

Thermochemical Equilibrium for Multiphysics Simulations of Nuclear Materials

Development of the Corrosion Modelling Application Yellowjacket

Thesis Proposal

Submitted in partial fulfilment of the requirements for the degree of

Doctor of Philosophy
in
Modelling and Computational Science

by

Parikshit Bajpai, MSc

School of Graduate and Postdoctoral Studies
University of Ontario Institute of Technology
Oshawa, Ontario, Canada
November 2019

This proposal has been submitted to the candidacy examination committee.

Members of the candidacy committee

Dr. Edward J. Waller	Chairman
Dr. Markus H.A. Piro	Supervisor
Dr. Lennaert van Veen	Member of Supervisory Committee
Dr. Hendrick W. de Haan	Member of Supervisory Committee
Dr. Kirk D. Atkinson	External Examiner

ACKNOWLEDGEMENTS

I am greatly thankful to Prof. Markus Piro for his constant guidance and support and for giving me the opportunity to work on this project. I am also grateful to the members of my candidacy examination committee, Professors Edward Waller, Lennaert van Veen, Hendrick de Haan and Kirk Atkinson. I appreciate your willingness to be on the committee and look forward to your suggestions and remarks.

I also appreciate Drs. David Andrš from Idaho National Laboratory and Prof. Michael Tonks from University of Florida for their help and support in the development of Yellowjacket. I'd also like to acknowledge Drs. Rich Martineau and David Andersson of Idaho National Laboratory and Los Alamos National Laboratory, respectively, for their role in facilitating this effort.

This work was funded by the Department of Energy Nuclear Energy Advanced Modeling and Simulation program under Contract No. DE-AC07-05ID14517 with the US Department of Energy. This research made use of the resources of the High-Performance Computing Center at Idaho National Laboratory, which is supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities under Contract No. DE-AC07-05ID14517.

This research was undertaken, in part, thanks to funding from the Canada Research Chairs (950-231328) program of the Natural Sciences and Engineering Research Council of Canada.

EXECUTIVE SUMMARY

INTRODUCTION AND MOTIVATION

Nuclear materials are highly complex multiscale, multiphysics systems and there has been an increasing interest in adopting a multiscale approach to better simulate the behaviour of nuclear materials. Material behaviour is influenced by many different physics, for example, mechanics such as dislocations, cracking, stress driven diffusion; chemistry such as corrosion, oxidation, reactive transport; heat conduction and species transport resulting in melting, precipitation; etc. Furthermore, the phenomena at the atomistic and micro scales drive the macro scale response. The multiscale modelling approach aims at using information from smaller scales to inform the models at increasing length scales and helps in effective prediction of performance of nuclear materials [1].

The evolution of the composition of nuclear materials due to irradiation plays a significant role in driving the above mentioned phenomena and thermochemical equilibrium calculations help in providing the information such as material properties and boundary conditions for continuum and mesoscale codes. As a result, recent trends in modelling and simulation of nuclear materials have exhibited a desire to couple thermochemical equilibrium codes within multiphysics frameworks.

Many emerging nuclear technologies, such as the Molten Salt Reactor (MSR), use high temperature fluids such as molten fluoride/chloride salts, which lead to corrosion of the metal containment leading to problematic behaviours during reactor operations. Corrosion is an electrochemical process composed of oxidation and reduction reactions, which are defined by the thermodynamics and kinetics of the reactions. While thermodynamics determines whether or not a material can 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. The Multiphysics Object Oriented Simulation Environment (MOOSE) developed by the Idaho National Laboratory provides a framework for multiphysics simulations but lacks the tools for predicting corrosion at the microstructure scale. A new MOOSE-based tool, *Yellowjacket*, is currently being developed to perform such simulations and to predict quantities such as the rate of material loss, corrosion product production, and precipitate production in liquid. As part of *Yellowjacket*, a new thermochemical equilibrium solver is being developed to quantitatively provide quantities of interest, for example chemical potential of stable species, by using the principles of computational thermodynamics.

MOOSE FRAMEWORK

MOOSE is a tool for solving complex coupled Multiphysics equations using the finite element method. MOOSE uses an object-oriented design to abstract data structure management, parallelism, threading and compiling while providing an easy to use interface targeted at engineers that may not have a lot of software development experience. MOOSE provides extreme scalability and flexibility when compared to other finite element method (FEM) frameworks. For instance, MOOSE has the ability to run extremely complex material models, or even third-party applications within a parallel simulation without sacrificing parallelism. This 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 [2, 3].

The design goal of MOOSE is to give developers ultimate control over their physical models and applications. Designing new models or solving completely new classes of problems is accomplished by writing standard C++ source code within the framework's class hierarchy. Scientists and engineers are free to implement completely new algorithms using pieces of the framework where possible, and extending the framework's capabilities where it makes sense to do so. Commercial applications do not have this capability, and instead opt for either a more rigid parameter system or a limited application-specific metalanguage [3].

YELLOWJACKET

The MOOSE framework currently lacks a quantitative tool for corrosion prediction at the microstructure scale. To bridge this gap, a new mesoscale framework for thermodynamics based modelling of corrosion in advanced reactor materials namely *Yellowjacket* is under development. *Yellowjacket* is a MOOSE based application that couples quantitative models of corrosion with thermodynamic and kinetic databases to predict the rate of material loss, corrosion product production and precipitate production for advanced reactors. *Yellowjacket* relies on phase field models for structure evolution, coupling it with Poisson equation for electrostatics, fracture models and thermochemical equilibrium solvers to provide a holistic environment for corrosion modelling and simulation.

Yellowjacket combines thermochemistry and phase field simulation and is being developed through a collaboration of the Nuclear Fuel and Materials group of Ontario Tech University, University of Florida, and Idaho National Laboratory. The role of Nuclear Fuels and Materials Group is the development of thermochemistry component of *Yellowjacket* and is the primary focus of this thesis. The phase field part of the work is being performed at University of Florida.

THERMOCHEMISTRY IN YELLOWJACKET

The composition of nuclear materials constantly evolves due to irradiation. This results in an evolution of the material properties, which constantly change as the stable phases in the system evolve as a function of temperature, pressure and composition of the system. Thermodynamic computations provide quantitative capabilities for predicting phase distribution and chemical potentials in fuels and other materials. Coupling thermodynamics with other multiphysics codes can provide material properties (e.g. heat capacity, oxygen to metal ratio) and boundary conditions as the composition evolves, thereby improving the predictions of nuclear material performance and improving safety.

Thermochemical equilibrium calculations are based on minimising the integral Gibbs energy of a closed system at constant temperature and hydrostatic pressure. From a numerical point of view, the objective of computing thermochemical equilibrium is to determine a unique combination of phases and their composition that yields a global minimum in the integral Gibbs energy subject to various linear and non-linear equality constraints. As shown in fig. 1, by relying on the fundamental laws of thermodynamics, equilibrium computations use the system information, namely, Gibbs energy functions of the species that can be present in the system, temperature, pressure and composition to provide quantities such as the stable phases and species, Gibbs energy of the system, chemical potentials of the species and can be used to provide information such the enthalpy, heat capacity, etc. A detailed description of the thermodynamic equilibrium computation is provided in the following section.

The thermochemical equilibrium solver in *Yellowjacket* leverages the experience from the development of a similar code *Thermochimica* [4]. By using the standard tools and libraries being used in MOOSE, the aim is to develop an improved thermochemical equilibrium solver for complete inte-

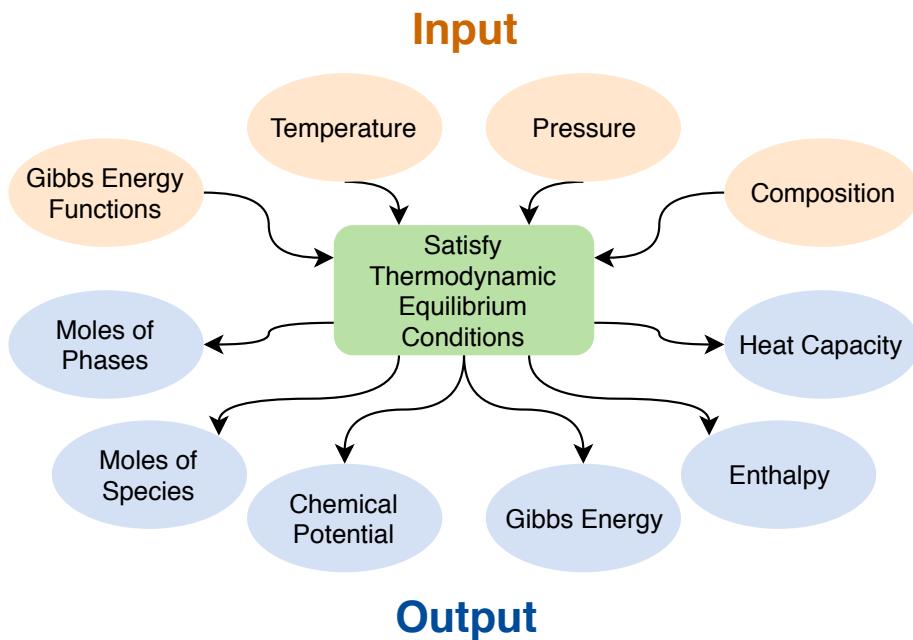


Figure 1: Input and output parameters of thermodynamic equilibrium calculations.

gration with other MOOSE based codes. This provides the foundation for future researchers to couple thermochemical simulations with fuel performance simulations in Bison, etc.

GOALS AND EXPECTED OUTCOMES

The primary goal of this thesis is to develop a new state-of-the-art thermodynamic equilibrium code built on the MOOSE platform for direct coupling to Marmot for nuclear corrosion problems. Though the thermodynamic equilibrium code is being developed within the corrosion modelling application Yellowjacket, it could be easily coupled to other applications, such as the fuel performance code Bison. The code will rely on the MOOSE framework and exploit the multitude of mathematical and development tools of the framework to ensure that the code meets the stringent requirements of the nuclear industry. It must be mentioned that while MOOSE and other MOOSE based applications solve systems of partial differential equations (PDE) using the finite element method, the computational thermodynamics calculations are essentially non-convex optimisation and require much more developmental effort than many other MOOSE applications where essentially just new PDEs need to be implemented.

The anticipated major contributions of the work are as follows:

1. Development of a new advanced Gibbs energy minimiser written in C++, built off MOOSE, and developed for multiscale, multiphysics simulations of nuclear materials.
2. Full integration within the multiphysics framework MOOSE and direct coupling to Marmot.
3. Enhanced initialisation algorithms to improve the computational performance.
4. Investigation and implementation of robust global optimisation algorithms to increase reliability and performance.
5. Software Quality Assurance with rigorous verification and testing to comply with the United States' NQA-1 guidelines required to be met for licensing.

TIMELINE

The major research milestones are shown in the following table:

Research Milestones		
Item	Timeline	Status
Implement data file parsing code	Feb. - Mar. 2019	Completed
Implement linear solver (levelling)	Apr. - Jun. 2019	Completed
Implement non-linear solver for GEM (homogeneous)	Sep. 2019 - Mar. 2020	In-progress
Demonstration of non-linear solver capabilities	Mar. - May 2020	Planned
Begin integration of thermodynamic solver with phase field	Jun. - Aug. 2020	Planned
Implementation of global optimisation algorithm	Sep. 2020 - Mar. 2021	Planned
Demonstration of global optimisation capabilities	Apr. - May 2021	Planned
Complete integration of Yellowjacket into MOOSE	Jun. - Aug. 2021	Planned
Verification and testing	Sep. - Dec. 2021	Planned

PUBLICATION

Following is a list of already published and soon to be submitted papers where contributions have been made as either primary author or co-author. The papers are attached in [List of Publications](#).

1. M. Piro, M. Poschmann and **P. Bajpai**, *On the interpretation of chemical potentials computed from equilibrium thermodynamic codes: Applications to molten salts*, *Journal of Nuclear Materials*, 526 (2019) 151756.
2. **P. Bajpai**, M. Poschmann, M. Piro, *Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models*, To be submitted to *CALPHAD Computer Coupling of Phase Diagrams and Thermochemistry*. [In preparation]
3. **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*. [Accepted]
4. **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*.

In summary, with the aim of incorporating thermodynamic equilibrium calculations with the multiphysics simulation platform MOOSE, an advanced Gibbs energy minimiser is being developed as part of the under development corrosion modelling tool Yellowjacket. Through advanced algorithm development and efficient implementation of performance enhancing strategies, this research will focus on accelerating the performance of thermodynamic computations which are inherently very complex and can significantly impede the performance of multiphysics codes. A special focus will be on coupling to other MOOSE based codes and software quality assurance to comply with Nuclear Quality Assurance Level 1 standards. In the long run, the thermodynamic solver, and Yellowjacket in general, will support the development of advanced nuclear reactors.

CONTENTS

Acknowledgements	iii
Executive Summary	v
List of Figures	xi
List of Tables	xiii
1 Introduction	1
1.1 Introduction	1
1.2 Modelling of Nuclear Materials	2
1.2.1 Corrosion in materials	3
1.2.2 Thermodynamic modelling of materials	4
1.3 Multiphysics Object Oriented Simulation Environment	4
1.3.1 Bison	6
1.3.2 Marmot	6
1.3.3 Yellowjacket	7
2 Goals of Research	9
3 Basic Thermodynamics	11
3.1 Basic Thermodynamic	11
3.1.1 First Law of Thermodynamics	12
3.1.2 Second Law of Thermodynamics	13
3.1.3 Third Law of Thermodynamics	13
3.2 Enthalpy, Helmholtz and Gibbs Energies	13
3.3 Gibbs Energy and Chemical Potential	14
3.3.1 Excess mixing models for Gibbs energy	16
3.4 Thermodynamic Equilibrium	19
3.4.1 Conditions of thermodynamic equilibrium	19
3.4.2 Convergence criteria	20
3.4.3 Global optimisation	22
3.5 Summary of Thermodynamic Equilibrium	23
3.5.1 Necessary conditions	23
3.5.2 Sufficient conditions	23
4 Literature Review	25
4.1 Numerical Methods for Thermodynamic Equilibrium	25
4.1.1 Equilibrium Constants	26
4.1.2 Gibbs Energy Minimisation (GEM)	26
4.1.3 Partitioning of Gibbs Energy (PGE)	27
4.1.4 Other Methods	28

4.2	Gibbs Energy Minimisers	28
4.3	Global Optimisation	30
4.3.1	Deterministic Methods	30
4.3.2	Stochastic Methods	34
4.3.3	Global Optimisation Review	34
4.4	Integration of Thermodynamics in Multiphysics Codes	36
5	Computational Implementation	39
5.1	Opportunities for Novel Contributions	39
5.2	Parsing and Input	40
5.3	Initialisation	42
5.3.1	Linear solver	42
5.3.2	Post-levelling	46
5.3.3	Euclidean norm	46
5.3.4	Temporal series estimate	48
5.3.5	Boundary value estimate	48
5.4	Non-linear solver	49
5.4.1	Matrix representation	52
5.4.2	Numerical implementation	53
5.4.3	Adding/Removing phases	54
5.4.4	Convergence criterion	54
5.5	Global Optimisation	57
5.5.1	Particle Swarm Optimisation	57
5.5.2	Grid Construction	58
5.5.3	Branch and Bound	59
5.6	Integration in multiphysics codes	62
5.7	Summary	62
6	Proposal	65
6.1	Overall Timeline	65
6.2	Current Progress	66
6.2.1	Demonstration Problem	66
6.2.2	Results of Demonstration Problem	67
6.3	Work Plan	68
6.3.1	Year 2019-2020	68
6.3.2	Year 2020-2021	70
6.3.3	Year 2021-2022	71
6.4	Publication Plan	72
6.4.1	Journal Articles	72
6.4.2	Conference Proceedings	73
6.4.3	Technical Reports	74
7	Conclusion	75
References		77
List of Publications		87

LIST OF FIGURES

1	Input and output parameters of thermodynamic equilibrium calculations.	vii
1.1	Multiscale theoretical and computational methods used for materials model development and computer simulation [1].	3
1.2	Input and output parameters of thermodynamic equilibrium calculations.	5
1.3	Principle of CALPHAD method by Zinkevich [5]	5
1.4	Illustration showing the underlying interface provided by MOOSE and the physics modules of Yellowjacket.	8
3.1	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.	12
3.2	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 [6].	21
3.3	Fictive system with miscibility gap showing a possible false positive from thermodynamic equilibrium solver [7].	22
3.4	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 [7].	23
4.1	Approximation of the function β in Simplex method. Reproduced by Piro [8] from Dantzig et al. [9]	29
4.2	A flowchart of the Advanced Multi-Physics (AMP) code illustrating the interaction between the various modules is shown [8].	36
4.3	The predicted distribution of phases across the pellet is shown for an average pellet burnup of 102 GW d t(U) ⁷¹ . [10].	37
4.4	Oxygen vacancy concentration in UO ₂ fuel obtained by coupling Thermochimica with Bison [11].	37
5.1	Top-level architecture of the proposed thermodynamic equilibrium code.	40
5.2	A marked-up example of a ChemSage data file of the Ni–K–F system [12]	41
5.3	Illustration of the levelling algorithm [13]	43
5.4	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) [8].	45
5.5	Performance gains when employing post-levelling and Euclidean-norm algorithms [14].	47
5.6	Illustration of the temporal series initialisation algorithm.	48
5.7	Illustration of the boundary value initialisation on a finite element mesh [15].	49
5.8	Illustration of the proposed methodology for updating the phase assemblage. Adapted from Piro [15].	55
5.9	Illustration of the proposed Gibbs energy minimisation algorithm. Adapted from Loukusa [13].	56

5.10 Demonstration of the grid construction method for an arbitrary binary system at constant temperature and pressure. The domain has been discretised into 11 grid points and the pure stoichiometric phase A_3B_2 is found to be in equilibrium with the solution phase giving a false positive [7]	59
5.11 Demonstration of the branch and bound method for an arbitrary binary system at constant temperature and pressure. The domain has been partitioned into 2 subdomains [7].	61
5.12 Refinement of the subdomains in branch and bound method and the subsequent convergence to global minimum [7].	62
6.1 Current progress on the implementation of the thermochemistry solver.	66
6.2 The demonstration problem consists of a bar divided into 5 elements with Dirichlet boundary conditions imposed at both ends and a linear temperature gradient.	67
6.3 Stable phases and Gibbs energies predicted by the linear solver.	67

LIST OF TABLES

4.1	A review of the major thermodynamic equilibrium codes.	31
4.1	A review of the major thermodynamic equilibrium codes.	32
4.1	A review of the major thermodynamic equilibrium codes.	33
4.2	A review of the global optimisation methods applied to thermodynamic equilibrium calculations.	35
6.1	Overall timeline of the proposed work showing major academic and research milestones.	65
6.2	Summary of some of the proposed unit and system tests for the thermodynamic solver. .	72

1

INTRODUCTION

Recent years have seen a rapid shift in the engineering design of materials. Modelling and simulation have become essential tools in this context and are moving towards a multiscale, multiphysics approach where various physical phenomena are coupled to enhance the accuracy of predictions. Of particular interest in this regard is the increasing desire to couple thermodynamics codes with other multiphysics codes such as phase field, fuel performance codes, etc. This chapter provides a brief background to the proposal and presents the motivation behind the proposed work.

1.1. INTRODUCTION

Global population and per capita energy consumption are rising and electrical power generation not only plays a key role in the advancement of industry, agriculture, technology and the quality of living but is also an important measure of a country's economic development, power and independence. The global energy consumption has had significant impact on the environment in terms of greenhouse gas emissions and degradation of the quality of air, water and land. As the call for action on climate change has become more pronounced and more urgent, there have also been concerns about energy security resource sustainability and human health. This has generated a renewed interest in nuclear energy as a source of reliable, low carbon footprint electricity source.

As of 2018, 450 nuclear plants around the world supplied 2563 TWh of electricity, around 10% of the world's total electricity [16]. 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 in the last 10 years or so [16]. In its World Energy Outlook 2018, the Organisation for Economic Co-operation and Development (OECD) International Energy Agency (IEA) has proposed an ambitious *Sustainable Development Scenario* consistent with the provision of clean and reliable energy and a reduction of air pollution, among other aims. In this decarbonisation scenario, electricity generation from nuclear increases by almost 90% by 2040 to 4960 TWh, and capacity grows to 678 GWe [17]. Meeting these goals not only requires committing to a continued operation of current nuclear power plants, but also rapid expansion and development of new nuclear plants.

Though many nations across the globe, both industrialised and developing, are confident of the potential of nuclear energy, challenges exist to future large scale use. These challenges relate to the sustainability, reliability and economic competitiveness, safety, risk of proliferation, anticipated future needs beyonds electricity, and need for government support [18]. 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 [19]. While promising in terms of sustainability, economics, safety and reliability, and proliferation resistance and physical protection, the Gen-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. Of particular interest and pertinent to this work are the material design issues discussed in the following section with a specific focus on corrosion.

1.2. MODELLING OF NUCLEAR MATERIALS

The environment in a nuclear reactor induces complex multiphysics phenomena in nuclear materials, occurring over distances ranging from inter-atomic spacing to meters, and times scales ranging from microseconds to years. This multiphysics behaviour is often tightly coupled and many important aspects are inherently multidimensional [20]. Once in the reactor, nuclear materials are subjected to extreme radiation environments that continuously alter their thermo-mechanical properties [1]. Moreover, due to irradiation effects, the physics and chemistry of such materials become more complicated over time. The safe and reliable performance of nuclear power plants requires choice of suitable materials and the assessment of long-term materials damage.

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 [1]. While the traditional approach to discovery and design of materials was almost entirely experimental, recent developments in modelling and high performance computing has 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.

With material issues ranging from creep, swelling, fracture, fatigue to corrosion, impurity effects and correlation between nano and microstructural scale, it is evident that a multiscale approach is required for a fundamental understanding of all the relevant phenomena. However, due to significant limitations on availability of computing resources, a majority of materials modelling and simulation efforts in the past adopted an operator splitting approach wherein the various physical phenomena were disconnected from each other. Though these methods were suitable for previous generation of nuclear reactors, addressing the materials challenges for advanced reactors requires a tightly coupled multiscale, multiphysics approach.

Traditionally, nuclear material modelling has focussed on the macroscale behaviour of the materials. Such models rely on the principles of thermo-mechanics and are heavily rooted in experimental observations. For example, nuclear fuel behaviour is often 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. Recently, there has been an impetus on atomistically informing mesoscale and macroscale methods by optimising characteristic parameters of these scales against the output of atomistic calculations [1]. 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. Some of the theoretical and computational methods used in multiscale approach have been shown in figure 1.1.

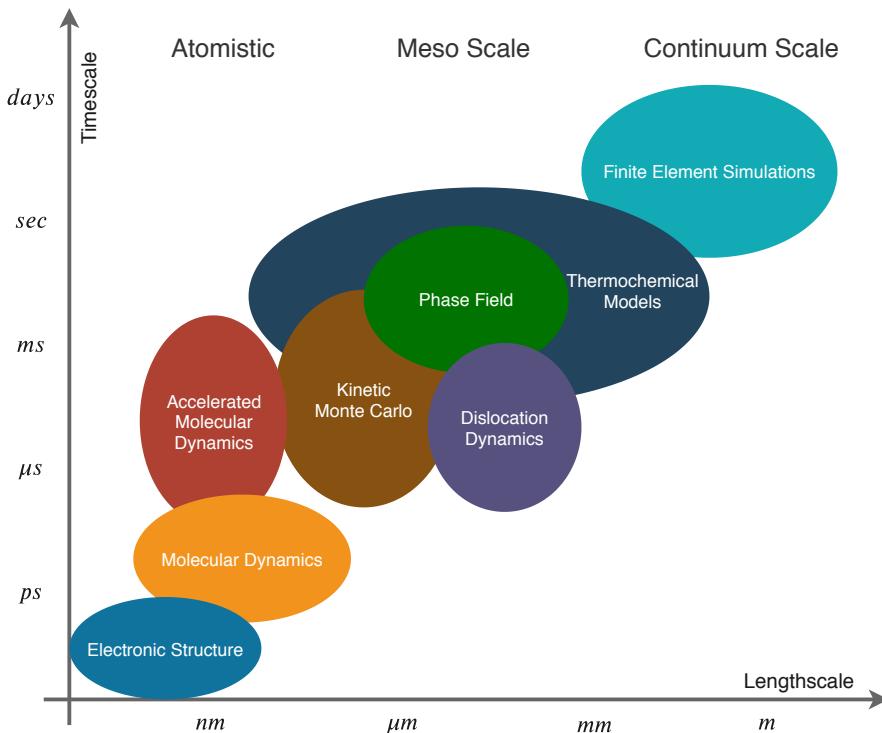


Figure 1.1: Multiscale theoretical and computational methods used for materials model development and computer simulation [1].

1.2.1. CORROSION IN MATERIALS

Many emerging nuclear technologies, such as the Molten Salt Reactors (MSR), use high temperature fluids, such as molten fluoride/chloride salts, which lead to corrosion of the metal containment leading to problematic behaviours during the reactor operations. Corrosion in molten salts is a fundamentally different process from that in conventional applications, and most of the methods to control corrosion developed over previous centuries are of limited value [21]. 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 [22]. 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. Another issue to be considered is the mass transfer of corrosion products from hotter sections of the nuclear reactor and subsequent deposition in the colder areas that can clog the heat exchanger systems. Therefore, effectively predicting corrosion and related phenomena like leaching and deposition requires a multiscale, multiphysics approach [23].

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.

1.2.2. THERMODYNAMIC MODELLING OF MATERIALS

The phase and chemical behaviour of nuclear materials is governed by the thermochemical equilibrium state. While in many systems, equilibrium is often not achieved due to transport and/or chemical kinetics phenomenon, a thorough understanding of both transport and chemical evolution, and subsequently material properties, is based on an accurate representation of thermochemical equilibria [24]. 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. In the specific context of corrosion modelling, the difference in the free energy of the salt fluoride/chloride constituents and the fluorides/chlorides of the alloying elements is a key driving force for corrosion. For closed systems, the equilibrium concentration of the corrosion product fluorides/chlorides in the salt melt dictates the maximum extent of corrosion and is important in the long-term corrosion of containment materials. Therefore, thermodynamic equilibrium calculations play an important role in the context of corrosion modelling in advanced reactors.

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 analysis 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 enabled the incorporation of these calculations which are of ever more importance in the discovery and design of materials for advanced reactors.

The inputs for a thermodynamic equilibrium calculation are shown in figure 1.2. Since thermodynamic equilibria 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. These thermodynamic models are generally developed using the Calculation of Phase Diagram (CALPHAD) approach shown in figure 1.3, which combines experimental and theoretical information to describe the thermodynamic properties through the Gibbs energy, applying a mathematical model containing adjustable parameters [25]. The multiscale approach also allows *ab initio* molecular dynamics calculations to inform and improvise the thermodynamic models developed using the CALPHAD approach.

Figure 1.2 also shows some of the outputs produced by thermodynamic equilibrium calculations. The main outputs include the phase assemblage, i.e. the number of moles of phases present at equilibrium and the mole fraction of the species in those phases. The equilibrium calculations also provide the Gibbs energy of the system, the chemical potentials of the species, etc. These quantities are useful in multiphysics calculations where, for example, the chemical potential of oxygen can be used to model oxygen diffusion in a UO₂ nuclear fuel pellet.

1.3. MULTIPHYSICS OBJECT ORIENTED SIMULATION ENVIRONMENT

The Multiphysics Object-Oriented Simulation Environment (MOOSE) is a tool for solving complex coupled multiphysics equations using the finite element method. MOOSE uses an object-oriented design to abstract data structure management, parallelism, threading and compiling while providing an easy to use interface targeted at engineers that may not have a lot of software development experience. MOOSE provides extreme scalability and flexibility when compared to other finite element method (FEM) frameworks. For instance, MOOSE has the ability to run extremely complex material models, or even

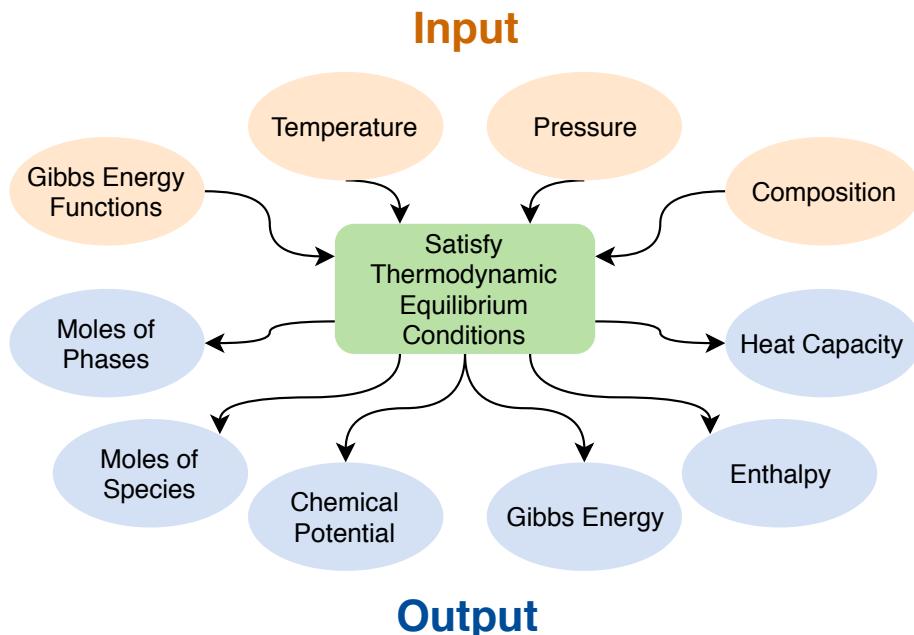


Figure 1.2: Input and output parameters of thermodynamic equilibrium calculations.

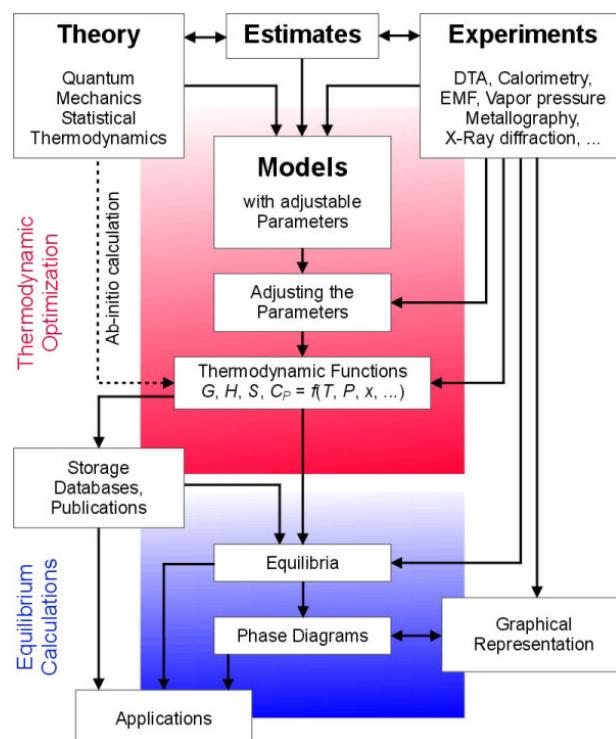


Figure 1.3: Principle of CALPHAD method by Zinkevich [5]

third-party applications within a parallel simulation without sacrificing parallelism. This 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 [2, 3].

The design goal of MOOSE is to give developers ultimate control over their physical models and applications. Designing new models or solving completely new classes of problems is accomplished by writing standard C++ source code within the framework's class hierarchy. Scientists and engineers are free to implement completely new algorithms using pieces of the framework where possible, and extending the framework's capabilities where it makes sense to do so. Commercial softwares do not have this capability, and instead opt for either a more rigid parameter system or a limited application-specific metalanguage [3].

Currently, apart from a number of other applications, such as RELAP [26] for system level thermal hydraulics, Rattlesnake [27] for neutronics, etc., the MOOSE framework consists of two main applications for materials applications - the macroscale fuel performance code Bison [28] and the mesoscale phase field code Marmot [29]. Together, MOOSE, Bison and Marmot, form the Fuels Product Line (FPL) to deliver an integrated set of increasingly predictive computational tools for nuclear fuel performance analysis and design. The FPL enable multiscale modelling and simulation of nuclear fuels where simulations of fuel performance at the engineering scale are informed by material property and behaviour models developed from mesoscale simulations of microstructure evolution under irradiation, which are themselves guided and enabled by inputs of fundamental materials parameters obtained from atomistic simulations. The multiscale, multiphysics approach allows an unprecedented degree of predictability of nuclear fuel performance.

1.3.1. BISON

The 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, Bison 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 [20].

Within the multiscale framework, Bison can be coupled with both mesoscale microstructure evolution tool Marmot as well as reactor core and system tools being developed under the Reactor Products Line to perform full scale simulations of the entire nuclear reactor. Coupling with Marmot allows Bison to easily and continuously incorporate new mechanistic, physics-based models produced by the mesoscale model development activities in order to extend its predictive capability to new fuels and operational regimes. While focussed on Light Water reactor (LWR) fuel, Bison is applicable to variety of fuel forms including the spherical TRISO fuel design [30].

1.3.2. MARMOT

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, martinstic transformation, two-phase flow, etc. The phase field approach treats all material interfaces as diffuse by representing structural features with continuous 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 framework has been developed to enable simu-

lations 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.

Despite the wide ranging capabilities of the FPL, there remains a gap in terms of modelling advanced nuclear reactors. The high temperature operations of reactors such as the Molten Salt Reactors (MSR), which use molten fluoride/chloride salts as the fuel and coolant, produce a conducive environment for corrosion. The current FPL lacks a tool for corrosion modelling at microstructure scale and efforts are underway to develop a new MOOSE based application called *Yellowjacket* to bridge this gap.

1.3.3. YELLOWJACKET

Yellowjacket is a mesoscale framework for thermodynamics based modelling of corrosion in advanced reactor materials. Currently under development, it is a MOOSE based application 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 phase field models for structure evolution, coupling it with Poisson equation for electrostatics, fracture models and thermochemical equilibrium solvers to provide a holistic environment for corrosion modelling and simulation. As shown in figure 1.4, *Yellowjacket* depends on the MOOSE framework for the development infrastructure and follows the Nuclear Quality Assurance Level 1 (NQA 1) [31] development process.

Yellowjacket is being developed through a joint collaboration between the Nuclear Fuels and Materials Group at Ontario Tech University, University of Florida, Idaho National Laboratory and Los Alamos National Laboratory, and is funded primarily by the United States Department of Energy (US-DOE) through the Nuclear Energy Advanced Modelling and Simulation (NEAMS) program.

This thesis is aimed at developing a thermodynamic equilibrium solver for the corrosion modelling tool *Yellowjacket* and the goals of this research are specified in the following chapter. The phase field component of *Yellowjacket* is being investigated by another PhD student at University of Florida.

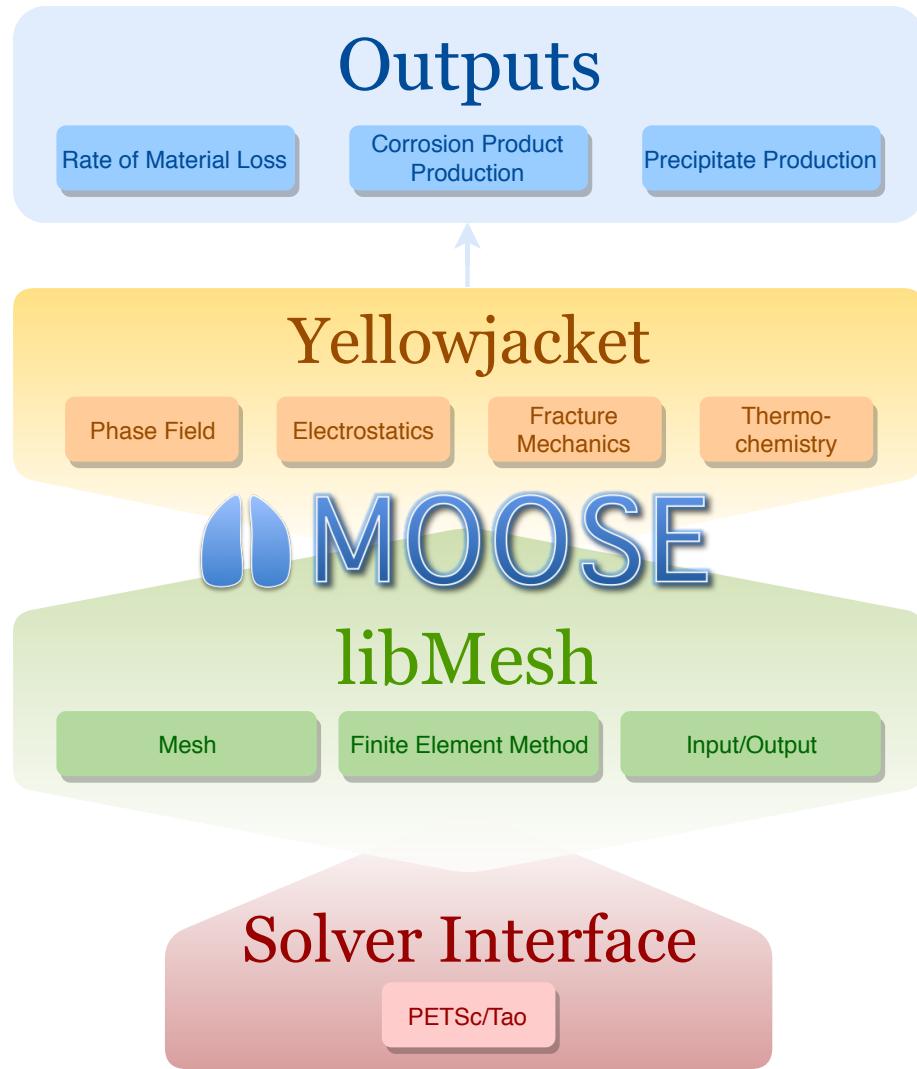


Figure 1.4: Illustration showing the underlying interface provided by MOOSE and the physics modules of Yellowjacket.

2

GOALS OF RESEARCH

Facilitating the discovery and design of nuclear materials for innovative nuclear materials requires use of multiscale, multiphysics models and simulations and chemical thermodynamics forms an integral part of such simulations. The motivation behind this research is to directly integrate thermodynamic equilibrium computations in the Multiphysics Object Oriented Simulation Environment (MOOSE) which is a generic finite element method based simulation framework. By computing various thermodynamic values on a finite element mesh and using these values to inform macroscale and mesoscale models, an unprecedented level of sophistication can be achieved in multiscale, multiphysics models for materials.

Some of the challenges in achieving this objective include computational expense, predictive capabilities and reliability. First, relatively limited capabilities are currently available to perform such coupling. Within the MOOSE framework, the thermodynamic equilibrium code *Thermochimica* has only recently been integrated with the macroscale code *Bison* while the mesoscale code *Marmot* still relies on empirical correlations for thermodynamic inputs and coupling *Thermochimica* with it would require starting the process of coupling from scratch. Second, the computational expense of thermodynamic equilibrium dramatically increases the computational burden of the multiphysics simulations. Finally, reliability is of utmost importance for simulation of nuclear materials and requires an enormous number of function evaluations.

While there are a number of existing thermodynamic equilibrium tools, all but a handful of them are standalone codes and since computational time for such computations is not of high importance, there has been no interest in optimising their performance. In order to maintain numerical stability, most of the codes restrict the number of system components but the intended application also requires that the new code be able to handle systems with a very large number of components. Another issue that needs to be addressed is the challenge associated with initialisation algorithms for the code. A far from accurate initial estimate can significantly reduce the convergence rate impeding the performance of the simulations and the current schemes used for initialisation often increase the computational cost when used at every iteration in the multiphysics simulations. Finally, the convergence of solution to the true solution and not a false positive must be ensured which requires the use of global optimisation methods.

The goal of this work is to develop a new state-of-the-art thermodynamic equilibrium code by leveraging the experience with the development and utilisation of *Thermochimica*. Though the thermodynamic equilibrium code is being developed within the corrosion modelling tool *Yellowjacket*, it would be easily couple-able with other applications such as *Bison* and *Rattlesnake*. The code will

rely on the MOOSE framework and exploit the multitude of mathematical and development tools of the framework to ensure that the code meets the stringent requirements of the nuclear industry. It must be mentioned that while MOOSE and other MOOSE based applications solve systems of partial differential equations (PDE) using finite element method, thermodynamic equilibrium calculation is essentially a non-convex optimisation problem and requires much more developmental effort than many other MOOSE applications where essentially just new PDEs need to be implemented.

The major contributions of the work would be as follows:

1. Development of a new advanced Gibbs energy minimiser written in C++ within the framework of MOOSE platform.
2. Full integration within the multiphysics framework MOOSE, with the intent of coupling to the phase field code Marmot¹.
3. Enhanced initialisation algorithms to improve the computational performance.
4. Investigation and implementation of robust global optimisation schemes to increase reliability and robustness.
5. Software Quality Assurance with rigorous verification and testing to comply with the NQA-1 guidelines required to be met for licensing.

¹The phase field module development and coupling is being investigated at University of Florida.

3

BASIC THERMODYNAMICS

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*”. This chapter summarises the fundamentals of classical thermodynamics and gives a brief review of the various thermodynamic models used to describe materials. Finally, the conditions for thermodynamic equilibrium are discussed.

3.1. BASIC THERMODYNAMIC

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 3.1 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.

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.

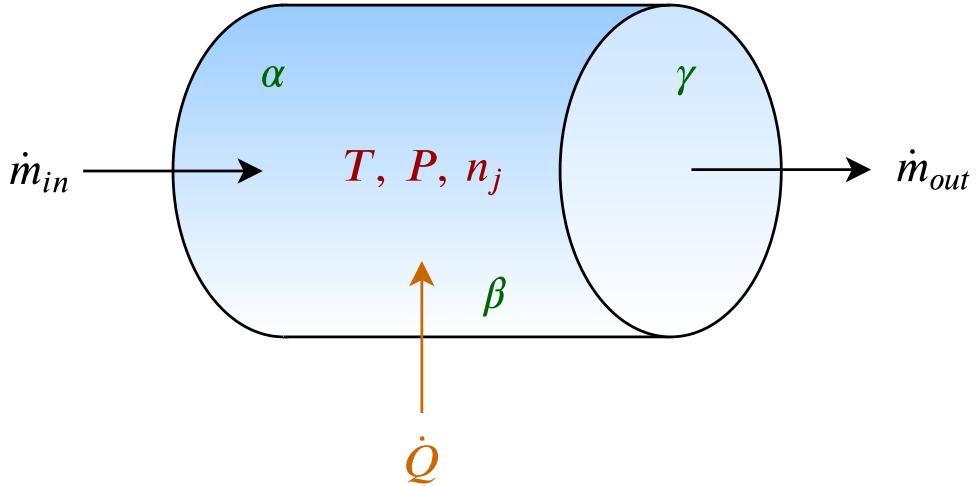


Figure 3.1: Volume element of a general thermodynamic system with mass flow of chemical components \dot{m} and heat flux \dot{Q} . The Greek letters indicate presence of separate phases.

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.

3.1.1. 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:

$$dU = dQ + dW + \sum H_i dN_i \quad (3.1)$$

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:

$$dU = dQ + dW \quad (3.2)$$

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

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.

3.1.2. 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:

$$dS = dS_{sys} + dS_{surr} \geq 0 \quad (3.3)$$

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 defined as the heat exchange divided by temperature:

$$dS_{sys} = \frac{dQ}{T} \quad (3.4)$$

3.1.3. 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.

3.2. ENTHALPY, HELMHOLTZ AND GIBBS ENERGIES

Three important state functions of great practical importance in thermodynamics are the *enthalpy* H , *Helmholtz energy* A , 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 defined as:

$$H = U + PV \quad (3.5)$$

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:

$$A = U - TS \quad (3.6)$$

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:

$$G = H - TS \quad (3.7)$$

The equilibrium criterion 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.

$$dS_{sys} + dS_{surr} > 0 \quad (3.8)$$

For a closed system in thermal and mechanical equilibrium but not in chemical equilibrium which acquires an infinitesimal quantity of heat from the surroundings,

$$dS_{surr} = -\frac{dQ_{sys}}{T} \quad (3.9)$$

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,

$$dQ_{sys} - TdS_{sys} < 0 \quad (3.10)$$

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,

$$dU_{sys} = dQ_{sys} + dW_{sys} \quad (3.11)$$

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:

$$dU_{sys} + PdV_{sys} - TdS_{sys} < 0 \quad (3.12)$$

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

$$dU_{sys} - TS_{sys} < 0 \quad (3.13)$$

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:

$$dA_{sys} < 0 \quad (3.14)$$

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

$$dU_{sys} + PV_{sys} - TS_{sys} < 0 \quad (3.15)$$

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

$$dG_{sys} < 0 \quad (3.16)$$

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.

3.3. 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. Willard used the term *thermodynamic potential* to represent all the relevant system potentials to characterise the conditions of thermodynamic equilibrium [32]. Thermodynamic equilibrium calculations are based on the principle that the potential for each component must be uniform throughout the system at thermodynamic equilibrium. This and the following section describe the relation between Gibbs energy and chemical potentials and their use in computing thermodynamic equilibrium.

The Gibbs energy, $G_{i(\phi)}$ [J mol^{-1}], of a pure species i is defined as [33]:

$$G_{i(\phi)} = \Delta H_{i(\phi)} - TS_{i(\phi)} \quad (3.17)$$

where, T [K] is the absolute temperature, $\Delta H_{i(\phi)}$ [J mol^{-1}] and $S_{i(\phi)}$ [$\text{J mol}^{-1} \text{ K}^{-1}$] represent the enthalpy and absolute entropy of species i in phase ϕ respectively. Since thermodynamic quantities are relative in nature, equation (3.17) can be expanded as:

$$G_{i(\phi)} = \left(\Delta H_{i(\phi)}^0 + \int_{T_0}^T C_{p,i(\phi)} dT \right) - T \left(S_{i(\phi)}^0 + \int_{T_0}^T \frac{C_{p,i(\phi)}}{T} dT \right) + \int_{P_0}^P V_i dP \quad (3.18)$$

where, $\Delta H_{i(\phi)}^0$ [J mol^{-1}] and $S_{i(\phi)}^0$ [$\text{J mol}^{-1} \text{ K}^{-1}$] 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 0 represents a quantity at standard temperature and pressure, a notation that is used hereafter. $C_{p,i(\phi)}$ [$\text{J mol}^{-1} \text{ K}^{-1}$] 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 (3.19) 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:

$$G_{i(\phi)} = \left(\Delta H_{i(\phi)}^0 + \int_{T_0}^T C_{p,i(\phi)} dT \right) - T \left(S_{i(\phi)}^0 + \int_{T_0}^T \frac{C_{p,i(\phi)}}{T} dT - R \ln \left(\frac{P}{P_0} \right) \right) \quad (3.19)$$

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 Gibbs energy of the pure species incorporates the reference Gibbs energy of pure species, $g_{i(\lambda)}^0$, 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 [33]:

$$\mu_{i(\lambda)} = \left(\frac{\partial G_{sys}}{\partial n_{i(\lambda)}} \right)_{T,P,n_{j\neq i}} \quad (3.20)$$

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

$$\mu_{i(\lambda)} = g_{i(\lambda)}^0 + \ln x_{i(\lambda)} \quad (3.21)$$

For non-ideal solution phases, the chemical potential also includes the partial molar excess Gibbs energy of mixing, $g_{i(\lambda)}^{ex}$ [J mol^{-1}], to account for non-ideal mixing

$$\mu_{i(\lambda)} = g_{i(\lambda)}^0 + \ln x_{i(\lambda)} + g_{i(\lambda)}^{ex} \quad (3.22)$$

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 [34–38], the Compound Energy Formalism [39], etc.

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

$$G_{sys} = RT \left(\sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \tilde{\mu}_i + \sum_{\omega=1}^{\Omega} n_{\omega} \tilde{\mu}_{\omega} \right) \quad (3.23)$$

where, R [$\text{J mol}^{-1}\text{K}^{-1}$] is the ideal gas constant, T [K] is the absolute temperature, N_λ denotes the number of species in the solution phase λ and $x_{i(\lambda)}$ 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. Finally, $\tilde{\mu}_i$ and $\tilde{\mu}_j$ 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:

$$G_{sys} = \sum_{j=1}^C \Gamma_j b_j \quad (3.24)$$

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.

3.3.1. 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 since a detailed discussion of all the models is beyond the scope of this thesis proposal and has therefore been omitted.

1. Regular 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.

- **Kohler-Toop Interpolation**

$$g_\lambda^{ex} = \sum_{z=1}^Z \phi_z (x_1^{d_1} x_2^{d_2} x_3^{d_3}) \quad (3.25)$$

- **Redlich-Kister-Muggiano Interpolation**

$$g_\lambda^{ex} = \sum_{z=1}^Z x_j x_k \sum_{v=0}^v L_j \quad (3.26)$$

2. Compound Energy Formalism (CEF)

Compound Energy Formalism is a multi-sublattice model proposed by Hillert [39] 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:

$$g_\lambda = \sum_{i=1}^{N_\lambda} g_{i(\lambda)}^\circ \prod_{s=1}^{N_s} y_{i(s)} + RT \left(\sum_{s=1}^{N_s} a_s \sum_{c=1}^{N_c} y_{c(s)} \ln(y_{c(s)}) \right) + g_\lambda^{ex} \quad (3.27)$$

where $g_{i(\lambda)}^\circ$ 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:

$$g_\lambda^{ex} = \sum_{p=1}^{N_p} \left(\prod_{m=1}^{N_p} y_{m(s)} \right) \sum_{z=0}^{N_z} {}^z L_{j,k} (y_j - y_k)^z \quad (3.28)$$

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. As already mentioned, a detailed description of CEF is beyond the scope of this proposal and can be found in the paper by Hillert [39].

3. Modified Quasichemical Model (MQM)

The Modified Quasichemical Model (MQM) in the quadruplet approximation is the most generalized 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.* [34–37]

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:

$$(A - [X] - A) + (B - [X] - B) = 2(A - [X] - B); \Delta g_{AB/X} \quad (3.29)$$

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:

$$(X - [A] - X) + (Y - [A] - Y) = 2(X - [A] - Y); \Delta g_{A/XY} \quad (3.30)$$

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:

$$(A - X) + (B - Y) = (A - Y) + (B - X); \Delta g_{A/XY}^{exchange} \quad (3.31)$$

where $\Delta g_{A/XY}^{exchange}$ 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_{ijkl} be the number of moles of the quadruplets. The relationship between the foregoing terms is [37]

$$Z_A n_A = 2n_{A_2/X_2} + 2n_{A_2/Y_2} + 2n_{A_2/XY} + n_{AB/X_2} + n_{AB/Y_2} + n_{AB/XY} + \dots \quad (3.32)$$

$$Z_X n_X = 2n_{A_2/X_2} + 2n_{B_2/X_2} + 2n_{AB/X_2} + n_{A_2/XY} + n_{B_2/XY} + n_{AB/XY} + \dots \quad (3.33)$$

where Z_A and Z_B are the coordination numbers for A and B, respectively. A generic statement for a multi-component system is:

$$Z_i n_i = 2n_{ii} + \sum_{j \neq i} n_{ij} \quad (3.34)$$

The mole fractions then follow:

$$x_i = \frac{n_i}{\sum n_j} \quad (3.35)$$

$$x_k = \frac{n_k}{\sum n_l} \quad (3.36)$$

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:

$$x_{i/k} = \frac{n_{i/k}}{\sum_j \sum_l n_{j/l}} \quad (3.37)$$

$$x_{ij/kl} = \frac{n_{ij/kl}}{\sum n_{ij/kl}} \quad (3.38)$$

Another useful term is the coordination equivalent fraction, which is

$$y_i = \frac{Z_i n_i}{\sum Z_j n_j} \quad (3.39)$$

$$y_k = \frac{Z_k n_k}{\sum Z_l n_l} \quad (3.40)$$

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

$$G_\lambda = (n_A g_A^\circ + n_B g_B^\circ) - T \Delta S^{config} + \frac{n_{AB} \Delta g_{AB}}{2} \quad (3.41)$$

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:

$$\Delta S^{config} = -R \left(n_A \ln(x_A) + n_B \ln(x_B) + n_{AA} \ln(x_{AA}/y_A^2) + n_{BB} \ln(x_{BB}/y_B^2) + n_{AB} \ln(x_{AB}/(2y_A y_B)) \right) \quad (3.42)$$

MQM is of particular interest in this work because it is the preferred model for thermodynamic 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 [40]. A solution to this problem has been proposed by Piro *et al.* and the paper has been attached in the publications section at the end of this proposal [40].

3.4. THERMODYNAMIC EQUILIBRIUM

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.

3.4.1. CONDITIONS OF THERMODYNAMIC EQUILIBRIUM

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

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} v_{i,j} + \sum_{\omega=1}^{\Omega} n_{\omega} v_{\omega} \quad (3.43)$$

where, $v_{i,j}$ and v_{ω} represent the stoichiometric coefficients of element j in solution phase species j and stoichiometric phase ω respectively. In an electrochemical system where the electrons form a system component with zero moles overall in the system, the mass balance constraint represents charge neutrality constraint.

Thermodynamic equilibrium conditions also require that the **Gibbs' phase rule** must also 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 [32]. in general, the phase rule can be written as:

$$F = C - \Phi + 2 + \Xi \quad (3.44)$$

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 :

$$F = C - \Phi \quad (3.45)$$

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.

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 $dG_{sys} = 0$ [32]. Thus, differentiating equation 3.23

$$dG_{sys} = \sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_{\phi}} (dn_{i(\phi)} \mu_{i(\phi)} + n_{i(\phi)} d\mu_{i(\phi)}) = 0 \quad (3.46)$$

The chemical potentials are related through the *Gibbs-Duhem equation* which, at constant temperature and pressure, can be written as [41]:

$$\sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_{\phi}} (n_{i(\phi)} d\mu_{i(\phi)}) = 0 \quad (3.47)$$

Substituting the Gibbs-Duhem equation in equation 3.47 gives:

$$dG_{sys} = \sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_{\phi}} (dn_{i(\phi)} \mu_{i(\phi)}) = 0 \quad (3.48)$$

The chemical potentials of the species can be written in terms of the chemical potentials of the system components. Therefore, substituting equation refeq:massbalance into equation 3.24, differentiating with respect to $n_{i(\phi)}$ at constant temperature and pressure and equating to zero gives:

$$dG_{sys} = \sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_{\phi}} dn_{i(\phi)} \sum_{j=1}^C \nu_{i,j} \Gamma_j = 0 \quad (3.49)$$

Rearranging gives:

$$\sum_{\phi=1}^{\Phi} \sum_{i=1}^{N_{\phi}} dn_{i(\phi)} \left(\mu_{i(\phi)} - \sum_{j=1}^C \nu_{i,j} \Gamma_j \right) = 0 \quad (3.50)$$

Since both $\nu_{i,j}$ and $\mu_{i(\phi)}$ 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 [42]:

$$\mu_{i(\phi)} = \sum_{j=1}^C \nu_{i,j} \Gamma_j \quad (3.51)$$

Ensuring that equation 3.51 is satisfied for all species in the system is equivalent to satisfying the equilibrium criterion that the Gibbs energy of the system is at a global minimum. This is useful in developing a convergence criterion for thermodynamic equilibrium calculations and is discussed in the following section.

3.4.2. 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 3.51 and requires that the chemical potentials of all species lie on or above the Gibbs plane formed by chemical potentials of system components.

EVALUATION OF THE 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:

$$\Psi_G = \left| \frac{G_{sys}^m - G_{sys}^{m-1}}{G_{sys}^m} \right| < \epsilon \quad (3.52)$$

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.* [43], 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:

$$\Psi_{\pi} = \left| \frac{\pi_j^m - \pi_j^{m-1}}{\pi_j^m} \right| < \epsilon \quad (3.53)$$

Though intuitive, this approach to judging convergence suffers from two potential issues. 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.

THE GIBBS CRITERIA

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:

$$\hat{\mu}_{i(\phi)} = \frac{\mu_i(\phi)}{a_{i(T)}} \quad (3.54)$$

where, $\hat{\mu}_{i(\phi)}$ [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 $\hat{\mu}_{i(\phi)}$ 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 3.2 for a three dimensional space.

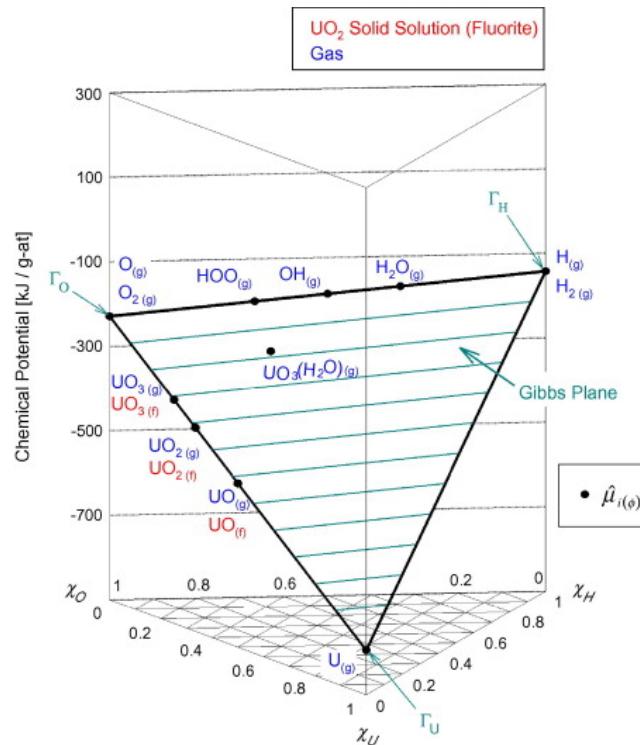


Figure 3.2: The Gibbs criteria is satisfied when the chemical potentials for all species represented per gram-atom lie on the Gibbs Plane within an acceptable tolerance [6].

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:

$$\Psi_\Gamma = |\hat{\mu}_{i(\phi)}(\Gamma) - \hat{\mu}_{i(\phi)}| < \epsilon \quad (3.55)$$

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.

3.4.3. GLOBAL OPTIMISATION

The Gibbs energy function of a system is often non-convex and therefore global optimisation schemes must be used to verify that the converged results from thermodynamic equilibrium codes yield a true global minimum and not a false positive. To illustrate this, a couple of scenarios where a false positive is obtained are described in this section.

1. In the fictive system shown in figure 3.3 which can possibly have a solution phase and a stoichiometric phase, the pure stoichiometric phase A_3B_2 and solution phase α are predicted to be stable (as represented by the dashed tangent line). However, they are in fact metastable and a miscibility gap would yield a lower value of G_{sys} .

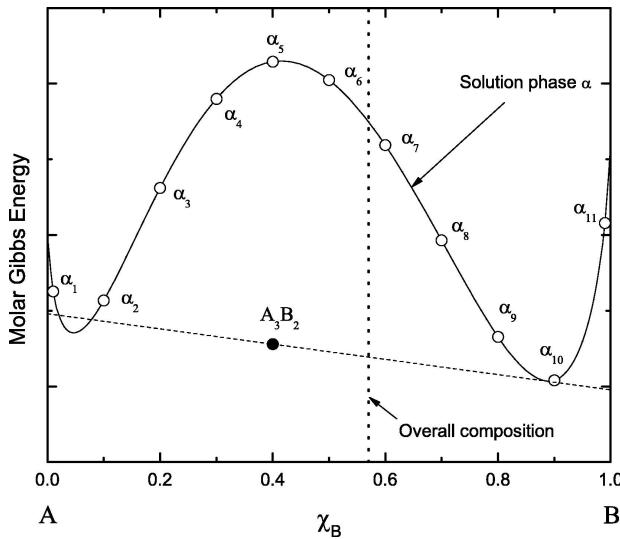


Figure 3.3: Fictive system with miscibility gap showing a possible false positive from thermodynamic equilibrium solver [7].

2. In the fictive system shown in figure 3.4 which can possibly have a three solution phases, the δ phase is believed to be metastable and one must confirm that a combination of β and γ is most stable or if a different combination is more stable. It can be seen that inserting δ phase into the system and replacing one of the other two phases would yield a lower value of G_{sys} .

The above examples show a couple of scenarios of false positives and illustrate why global optimisation strategies are a must for thermodynamic equilibrium solvers. Some of these strategies have been discussed in the following chapters.

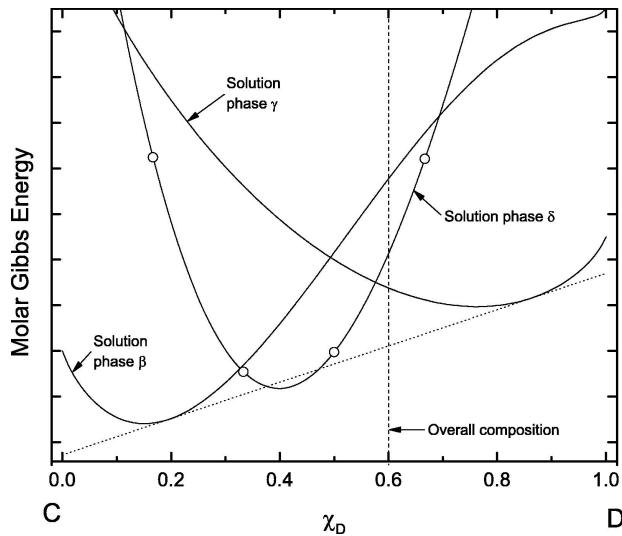


Figure 3.4: Fictive system with three possible phases showing a false positive from thermodynamic equilibrium solver wherein a wrong phase is believed to be present at equilibrium [7].

3.5. SUMMARY OF THERMODYNAMIC EQUILIBRIUM

Achieving thermochemical equilibrium in a system requires satisfaction of several conditions which are as follows:

3.5.1. NECESSARY CONDITIONS

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

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} v_{i,j} + \sum_{\omega=1}^{\Omega} n_{\omega} v_{\omega} \quad (3.56)$$

where, $v_{i,j}$ and v_{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

$$F = C - \Phi + 2 + \Xi \quad (3.57)$$

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 [44], 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

$$\mu_i = \sum_{j=1}^C v_{i,j} \Gamma_j \quad (3.58)$$

3.5.2. SUFFICIENT CONDITIONS

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 equiva-

lent 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

$$\pi_\lambda = \min_{\lambda} \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C v_{i,j} \Gamma_j \right)$$

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

$$\begin{aligned} \sum_{i=1}^{N_\lambda} x_{i(\lambda)} &= 1 \\ x_{i(\lambda)} &\geq 0 \quad \forall i \end{aligned} \tag{3.59}$$

i.e., the sum of mole fraction of all the species in a phase λ 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.

4

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 the World War II that numerical approaches amenable to computer programming were developed. This chapter provides a literature review describes the main methods adopted for chemical equilibrium calculations and reviews the many existing thermodynamic equilibrium codes.

4.1. 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 [42]. 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 [42]. 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.

4.1.1. 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:

$$K = \frac{\prod^{N_p} x_{i,p}^{\nu_i}}{\prod^{N_r} x_{i,r}^{\nu_i}} \quad (4.1)$$

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 (4.1) 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 [42]. 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.

4.1.2. 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 [42, 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 [42, 56]. Another variation 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.

4.1.3. 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 [42, 60]. The significant disadvantages of this method compared to GEM led to it being mostly dismissed by the thermodynamic community until Piro [8] reconsidered a modified form of the method by incorporating principles of the levelling method and employed it in the development of thermochemistry library *Thermochimica* [4].

In the approach taken by Piro, 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 optimising procedure while PGE solves for the roots of a simultaneous system of linear equation [42]. 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 since not been used in any other thermodynamic equilibrium solver.

4.1.4. 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 [61]. 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 [9, 62]. 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:

$$\beta_i = \alpha_i \ln \alpha_i \quad (4.2)$$

which is represented as a piecewise linear approximation as shown in fig. 4.1. Though the Simplex method has been successful in many optimisation problems [63], 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 [42]. As a result, the Simplex method has not received widespread usage in thermodynamic equilibrium calculations.

4.2. 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 4.1. The most noticeable of these codes include SOLGAS [64] 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 [65], ChemSage [54] and FACT [66]. 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

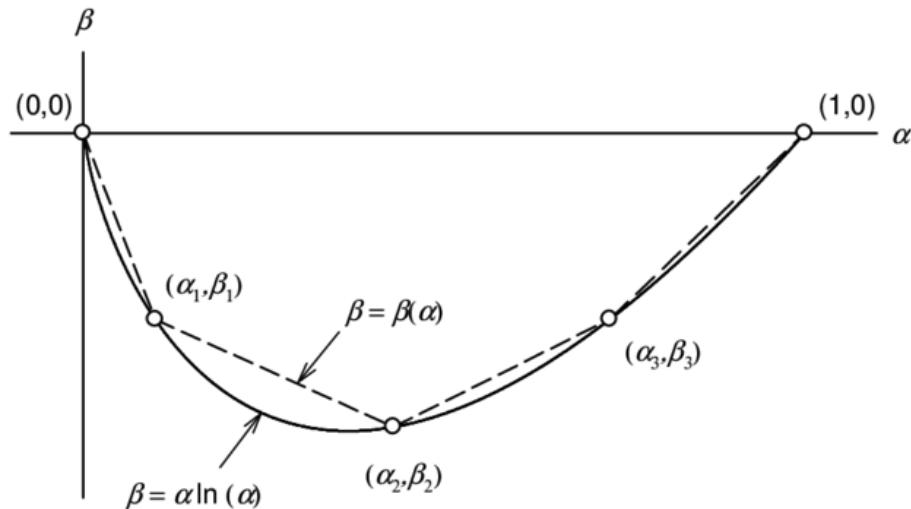


Figure 4.1: Approximation of the function β in Simplex method. Reproduced by Piro [8] from Dantzig *et al.* [9]

FACT a popular choice in the thermodynamics community. FACT merged with ChemSage to create a new standalone software called FactSage [67], which is the current version of the SOLGAS family. Another app in the family, called ChemApp [68, 69], 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 [70] 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 [71] 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.

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 - GEM-

INI [72], ThermoCalc [70] and FactSage [67]. 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.

4.3. 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. [73, 74]. 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.

4.3.1. DETERMINISTIC METHODS

Deterministic optimisation methods exploit the analytical properties of the problem to generate a deterministic sequence of points converging to a global optimum [75]. 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* [76].

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 [76]. 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 [73, 77] 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 [78, 79]. 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 [80].

For the case of thermodynamic equilibrium calculations, Piro and Simunovic [7] have shown that the branch and bound algorithm has proven to be the most promising of all deterministic methods and will be discussed in more detail in chapter 5.

Table 4.1: A review of the major thermodynamic equilibrium codes.

Code / Author	Applications	Optimisation Method	Thermodynamic Models				Charged
			Stoichiometric	Ideal Solution	Non-ideal Solution		
ANGE [81]	Used for coupled simulations of fission product elements. Formerly, SAGE.	GEM	Yes	Yes		Yes	Yes
CALMIX [82]		GEM	Yes	Yes		Yes	No
Cantera [83]	Used for applications including combustion, detonations, electrochemical energy conversion and storage, fuel cells, etc.	GEM	No	Yes		Yes	No
Castier <i>et al.</i> [84]	Simultaneous chemical and phase equilibria in organic chemistry.	GEM	No	Yes		No	No
CatCalc [85]		GEM	Yes	Yes		Yes	No
CEA [86]	Rocket design and combustion	GEM	Yes	Yes		No	No
ChemApp [68]	General purpose. Direct coupling to external softwares.	GEM	Yes	Yes		Yes	Yes
ChemSage [54]	General purpose standalone software	GEM	Yes	Yes		Yes	Yes
ChemSheet [87]	General purpose Microsoft Excel add-in for ChemApp	GEM	Yes	Yes		Yes	Yes
COEXIST [88]	Metallurgy	Levelling	Yes	No		No	No
Dantzig <i>et al.</i> [62]	Combustion	Simplex	No	Yes		No	No
Ebel <i>et al.</i> [89]	Cosmic nebular gases enriched in dust	BNR	Yes	Yes		No	No
ESP [90]	Aqueous, corrosion, oil & gas, pharmaceuticals	LMA	No	Yes		No	No
FACT [66]	General purpose standalone software. Also capable of database development and phase diagram construction.	GEM	Yes	Yes		Yes	Yes
FactSage [91]	General purpose standalone software. Also capable of database development and phase diagram construction.	GEM	Yes	Yes		Yes	Yes
GEMINI 1 [72]	Inorganic chemistry	GEM	Yes	Yes		No	No

Table 4.1: A review of the major thermodynamic equilibrium codes.

Code / Author	Applications	Optimisation Method	Thermodynamic Models				Charged
			Stoichiometric	Ideal Solution	Non-ideal Solution		
GEMINI 2 [72]	Metallurgy, inorganic chemistry, nuclear materials, etc.	GEM	Yes	Yes		Yes	Yes
GEM-Selektor [92]	Geology, nuclear waste management	GEM	Yes	Yes		No	Yes
GEMIPM2K [92]	Direct coupling of GEM-Selektor to external software	GEM	Yes	Yes		No	Yes
Gibbs [93]	Symbolic thermodynamics and phase diagram construction	Convex hull		Yes		Yes	
GLOPEQ [94]	Oil and gas	Modified GEM	No	Yes		No	No
HALTA [95]	Inorganic chemistry	LMA	No	Yes		No	No
HALTAFALL [96]	Inorganic chemistry	LMA	Yes	Yes		No	No
Han <i>et al.</i> [97]	Distillation, chemical extraction	Modified LMA	No	Yes		No	No
HSC [65]	General (uses SOLGASMIX)	GEM	Yes	Yes		Yes	Yes
Koukkari <i>et al.</i> [53]	Modelling of chemical processes and materials. Also accounts for work terms and additional constraints.	Constrained GEM	Yes	Yes		Yes	Yes
Lantagne <i>et al.</i> [57]		GEM	No	Yes		Yes	No
Lee <i>et al.</i> [98]	Organic Chemistry	GEM	No	Yes		Yes	No
Lukas <i>et al.</i> [99]	Phase diagram construction	GEM	Yes	Yes		Yes	No
MatCalc	Metallurgy [100]	GEM		Yes		Yes	
MTDATA [101]	General purpose. Direct coupling to external softwares.	GEM	No	Yes		Yes	No
NUTS [13]	Nuclear fuels	GEM	Yes	Yes		Yes	Yes
OpenCalphad [71]	General purpose, model development.	GEM	Yes	Yes		Yes	Yes
PANDAT [102]	Metallurgy, phase diagram construction	GEM	Yes	Yes		Yes	Yes
Pereira <i>et al.</i> [103]	Fluid phase equilibria, liquid crystals	HEM	No	Yes		No	No
pycalphad [104]	Metallurgy, phase diagram construction	Lower convex hull	Yes	Yes		Yes	No

Table 4.1: A review of the major thermodynamic equilibrium codes.

Code / Author	Applications	Optimisation Method	Thermodynamic Models				Charged
			Stoichiometric	Ideal Solution	Non-ideal Solution		
Rossi <i>et al.</i> [105]	Organic chemical separation	GEM	Yes	Yes		No	No
Schnedler [106]	Integration of thermodynamic equilibrium into finite element calculations and CFD.	GEM	Yes	Yes		No	No
Smith and Missen [107]	Combustion	GEM	No	Yes		No	No
SOLGAS [64]	Metalurgy	GEM	No	Yes		No	No
SOLGASMIX [50]	General purpose	GEM	Yes	Yes		Yes	No
SOLGASMIX-PV [108]	General purpose	GEM	Yes	Yes		Yes	No
SOLGASWATER [52]	General purpose, aqueous	GEM	Yes	Yes		Yes	Yes
Song <i>et al.</i> [109]		Modified GEM	Yes	Yes		No	No
Srinivas <i>et al.</i> [61]		GEM-RTA	No	Yes		No	No
STANJAN / EQUIL [110]	Combustion	PGE	No	Yes		No	No
Storey <i>et al.</i> [56]	Combustion	First order GEM	Yes	Yes		No	No
THERIAK [111]	Combustion, metallurgy, geology	GEM	No	Yes		Yes	No
ThermoCalc [70]	General purpose, model development, phase diagram construction	GEM	Yes	Yes		Yes	Yes
Thermochimica [4]	General purpose, integration in multiphysics codes	GEM	Yes	Yes		Yes	Yes
ThermoSolver [8]	General purpose, integration in multiphysics codes	PGE	Yes	Yes		Yes	Yes
VICTORIA [112]	Fission gas release in nuclear fuels	LMA	Yes	Yes		No	No
White <i>et al.</i> [43]	Organic chemistry, combustion	GEM	No	Yes		No	No
Zeleznik <i>et al.</i> / NASA [48]	Combustion, rocket propellant	NASA	No	Yes		No	No

4.3.2. 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 [113]. 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 [114]. 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 [115] 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 [116].

The Tabu search algorithm proposed by Glover and Laguna [117] 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 [118, 119]. One of the other notable algorithms is the random tunnelling algorithm which is a derivative of the TRUST algorithm. The TRUST algorithm [120] 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 [7] 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 5.

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 [80, 114].

4.3.3. GLOBAL OPTIMISATION REVIEW

A few of the studies on global optimisation in thermodynamic equilibrium calculation have been summarised in tab. 4.2. 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.* [121] applied a hybrid algorithm based on non-linear parametric optimisation routines which solves the Kuhn-Tucker conditions by minimising a quadratic sub-problem with linearised equality and inequality constraints. While the method can equilibrium solutions, a global solution cannot be guaranteed [80]. Another no-

table study is by Nichita *et al.* [77] who tested the tunnelling method for multi-phase equilibrium calculation by direct minimisation of Gibbs energy of the components. Rossi *et al.* [105] 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.* [103] can guarantee the global optimum but requires a differentiable objective function [80].

Amongst the stochastic methods, the most notable works are from Teh and Rangaiah [119] 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 [61] 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 [7] and they found the PSO and the Branch and Bound algorithms to be the most promising stochastic and deterministic methods respectively.

Table 4.2: A review of the global optimisation methods applied to thermodynamic equilibrium calculations.

Method	Class	Problem Formulation
Branch and Bound [122]	Deterministic	Potential energy
Branch and Bound [7]	Deterministic	Gibbs energy
Convex optimisation [105]	Deterministic	Gibbs energy
Differential evolution and tabu search [118]	Stochastic	Gibbs energy
Differential evolution with tabu list [123]	Stochastic	Gibbs energy
Duality based optimisation [103]	Deterministic	Helmholtz energy
Enhanced simulated annealing [124]	Stochastic	Gibbs energy
Enhanced tabu search [119]	Stochastic	Gibbs energy
Genetic algorithm and simulated annealing [125]	Stochastic	Gibbs energy
Genetic algorithm and differential evolution with tabu list [126]	Stochastic	Gibbs energy with reaction
Hybrid artificial immune system [127]	Stochastic	Gibbs energy with reaction
Hybrid genetic algorithm with interior point method [128]	Stochastic	Gibbs energy
Interval analysis [129]	Deterministic	Gibbs energy surface
Nonlinear parametric optimisation [121]	Deterministic	Gibbs energy
Particle swarm optimisation [7, 130]	Stochastic	Gibbs energy
Random tunnelling algorithm [61]	Stochastic	Gibbs energy
Simulated annealing [131]	Stochastic	Gibbs energy
Successive quadratic programming [132]	Deterministic	Gibbs energy
Tunnelling method [77, 133]	Deterministic	Gibbs energy

4.4. INTEGRATION OF THERMODYNAMICS IN MULTIPHYSICS CODES

Recently significant effort has been invested in integrating thermodynamic equilibrium computations in multiphysics codes. To highlight the relevance of coupling thermodynamic equilibrium calculations in multiphysics codes, some of the notable works are discussed in this section.

Piro integrated the thermochemistry solver *Thermochimica* into the Advance Multi-Physics AMP code developed by Oak Ridge National Laboratory [8]. 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 4.2 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 4.3.

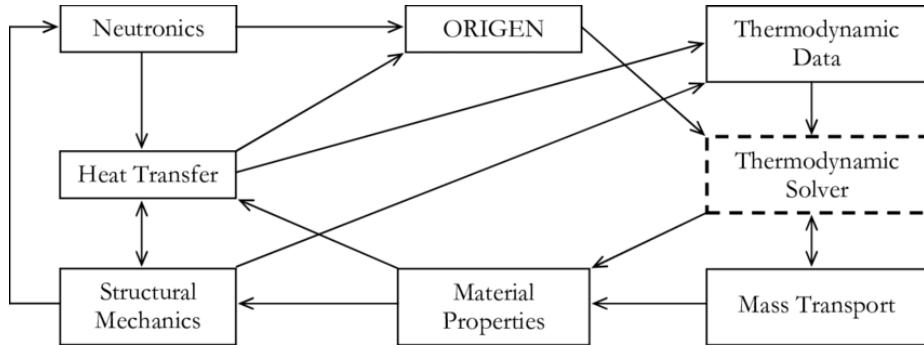


Figure 4.2: A flowchart of the Advanced Multi-Physics (AMP) code illustrating the interaction between the various modules is shown [8].

The software integration of *Thermochimica* with *Bison* was performed by Simunovic and Beßmann [134]. 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 [135] system.

In France, 3D coupled multiphysics simulations of power ramps in Pressurised Water Reactors (PWR) were performed by Konarski *et al.* [136]. 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 of PWR power ramps on Cr-doped UO₂ 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.* [11] have demonstrated the acceleration of *Thermochimica* and coupled it with *Bison* to simulate oxygen diffusion in irradiated fuel rods. Figure 4.4 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

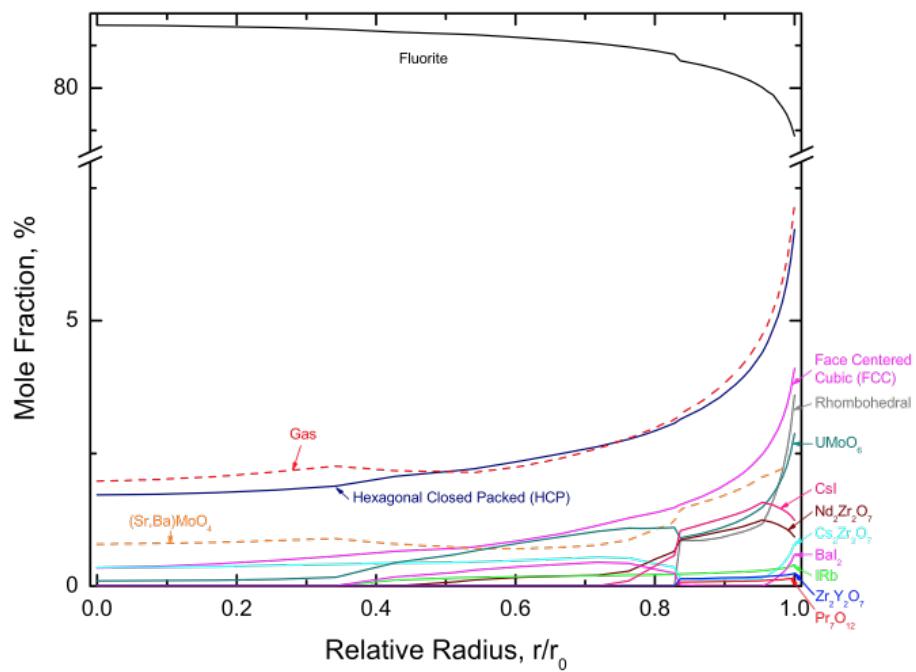


Figure 4.3: The predicted distribution of phases across the pellet is shown for an average pellet burnup of $102 \text{ GW d t(U)}^{21}$. [10].

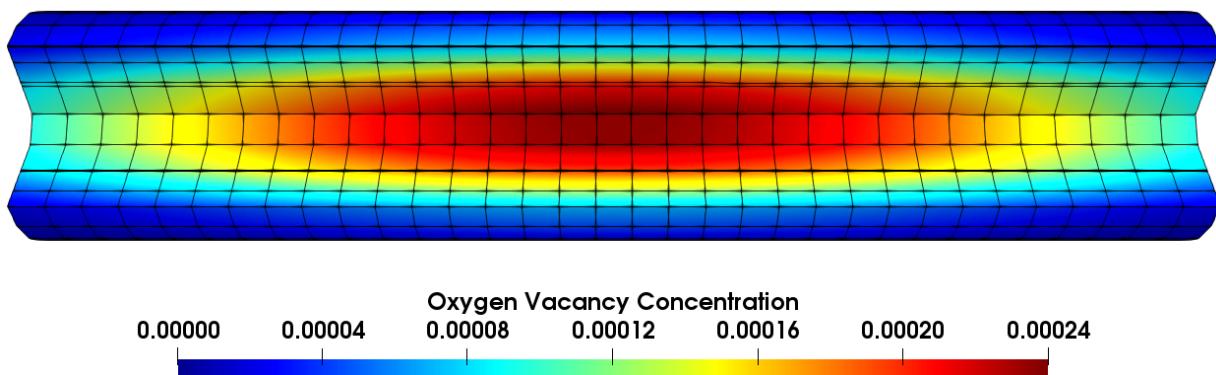


Figure 4.4: Oxygen vacancy concentration in UO_2 fuel obtained by coupling Thermochimica with Bison [11].

Fitzpatrick *et al.* [137] 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.

5

COMPUTATIONAL IMPLEMENTATION

This chapter presents the numerical algorithms that can be employed in computing thermodynamic equilibria. While most of these algorithms embody the concepts previously presented in the 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. This chapter discusses the computational implementation of the proposed thermodynamic equilibrium solver, the top-level architecture of which has been outlined in figure 5.1. The program essentially consists of a parsing and input module to read the required thermodynamic data and system information followed by initialisation routines which provide the initial assemblage to a non-linear GEM routine. The assemblage from the non-linear solver is then checked to ensure global minimum is achieved at which stage the outputs are produced.

5.1. OPPORTUNITIES FOR NOVEL CONTRIBUTIONS

Before delving into the details of a thermodynamic solver, a number of opportunities for novel contributions are presented here. The first and the foremost is integration of the thermodynamic solver within multiphysics framework MOOSE. MOOSE based applications currently leverage the thermochemistry library *Thermochimica* to perform thermodynamic equilibrium calculations. However, since *Thermochimica* was developed in FORTRAN and wasn't developed within the MOOSE framework, coupling it requires writing wrapper classes for every intended application. Not only does this lead to waste of time and resources, it also needs a lot of effort to maintain reliability and achieve desired performance. The new thermodynamic solver will be built within the MOOSE framework and will eliminate the need to write multiple wrapper classes. Furthermore, since it will use the same software quality assurance practices as MOOSE, it will be able to meet the desired performance standards.

In addition to coupling, the development of the new thermodynamic code will try to achieve performance gain through advanced algorithm development. While the GEM method has little scope of improvement in itself, the performance of thermodynamic equilibrium codes can be significantly improved by improving the initialisation routines and focussing on strategies for updating the estimated phase assemblage. The strategies to achieve this goal have been presented in the following sections. Novel contributions can also be made towards global optimisation routines for thermodynamic equilibrium solvers. As shown in section 3.4.3, ensuring that a global minimum of Gibbs energy has been achieved is a challenging task and the global optimisation methods available in the literature have mostly been problem specific. Since a thermodynamic equilibrium solver needs to perform well for

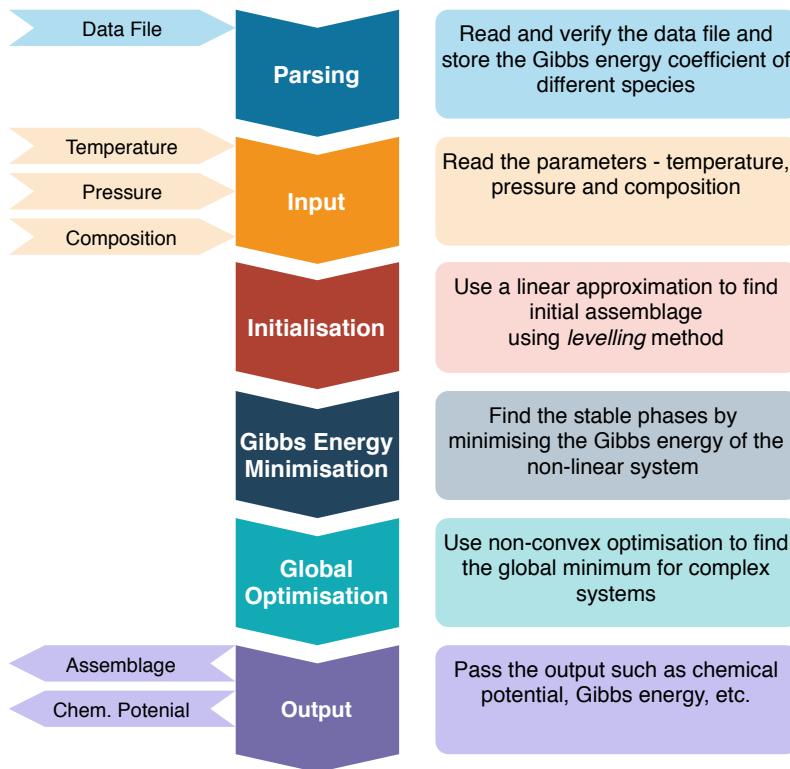


Figure 5.1: Top-level architecture of the proposed thermodynamic equilibrium code.

different kinds of problems, significant contributions can be made by implementing robust global optimisation algorithms. These strategies are discussed in the following sections.

5.2. PARSING AND INPUT

Calculation of thermodynamic equilibrium requires a thermodynamic database, which includes Gibbs energy expressions of the different phases and species that can exist in the system. These thermodynamic databases are developed using the well established CALculation of PHase Diagrams (CAL-PHAD) method [138] and are available in different formats, the most commonly used being Thermo-Calc (*.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 5.2 and consists of a header block followed by information blocks for every possible phase in the system.

The data file parser for the thermodynamic equilibrium part of Yellowjacket has been developed in C++ and it performs the extraction of free energy expressions from *.dat thermodynamic database files (ChemSage format) and exports a list of free energy terms for each phase (or a user specified subset of phases). The data-file parser has the following capabilities:

- Extract system information from *.dat files and ensure that the data is consistent with the inputs and appropriate for consideration.
- Extract Gibbs energy terms for different phases and all the species within each phase.
- Store the Gibbs energy terms to ensure that terms corresponding to each phase can be selectively and conveniently retrieved.

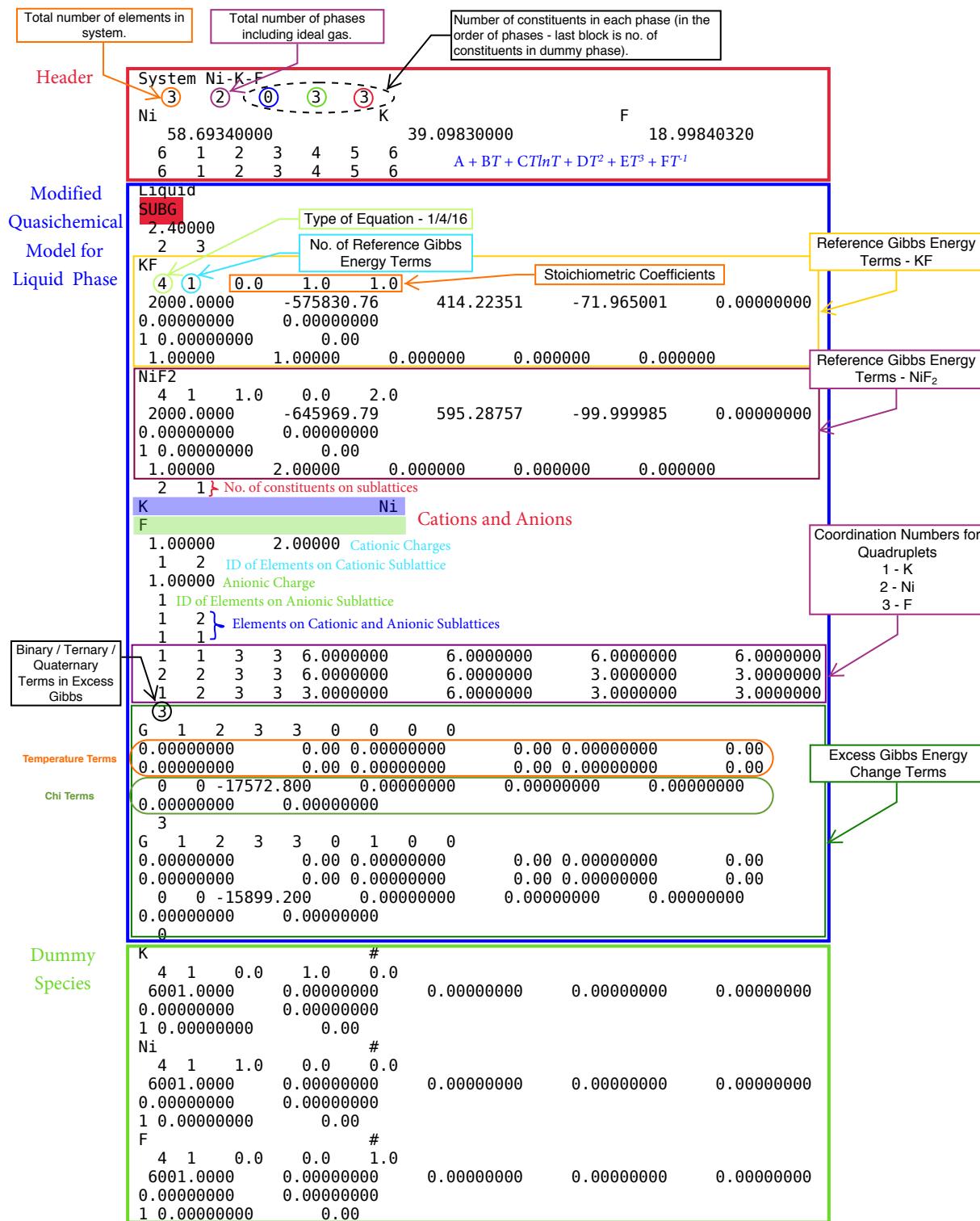


Figure 5.2: A marked-up example of a ChemSage data file of the Ni–K–F system [12]

Another requirement for Gibbs energy minimisation is physical parameters of the system, namely, the temperature, pressure and composition. Within a multiphysics framework, these informations are required for each finite element at every time-step. In the context of the proposed Gibbs energy minimiser, the system inputs are provided by MOOSE which passes the information at the time the Gibbs energy minimiser is called. For standalone applications, this information can be provided as an input through the MOOSE input file.

5.3. 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 need for providing initial estimates of the number of moles of phases and the mole fractions of the species in those phases 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. Providing such initial estimates relied on the intuition of the user and was often very inconvenient for the user, especially when working with complex systems and/or systems where finding estimates from intuition was not straightforward. To overcome the need for the user to enter the initial estimates, Eriksson and Thompson [59] proposed an initialisation algorithm called *levelling* that has found widespread application in thermodynamic equilibrium softwares. Subsequently, Piro and Simunovic [14] proposed the *post-levelling* method as an extension to levelling in order to further improve the initial estimate.

5.3.1. LINEAR SOLVER

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 5.3.

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 (5.1)

$$\hat{G}_i = \frac{G_j}{\sum_{j=1}^C v_{ij}} \quad (5.1)$$

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 [14]. At iteration $m+1$, the adjustment to be applied

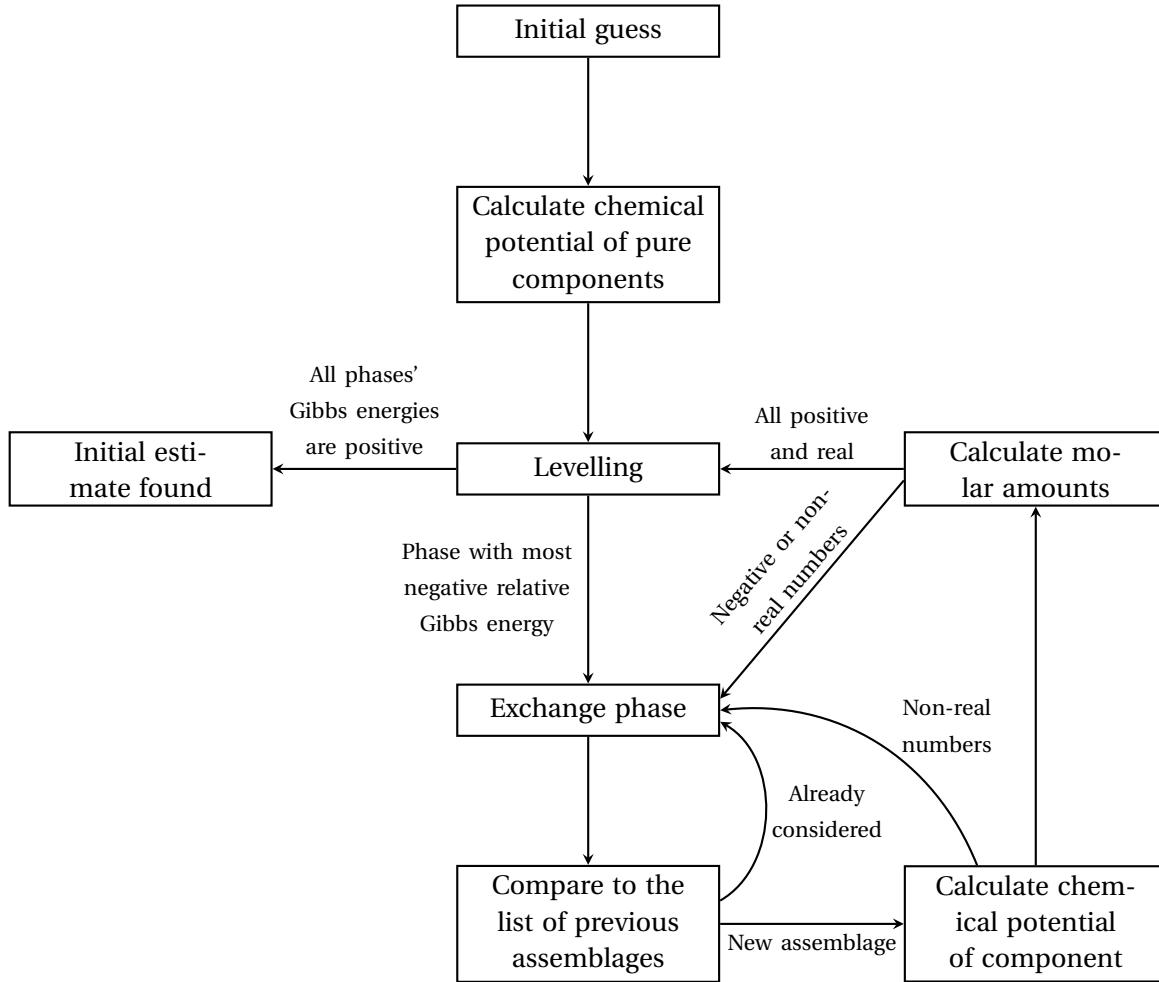


Figure 5.3: Illustration of the levelling algorithm [13]

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

$$\begin{aligned} d\hat{G}_i^{m \rightarrow m+1} &= \sum_{j=1}^C c_{i,j} d\Gamma_j^{m \rightarrow m+1} \\ \hat{G}_i^{m+1} &= \hat{G}_i^m - d\hat{G}_i^{m \rightarrow m+1} \end{aligned} \quad (5.2)$$

where, $c_{i,j}$ 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 [14]

$$\mathbf{A}^T \mathbf{n} = \mathbf{b} \quad (5.3)$$

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 5.3 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 (5.3) 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:

$$\mathbf{A}^T \boldsymbol{\Gamma} = \boldsymbol{\mu} \quad (5.4)$$

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 (5.2). 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 [14]. This method has been described in sec. 5.3.3

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 5.4. 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 UO₂ as the phase with the most negative relative Gibbs energy and arbitrarily choosing solid UO₃ 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 U₃O₈ is negative with respect to the combination of solid UO₂ and solid UO₃, 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 5.4, 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.

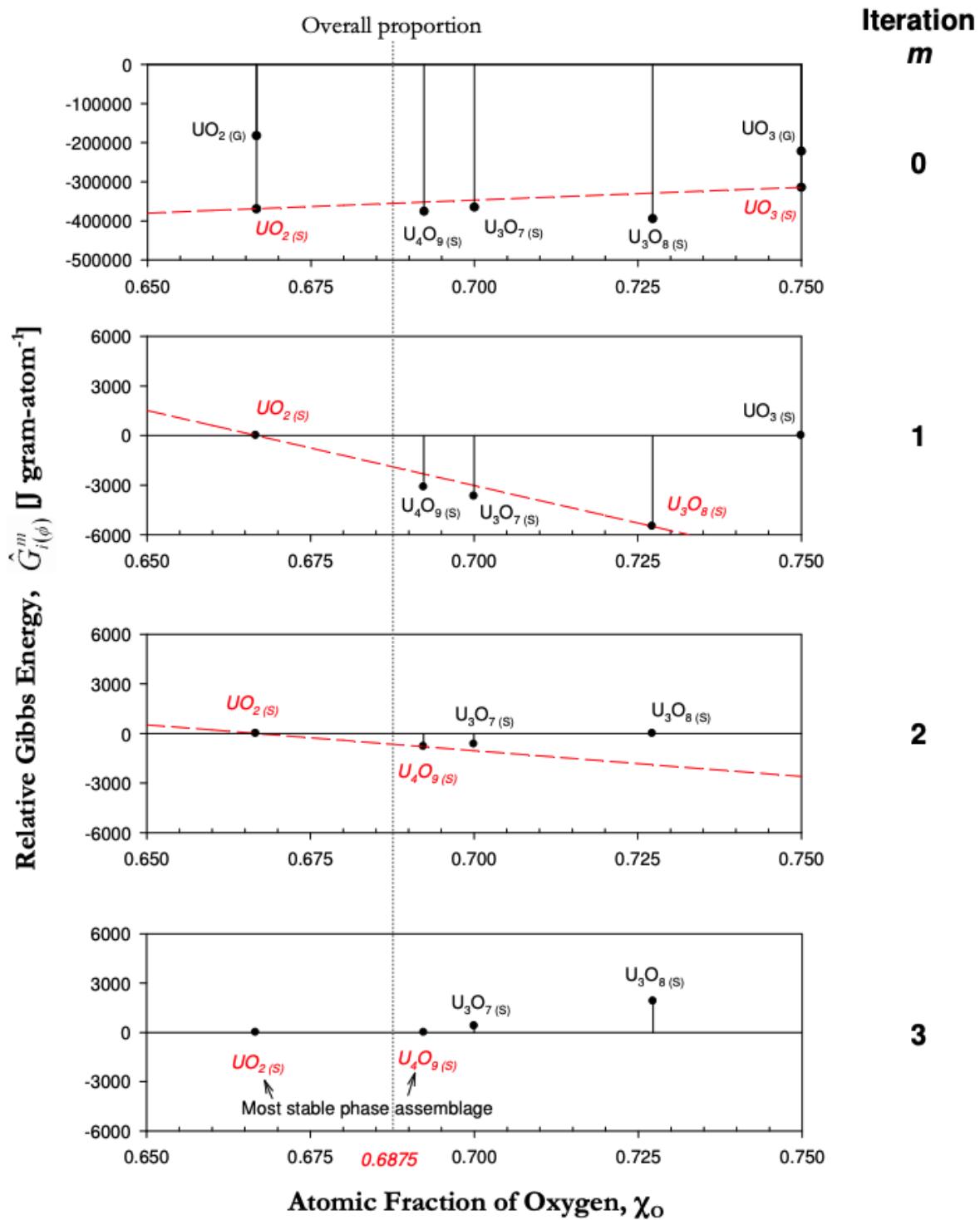


Figure 5.4: Illustration of the levelling process for a binary system of U–O at each iteration (1 mol U, 2.2 mol O, 298.15 K, 1 atm) [8].

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.

5.3.2. POST-LEVELLING

Developed by Piro and Simunovic [14], the post-levelling method is an extension to the levelling method and can be used to refine the assemblage provided by the levelling method by accounting for the ideal mixing of the phases and relaxing the assumption that the phases are pure. Thus, post-levelling acts as an intermediate step between levelling and the non-linear solver. While post-levelling resembles the non-linear solver in the incorporation of compositional component in the chemical potential of the solution phase constituents, the primary distinction between them is that post-levelling considers only dominant phases identified by levelling as compared to the non-linear solver which considers all the constituents. Furthermore, the non-linear solver also considers non-ideal behaviour.

The chemical potential term in post-levelling takes the following form:

$$\begin{aligned}\mu_{i(\lambda)} &= g_{i(\lambda)}^0 + RT \ln(x_{i(\lambda)}) \\ x_{i(\lambda)} &= \frac{n_{i(\lambda)}}{\sum_{k=1}^{N_\lambda} n_{k(\lambda)}}\end{aligned}\quad (5.5)$$

where N_λ is the number of constituents in solution phase λ identified by levelling and is less than the actual constituents in the phase. The element potentials can then be computed using equation (5.4) and an iterative process similar to levelling can be followed.

A demonstration of the post-levelling method in predicting the element potentials of combustion products from a coal fire shows that compared to levelling, post levelling calculations provide values much closer to the equilibrium values. As a result, the rate of convergence of the non-linear solver improves by a large factor. While exact gains depend on the non-linear solver, line-search algorithm and the strategy for updating the estimated phase assemblage, relative performance gains can be easily envisaged even though post-levelling process incurs additional computational cost. This can be attributed to the fact that the cost of post-levelling is negligible in comparison to the cost of a single iteration in a non-linear solver [14].

5.3.3. EUCLIDEAN NORM

The Euclidean norm method was proposed by Piro and Simunovic [14], 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 [14]. 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:

$$c_{\omega,j} = \frac{c_{\omega,j}}{\sum_{k=1}^E x_{i(\omega)} v_{\omega,j}} \quad (5.6)$$

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

$$c_{\lambda,j} = \frac{\sum_{i=1}^{N_\lambda} v_{i,j}}{\sum_{i=1}^{N_\lambda} \sum_{k=1}^E x_{i(\lambda)} v_{i,k}} \quad (5.7)$$

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

$$\|c_\phi\|_2 = \sqrt{\sum_{j=1}^E (c_{\phi,j} - c_{\phi,j}^*)^2} \quad (5.8)$$

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.

As shown in figure 5.5, the overall computational expense of thermodynamic calculations is significantly reduced when post-levelling and Euclidean norm methods are utilised [14]. These performance gains can offer a significant advantage when considering multiphysics simulations where thermodynamic equilibrium is often the most computationally expensive calculation.

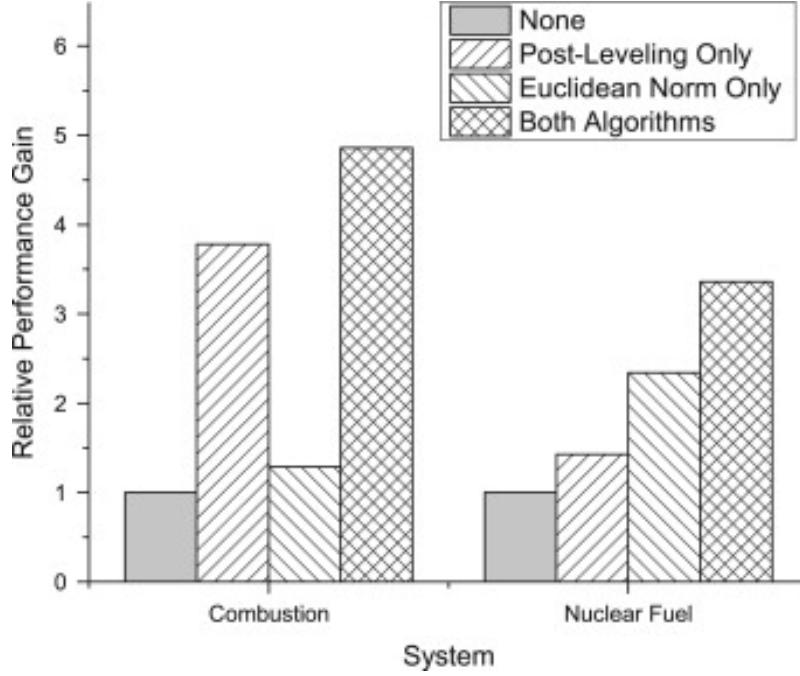


Figure 5.5: Performance gains when employing post-levelling and Euclidean-norm algorithms [14].

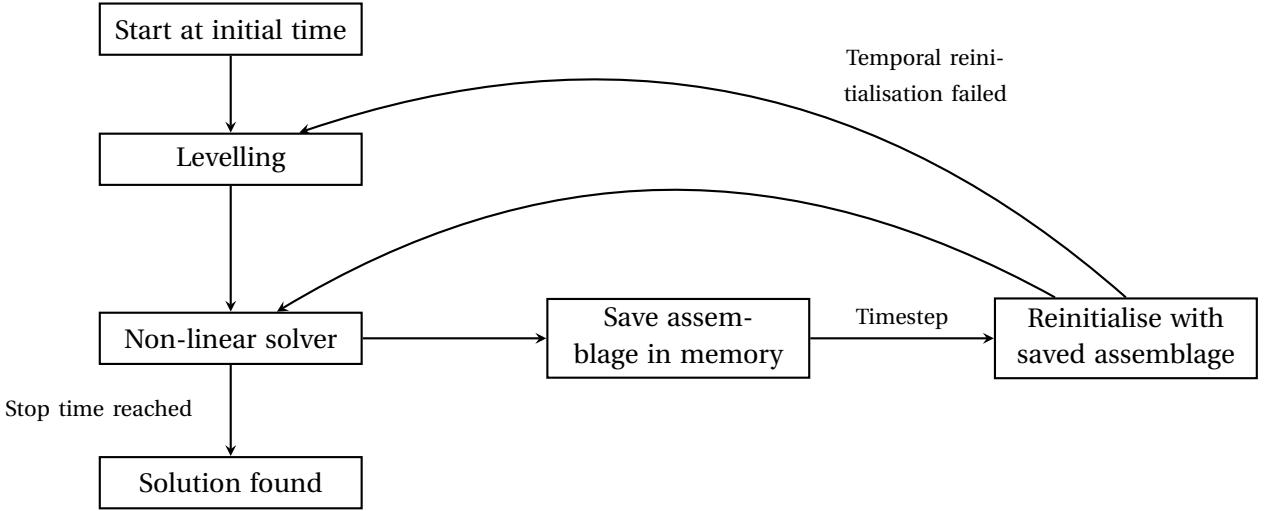


Figure 5.6: Illustration of the temporal series initialisation algorithm.

5.3.4. TEMPORAL SERIES ESTIMATE

While in most cases levelling and post-levelling methods can provide initial assemblages close to the final assemblage, using the assemblage from a previous time step in multiphysics codes can often provide much closer estimates to the final assemblage. In time-dependent multiphysics simulations, this can result in significant performance gains as has been recently shown through the implementation of this strategy in *Thermochimica* [11]. These performance gains can be attributed to the fact that the convergence of the non-linear solver can be significantly accelerated by providing initial estimates close enough to the final assemblage. This temporal initialisation strategy has been illustrated in figure 5.6

The details of the implementation of the temporal initialisation strategy in *Yellowjacket* have not yet been set in stone but, based on *Thermochimica* acceleration results obtained by Poschmann et al. [11], a significant performance gain is foreseen which justifies the use of this strategy especially in coupled multiphysics problems where thermodynamic equilibrium calculations are impediment to significant performance gains. However, this might also lead to a drastic increase in memory requirement and a compromise must be made between computing time gains and increased memory requirements.

5.3.5. BOUNDARY VALUE ESTIMATE

For the case where Gibbs energy minimisation is performed on a 2D/3D mesh, very good initial estimates can conceivably be provided to the non-linear solver by exploiting the results from the neighbouring solutions in space at the same time step. As an example, the final assemblage of element A on the finite element mesh shown in figure 5.7 can be used as the initial assemblage for element B. This initialisation scheme relies on the principles of continuum between adjacent cells, i.e., if the mesh is sufficiently resolved, the difference between system potentials (temperature, pressure and chemical potentials) between two neighbouring cells must be small.

While this approach is well suited to simulations on finite element meshes and reduces the need to re-evaluate the estimated assemblage of stable phases, it might lead to a less than optimal estimate for elements close to a moving interface (for example, close to a melting boundary). Also, this approach does not lend itself well to parallel computing using MPI and thus might actually be ineffective for large

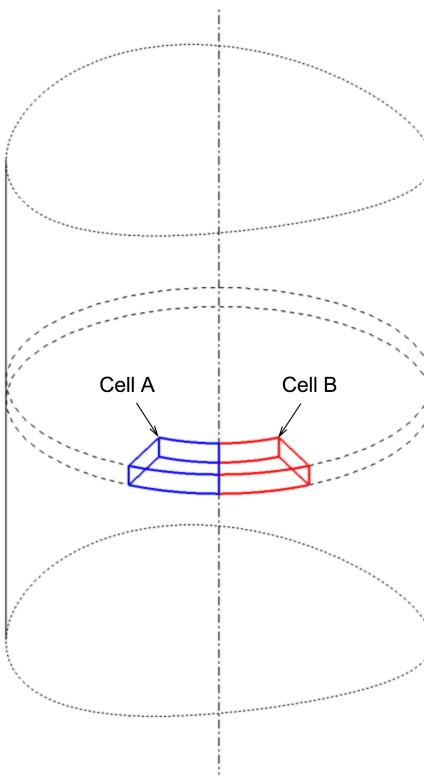


Figure 5.7: Illustration of the boundary value initialisation on a finite element mesh [15].

problems where MPI can significantly speed up calculations. However, the approach is a potential avenue that can be explored but is not the primary focus.

5.4. 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).

The GEM method presented by White *et al.* [45] can constrain conditions 1 and 2 while optimising condition 3. The subsidiary condition B is inherent in the method and is always satisfied but care must be taken to ensure that subsidiary condition A is met. However, in most cases, condition 1 is not initially satisfied and GEM optimises conditions 1 and 3 simultaneously [64]. The derivation of the GEM method is given below [8].

The quantity to be minimised, the integral Gibbs energy of the system, depends on the molar amounts n_i of the species in the system, which are subject to the mass balance constraints given by the individual components in the system. In dimensionless form, the Gibbs energy can be represented as:

$$G^m = \sum_{\lambda=1}^{\Lambda} \left(\frac{\mu_{i(\lambda)}^m}{RT} \right) n_{i(\lambda)}^m + \sum_{\omega=1}^{\Omega} \left(\frac{\mu_{i(\omega)}^m}{RT} \right) n_{i(\omega)}^m \quad (5.9)$$

where, the variable G^m represents the Gibbs energy at iteration m and is expressed in the dimensionless form as by doing so we can avoid the division by RT at every iteration step, thus increasing efficiency. It must be noted that the chemical potential of the stoichiometric phase, $\mu_{i(\omega)}^m$, is by definition fixed but the superscript has been retained for the uniformity of notation. The mass balance for component j is given as:

$$b_j^m = \sum_{\lambda=1}^{\Lambda} n_{i(\lambda)}^m v_{i,j} + \sum_{\omega=1}^{\Omega} n_{i(\omega)}^m v_{\omega,j} \quad (5.10)$$

where b_j^m is the estimated molar quantity and not the true mass of element j in the system [8]. The mass constraint (condition A) requires that

$$b_j - b_j^m = 0 \quad (5.11)$$

To arrive at the quadratic approximation of the Gibbs energy function, a Taylor expansion is performed:

$$\begin{aligned} Q^{m+1} &= G^m + \sum_{\omega=1}^{\Omega} \delta_{\omega} \frac{\partial G^m}{\partial n_{\omega}^m} \Bigg|_{n_{\omega}^m = n_{\omega}^{m+1}} \\ &+ \sum_{\lambda=1}^{\Lambda} \delta_i \frac{\partial G^m}{\partial n_{i(\lambda)}^m} \Bigg|_{n_{i(\lambda)}^m = n_{i(\lambda)}^{m+1}} \\ &+ \frac{1}{2} \sum_{\omega=1}^{\Omega} \delta_{\omega}^2 \frac{\partial^2 G^m}{\partial (n_{\omega}^m)^2} \Bigg|_{n_{\omega}^m = n_{\omega}^{m+1}} \\ &+ \frac{1}{2} \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} \sum_{l=1}^{N_{\lambda}} \delta_i \delta_l \frac{\partial^2 G^m}{\partial n_{i(\lambda)}^m \partial n_{l(\lambda)}^m} \Bigg|_{n_{i(\lambda)}^m = n_{i(\lambda)}^{m+1}} \end{aligned} \quad (5.12)$$

where $\delta_i = n_{i(\lambda)}^{m+1} - n_{i(\lambda)}^m$ and $\delta_{\omega} = n_{\omega}^{m+1} - n_{\omega}^m$. By the definition of chemical potential, the first order derivatives take the following form:

$$\frac{\partial G^m}{\partial n_{i(\lambda)}^m} = \frac{\mu_{i(\lambda)}^m}{RT} \quad (5.13)$$

$$\frac{\partial G^{\omega}}{\partial n_{\omega}^m} = \frac{\mu_{\omega}^m}{RT} \quad (5.14)$$

and the second order derivatives can be represented as:

$$\frac{\partial^2 G^m}{\partial (n_{i(\lambda)}^m)^2} = \frac{1}{n_{i(\lambda)}^m} - \frac{1}{n_\lambda^m} \quad (5.15)$$

$$\left. \frac{\partial^2 G^m}{\partial n_{i(\lambda)}^m \partial n_{l(\lambda)}^m} \right|_{l \neq i} = -\frac{1}{n_\lambda^m} \quad (5.16)$$

$$\frac{\partial^2 G^m}{\partial (n_\omega^m)^2} = 0 \quad (5.17)$$

Substituting these expressions into the Taylor expansion results in the following:

$$\begin{aligned} Q^{m+1} &= G^m + \sum_{\omega=1}^{\Omega} \delta_\omega \frac{\mu_\omega^m}{RT} \\ &\quad + \sum_{\lambda=1}^{\Lambda} \delta_\lambda \frac{\mu_{i(\lambda)}^m}{RT} \\ &\quad + \frac{1}{2} \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_\lambda} n_{i(\lambda)}^m \left(\frac{\delta_i}{n_{i(\lambda)}^m} - \frac{\delta_\lambda}{n_\lambda^m} \right)^2 \end{aligned} \quad (5.18)$$

where, $\delta_\lambda = n_\lambda^{m+1} - n_\lambda^m$

To find the next approximation to the desired solution, we can minimise Q^{m+1} subject to the mass balance constraint and restricting n to positive values [45]. The constrained optimisation problem can be solved using the Lagrange method of undetermined multipliers [58] where the Lagrangian function in terms of the objective function and the constraints is written as follows:

$$L = Q^{m+1} + \sum_E \pi_{m+1}^j (b_j - b_j^m) \quad (5.19)$$

where the undetermined Lagrange multipliers are denoted by π_{m+1}^j . This formulation allows for the mass balances to be corrected when the initial estimates of mole numbers do not satisfy the mass balance constraints thereby helping in simultaneously minimising the Gibbs energy of the system and residuals of the mass constraints [8]. The minimum of the Lagrangian can be found by finding the points where the partial derivatives of the Lagrangian with respect to the molar amounts and the Lagrange multiplier are zero. This results in the following system of equations:

$$\frac{\partial L}{\partial n_{i(\lambda)}^m} = \frac{\mu_{i(\lambda)}^m}{RT} - \sum_{j=1}^E \nu_{i,j} \pi_{m+1}^{j+1} + \left(\frac{n_{i(\lambda)}^{m+1}}{n_{i(\lambda)}^m} - \frac{n_\lambda^{m+1}}{n_\lambda^m} \right) = 0 \quad (5.20)$$

$$\frac{\partial L}{\partial n_\omega^m} = \frac{\mu_\omega^m}{RT} - \sum_{j=1}^E \nu_{\omega,j} \pi_{m+1}^j = 0 \quad (5.21)$$

Rearranging and solving the above equation gives:

$$n_{i(\lambda)}^{m+1} = n_{i(\lambda)}^m \left(-\frac{\mu_{i(\lambda)}^m}{RT} + \frac{n_\lambda^{m+1}}{n_\lambda^m} + \sum_{j=1}^E \nu_{i,j} \pi_{m+1}^{j+1} \right) \quad (5.22)$$

and using the mass balance:

$$b_j = \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} \left(-\frac{\mu_{i(\lambda)}^m}{RT} + \frac{n_{\lambda}^{m+1}}{n_{\lambda}^m} + \sum_{j=1}^E v_{i,j} \pi_j^{m+1} \right) n_{i(\lambda)}^m v_{i,j} + \sum_{\omega=1}^{\Omega} n_{\omega}^m v_{\omega,j} \quad (5.23)$$

The above equation can be rearranged to arrive at the form used by Eriksson and Rosén [51]:

$$\sum_{j=1}^E r_{j,k} \pi_j^{m+1} + \sum_{\lambda=1}^{\Lambda} \pi_{\lambda}^{m+1} \varphi_{\omega,j}^m + \sum_{\omega=1}^{\Omega} n_{\omega}^m v_{\omega,j} = b_j + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} \left(\frac{\mu_{i(\lambda)}^m}{RT} - 1 \right) n_{i(\lambda)}^m v_{i,j} \quad (5.24)$$

where,

$$\begin{aligned} r_{j,k} &= \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)}^m v_{i,j} v_{i,k} \\ \varphi_{\omega,j}^m &= \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)}^m v_{i,j} \\ \pi_{\lambda}^{m+1} &= \left(\frac{n_{\lambda}^{m+1}}{n_{\lambda}^m} \right) - 1 \end{aligned}$$

The form of the minimisation problem in equation (5.24) is relevant to programming since the set of the undetermined Lagrange multipliers π_j^{m+1} are in fact the chemical potentials and the mass balance can be enforced using the undetermined Lagrange multipliers π_{λ}^{m+1} . The chemical potential of the elements can then be computed using:

$$\sum_{j=1}^E \pi_j^{m+1} \varphi_{\lambda,j}^m = \sum_{i=1}^{N_{\lambda}} \left(\frac{\mu_{i(\lambda)}^m}{RT} \right) n_{i(\lambda)}^m \quad (5.25)$$

Conversely, the chemical potential of the system components can be constrained since the chemical potential of pure stoichiometric phases is fixed [8]:

$$\frac{\mu_{\omega}^m}{RT} = \sum_{j=1}^E v_{\omega,j} \pi_j^{m+1} \quad (5.26)$$

5.4.1. MATRIX REPRESENTATION

The system of $(E + \Lambda + \Omega)$ linear equations formed by equations (5.24), (5.25) and (5.26) contains $(E + \Lambda + \Omega)$ variables and can conveniently be represented in the matrix representation as follows:

$$\mathbf{H} \cdot \boldsymbol{\pi} = \boldsymbol{\zeta} \quad (5.27)$$

where the Hessian matrix (\mathbf{H}) can be written as:

$$\mathbf{H} = \begin{bmatrix} r_{j=1,k=1} & \dots & r_{j=1,k=C} & \phi_{j=1,\lambda=1} & \dots & \phi_{j=1,\lambda=\Lambda} & v_{j=1,\omega=1} & \dots & v_{j=1,\omega=\Omega} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ r_{j=C,k=1} & \dots & r_{j=C,k=C} & \phi_{j=C,\lambda=1} & \dots & \phi_{j=C,\lambda=\Lambda} & v_{j=C,\omega=1} & \dots & v_{j=C,\omega=\Omega} \\ \phi_{\lambda=1,j=1} & \dots & \phi_{\lambda=1,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \phi_{\lambda=\Lambda,j=1} & \dots & \phi_{\lambda=\Lambda,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ v_{\omega=1,j=1} & \dots & v_{\omega=1,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ v_{\omega=\Omega,j=1} & \dots & v_{\omega=\Omega,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \end{bmatrix} \quad (5.28)$$

and $\boldsymbol{\pi}$ and $\boldsymbol{\zeta}$ which denote the unknown and constraint vectors respectively take the following forms:

$$\boldsymbol{\pi} = \begin{bmatrix} \pi_{j=1}^{m+1} \\ \vdots \\ \pi_{j=E}^{m+1} \\ \pi_{\lambda=1}^{m+1} \\ \vdots \\ \pi_{\lambda=\Lambda}^{m+1} \\ \pi_{\omega=1}^{m+1} \\ \vdots \\ \pi_{\omega=\Omega}^{m+1} \end{bmatrix} \quad (5.29)$$

$$\boldsymbol{\zeta} = \begin{bmatrix} b_{j=1} + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} \left(\frac{\mu_{i(\lambda)}^m}{RT} - 1 \right) n_{i(\lambda)}^m v_{i,j=1} \\ \vdots \\ b_{j=E} + \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} \left(\frac{\mu_{i(\lambda)}^m}{RT} - 1 \right) n_{i(\lambda)}^m v_{i,j=E} \\ \sum_{i=1}^{N_{\lambda=1}} \left(\frac{\mu_{i(\lambda=1)}^m}{RT} - 1 \right) n_{i(\lambda=1)}^m \\ \vdots \\ \sum_{i=1}^{N_{\lambda=\Lambda}} \left(\frac{\mu_{i(\lambda=\Lambda)}^m}{RT} - 1 \right) n_{i(\lambda=\Lambda)}^m \\ \frac{\mu_{\omega=1}^m}{RT} \\ \vdots \\ \frac{\mu_{\omega=\Omega}^m}{RT} \end{bmatrix} \quad (5.30)$$

The unknown column vector $\boldsymbol{\pi}$ is computed through a linear equation solver and used to update the molar quantities of each species and phase at each iteration. The matrix \mathbf{H} being a Hessian is necessarily square and symmetric and solving equation (5.27) can be viewed as solving the Karush-Kahn-Tucker (KKT) optimality condition via Newton's method [58].

5.4.2. NUMERICAL IMPLEMENTATION

The system of non-linear equations can be solved using either the Newton-Raphson method. Newton-Raphson method depends on solving equation (5.27) and is an $\mathcal{O}(N^3)$ operation. 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 [15]:

$$\|f\|^2 = \sum_{j=1}^C \left(\sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} v_{i,j} + \sum_{\omega=1}^{\Omega} n_{\omega} v_{\omega,j} - b_j \right)^2 + \sum_{\lambda=1}^{\Lambda} \left(\sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \left| \mu_{i(\lambda)} - \sum_{j=1}^C v_{i,j} \Gamma_j \right| \right)^2 + \sum_{\omega=1}^{\Omega} \left(g_{\omega} - \sum_{j=1}^C v_{\omega,j} \Gamma_j \right)^2 \quad (5.31)$$

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 can be decided.

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

$$\min_{\alpha} f(\mathbf{x}^m + \alpha \mathbf{p}^m) \quad (5.32)$$

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 are a set of inequalities for performing inexact line search 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:

$$f(\mathbf{x}^m + \alpha^m \mathbf{p}^m) \leq f(\mathbf{x}^m) + c_1 \alpha^m (\mathbf{p}^m)^T \nabla f(\mathbf{x}^m) \quad (5.33)$$

$$-(\mathbf{p}^m)^T \nabla f(\mathbf{x}^m + \alpha^m \mathbf{p}^m) \leq -c_2 (\mathbf{p}^m)^T \nabla f(\mathbf{x}^m) \quad (5.34)$$

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].

5.4.3. 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 [15] will be adopted. This strategy has been illustrated in figure 5.8

5.4.4. CONVERGENCE CRITERION

The convergence of the solver is tested in accordance with conditions for convergence described in chapter 3. 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 are 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 can help 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 fig. 5.9

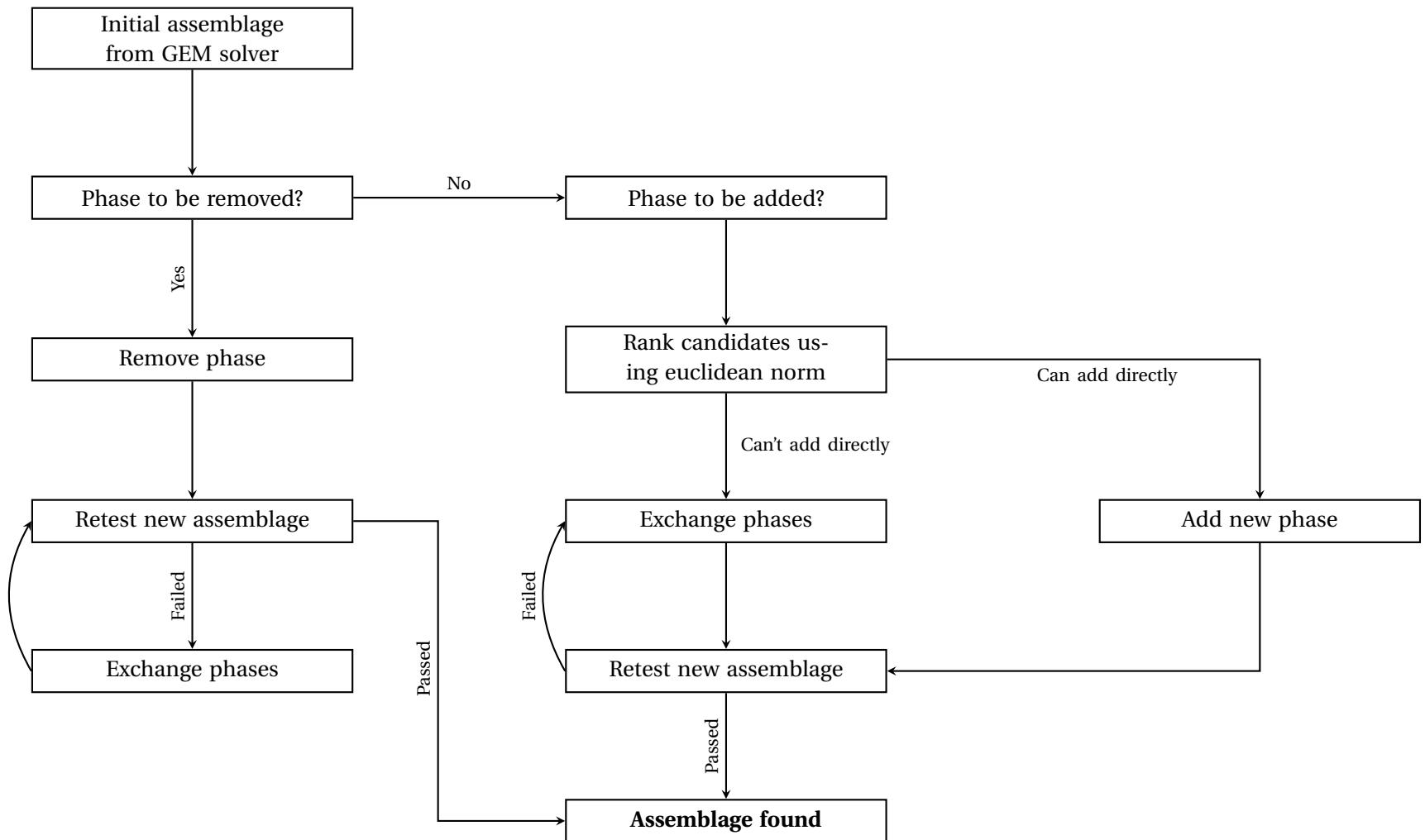


Figure 5.8: Illustration of the proposed methodology for updating the phase assemblage. Adapted from Piro [15].

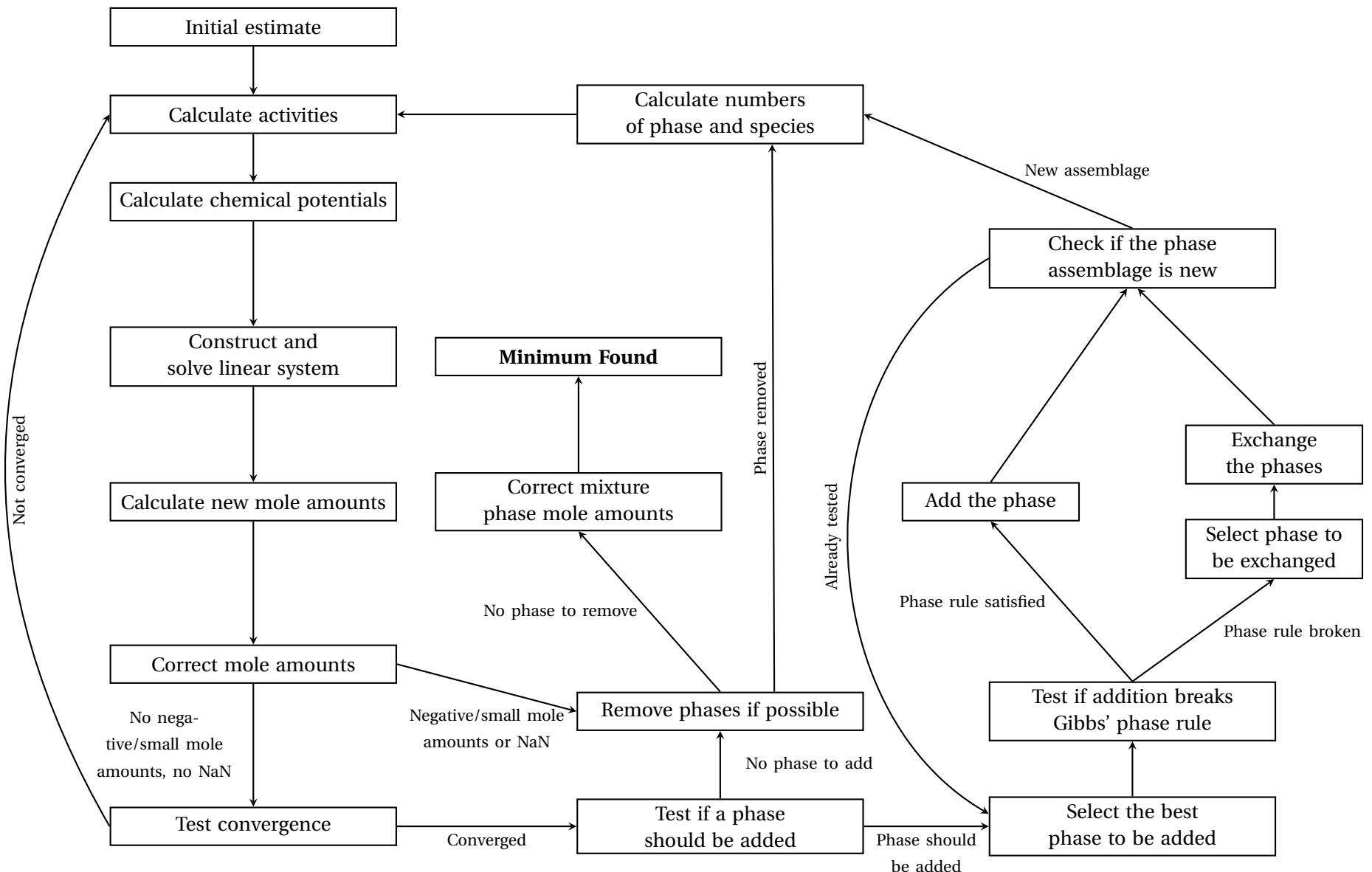


Figure 5.9: Illustration of the proposed Gibbs energy minimisation algorithm. Adapted from Loukusa [13].

5.5. GLOBAL OPTIMISATION

The computation of thermodynamic equilibrium, as discussed in sec. 3.4.3, is a global optimisation problem where the focus is on systems that can attain equilibrium state under conditions of constant temperature and pressure, where the global minimum value of the Gibbs energy describes the true equilibrium state. The problem can be stated as follows [76]:

Objective. Given C components participating in up to Φ potential phases under isothermal and isobaric conditions find the mole vector \mathbf{n} that minimises the value of the Gibbs energy while also satisfying the appropriate material balance constraints.

Constraints. The mole fraction of a species in phase λ , $x_{i(\lambda)}$, must satisfy the following linear equality and inequality constraints

$$\sum_{i=1}^{N_\lambda} x_{i(\lambda)} = 1 \quad x_{i(\lambda)} > 0 \quad \forall i \quad (5.35)$$

The component set is represented by the index set $C = \{i\}$ and the elements that constitute these components are given by $E = \{e\}$. The set of phases is denoted by $\Phi = \{\lambda\}$ where it is composed of solution and stoichiometric phases, labelled Λ and Ω respectively, so that $\Phi \equiv \Lambda \cup \Omega$.

The conditions for thermodynamic equilibrium discussed in section 3.4.1 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* [25] or *tangent plane distance function* [25, 80]. The driving force for solution phase λ is represented by π_λ and is computed as [7]:

$$\pi_\lambda = \min_x \sum_{i=1}^{N_\lambda} \left(\mu_{i(\lambda)} - \sum_{j=1}^C v_{i,j} \Gamma_j \right) \quad (5.36)$$

which is subject to the mass balance constraints. The sufficient condition for equilibrium requires that the driving force π_λ computed with equation (5.36) is positive for all phases believed to be metastable and zero for all the stable phases. According to Hillert [139], 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 and forms the basis of the methods discussed below.

This section describes three global optimisation methods that have been shown to be promising in thermodynamic equilibrium calculations. These methods are both stochastic - *particle swarm optimisation* and deterministic - *grid construction* and *branch and bound*.

5.5.1. PARTICLE SWARM OPTIMISATION

Particle Swarm Optimisation (PSO) has been inspired by the swarm like behaviour in the animal kingdom such the migration of swarm of bees [140]. In this method, a population of candidate solutions, dubbed particles, moves around the search space as function of the position and velocity of the particle. the movement of each particle is influenced by it's best known local position and guided towards the best global position as other particles find better solutions.

The position vector of the particles at iteration m , \mathbf{x}_p^m , is updated based on the velocity vector, \mathbf{v}_p^m , by [7]:

$$\mathbf{v}_p^m = \psi \mathbf{v}_p^{m-1} + \phi_p r_p (\mathbf{x}_p^* - \mathbf{x}_p^m) + \phi_s r_s (\mathbf{x}_s^* - \mathbf{x}_p^m) \quad (5.37)$$

$$\mathbf{x}_p^{m+1} = \mathbf{x}_p^m + \mathbf{v}_p^m \quad (5.38)$$

where, x_p^* denotes the best known position of a particle (local minima) and x_s^* denotes the best known position of the swarm (global maximum). The first term in the above equation can be interpreted as the inertia term while the second and the third terms act as the driving force towards the local minima and global minimum respectively. These terms are weighted by the parameters ψ , ϕ_p and ψ_s which can be tuned according to the problem. These parameters affect the behaviour and efficacy of the PSO algorithm. Finally, randomly generated numbers r_p , $r_s \in (0, 1)$ influence the movement of the swarm towards the local or global optima.

The implementation of PSO is an iterative process where N_λ are initially released at N_λ corners in domain and allowed to traverse the domain with the velocity and position being updated through (5.37) and (5.38) respectively. At each iteration, the velocity vector must also be scaled to ensure that the particle stays within the feasible region, i.e., $0 < x_{i(\lambda)} < 1$ [7].

A challenge in the implementation of the PSO algorithm will be to tune the parameters ψ , ϕ_p and ψ_s to achieve a compromise between good convergence rate and thoroughness in traversing the search space. Piro and Simunovic [7] have found that $\psi = 0.5$, $\phi_p = 2$ and $\psi_s = 2$ provides the desired behaviour and that the parameters can be tuned effectively by progressively relaxing the constraints imposed on the velocity magnitude using the following equation [58]:

$$\|\mathbf{v}\| \leq v_{min} + \frac{v_{max} - v_{min}}{m_{max} - 1} (m - 1) \quad (5.39)$$

where, v_{max} and v_{min} are the pre-specified maximum and minimum velocity magnitudes respectively and m_{max} is the maximum number of iteration allowed in PSO. Thereby, the optimisation neighbourhood gradually increases in size as the iteration cycle progresses.

5.5.2. GRID CONSTRUCTION

Grid construction 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 [85, 141–144]. 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 5.10, in the grid construction method, the surface of π_λ is discretised with each point treated as a stoichiometric compound and the ensemble of these compounds collectively approximates the driving force surface [7]. 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 divided into 11 grid points.

The discretisation of the grid plays an important role in the efficacy of this method and it has been shown by Chen *et al.* [144] that the grid must be sufficiently resolved to avoid missing critical features such as the minimum between α_1 and α_2 in fig. 5.10. However, this requirement leads to commercial 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 [7] have demonstrated how uniformly spaced grid for a solution phase λ in N_λ dimensional Euclidean phase (each dimension corresponds to a species in phase λ) can result in an enormously large number of grid points depending on the grid size. While Chen *et al.* [143] and the open-source code OpenCalphad [71] use 8 grid points, it becomes clear from figure 5.10 that global minimum would not be found. Therefore, 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.

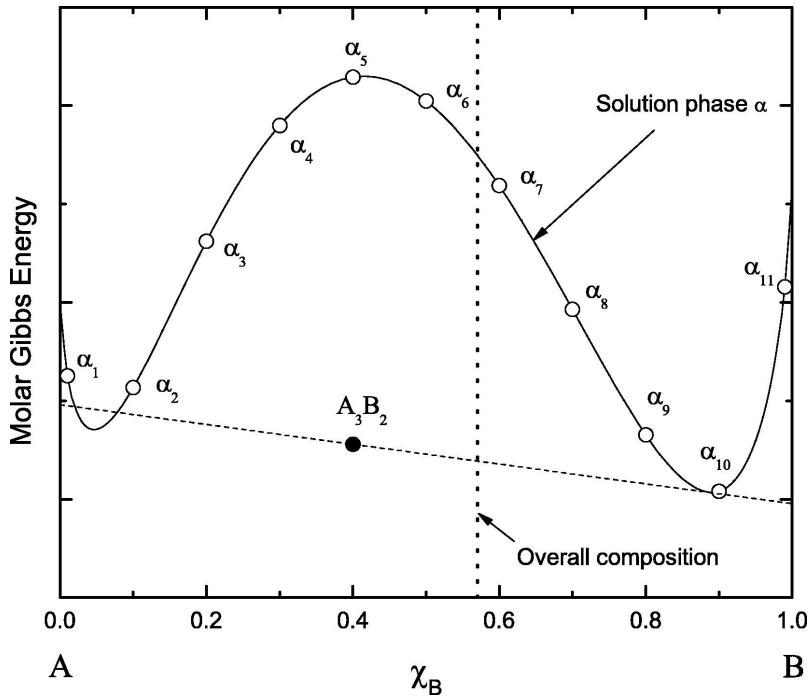


Figure 5.10: Demonstration of the grid construction method for an arbitrary binary system at constant temperature and pressure. The domain has been discretised into 11 grid points and the pure stoichiometric phase A_3B_2 is found to be in equilibrium with the solution phase giving a false positive [7].

5.5.3. BRANCH AND BOUND

The Branch and Bound (B&B) algorithm was proposed to solve constrained optimisation problems for non-convex functions by solving a sequence of problems in each of which the objective function is convex [145]. The algorithm involves two procedures to solve global optimisation problems:

1. **Branching:** The domain D is partitioned into two or more smaller disjoint domains D_1, D_2, \dots , such that $D = D_1 \cup D_2 \cup \dots$. Thus, the partitioned objective function can be considered a convex approximation of the objective function within the subdomain D_i .
2. **Bounding:** The upper and lower bound of the objective function are found within a subset of the domain D . 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.

While the B&B method was originally applied to mixed integer linear programming (MINLP) problems [146], McDonald and Floudas [147] applied it to solve thermochemical equilibrium problems. Piro and Simunovic [7] proposed a modified version of the classical B&B for Thermochimica which uses a different initialisation procedure and relaxation scheme for the bounds. Furthermore, instead of relying on pruning, every subdomain is evaluated till stopping criteria are met and if necessary, recursive partitioning technique is applied.

The approach adopted by Piro and Simunovic [7] partitions the domain for each solution phase λ into N_λ subdomains and the driving force π_λ is minimised in each subdomain. The Lagrangian

function of the driving force of the solution phase λ can be defined as follows [7]:

$$L_\lambda = \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C \nu_{i,j} \Gamma_j \right) - \pi_\lambda \left(\sum_{i=1}^{N_\lambda} x_{i(\lambda)} - 1 \right) \quad (5.40)$$

In the branch and bound method, the local variables (mole fraction of species, $x_{i(\lambda)}$, and driving force π_λ) are optimised while holding the global variables (element potentials i.e. Γ_j) constant. This results in a system of $N_\lambda + 1$ equations for a particular phase λ . To find the minimum, differentiating L_λ with respect to $x_{i(\lambda)}$ and π_λ and applying the Gibbs-Duhem equation:

$$\frac{\partial L_\lambda}{\partial x_{i(\lambda)}} = \mu_{i(\lambda)} - \sum_{j=1}^C \nu_{i,j} \Gamma_j + 1 - \pi_\lambda \quad (5.41)$$

$$\frac{\partial L_\lambda}{\partial \pi_\lambda} = 1 - \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \quad (5.42)$$

Taking a second order Taylor approximation of the Lagrangian function,

$$\nabla^2 L_\lambda \delta y = -\nabla L_\lambda \quad (5.43)$$

where the column vector of unknown variables $\delta y = [\delta x, \delta \pi]^T$. The second order partial derivatives are equal to:

$$\frac{\partial^2 L_\lambda}{\partial x_{i(\lambda)}^2} = \frac{1}{x_{i(\lambda)}} \quad \frac{\partial^2 L_\lambda}{\partial x_{i(\lambda)} \partial x_{j(\lambda)}} = 0 \quad (5.44)$$

$$\frac{\partial^2 L_\lambda}{\partial \pi_\lambda \partial x_{i(\lambda)}} = 0 \quad \frac{\partial^2 L_\lambda}{\partial \pi_\lambda^2} = 0 \quad (5.45)$$

The discussion can be extended to incorporate charge neutrality constraints through the following equation:

$$L_\lambda = \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C \nu_{i,j} \Gamma_j \right) - \pi_\lambda \left(\sum_{i=1}^{N_\lambda} x_{i(\lambda)} - 1 \right) - \pi_e \left(\sum_{i=1}^{N_\lambda} \nu_{i,e} x_{i(\lambda)} - 1 \right) \quad (5.46)$$

where π_e denotes the Lagrange multiplier of the electronic component.

Solving the first order partial differential gives:

$$\frac{\partial L_\lambda}{\partial \pi_e} = 1 - \sum_{i=1}^{N_\lambda} \nu_{i,e} x_{i(\lambda)} \quad (5.47)$$

The second order terms are the following:

$$\frac{\partial^2 L_\lambda}{\partial \pi_e^2} = 0 \quad \frac{\partial^2 L_\lambda}{\partial \pi_e \partial x_i} = -\nu_{i,e} \quad (5.48)$$

The Hessian in the above system of equations can be represented as a symmetric arrow matrix:

$$\mathbf{H} = \begin{bmatrix} \frac{1}{x_{1(\lambda)}} & & & & -1 \\ & \frac{1}{x_{1(\lambda)}} & & & -1 \\ & & \ddots & & \vdots \\ & & & \frac{1}{x_{N(\lambda)}} & -1 \\ -1 & -1 & \dots & -1 & 0 \end{bmatrix} \quad (5.49)$$

Therefore, by exploiting the structure of this matrix, the combination of $x_{i(\lambda)}$ that minimises π_λ can be easily determined. To solve the above 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 $0 < x_{i(\lambda)} < 1$. In addition, the step length must be suitably constrained to avoid missing any local minimums [7].

The application of the branch and bound method to the arbitrary binary problem presented before has been illustrated in figure 5.11. Piro and Simunovic implemented an iterative technique where the domain was initially divided into 2 subdomains with the initialisation of each sub-domain at the corners. To improve numerical stability, the bounds of each subdomain were relaxed while the domain bounds were strictly enforced. The stopping criteria within a subdomain was convergence to local minimum or departure of the local minimiser from the subdomain. In case multiple minima were encountered within a subdomain, the subdomain was further split at the next iteration.

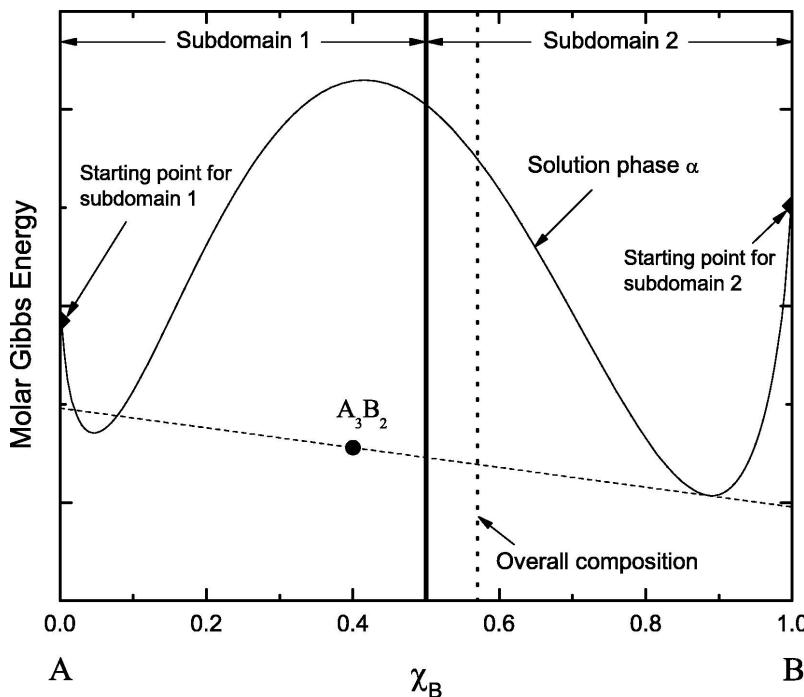


Figure 5.11: Demonstration of the branch and bound method for an arbitrary binary system at constant temperature and pressure. The domain has been partitioned into 2 subdomains [7].

The branch and bound method was able to identify the local minima in both the domains and subsequently the predicted phase assemblage was found to be at the global minimum as shown in figure 5.12

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 [7]. 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. Therefore, apart from the non-linear solver, this

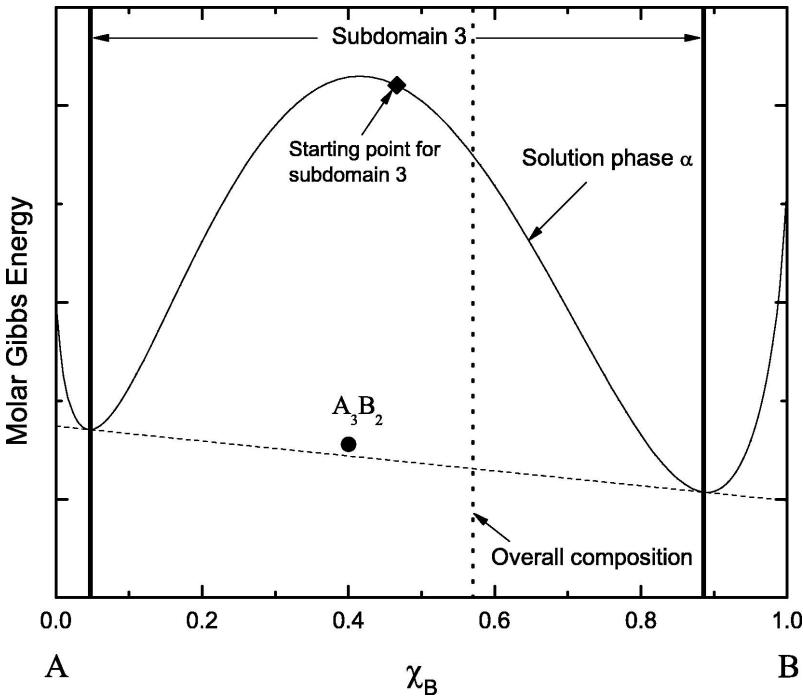


Figure 5.12: Refinement of the subdomains in branch and bound method and the subsequent convergence to global minimum [7].

work will also focus on a quantitative comparison of global optimisation methods in terms of application to thermodynamic equilibrium calculations. This comparison will be based on evaluating the reliability, capability and performance of the methods and some preliminary details of the methodology will be discussed in section 6.3

5.6. INTEGRATION IN MULTIPHYSICS CODES

The thermodynamic solver is being developed with the primary aim of being incorporated within the finite element multiphysics framework MOOSE. The first level of integration of the thermodynamic solver within Yellowjacket will be coupling thermodynamic equilibrium calculations with kinetics and phase field modules being developed by at the Idaho National Laboratory and the University of Florida. This would involve procedures to transfer information between the thermodynamic solver and the other modules. Though MOOSE contains the tools required to enable such computations with minimum effort, there always remains a probability of conflicts arising during coupling, such as conflicting variables, etc. Also, different MOOSE apps have different requirements from the thermodynamic equilibrium solver. While Marmot and Bison computations are mostly require partial derivatives of Gibbs energies (chemical potential, driving force, etc.) and assemblages, other codes might require quantities such as the heat capacity, thermal conductivity, etc. Therefore, though the procedures have not yet been finalised, complete integration of the thermodynamic solver in MOOSE will be a major focus towards the end of this project.

5.7. 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.

6

PROPOSAL

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.

6.1. OVERALL TIMELINE

Table 6.1: Overall timeline of the proposed work showing major academic and research milestones.

Item	Timeline	Status
Coursework		
MCSC-6010G: Mathematical Modelling	Sep. - Dec. 2018	Complete
MCSC-6030G: High Performance Computing	Sep. - Dec. 2018	Complete
NUCL-6005G: Computational Thermodynamics [PhD level elective]	Sep. - Dec. 2018	Complete
MCSC-6020G: Numerical Analysis	Sep. - Dec. 2019	In progress
Research		
Literature review of computational thermodynamics and GEM	Sep. - Dec. 2018	Complete
Implement data file parsing code	Feb. - Mar. 2019	Complete
Implement linear solver (levelling)	Apr. - Jun. 2019	Complete
Implement communication between Yellowjacket and MOOSE	Jul. - Aug. 2019	Complete
Implement non-linear solver for GEM (homogeneous)	Sep. - Dec. 2019	In progress
Implement non-linear solver for GEM (heterogeneous)	Jan. - Mar. 2020	Planned
Demonstration of non-linear solver capabilities	Mar. - May 2020	Planned
Begin integration of thermodynamic solver with Marmot	Jun. - Aug. 2020	Planned
Comparative study of global optimisation strategies	Sep. - Dec. 2020	Planned
Implementation of global optimisation algorithm	Jan. - Mar. 2021	Planned
Demonstration of global optimisation capabilities	Apr. - May 2021	Planned
Complete integration into MOOSE	Jun. - Aug. 2021	Planned
Verification and testing	Sep. - Dec. 2021	Planned

6.2. CURRENT PROGRESS

Over the last one year, since starting my PhD at Ontario Tech, significant progress has been made towards the development of the Gibbs energy minimisation code. This includes the development of a robust parser for parsing the data files and the linear solver for initialisation. The current progress in development of the thermodynamic solver for *Yellowjacket* has been shown in figure 6.1. The thermochemistry code has been partly integrated with MOOSE and thermochemical equilibrium can be calculated on a MOOSE mesh using the levelling solver. Currently only the ideal mixture phases (denoted with IDMX in ChemSage data files) and the Modified Quasichemical Model (denoted with SUBG in ChemSage data files) for molten salts are supported. These models were selected for the initial development since MQM are as the development is underway to expand support to a large number of thermodynamic models.

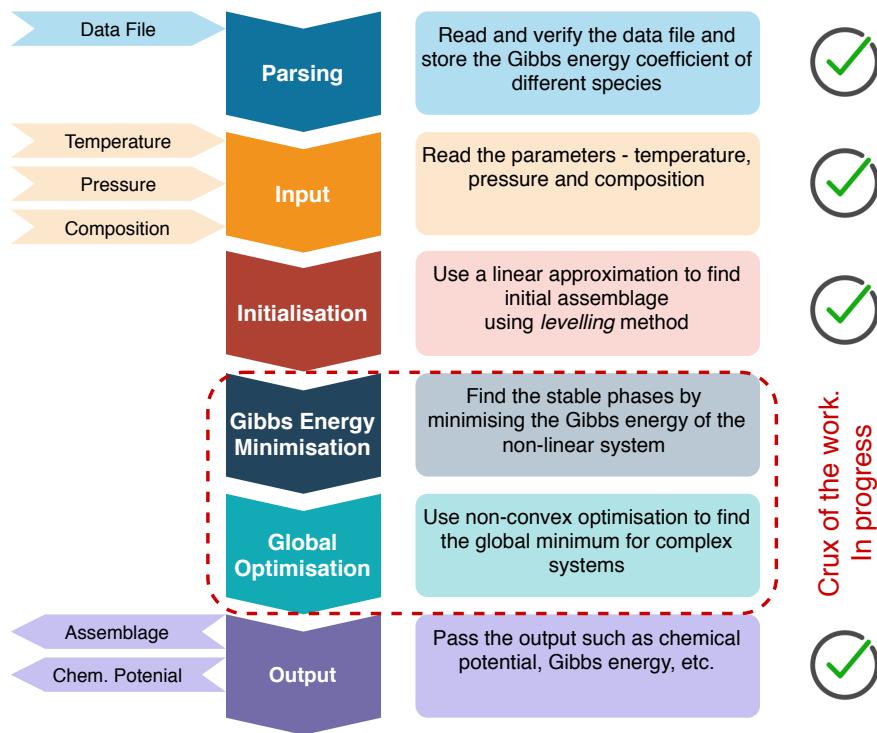


Figure 6.1: Current progress on the implementation of the thermochemistry solver.

It is imperative to advise a word of caution with respect to the progress represented above. While figure 6.1 might make the reader believe that a major part of the work has already been completed, in reality, Gibbs energy minimisation and global optimisation are the major and the most challenging parts of this work and they will be the primary focus over the next year along with expansion of capabilities.

6.2.1. DEMONSTRATION PROBLEM

The reference fuel and coolant proposed for the different MSR concepts are fluoride salts due to their advantageous neutronic and physico-chemical properties [148]. LiF–BeF₂ and LiF–NaF–KF are amongst the different salt compositions under study for the primary and secondary coolant and their suitability with respect to their corrosion properties for the structural material is an essential requirement for reactor safety and operation. Since Ni is the main element for prospective alloys for structural materials,

and the rate of corrosion is defined by the redox potential of the molten salt, the phase equilibrium of the salt with potential corrosion products must be studied as a function of temperature and pressure [12]. Therefore, the initial focus is on Ni alloys interacting with molten $\text{LiF}_2 - \text{KF}$ salts and for the present demonstration the $\text{KF} - \text{NiF}_2$ binary system has been selected. This system is not only relevant to the MSR but has also been studied experimentally and the required thermodynamic data is available in literature [12].

The demonstration problem presented here was a milestone in the first year development plan of Yellowjakcte and was submitted to the Idaho National Lab as part of a progress report. For the demonstration problem, a bar with molar composition $0.8\text{KF} + 0.2\text{NiF}_2$ under a temperature gradient as shown in figure 6.2 has been solved for thermodynamic equilibrium using the linear levelling solver.

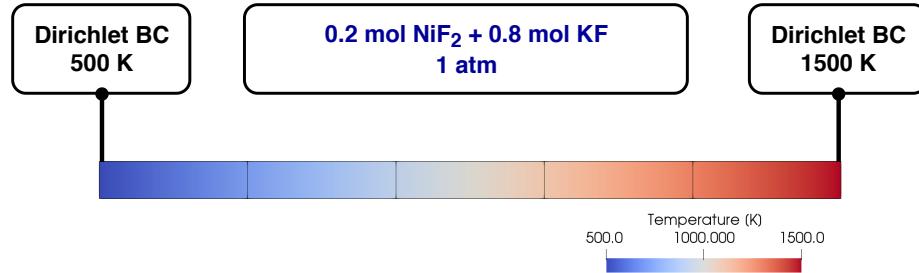


Figure 6.2: The demonstration problem consists of a bar divided into 5 elements with Dirichlet boundary conditions imposed at both ends and a linear temperature gradient.

6.2.2. RESULTS OF DEMONSTRATION PROBLEM

The stable phases and the Gibbs energies predicted by the levelling solver are shown in figure 6.3. As expected from the phase diagram shown below, a transition from a solid phase to a mixture of solid and liquid phase around 1100°C and a transition from a two-phase region to a single liquid phase region around 1200°C is observed.

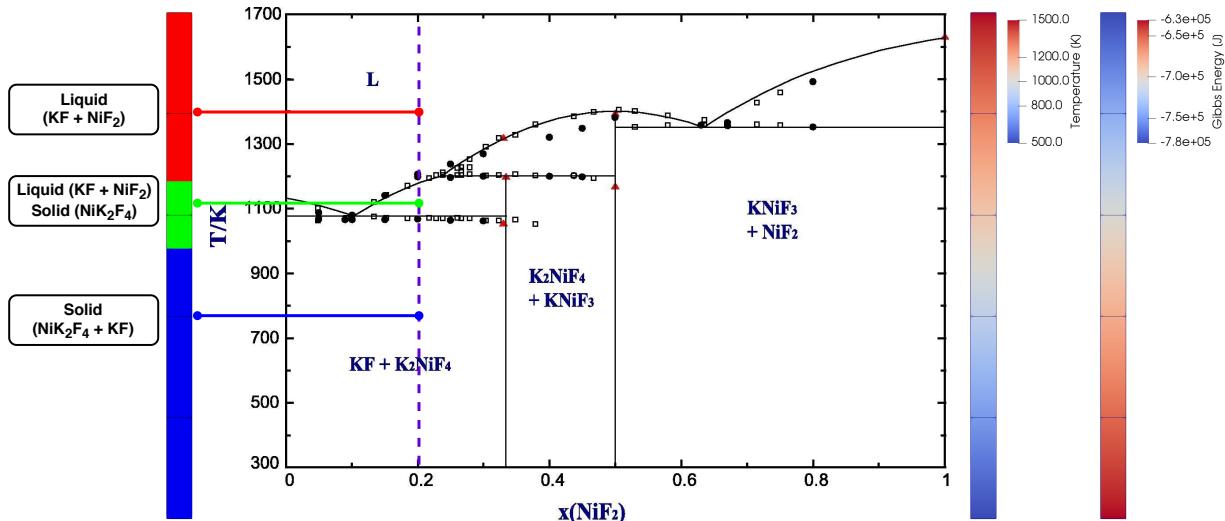


Figure 6.3: Stable phases and Gibbs energies predicted by the linear solver.

It must be mentioned that though the Gibbs energy profile shown on the extreme right in figure 6.3

is continuous, the actual results on the finite element mesh are discretised due to a step change in the temperature as we move from one element to the other. The continuous profile, has been plotted through Paraview, by interpolation during post processing and is a better representation of the physical conditions where we expect no step changes if a temperature gradient is applied.

It must also be clarified that the in the current state, the under-development thermodynamic solver cannot fully reproduce the phase diagram presented above. The levelling solver converts all species to ideal phases and therefore any non-linear behaviour (the curved lines on the phase diagram) cannot be reproduced. However, the demonstration problem is successful in showing that the code development is on the correct path and once the non-linear GEM part has been implemented, it will be possible to reproduce the non-ideal behaviour too.

6.3. WORK PLAN

6.3.1. YEAR 2019-2020

The primary focus of 2019-2020 will be the implementation of the non-linear solver for thermochemical equilibrium. Using the levelling solver's results as initial estimates, the non-linear solver will be able to provide the final phase assemblage. Also, the integration of thermodynamic equilibrium code with phase field part of Yellowjacket will be done in the last quarter of 2019-2020.

NON-LINEAR SOLVER

The implementation of the non-linear solver is relatively straightforward. The implementation of Gibbs energy minimisation method results in system of equations given by equation (5.27) and the initial estimates are provided by the levelling solver. The principle tasks in the implementation of the non-linear solver are as follows:

1. The first requirement of the non-linear solver is to have the partial molar excess Gibbs energy functions for the different thermodynamic models supported by the solver. Therefore, as the first task I will implement a number of functions that compute the excess Gibbs energy terms and the resulting chemical potentials. While this task seems relatively straightforward, the peculiarities of the thermodynamic models make it less so. For example, the interaction terms in the modified quasichemical models take different forms depending on a number of factors. This difference in implementation does not find a mention in the literature and has been identified only through a rigorous debugging process during the development of Thermochimica. Therefore proper care must be taken to ensure that the terms take the correct form. In this direction, I'm working on a soon to be submitted paper which goes through the nuances of each thermodynamic model and the exercise will then be useful in the implementation of the required functions.
2. A function will be implemented to check the convergence of the initial estimate at the start of the non-linear solver. If the system consists of only pure stoichiometric species, the levelling estimate results in the actual assemblage and the costly non-linear step can be avoided. The implementation of this routine will simply test for the convergence criteria and if satisfied the non-linear steps will be skipped. The subroutine for the convergence check will also be useful when verifying the convergence of the iterative Newton method that will be used in the non-linear solver.
3. The first function that forms a direct part of the non-linear solution module is a Newton method function to compute the direction vector for the solver. The Hessian matrix and its corresponding constraint vector will first be constructed and then the direction vector representing the system parameters will be solved with the DGESV driver routine from LAPACK. One of the possible issues

with this function is the possibility of numerical singularity in the Hessian matrix and to avoid it a simple check will be performed which would test for zero rows in the Hessian matrix. Also, since support for ionic phases is envisaged in the future, additional charge neutrality constraints will need to be coded within the implementation. This would be done by adding an electron as a system component for every charged phase in the system. At a later stage, I might consider using PETSc for this function.

4. The updated element potentials, adjustments to the number of moles of solution phases and the number of moles of pure stoichiometric phases will be applied in this function which will perform a line search using the direction vector computed by the Newton solver. The system will be updated using an appropriate step length that satisfies the Wolfe conditions. It might be possible for the system of equations to be ill-behaved and yield inappropriate results and the maximum change to the element potentials will be appropriately constrained.
5. Finally a convergence check will be performed to verify that the following criteria are satisfied:
 - (a) The phases in the assemblage should not be dummy species present in the ChemSage data files.
 - (b) The number of moles of all species and phases are positive and non-zero.
 - (c) Gibbs' Phase Rule has been satisfied.
 - (d) The Gibbs energies of all the phases must be above the Gibbs' plane.
 - (e) The residuals of the chemical potential terms are below a specified tolerance.
 - (f) The relative errors of the mass balance equations are within tolerance.

The implementation of the non-linear solver is scheduled to be completed by the first quarter of 2020 and will be performed in two stages - initially for only homogeneous systems and then extended to heterogeneous systems as well.

INTEGRATION WITH PHASE FIELD

Within Yellowjacket, the thermochemistry solver will be used for predicting microstructure evolution using phase field. Yellowjacket will use MOOSE to solve phase-field equations to describe the evolution of the chemical components and phases. The chemical components in the system are represented by conserved variables that evolve based on the Cahn-Hilliard equation as follows:

$$\frac{dc}{dt} = \nabla M(c_i) \nabla \frac{\delta F}{\delta c_i} \quad (6.1)$$

where M is the mobility of the component, c_i represents the concentration of the component i , F denotes the free energy density of the system, and the $\frac{\delta F}{\delta c_i}$ denotes chemical potential of species i . The phases are represented as non-conserved order parameters, and are evolved using the Allen-Cahn equation

$$\frac{d\eta_j}{dt} = -L \frac{\delta F}{\delta \eta_j} \quad (6.2)$$

where η_j denotes the order parameter for the phase j , and L is the Allen-Cahn mobility of the interface. The order parameters are used to interpolate between the thermodynamic model for each phase.

Thus, the primary thermodynamic inputs required to the evolution equations are the Gibbs free energy of the system and chemical potentials of the species as a function of the concentrations of

components and the phase order parameters. Typically, the free energy functions for each phase are obtained for the given system of components using a CALPHAD thermodynamic assessment before running the simulation. However, for multicomponent metal alloy systems, the free energy functions are often very complex. The coupled thermodynamic solver would directly provide the values from the database and would help in simplifying the development of the phase field models by distributing the complex coupled problem into two simpler problems.

Values for derivatives of thermodynamic variables within the phase field simulation would be directly communicated from the thermodynamic solver through MOOSE. These derivatives would be output as *aux variables* which allow explicit calculation and can be used by MOOSE kernels, BCs and material properties allowing them to be accessed from phase field and/or other MOOSE based codes. However, coupling of the two modules of Yellowjacket might have potential issues such as conflicting variable names, function structures etc. To iron out these issues, the coupling would be performed in collaboration with Idaho National Laboratory and University of Florida and exchange visits at these institutions are foreseen around the summer and fall of 2020.

6.3.2. YEAR 2020-2021

The focus in 2020-2021 will be two-fold. First, implementation of global optimisation strategies for the thermodynamic solver and second, completing the integration of thermodynamic solver in the multiphysics environment. Also, during this time new thermodynamic models will be continuously added to the solver.

GLOBAL OPTIMISATION

The first task in implementation of global optimisation strategy will be performing a comprehensive review of the various stochastic and deterministic methods of global optimisation available in literature. As of now, based on the available literature, the following test cases are under consideration [7]:

1. A relatively simple binary system where a stoichiometric species might result in a false positive, such as, the case shown in figure 5.10.
2. A relatively binary system where a phase which must be present in the assemblage gets replaced by another phase which should actually be metastable.
3. A fictive binary system with multiple miscibility gaps.
4. A fictive system with a knife edge phase, i.e. a phase with extremely narrow convex Gibbs energy profile resulting in a system with metastable equilibrium.
5. A quinary solution phase represented by a regular substitutional model.
6. An ionic solid solution phase represented by a multi-sublattice model containing a moderate number of species.
7. An ionic solid solution phase represented by a multi-sublattice model containing a large number of species.

A comparison of rate of convergence, convergence time and success rate for the above test cases will help in identifying the most suitable global optimisation method in terms of reliability, efficacy and speed. The selected model will then be implemented within Yellowjacket. However, the implementation would also require further study of the selected method to optimise a number of method

parameters that used in all the systems. As a backup solution in case of inconclusive results from the above mentioned comparative study, the efforts will be dedicated towards implementing the Branch and Bound algorithm and the efforts will then be dedicated towards improving the performance and robustness of the algorithm.

6.3.3. YEAR 2021-2022

While the work plan for 2021-2022 has not been set in stone, the primary focus will be verification and testing of the developed thermochemistry solver. It is expected that the majority of development work would be completed by September 2021 after which a number of different applications of the developed code would be explored. However, as a contingency plan in case of unforeseen delays in the code development, some of the time dedicated to demonstration problems could be reallocated to code development.

VERIFICATION AND TESTING

The verification of the developed code will consist of both unit tests performed on individual modules and functions of the code and system tests which simulate the behaviour of end-user without the knowledge of internal programming. The Continuous Integration, Verification, Enhancement, and Testing (CIVET) tool has been developed to support MOOSE and its applications. MOOSE uses tests to do both continuous integration (CI) and continuous deployment (CD). Each and every change to MOOSE is tested across multiple operating systems, in parallel, with threads, in debug, with Valgrind and several other configurations. The same development philosophy is being followed for Yellowjacket and the following testing ideas are being used:

- *Regression tests* consisting of input files and known good outputs (“gold” files).
- *Unit tests* that test the functionality of small separable pieces.
- A test harness to run all the tests and aggregate the results.

The gold files for the testing will be generated using the commercial software FactSage and will be used to compare the outputs from the system tests. Some of the proposed tests for the thermodynamics code have been listed in table 6.2. While the table does not cover all the tests, as a number of tests will be developed as the code matures, it gives a clear idea of the testing philosophy.

DEMONSTRATION PROBLEMS

The primary demonstration problem for Yellowjacket is corrosion of metallic structures by molten fluoride/chloride salts and multiphysics simulations will be performed to demonstrate the capability of Yellowjacket in predicting the rate of material loss, simulating leaching and deposition of corrosion products, etc.

Furthermore, a few other demonstration problems will be explored to exhibit the broader capabilities of thermodynamic equilibrium module and its integration within MOOSE. These demonstration problems will include but are not limited to:

1. Coupled thermochemical, isotopic evolution and heat transfer simulations in highly irradiated UO₂ nuclear fuel. This demonstration problem would provide an example of coupling the thermodynamics code with Bison and will also provide an excellent example for verifying the predictions of the thermochemistry code by comparison with previous experimental investigations [149] and computational studies [10].
2. Coupling with isotopic evolution and thermal-hydraulics codes to predict fission product inventory in a MSR. A similar study has been performed to demonstrate the coupling of Thermochimica

Table 6.2: Summary of some of the proposed unit and system tests for the thermodynamic solver.

System	Description
Unit Tests	
None	Ensure graceful exit if no data-file specified or wrong pathname specified.
Simple	Ensure graceful exit if input parameters not specified.
Simple	Ensure graceful exit if input parameters if inconsistent or unspecified units.
Simple	Ensure graceful exit if NaN/Inf is encountered in data file.
Complex	Ensure graceful exit if data file contains unsupported models.
Complex	Ensure graceful exit if expected information is missing from data file.
Complex	Ensure that a data-file containing a large number of phases and species can be read.
System Tests	
Simple	Ensure that the phase assemblage matches gold files.
Simple	Ensure that the thermodynamic quantities match gold files.
Complex	Ensure that the phase assemblage matches gold files.
Complex	Ensure that the thermodynamic quantities match gold files.
Complex	Ensure that dummy species are not present in the assemblage. Use Valgrind to check that there are no memory leaks.

with Origen and Cobra-TF. The problem would help in exhibiting the robustness of the thermodynamic solver and again be a great verification problem.

Finally, starting the first quarter of 2022, I will also focus on consolidating the research and preparing the dissertation in order to defend my thesis around September 2020 which is roughly 2 years and 9 months from the present.

6.4. PUBLICATION PLAN

The planned publications over the period of this PhD fall into three categories - Journal articles, Conference proceeding and presentations, and US-DOE reports.

6.4.1. JOURNAL ARTICLES

Recently, contribution was made to a paper titled *On the interpretation of chemical potentials computed from equilibrium thermodynamic codes: Applications to molten salts* [40] which has been published in the *Journal of Nuclear Materials*, a leading journal in the field of materials research for nuclear applications. The paper has been attached in [List of Publications](#).

Currently, a first author journal paper titled *Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models* is under preparation and will be submitted to *Calphad*, one of the most respected journals in the field of computational thermodynamics. The papers available in open literature have focussed on describing the various thermodynamic models and on their applications in modelling various materials. However, none of them presents the equations in a form amenable to programming. This paper will present the derivations of the partial molar excess Gibbs energy of mixing of multiple common classes of thermodynamic models for use in a Gibbs energy minimiser. A very rough first draft of the paper has been attached in [List of Publications](#).

Also, within the first quarter of 2020, the candidate intends to submit a short communication to

the *Computational Materials Science* journal highlighting the numerical issues that arise in the implementation of the Partitioning of Gibbs Energy (PGE) method. The paper would critically and objectively compare the PGE approach to the GEM approach and point out the reasons why, despite its apparent numerical advantages, the PGE method falls short of converging in certain cases and illustrate why the PGE method was discarded in favour of the GEM method over the course of development of the thermochemistry library *Thermochimica*. The accepted draft of the paper is attached in [List of Publications](#).

At this stage, the exact details of journal articles apart from the ones discussed above haven't been finalised. However, at least two other first author journal papers are foreseen:

1. There has been a lack of quantitative comparison of global optimisation methods in terms of their applicability to thermodynamic equilibrium problems and most of the publications have focussed on the application of specific methods to either relatively small system or applicable to a specific problem. A proposed paper (in 2021) will aim at bridging this gap by comparing the different stochastic and deterministic global optimisation methods in terms of their efficacy, reliability and computational performance through a series of methodological numerical experiments.
2. Towards the end of the research, a paper on the capabilities of the thermodynamic equilibrium solver will be published with a detailed description of the numerical methods, performance enhancing algorithms and optimisation schemes implemented in the solver. The paper would also demonstrate the capabilities of the code through various verification and validation problems.

Apart from the aforementioned papers, contributions as a co-author are foreseen in a number of papers that will be published as part of the Molten Salt Chemistry and Corrosion campaign of the US Department of Energy, which is the umbrella program for all efforts related to materials and corrosion modelling for the MSRs and include the development of *Yellowjacket*.

6.4.2. CONFERENCE PROCEEDINGS

In 2019, the candidate attended the *39th Annual Conference of the Canadian Nuclear Society and 43rd Annual CNS/CNA Student Conference* held in Ottawa from June 23 to June 26. The CNS Annual Conference is the largest gathering of nuclear industry professionals in Canada and provides a forum for communicating progress, achievements and new ideas across a broad range of nuclear technology areas. At the conference, a proceedings paper and a poster on *Progress in developing a new thermochemistry code for corrosion modelling and multiphysics simulation of nuclear fuels* were presented. The paper was coauthored with scientists at the Idaho National Laboratory. The poster and the paper are attached in [List of Publications](#).

In February 2020, the candidate will attend the *TMS 2020 Annual Meeting & Exhibition*, which is a gathering of more than 4,000 engineers, scientists, business leaders, and other professionals in the minerals, metals, and materials fields for a comprehensive, cross-disciplinary exchange of technical knowledge. A poster will be presented at the *Computational Materials Science and Engineering of Materials in Nuclear Reactors* symposium which focusses on the current computational materials science and engineering efforts towards understanding the materials behaviours and microstructure evolutions in nuclear reactors. Also, a paper titled *Development of a new thermochemistry solver for multiphysics simulations of nuclear materials* has been accepted for publication in the proceedings of the conference. The paper is coauthored with scientists at the Idaho National Laboratory and the University of Florida.

In the future, the candidate is expecting to attend the International Conference on Mathematics and Computational Methods applied to Nuclear Science and Engineering (M&C 2021). M&C, organised by the American Nuclear Society, represents a series of international forums that bring together worldwide expertise related to nuclear science or technology including mathematical and computational methods, numerical analysis, computer codes, computer architectures, and benchmarks for computationally solving problems. Presentations at nuclear materials conference NuMat or the ANS Annual/Winter meetings, and the ANS Student Conference or the SIAM Conference on Mathematical Aspects of Materials Science are also expected.

6.4.3. TECHNICAL REPORTS

In August 2019, a progress report titled *Development of a thermochemical equilibrium Solver for MOOSE-based corrosion modelling app Yellowjacket* was submitted to the Idaho National Laboratory. In the future, a number of such reports detailing the progress made towards the development of thermodynamic solver in Yellowjacket and reports describing the results of various demonstration problems solved through the thermodynamics code will also be submitted to Idaho National Laboratory.

7

CONCLUSION

Recent trends in modelling and simulation of various materials have adopted the multiscale approach wherein the information from smaller scales is used to develop and improve the models at larger scale in order to better simulate material behaviour. Nuclear materials, in particular, stand to benefit from these multiscale, multiphysics simulation models and have therefore driven the development of advanced modelling and simulation tools. The Multiphysics Object Oriented Programming Environment (MOOSE) developed by the Idaho national Laboratory enables such high fidelity simulations of nuclear materials and contains dedicated applications to model the behaviour of nuclear materials at various scales. However, it has, until now, lacked an application that can model corrosion at the meso-scale and efforts are now underway to develop a new application called *Yellowjacket*. An essential requirement of many nuclear material simulations is the ability to reliably predict the material properties as material composition evolves and it requires thermodynamic equilibrium calculations to predict the phase distribution at given temperatures and pressure. Particularly, for the case of corrosion modelling, the chemical potentials of various species that exist in the system acts as the driving force for corrosion. Therefore, there is considerable interest in integrating thermodynamic equilibrium computations in MOOSE and specifically *Yellowjacket*.

The proposed research is aimed at developing a thermodynamic equilibrium solver to predict the phase assemblage of a multicomponent system for a given composition at isothermal, isobaric conditions. Through advanced algorithm development and efficient implementation of performance enhancing strategies, this research will focus on accelerating the performance of thermodynamic computations which are inherently very complex and can significantly impede the computational performance in coupled multiphysics codes. The need to minimise computation time while ensuring that the highly non-linear and non-convex system satisfies the conditions of thermodynamic equilibrium results in a challenging global optimisation problem. Over the course of this work, the Gibbs energy minimisation approach for computing thermodynamic equilibrium will be coupled with the proposed performance enhancing strategies and global optimisation schemes to efficiently and reliably predict the thermodynamic equilibrium in large multicomponent systems.

The research will enable coupling thermodynamic equilibrium calculations within multiphysics codes and enable high fidelity material and process simulations to support the development of advanced nuclear reactors.

REFERENCES

- [1] M. Stan, “Discovery and design of nuclear fuels,” *Materials Today*, vol. 12, no. 11, pp. 20 – 28, 2009.
- [2] D. R. Gaston, C. J. Permann, J. W. Peterson, A. E. Slaughter, D. Andrš, Y. Wang, M. P. Short, D. M. Perez, M. R. Tonks, J. Ortensi, L. Zou, and R. C. Martineau, “Physics-based multiscale coupling for full core nuclear reactor simulation,” *Annals of Nuclear Energy*, vol. 84, pp. 45–54, 2015.
- [3] B. Alger, D. Andrš, R. W. Carlsen, D. R. Gaston, F. Kong, A. D. Lindsay, J. M. Miller, C. J. Permann, J. W. Peterson, A. E. Slaughter, and R. Stogner, “MOOSE Web page.” <https://mooseframework.org>, 2019.
- [4] M. Piro, S. Simunovic, T. Besmann, B. Lewis, and W. Thompson, “The Thermochemistry Library THERMOCHIMICA,” *Computational Materials Science*, vol. 67, pp. 266–272, 2013.
- [5] M. Zinkevich, “Computational thermodynamics: Learning, doing and using.” Presentation at the International Max Planck Research School for Advanced Materials, 06 2003.
- [6] M. Piro, T. Besmann, S. Simunovic, B. Lewis, and W. Thompson, “Numerical verification of equilibrium thermodynamic computations in nuclear fuel performance codes,” *Journal of Nuclear Materials*, vol. 414, no. 3, pp. 399 – 407, 2011.
- [7] M. Piro and S. Simunovic, “Global optimization algorithms to compute thermodynamic equilibria in large complex systems with performance considerations,” *Computational Materials Science*, vol. 118, pp. 87–96, 2016.
- [8] M. Piro, *Computation of Thermodynamic Equilibria Pertinent to Nuclear Materials in Multi-Physics Codes*. PhD thesis, Royal Military College of Canada, 2011.
- [9] G. B. Dantzig, S. Johnson, and W. B. White, “A linear programming approach to the chemical equilibrium problem,” Tech. Rep. Paper P-1060, The RAND Corporation, 1957.
- [10] M. Piro, J. Banfield, K. Clarno, S. Simunovic, T. Besmann, B. Lewis, and W. Thompson, “Coupled thermochemical, isotopic evolution and heat transfer simulations in highly irradiated UO₂ nuclear fuel,” *Journal of Nuclear Materials*, vol. 441, pp. 240–251, 2013.
- [11] M. Poschmann, S. Simunovic, and M. Piro, “Acceleration of thermochimica calculations in Bison,” tech. rep., Oak Ridge National Laboratory, 2019.
- [12] J. Ocadiz-Flores, E. Capelli, P. Raison, R. Konings, and A. Smith, “Thermodynamic assessment of the LiF–NiF₂, NaF–NiF₂ and KF–NiF₂ systems,” *Journal of Chemical Thermodynamics*, vol. 121, pp. 17–26, 2018.
- [13] H. Loukusa, “Computational module for the calculation of thermochemical equilibria in nuclear fuel,” Master’s thesis, Aalto University, Finland, 2014.

- [14] M. Piro and S. Simunovic, “Performance enhancing algorithms for computing thermodynamic equilibria,” *CALPHAD*, vol. 39, pp. 104–110, 2012.
- [15] M. Piro, “Updating the estimated assemblage of stable phases in a gibbs energy minimizer,” *CALPHAD*, vol. 58, pp. 115–121, 2017.
- [16] W. N. Association, “Nuclear power in the world today.” <https://www.world-nuclear.org/information-library/current-and-future-generation/nuclear-power-in-the-world-today.aspx#targetText=Nuclear%20energy%20now%20provides%20about,in%20about%20225%20research%20reactors.>, 09 2019.
- [17] International Energy Agency, “World energy outlook 2018.” Report, 2018.
- [18] Generation IV International Forum (GIF), “GIF R&D Outlook for Generation IV Nuclear energy systems.” Report, 08 2009.
- [19] Generation IV International Forum (GIF), “GIF Web page.” https://www.gen-4.org/gif/jcms/c_9261/home, 2019.
- [20] R. Williamson, J. Hales, S. Novascone, M. Tonks, D. Gaston, C. Permann, D. Andrs, and R. Martineau, “Multidimensional multiphysics simulation of nuclear fuel behavior,” *Journal of Nuclear Materials*, vol. 423, no. 1, pp. 149 – 163, 2012.
- [21] R. Yoshioka, M. Kinoshita, and I. Scott, *Molten Salt Reactors and Thorium Energy*, ch. Materials. Elsevier, 2017.
- [22] K. Sridharan and T. Allen, *Molten Salts Chemistry From Lab to Applications*, ch. Corrosion in Molten Salts. Elsevier, 2013.
- [23] J. W. McMurray, T. M. Besmann, J. Ard, B. Fitzpatrick, M. Piro, J. Jerden, M. Williamson, B. S. Collins, B. R. Betzler, and A. L. Qualls, “Multi-physics simulations for molten salt reactor evaluation: Chemistry modeling and database development,” Tech. Rep. ORNL/SPR-2018/864, Oak Ridge National Laboratory, 2018.
- [24] R. Devanathan, L. Van Brutzel, A. Chartier, C. Guéneau, A. E. Mattsson, V. Tikare, T. Bartel, T. Besmann, M. Stan, and P. Van Uffelen, “Modeling and simulation of nuclear fuel materials,” *Energy Environ. Sci.*, vol. 3, pp. 1406–1426, 2010.
- [25] H. Lukas, S. Fries, and B. Sundman, *Computational Thermodynamics: The CALPHAD Method*. Cambridge University Press, 2007.
- [26] H. Zhang, D. Andrs, J. Hansel, L. Zou, R. Berry, and R. Martineau, “RELAP-7 Web page.” <https://moose.inl.gov/relap7/>, 2019.
- [27] Y. Wang, S. Schunert, V. Laboure, M. D. DeHart, and R. C. Martineau, “Rattlesnake Web page.” <https://rattlesnake.inl.gov/>, 2019.
- [28] C. Newman, G. Hansen, and D. Gaston, “Three dimensional coupled simulation of thermo-mechanics, heat and oxygen diffusion in UO₂ nuclear fuel rods,” *Journal of Nuclear Materials*, vol. 392, pp. 6–15, 2009.

- [29] M. Tonks, D. Gaston, P. Millett, D. Andrs, and P. Talbot, “An object-oriented finite element framework for multiphysics phase field simulations,” *Journal of Nuclear Materials*, vol. 51, pp. 20–29, 2012.
- [30] U.S. Department of Energy, “NEAMS Fuel Products Line.” <https://neams.inl.gov/SitePages/FuelsProductLine.aspx>.
- [31] American Society of Mechanical Engineers, “Nuclear Quality Assurance (NQA-1) certification.” <https://www.asme.org/certification-accreditation/nuclear-quality-assurance-nqa1-certification>, 2019.
- [32] J. W. Gibbs, “On the equilibrium of heterogeneous substances,” *American Journal of Science*, vol. 16, no. 96, pp. 441–458, 1878.
- [33] M. Zemansky and R. Dittman, *Heat and thermodynamics*. McGraw-Hill, 6th ed., 1981.
- [34] A. Pelton, S. Degterov, G. Eriksson, C. Robelin, and Y. Dessureault, “The modified quasichemical model I – binary solutions,” *Metallurgical and Materials Transactions B*, vol. 31B, pp. 651–659, 2000.
- [35] A. Pelton and P. Chartrand, “The modified quasichemical model II – multicomponent solutions,” *Metallurgical and Materials Transactions A*, vol. 32A, pp. 1355–1360, 2001.
- [36] P. Chartrand and A. Pelton, “The modified quasichemical model III – two sublattices,” *Metallurgical and Materials Transactions A*, vol. 32, pp. 1397–1407, 2001.
- [37] A. Pelton, P. Chartrand, and G. Eriksson, “The modified quasichemical model IV – two-sublattice quadruplet approximation,” *Metallurgical and Materials Transactions A*, vol. 32, pp. 1409–1416, 2001.
- [38] G. Lambotte and P. Chartrand, “Thermodynamic optimization of the (Na₂O + SiO₂ + NaF + SiF₄) reciprocal system using the modified quasichemical model in the quadruplet approximation,” *Journal of Chemical Thermodynamics*, vol. 43, pp. 1678–1699, 2011.
- [39] M. Hillert, “The compound energy formalism,” *Journal of Alloys and Compounds*, vol. 320, no. 2, pp. 161 – 176, 2001.
- [40] M. Piro, M. Poschmann, and P. Bajpai, “On the interpretation of chemical potentials computed from equilibrium thermodynamic codes: Applications to molten salts,” *Journal of Nuclear Materials*, vol. 526, p. 151756, December 2019.
- [41] D. Olander, *General Thermodynamics*. CRC Press, 2008.
- [42] F. van Zeggeren and S. Storey, *The Computation of Chemical Equilibria*. Cambridge University Press, 2011.
- [43] W. White, S. Johnson, and G. Dantzig, “Chemical equilibrium in complex mixtures,” *Journal of Chemical Physics*, vol. 28, no. 5, pp. 751–755, 1958.
- [44] M. Hillert, “Some viewpoints on the use of a computer for calculating phase diagrams,” *Physica B+C*, vol. 103, no. 1, pp. 31 – 40, 1981.

- [45] W. B. White, S. M. Johnson, and G. B. Dantzig, "Chemical equilibrium in complex mixtures," *The Journal of Chemical Physics*, vol. 28, no. 5, pp. 751–755, 1958.
- [46] S. R. Brinkley, "Calculation of the equilibrium composition of systems of many constituents," *The Journal of Chemical Physics*, vol. 15, no. 2, pp. 107–110, 1947.
- [47] F. J. Krieger and W. B. White, "A simplified method for computing the equilibrium composition of gaseous systems," *The Journal of Chemical Physics*, vol. 16, no. 4, pp. 358–360, 1948.
- [48] F. J. Zeleznik and S. Gordon, "Calculation of complex chemical equilibria," *Industrial & Engineering Chemistry*, vol. 60, no. 6, pp. 27–57, 1968.
- [49] F. P. Boynton, "Chemical equilibrium in multicomponent polyphase systems," *The Journal of Chemical Physics*, vol. 32, no. 6, pp. 1880–1881, 1960.
- [50] G. Eriksson, "Thermodynamic studies of high temperature equilibria. xii. solgasmix, a computer program for calculation of equilibrium compositions in multiphase systems.,," *Chemica Scripta*, vol. 8, no. 3, pp. 100–103, 1975.
- [51] G. Eriksson and E. Rosen, "General equations for the calculation of equilibria in multiphase systems," *Chemica Scripta*, vol. 4, pp. 193–194, 1973.
- [52] G. Eriksson, "An algorithm for the computation of aqueous multi-component, multiphase equilibria," *Analytica Chimica Acta*, vol. 112, no. 4, pp. 375 – 383, 1979.
- [53] P. Koukkari and R. Pajarre, "Calculation of constrained equilibria by gibbs energy minimization," *CALPHAD*, vol. 30, no. 1, pp. 18 – 26, 2006.
- [54] G. Eriksson and K. Hack, "Chemsage – a computer program for the calculation of complex chemical equilibria," *Metallurgical and Materials Transactions B*, vol. 21B, pp. 1013–1023, 1990.
- [55] R. Pajarre, P. Koukkari, and E. Räsänen, "Inclusion of the donnan effect in gibbs energy minimization," *Journal of Molecular Liquids*, vol. 125, no. 1, pp. 58 – 61, 2006. Selected Papers on Molecular Liquids.
- [56] S. H. Storey and F. Van ZEGGEREN, "Computation of chemical equilibrium compositions," *The Canadian Journal of Chemical Engineering*, vol. 42, no. 2, pp. 54–55, 1964.
- [57] G. Lantagne, B. Marcos, and B. Cayrol, "Computation of complex equilibria by nonlinear optimization," *Computers & Chemical Engineering*, vol. 12, no. 6, pp. 589 – 599, 1988.
- [58] J. Nocedal and S. Wright, *Numerical Optimization*. Springer, 2006.
- [59] G. Eriksson and W. Thompson, "A procedure to estimate equilibrium concentrations in multi-component systems and related applications," *CALPHAD*, vol. 13, no. 4, pp. 389 – 400, 1989.
- [60] W. White, "Numerical determination of chemical equilibrium and the partitioning of free energy," *Journal of Chemical Physics*, vol. 46, no. 11, pp. 4171–4175, 1967.
- [61] M. Srinivas and G. Rangaiah, "Implementation and evaluation of random tunneling algorithm for chemical engineering applications," *Computers and Chemical Engineering*, vol. 30, pp. 1400–1415, 2006.

- [62] G. Dantzig, S. Johnson, and W. White, "A linear programming approach to the chemical equilibrium problem," *Management Science*, vol. 5, no. 1, pp. 38–43, 1958.
- [63] G. Dantzig, *Linear Programming and Extensions*. Princeton University Press, 2016.
- [64] G. Eriksson, "Thermodynamic studies of high temperature equilibria: iii. solgas, a computer program for calculating the composition and heat condition of an equilibrium mixture," *Acta Chemica Scandinavica*, vol. 25, pp. 2651–2658, 1971.
- [65] Chemistry Software, "HSC Chemistry 9 Web page." <http://hsc-chemistry.net/index.html>.
- [66] W. Thompson, A. Pelton, and C. Bale, "Extension to solgasmix for interactive calculations with the F*A*C*T thermodynamic database," *CALPHAD*, vol. 7, no. 2, 1983.
- [67] C. Bale, P. Chartrand, S. Degterov, G. Eriksson, K. Hack, R. Mahfoud, J. Melançon, A. Pelton, and S. Peterson, "FactSage thermochemical software and databases," *CALPHAD*, vol. 26, no. 2, 2002.
- [68] G. Eriksson and E. Koenigsberger, "Factsage and chemapp: Two tools for the prediction of multiphase chemical equilibria in solutions," *Pure and Applied Chemistry*, vol. 80, pp. 1293–1302, 2008.
- [69] S. Petersen and K. Hack, "The thermochemistry library ChemApp and its applications," *International Journal of Materials Research*, vol. 98, pp. 935–945, 2007.
- [70] J.-O. Andersson, T. Helander, L. Höglund, P. Shi, and B. Sundman, "ThermoCalc & DICTRA, computational tools for materials science," *CALPHAD*, vol. 26, no. 2, pp. 273 – 312, 2002.
- [71] B. Sundman, U. R. Kattner, M. Palumbo, and S. G. Fries, "OpenCalphad - a free thermodynamic software," *Integrating Materials and Manufacturing Innovation*, vol. 4, no. 1, 2015.
- [72] B. Cheynet, C. Bonnet, and M. Stankov, "GEMINI - DiagPlot: 2D & 3D ternary phase diagrams," *CALPHAD*, vol. 33, no. 312-316, 2009.
- [73] W. A. Wakeham and R. P. Stateva, "Numerical solution of isothermal, isobaric, phase equilibrium problem," *Reviews in Chemical Engineering*, vol. 20, no. 1-2, pp. 1–56, 2004.
- [74] Y. Teh and G. Rangaiah, "A study of equation-solving and gibbs free energy minimization methods for phase equilibrium calculations," *Chemical Engineering Research and Design*, vol. 80, no. 7, pp. 745 – 759, 2002.
- [75] P. M. Pardalos, H. Romeijn, and H. Tuy, "Recent developments and trends in global optimization," *Journal of Computational and Applied Mathematics*, vol. 124, no. 1, pp. 209 – 228, 2000. Numerical Analysis 2000. Vol. IV: Optimization and Nonlinear Equations.
- [76] C. Floudas, *Deterministic Global Optimization: Theory, Methods and Applications*. Springer, 1999.
- [77] D. Nichita, S. Gomez, and E. Luna, "Multiphase equilibria calculations by direct minimization of Gibbs free energy with a global optimization," *Computers and Chemical Engineering*, vol. 26, pp. 1703–1724, 2002.

- [78] J. B. Riggs, *An Introduction to Numerical Methods for Chemical Engineers*. Texas Tech University Press, 2nd ed., 1994.
- [79] F. Jalali, J. Seader, and S. Khaleghi, “Global solution approaches in equilibrium and stability analysis using homotopy continuation in the complex domain,” *Computers & Chemical Engineering*, vol. 32, no. 10, pp. 2333 – 2345, 2008.
- [80] H. Zhang, A. Bonilla-Petriciolet, and G. Rangaiah, “A review on global optimization methods for phase equilibrium modeling and calculations,” *The Open Thermodynamics Journal*, vol. 5, pp. 71–92, 2011.
- [81] B. Baurens, J. Sercombe, C. Riglet-Martial, L. Desgranges, L. Trotignon, and P. Maugis, “3d thermo-chemical-mechanical simulation of power ramps with alcyone fuel code,” *Journal of Nuclear Materials*, vol. 452, no. 1, pp. 578 – 594, 2014.
- [82] H. Greiner, “Computing complex chemical equilibria by generalized linear programming,” *Mathematical and Computer Modelling*, vol. 10, no. 7, pp. 529 – 550, 1988.
- [83] D. G. Goodwin, H. K. Moffat, and R. L. Speth, “Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes.” <http://www.cantera.org>, 2017.
- [84] M. Castier, P. Rasmussen, and A. Fredenslund, “Calculation of simultaneous chemical and phase equilibria in nonideal systems,” *Chemical Engineering Science*, vol. 44, no. 2, pp. 237 – 248, 1989.
- [85] K. Shobu, “CatCalc: New thermodynamic equilibrium calculation software,” *CALPHAD*, vol. 33, pp. 279–287, 2009.
- [86] S. Gordon and B. McBride, “Computer program for calculation of complex chemical equilibrium compositions and applications,” Tech. Rep. 1311, NASA, 1994.
- [87] P. Koukkari, K. Penttila, K. Hack, and S. Petersen, *CHEMSHEET – An Efficient Worksheet Tool for Thermodynamic Process Simulation*, pp. 323–330. John Wiley & Sons, Ltd, 2005.
- [88] M. Ahafat, *Computation of Stoichiometric Phase Coexistence in Multicomponent Systems*. PhD thesis, Queen's University, Kingston, ON, Canada, 1992.
- [89] D. S. Ebel, M. S. Ghiorso, R. O. Sack, and L. Grossman, “Gibbs energy minimization in gas + liquid + solid systems,” *Journal of Computational Chemistry*, vol. 21, no. 4, pp. 247–256, 2000.
- [90] M. Rafal, J. Berthold, and D. Linz, “Introduction to electrolytes,” technical white paper, OLI Systems Inc., 2003.
- [91] C. Bale and A. Pelton, “Optimization of binary thermodynamic and phase diagram data,” *Metallurgical Transactions B*, vol. 14B, pp. 77–83, 1983.
- [92] I. K. Karpov, K. V. Chudnenko, D. A. Kulik, and V. A. Bychinskii, “The convex programming minimization of five thermodynamic potentials other than Gibbs energy in geochemical modeling,” *American Journal of Science*, vol. 302, no. 4, pp. 281–311, 2002.
- [93] T. Cool, A. Bartol, M. Kasenga, K. Modi, and R. E. García, “Gibbs: Phase equilibria and symbolic computation of thermodynamic properties,” *CALPHAD*, vol. 34, no. 4, pp. 393 – 404, 2010.

- [94] C. M. McDonald and C. A. Floudas, "Glopeq: A new computational tool for the phase and chemical equilibrium problem," *Computers & Chemical Engineering*, vol. 21, no. 1, pp. 1 – 23, 1997.
- [95] L. G. Sillén, "High-speed Computers as a Supplement to Graphical Methods," *Acta Chemica Scandinavica*, vol. 16, pp. 159–172, 1962.
- [96] N. Ingri, W. Kakolowicz, L. G. Sillén, and B. Warnqvist, "High-speed computers as a supplement to graphical methods – V: Haltafall, a general program for calculating the composition of equilibrium mixtures," *Talanta*, vol. 14, no. 11, pp. 1261 – 1286, 1967.
- [97] G. Han and G. P. Rangaiah, "A method for multiphase equilibrium calculations," *Computers & Chemical Engineering*, vol. 22, no. 7, pp. 897 – 911, 1998.
- [98] Y. P. Lee, G. P. Rangaiah, and R. Luus, "Phase and chemical equilibrium calculations by direct search optimization," *Computers & Chemical Engineering*, vol. 23, no. 9, pp. 1183 – 1191, 1999.
- [99] H. Lukas, E. Henig, and B. Zimmermann, "Optimization of phase diagrams by a least squares method using simultaneously different types of data," *CALPHAD*, vol. 1, no. 3, pp. 225–236, 1977.
- [100] E. Kozeschnik and B. Buchmayr, "MatCalc - a simulation tool for multicomponent thermodynamics, diffusion and phase transformation kinetics," in *Mathematical Modeling of Weld Phenomena*, pp. 349–361, 2001.
- [101] R. Davies, A. Dinsdale, and J. Gisby, "MTDATA - thermodynamic and phase equilibrium software from the national physical laboratory," *CALPHAD*, vol. 26, no. 2, pp. 229–271, 2002.
- [102] W. Cao, S.-L. Chen, F. Zhang, K. Wu, Y. Yang, Y. Chang, R. Schmid-Fetzer, and W. Oates, "PANDAT software with panengine, panoptimizer and panprecipitation for multi-component phase diagram calculation and materials property simulation," *CALPHAD*, vol. 33, no. 328-342, 2009.
- [103] F. E. Pereira, G. Jackson, A. Galindo, and C. S. Adjiman, "A duality-based optimisation approach for the reliable solution of (p, t) phase equilibrium in volume-composition space," *Fluid Phase Equilibria*, vol. 299, no. 1, pp. 1 – 23, 2010.
- [104] R. Otis and Z.-K. Liu, "pycalphad: CALPHAD-based Computational Thermodynamics in Python," *Journal of Open Research Software*, vol. 5, no. 1, 2017.
- [105] C. Rossi, M. Berezuk, L. Cardozo-Filho, and R. Guirardello, "Simultaneous calculation of chemical and phase equilibria using convexity analysis," *Computers & Chemical Engineering*, vol. 35, no. 7, pp. 1226 – 1237, 2011.
- [106] E. Schnedler, "The calculation of complex chemical equilibria," *CALPHAD*, vol. 8, no. 3, pp. 265 – 279, 1984.
- [107] W. R. Smith and R. W. Missen, "Strategies for solving the chemical equilibrium problem and an efficient microcomputer-based algorithm," *The Canadian Journal of Chemical Engineering*, vol. 66, no. 4, pp. 591–598, 1988.
- [108] T. M. Besmann, "SOLGASMIX-PV, a computer program to calculate equilibrium relationships in complex chemical systems," Tech. Rep. ORNL/TM-5775, Oak Ridge National Laboratory, 1977.

- [109] W. Song and M. A. Larson, "Phase equilibrium calculation by using large-scale optimization technique," *Chemical Engineering Science*, vol. 46, no. 10, pp. 2513 – 2523, 1991.
- [110] W. Reynolds, "The element potential method for chemical equilibrium analysis: Stanjan," tech. rep., Stanford University, 1986.
- [111] C. de Capitani and T. H. Brown, "The computation of chemical equilibrium in complex systems containing non-ideal solutions," *Geochimica et Cosmochimica Acta*, vol. 51, no. 10, pp. 2639 – 2652, 1987.
- [112] T. J. Heams, D. A. Williams, N. A. Johns, A. Mason, N. E. Bixler, A. J. Grimley, C. J. Wheatley, L. W. Dickson, I. Osborn-Lee, P. Domagala, S. Zawadzki, J. Rest, C. A. Alexander, and R. Y. Lee, "VICTORIA: A mechanistic model of radionuclide behavior in the reactor coolant system under severe accident conditions," Tech. Rep. NUREG/CR-5545-Rev.1, Nuclear Regulatory Commission, 1992.
- [113] G. P. Rangaiah, *Stochastic Global Optimization: Techniques And Applications In Chemical Engineering*. World Scientific, 2010.
- [114] C. Blum and A. Roli, "Metaheuristics in combinatorial optimization: Overview and conceptual comparison," *ACM Computing Surveys*, vol. 35, no. 3, pp. 268–308, 2003.
- [115] S. H. Brooks, "A discussion of random methods for seeking maxima," *Operations Research*, vol. 6, no. 2, pp. 244–251, 1958.
- [116] R. Luus and T. H. I. Jaakola, "Optimization by direct search and systematic reduction of the size of search region," *AIChE Journal*, vol. 19, no. 4, pp. 760–766, 1973.
- [117] F. Glover and M. Laguna, *Modern Heuristic Techniques for Combinatorial Problems*, ch. Tabu Search. Blackwell Scientific Publications, 1993.
- [118] M. Srinivas and G. Rangaiah, "A study of differential evolution and tabu search for benchmark, phase equilibrium and phase stability problems," *Computers & Chemical Engineering*, vol. 31, no. 7, pp. 760 – 772, 2007.
- [119] Y. Teh and G. Rangaiah, "Tabu search for global optimization of continuous functions with application to phase equilibrium calculations," *Computers and Chemical Engineering*, vol. 27, pp. 1665–1679, 2003.
- [120] J. Barhen, V. Protopopescu, and D. Reister, "TRUST: a deterministic algorithm for global optimization," *Science*, vol. 276, pp. 1094–1097, 1997.
- [121] S. Chaikunchuensakun, L. I. Stiel, and E. L. Baker, "A combined algorithm for stability and phase equilibrium by gibbs free energy minimization," *Industrial & Engineering Chemistry Research*, vol. 41, no. 16, pp. 4132–4140, 2002.
- [122] A. Cheung, C. S. Adjiman, P. Kolar, and T. Ishikawa, "Global optimization for clusters of flexible molecules—solvent–solute interaction energy calculations," *Fluid Phase Equilibria*, vol. 194–197, pp. 169 – 183, 2002. Proceedings of the Ninth International Conference on Properties and Phase Equilibria for Product and Process Design.

- [123] M. Srinivas and G. P. Rangaiah, "Differential evolution with tabu list for global optimization and its application to phase equilibrium and parameter estimation problems," *Industrial & Engineering Chemistry Research*, vol. 46, no. 10, pp. 3410–3421, 2007.
- [124] Y. Zhu, H. Wen, and Z. Xu, "Global stability analysis and phase equilibrium calculations at high pressures using the enhanced simulated annealing algorithm," *Chemical Engineering Science*, vol. 55, no. 17, pp. 3451 – 3459, 2000.
- [125] G. P. Rangaiah, "Evaluation of genetic algorithms and simulated annealing for phase equilibrium and stability problems," *Fluid Phase Equilibria*, vol. 187, pp. 83–109, 2001.
- [126] A. Bonilla-Petriciolet, G. P. Rangaiah, and J. G. Segovia-Hernández, "Constrained and unconstrained gibbs free energy minimization in reactive systems using genetic algorithm and differential evolution with tabu list," *Fluid Phase Equilibria*, vol. 300, no. 1, pp. 120 – 134, 2011.
- [127] K. Lin and D. Chen, "Hybrid artificial immune system and its application to calculation of chemical reaction and phase equilibrium," *Journal of Chemical Industry & Engineering*, vol. 58, pp. 1348–1352, 2007.
- [128] P. B. Staudt and R. de P. Soares, "Reliability vs. efficiency when solving multiphase equilibrium problems with hybrid optimization codes," in *10th International Symposium on Process Systems Engineering: Part A* (R. M. de Brito Alves, C. A. O. do Nascimento, and E. C. Bicaia, eds.), vol. 27 of *Computer Aided Chemical Engineering*, pp. 585 – 590, Elsevier, 2009.
- [129] A. M. Scurto, G. Xu, J. F. Brennecke, and M. A. Stadtherr, "Phase behaviour and reliable computation of high pressure solid fluid equilibrium with cosolvents," *Industrial and Engineering Chemistry Research*, vol. 42, pp. 6464–6475, 2003.
- [130] A. Bonilla-Petriciolet and J. G. Segovia-Hernández, "Particle swarm optimization for phase stability adn equilibrium calculations in reactive systems," 19th European Symposium on Computer Aided Process Engineering (ESCAPE19), 2009.
- [131] A. Bonilla-Petriciolet, G. A. Iglesias-Silva, and K. R. Hall, "Calculation of homogeneous azeotropes in reactive and non-reactive mixtures using a stochastic optimization approach," *Fluid Phase Equilibria*, vol. 281, no. 1, pp. 22 – 31, 2009.
- [132] A. Lucia, L. Padmanabhan, and S. Venkataraman, "Multiphase equilibrium flash calculations," *Computers & Chemical Engineering*, vol. 24, no. 12, pp. 2557 – 2569, 2000.
- [133] D. Nichita, S. Gomez, and E. Luna-Ortiz, "Multiphase equilibria calculation by direct minimization of gibbs free energy using the tunnelling global optimization method," *Journal of Canadian Petroleum Technology*, vol. 43, no. 05, pp. 13–16, 2004.
- [134] T. Besmann, J. McMurray, B. Gaston, S. Simunovic, and M. Piro, "Modeling thermochemistry of fuel and coupling to fuel performance codes," in *Proceedings of the Top Fuel Conference*, (Boise, Idaho), 2016.
- [135] SCALE, "SCALE: A modular code system for performing standardized computer analyses for licensing evaluation," Tech. Rep. ORNL/TM-2005/39, Version 6, Vols. I – III, Oak Ridge National Laboratory, 2005.

- [136] P. Konarski, J. Sercombe, C. Riglet-Martial, L. Noirot, I. Zacharie-Aubrun, K. Hanifi, M. Frégonèse, and P. Chantrenne, “3d simulation of a power ramp including fuel thermochemistry and oxygen thermodiffusion,” *Journal of Nuclear Materials*, vol. 519, pp. 104 – 120, 2019.
- [137] B. Fitzpatrick, M. Piro, and B. Collins, “Progress in coupling of thermodynamics, fluid dynamics and isotopics in molten salt reactor multi-physics simulations,” *Proceedings of American Nuclear Society*, Philadelphia, PA 2018.
- [138] Z.-K. Liu and Y. Wang, *Computational Thermodynamics of Materials*. Cambridge University Press, 2016.
- [139] M. Hillert, “Some viewpoints on the use of a computer for calculating phase diagrams,” *Physica*, vol. 103B, pp. 31–40, 1981.
- [140] J. Kennedy and R. Eberhart, “Particle swarm optimization,” Proceedings of IEEE International Conference on Neural Networks, 1995.
- [141] B. Sundman, B. Jansson, and J.-O. Andersson, “The Thermo-Calc databank system,” *CALPHAD*, vol. 9, no. 2, pp. 153–190, 1985.
- [142] B. Sundman, X.-G. Lu, and H. Ohtani, “The implementation of an algorithm to calculate thermodynamic equilibria for multi-component systems with non-ideal phases in a free software,” *Computational Materials Science*, vol. 101, pp. 127–137, 2015.
- [143] S. Chen, K. Chou, and Y. Chang, “On a New Strategy for Phase Diagram Calculation: 1. Basic Principles,” *CALPHAD*, vol. 17, no. 3, pp. 237–250, 1993.
- [144] S. Chen, K. Chou, and Y. Chang, “On a New Strategy for Phase Diagram Calculation: 2. Binary Systems,” *CALPHAD*, vol. 17, no. 3, pp. 287–302, 1993.
- [145] J. Falk and R. Soland, “An algorithm for separable nonconvex programming problems,” *Management Science*, vol. 15, no. 9, pp. 550–569, 1969.
- [146] L. Jaulin, M. Kieffer, O. Didrit, and E. Walter, *Applied Interval Analysis*. Berlin: Springer, 2001.
- [147] C. McDonald and C. Floudas, “Global optimization and analysis for the Gibbs free energy function using the UNIFAC, Wilson, and ASOG equations,” *Industrial and Engineering Chemistry Research*, vol. 34, pp. 1674–1687, 1995.
- [148] O. Beneš and R. Konings, “3.13 - Molten Salt Reactor Fuel and Coolant,” in *Comprehensive Nuclear Materials* (R. J. Konings, ed.), pp. 359 – 389, Oxford: Elsevier, 2012.
- [149] G. Ilas and I. Gauld, “Analysis of experimental data for high burnup PWR spent fuel isotopic validation-Vandellos II reactor,” Tech. Rep. NUREG/CR-7013, U.S. Nuclear Regulatory Commission, 2011.

LIST OF PUBLICATIONS

1. M. Piro, M. Poschmann and **P. Bajpai**, *On the interpretation of chemical potentials computed from equilibrium thermodynamic codes: Applications to molten salts*, *Journal of Nuclear Materials*, 526 (2019) 151756.
2. **P. Bajpai**, M. Poschmann, M. Piro, *Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models*, To be submitted to *CALPHAD Computer Coupling of Phase Diagrams and Thermochemistry*. [In preparation]
3. **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. [Accepted]
4. **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.

M. Piro, M. Poschmann and **P. Bajpai**

*On the interpretation of chemical potentials computed from equilibrium thermodynamic codes:
Applications to molten salts*
Journal of Nuclear Materials, 526 (2019) 151756.



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].

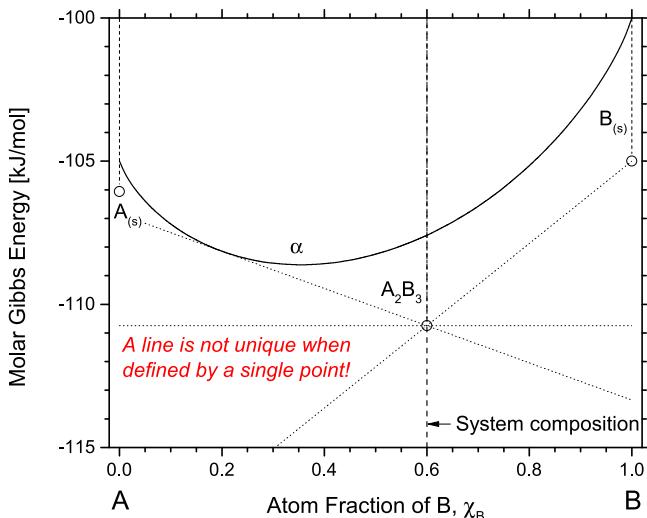


Fig. 1. The fictive A-B system is shown with the overall composition identified, which intersects the A_2B_3 phase. The lowest common tangent line intersects this phase, but is not uniquely defined. Copied from Piro et al. [1].

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.

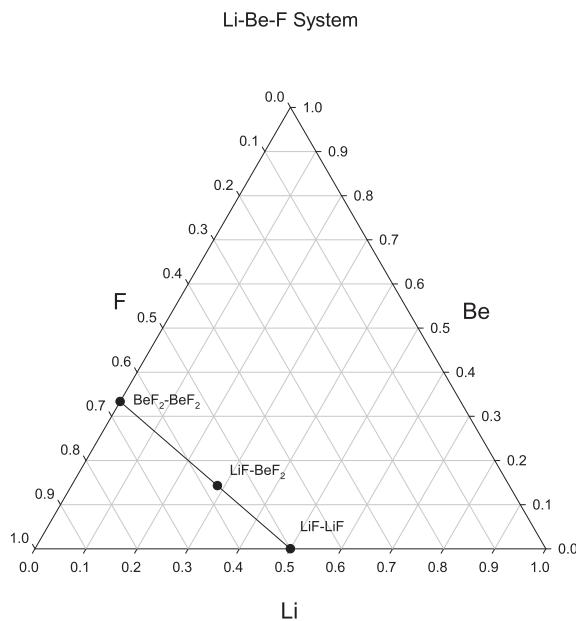


Fig. 2. A ternary plot of the Li-Be-F system with the three pair fractions corresponding to LiF-BeF_2 are indicated. A three dimensional Gibbs plane cannot be defined by three points because they are colinear.

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

This research was undertaken, in part, thanks to funding from the Canada Research Chairs (950–231328) program of the Natural Sciences and Engineering Research Council of Canada.

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.

References

- [1] M. Piro, M. Welland, M. Stan, On the interpretation of chemical potentials computed from equilibrium thermodynamic codes, *J. Nucl. Mater.* 464 (2015) 48–52.
- [2] J. McMurray, T. Besmann, J. Ard, B. Fitzpatrick, M. Piro, J. Jerden, M. Williamson, B. Collins, B. Betzler, A. Qualls, Multi-physics simulations for molten salt reactor evaluation: Chemistry modeling and database development, in: Tech. Rep. ORNL/SPR-2018/864, Oak Ridge National Laboratory, Oak Ridge, TN, 2018.
- [3] M. Piro, T. Besmann, S. Simunovic, B. Lewis, W. Thompson, Numerical verification of equilibrium thermodynamic computations in nuclear fuel performance codes, *J. Nucl. Mater.* 414 (3) (2011) 399–407.
- [4] Compendium of Chemical Terminology, Gold Book. No. Version 2.3.3, International Union of Pure and Applied Chemistry, 2014.
- [5] A. Pelton, S. Degterov, G. Eriksson, C. Robelin, Y. Desureault, The modified

- quasichemical model I – binary solutions, *Metall. Mater. Trans. B* 31B (2000) 651–659.
- [6] A. Pelton, P. Chartrand, The modified quasichemical model II – multicomponent solutions, *Metall. Mater. Trans. A* 32A (2001) 1355–1360.
- [7] P. Chartrand, A. Pelton, The modified quasichemical model III – two sublattices, *Metall. Mater. Trans. A* 32 (6) (2001) 1397–1407.
- [8] A. Pelton, P. Chartrand, G. Eriksson, The modified quasichemical model IV – two-sublattice quadruplet approximation, *Metall. Mater. Trans. A* 32A (2001) 1409–1416.
- [9] O. Beneš, Thermodynamics of Molten Salts for Nuclear Applications, PhD thesis, Institute of Chemical Technology, Prague, Czech Republic, 2008.
- [10] O. Beneš, M. Beilmann, R. Konings, Thermodynamic assessment of the LiF-NaF-ThF₄-UF₄ system, *J. Nucl. Mater.* 405 (2010) 186–198.
- [11] E. Capelli, O. Beneš, R. Konings, Thermodynamics of soluble fission products cesium and iodine in the molten salt reactor, *J. Nucl. Mater.* 501 (2018) 238–252.
- [12] O. Beneš, P. Soucek, 7: molten salt reactor fuels, in: M. Piro (Ed.), *Advances in Nuclear Fuel Chemistry*, Elsevier, 2019.
- [13] K. Johnson, M. Kahn, J. Leary, Phase equilibria in fused salt systems: binary systems of plutonium(III) chloride with the chlorides of magnesium, calcium, strontium, and barium, *J. Phys. Chem.* 65 (1961) 1461–1462.
- [14] C. Bale, P. Chartrand, S. Degterov, G. Eriksson, K. Hack, R. Mahfoud, J. Melançon, A. Pelton, S. Peterson, FactSage thermochemical software and databases, *Calphad* 26 (2) (2002).
- [15] M. Piro, S. Simunovic, T. Besmann, B. Lewis, W. Thompson, The thermochemistry library thermochimica, *Comput. Mater. Sci.* 67 (2013) 266–272.
- [16] O. Beneš, R. Konings, 3.13 – molten salt reactor fuel and coolant, in: R.J. Konings (Ed.), *Comprehensive Nuclear Materials*, Elsevier, Oxford, 2012, pp. 359–389.
- [17] M. Piro, Computation of Thermodynamic Equilibria Pertinent to Nuclear Materials in Multi-Physics Codes, PhD thesis, Royal Military College of Canada, 2011.
- [18] W. White, S. Johnson, G. Dantzig, Chemical equilibrium in complex mixtures, *J. Chem. Phys.* 28 (5) (1958) 751–755.

M.H.A. Piro*, M. Poschmann
Faculty of Energy Systems and Nuclear Sciences, Ontario Tech University, Oshawa, ON, Canada

P. Bajpai
Faculty of Science, Ontario Tech University, Oshawa, ON, Canada

* Corresponding author.
E-mail address: markus.piro@ontariotechu.ca (M.H.A. Piro).

8 August 2019
Available online 20 August 2019

P. Bajpai, M. Poschmann and M. Piro
*erivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic
models*

To be submitted to **CALPHAD Computer Coupling of Phase Diagrams and Thermochemistry**. [In
preparation]

Derivations of useful partial molar excess Gibbs energy of mixing expressions of common thermodynamic models

P. Bajpai^a, M. Poschmann^a, M.H.A. Piro^{a,*}

^a*University of Ontario Institute of Technology, Oshawa, ON, Canada*

Abstract

Numerous thermodynamic models have been developed to capture the behaviour of aqueous solutions, regular solid solutions, ionic ceramics, multi-sublattice metallic alloys, short and long range ordering, and much more. Classes of common thermodynamic models include regular solution, compound energy formalism, and modified quasi-chemical models. The mathematical formulation of the molar Gibbs energy of a phase represented by any of the aforementioned models takes on a unique form, which requires special consideration for use in a Gibbs energy minimizer. This paper provides derivations of the partial molar excess Gibbs energy of mixing of multiple common classes of thermodynamic models for use in a Gibbs energy minimizer.

Keywords: CALPHAD, Gibbs energy minimization, Regular Solution Model, Compound Energy Formalism, Modified Quasi-Chemical Model

Acronyms

FNN First Nearest Neighbour.

MQM Modified Quasichemical Model.

SNN Second Nearest Neighbour.

SRO Short-Range Ordering.

1. Introduction

Think about including a glossary. There will be a lot of variables, which will be difficult to keep sorted out.

*Corresponding author
Email address: markus.piro@uoit.ca ()

Specifically, one requires partial molar Gibbs energy terms to be used as input to a Hessian matrix to minimize G subject to appropriate constraints.

Consider submitting this a journal other than CALPHAD (e.g., Journal of Alloys and Compounds, Metallurgical and Materials Transactions, ...).

Give derivations of species, component, etc.

The partial molar excess Gibbs energy of mixing of species i in phase λ is by definition

$$g_{i(\lambda)}^{ex} = \left(\frac{\partial G_{\lambda}^{ex}}{\partial n_i} \right)_{T,P,n_j \neq i} \quad (1)$$

where n_i represents the number of moles of species i and the integral excess Gibbs energy of mixing is G_{λ}^{ex} , which is given by

$$G_{\lambda}^{ex} = n_{\lambda} g_{\lambda}^{ex} \quad (2)$$

2. Regular Solution Model with Kohler-Toop Interpolation

2.1. Background on QKTO

Briefly describe the QKTO.

2.2. Derivation of Equations for QKTO

2.2.1. Derivation of Partial Excess Gibbs Energy of Mixing in a Sub-System

Suppose the molar excess Gibbs energy of mixing of a non-ideal solution phase sub-system is generally given by

$$g_{\lambda}^{ex} = \sum_{z=1}^Z \phi_z (x_1^{d_1} x_2^{d_2} x_3^{d_3}) \quad (3)$$

Representing the first equation in terms of n_i for all components gives

$$G_{\lambda}^{ex} = \sum_{z=1}^Z \phi_z \frac{(n_1^{d_1} n_2^{d_2} n_3^{d_3})}{n_{\lambda}^{d_1+d_2+d_3-1}} \quad (4)$$

Differentiation of equation (X) with respect to n_1 gives the partial molar excess Gibbs energy of mixing,

$$g_{1(\lambda)}^{ex} = \sum_{z=1}^Z \phi_z \left(\frac{(d_1 n_1^{d_1-1} n_2^{d_2} n_3^{d_3})}{n_{\lambda}^{d_1+d_2+d_3-1}} - (d_1 + d_2 + d_3 - 1) \frac{n_1^{d_1} n_2^{d_2} n_3^{d_3}}{n_{\lambda}^{d_1+d_2+d_3-2}} \right) \quad (5)$$

Simplifying gives the partial molar excess Gibbs energy of mixing of component 1 in a particular sub-system (note that this may not be the same as the phase):

$$g_{1(\lambda)}^{ex} = \sum_{z=1}^Z \phi_z \left((d_1 x_1^{d_1-1} + (1-d_1-d_2-d_3)x_1^{d_1})x_2^{d_2}x_3^{d_3} \right) \quad (6)$$

2.2.2. Derivation of the Partial Excess Gibbs Energy of Mixing of a Component in a Ternary Phase with a Binary Sub-System Using Kohlers Interpolation

This section considers the scenario where the sub-system contains fewer constituents than that represented by the phase. This example considers a phase with three constituents and a mixing parameter representing two of them. First, the mole fractions of all constituents are related by the following equality,

$$x_1 + x_2 + x_3 = 1 \quad (7)$$

and the total number of moles of this phase is,

$$n_1 + n_2 + n_3 = n_\lambda \quad (8)$$

The molar excess Gibbs energy of an arbitrary phase is estimated using Kohlers interpolation scheme:

$$g_\lambda^{ex} = (x_1 + x_2)^2 g_{1,2}^{ex} \quad (9)$$

where is the molar excess Gibbs energy in the 1-2 binary sub-system and is related to the integral excess Gibbs energy of the 1-2 binary sub-system:

$$g_{1,2}^{ex} = \frac{G_{1,2}^{ex}}{n_1 + n_2} \quad (10)$$

and the partial excess Gibbs energy of component 1 in the 1-2 binary sub-system is

$$g_{1(1,2)}^{ex} = \left(\frac{\partial G_{1,2}^{ex}}{\partial n_1} \right)_{n_j \neq 1} \quad (11)$$

and is calculated with equation (X) using the equivalent mole fractions. Multiplying equation (x) by and substitution of equation (X) gives the integral excess Gibbs energy of the phase is

$$G_\lambda^{ex} = \frac{(n_1 + n_2)G_{1,2}^{ex}}{n_\lambda} \quad (12)$$

The partial excess Gibbs energy of component 1 in phase alpha is:

$$g_1^{ex} = \frac{(n_1 + n_2)g_{1,2}^{ex}}{n_\lambda} + \frac{(n_1 + n_2)g_{1(1,2)}^{ex}}{n_\lambda} - \frac{(n_1 + n_2)^2 g_{1,2}^{ex}}{n_\lambda^2} \quad (13)$$

which simplifies to:

$$g_1^{ex} = (x_1 + x_2) \left(g_{1(1,2)}^{ex} + (1 - (x_1 + x_2)) g_{1,2}^{ex} \right) \quad (14)$$

WHAT ABOUT COMPONENT 2???

Similarly, for component 3:

$$g_3^{ex} = -(x_1 + x_2)^2 g_{1(1,2)}^{ex} \quad (15)$$

2.2.3. Derivation of the Partial Excess Gibbs Energy of Mixing of a Component in a Multicomponent (more than three) Phase with a Ternary Sub-System Using Kohlers Interpolation

The molar excess Gibbs energy of an arbitrary phase is

$$g_\lambda^{ex} = (x_1 + x_2 + x_3)^3 g_{1,2,3}^{ex} \quad (16)$$

which is expanded to:

$$g_\lambda^{ex} = \left(\frac{n_1 + n_2 + n_3}{n_\lambda} \right)^3 \frac{G_{1,2,3}^{ex}}{n_1 + n_2 + n_3} \quad (17)$$

The integral excess Gibbs energy of an arbitrary phase is

$$G_\lambda^{ex} = \left(\frac{n_1 + n_2 + n_3}{n_\lambda} \right)^2 G_{1,2,3}^{ex} \quad (18)$$

The partial molar excess Gibbs energy of mixing of component 1 is

$$g_{1(\lambda)}^{ex} = 2 \left(\frac{n_1 + n_2 + n_3}{n_\lambda^2} \right) G_{1,2,3}^{ex} + \left(\frac{n_1 + n_2 + n_3}{n_\lambda} \right)^2 g_{1(1,2,3)^{ex}} - 2 \left(\frac{(n_1 + n_2 + n_3)^2}{n_\lambda^3} \right) G_{1,2,3}^{ex} \quad (19)$$

which simplifies to:

$$g_{1(\lambda)}^{ex} = (x_1 + x_2 + x_3)^2 \left(g_{1(1,2,3)}^{ex} + 2g_{1,2,3}^{ex}(1 - (x_1 + x_2 + x_3)) \right) \quad (20)$$

And where the partial molar excess Gibbs energy of mixing of component j ($\neq 1, 2, 3$) is:

$$g_{j(\lambda)}^{ex} = -(x_1 + x_2 + x_3)^3 (2g_{1,2,3}^{ex}) \quad (21)$$

3. Regular Solution Model with Muggiano Interpolation

3.1. Background on RKMP

Insert background here.

3.2. Derivation of Equations for RKMP

THINK ABOUT WHICH VARIABLES SHOULD BE USED. SHOULD v OR ν BE USED FOR EXPONENTS? SHOULD WE USE 1 AND 2 TO REPRESENT SPECIES, OR A AND B?

3.2.1. Binary mixing terms

An important distinction between the Muggiano interpolation scheme and the Kohler and Toop schemes is that if Redlich-Kister polynomials are used to represent mixing parameters, then the molar excess Gibbs energy of mixing involving binary interaction parameters is simply [1] [2].

$$g_{\lambda}^{ex} = \sum_{z=1}^Z x_j x_k \sum_{\nu=0}^{\nu} L_{j,k}(x_j - x_k)^{\nu} \quad (22)$$

and the equations are simplified in comparison to Kohler/Toop schemes. Kohler/Toop interpolation schemes require special consideration when relating binary interaction parameters for the molar Gibbs energy of a phase. For the above equation, x_j and x_k are the mole fractions of species j and k that correspond to parameter index z , the total number of mixing parameters is denoted by Z and is the temperature dependent mixing parameter for the ν -th order parameter. The partial molar excess Gibbs energy of mixing of constituent i in phase λ is by definition

$$g_{i(\lambda)}^{ex} = \left(\frac{\partial G_{\lambda}^{ex}}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (23)$$

where $n_{i(\lambda)}$ represents the number of moles of species i . The integral excess Gibbs energy of mixing for solution phase λ is,

$$G_{\lambda}^{ex} = n_{\lambda} g_{\lambda}^{ex} \quad (24)$$

where n_{λ} represents the total number of moles of phase λ . Representing equation X in terms of molar quantities instead of mole fractions gives,

$$G_{\lambda}^{ex} = n_{\lambda} g_{\lambda}^{ex} \quad (25)$$

Substituting equation X into equation X gives,

EQUATION (include?)

Substituting equation X into equation X gives the partial molar excess Gibbs energy of mixing of constituent 1 from parameter z in solution phase ,

EQUATION (include?)

Representing relative molar quantities by mole fractions and simplifying gives,

$$g_{1(\lambda,z)}^{ex} = {}^v L_{1,2}(x_1 - x_2)^{v-1} ((x_2 - x_1 x_2)(x_1 - x_2) + v x_1 x_2(1 - (x_1 - x_2))) \quad (26)$$

Similarly, the partial molar excess Gibbs energy of mixing for the second constituent in mixing parameter z is,

$$g_{2(\lambda,z)}^{ex} = {}^v L_{1,2}(x_1 - x_2)^{v-1} ((x_1 - x_1 x_2)(x_1 - x_2) - v x_1 x_2(1 + (x_1 - x_2))) \quad (27)$$

And finally any other species is,

$$g_{i \neq 1,2(\lambda,z)}^{ex} = -{}^v L_{1,2}(x_1 - x_2)^v (x_1 x_2)(1 + v) \quad (28)$$

Therefore, the partial molar excess Gibbs energy of mixing of any constituent is the sum of the partial molar excess Gibbs energy of that constituent for all mixing parameters in solution phase λ ,

$$g_{i(\lambda)}^{ex} = \sum_{z=1}^Z g_{i(\lambda,z)}^{ex} \quad (29)$$

3.2.2. Ternary Terms

Ternary terms are represented in an RKMP model with the following equation, which only contains zero-th order parameters (as opposed to higher order parameters permitted for binary interaction terms) [1] *CONFIRM that there are only zeroth order terms for ternary interaction parameters*

$$g_{(\lambda)}^{ex} = x_1 x_2 x_3 \left(\frac{1 - x_1 - x_2 - x_3}{3} + x_j \right)^0 L_{1,2,3} \quad (30)$$

where $j = 1, 2$, or 3 . FactSage-Solution does not allow the user to manually change the exponents of the mole fractions of constituents in a RKMP phase. According to Chartrand and Pelton [1], this constraint is imposed on the user due to the little theoretical justification of using higher order exponents.

The integral Gibbs energy of mixing for a ternary parameter is,

EQUATION (include?)

Inserting from equation X into equation X and differentiating with respect to X gives

EQUATION (include?)

Let the Kronecker-Delta term be defined for convenience,

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

Thus, simplifying the above equation using mole fractions and the Kronecker-Delta term gives,

$$g_{1(\lambda,z)}^{ex} = \left[(x_2x_3 - 3x_1x_2x_3) \left(\frac{1-x_1-x_2-x_3}{3} \right) + x_j \right]^0 L_{1,2,3} \quad (31)$$

Similarly, the partial molar excess Gibbs energy of mixing constituent 2 in a ternary phase is,

$$g_{2(\lambda,z)}^{ex} = \left[(x_1x_3 - 3x_1x_2x_3) \left(\frac{1-x_1-x_2-x_3}{3} \right) + x_j \right]^0 L_{1,2,3} \quad (32)$$

and for constituent 3 *WHY IS x_j MULTIPLIED BY THREE BELOW AND NOT ABOVE?*

$$g_{3(\lambda,z)}^{ex} = \left[(x_1x_2 - 3x_1x_2x_3) \left(\frac{1-x_1-x_2-x_3}{3} \right) + 3x_j \right]^0 L_{1,2,3} \quad (33)$$

and for any other constituent,

$$g_{i \neq 1,2,3(\lambda,z)}^{ex} = (x_1x_2x_3)(x_1 + x_2 + x_3 - \frac{2}{3})^0 L_{1,2,3} \quad (34)$$

Note that for any constituent not belonging to the ternary mixing parameter, necessarily equals zero because j = 1, 2 or 3 by definition.

3.2.3. Quaternary Terms

Quaternary terms are represented in an RKMP model with the following equation, which only contains zero-th order parameters (as opposed to higher order parameters permitted for binary interaction terms) [2],

$$g_{\lambda}^{ex} = x_1x_2x_3x_4^0 L_{1,2,3,4} \quad (35)$$

FactSage-Solution allows the user to enter exponents; however, they are not included in the model and are just confusing to the user. The integral Gibbs energy of mixing for a quaternary parameter is,

EQUATION (include?)

Inserting from equation (20) into equation (2) and differentiating with respect to gives

EQUATION (include?)

Thus, simplifying the above equation using mole fractions

$$g_{\lambda}^{ex} = x_1x_2x_3x_4 \left(\frac{1}{x_i} - 3 \right)^0 L_{1,2,3,4} \quad (36)$$

where i = 1, 2, or 3. Finally, the partial molar excess Gibbs energy of mixing for any other constituent,

$$g_{i \neq (1,2,34)(\lambda)}^{ex} = -3x_1x_2x_3x_4^0 L_{1,2,3,4} \quad (37)$$

3.2.4. Comments

Consider a special case where $x_1 = x_2$ and the equations above may yield infinite or non-real values. The solver must make provisions for such scenarios depending on the compiler that is used. Consider the following scenarios:

- i. Consider $x_1 = x_2$ and $v_{Li,j}$ where $v = 0$. Note that $00=1$ and $0/0 = 1$; although some may argue that these two special cases are undefined.
- ii. Consider $x_1 = x_2$ and $v_{Li,j}$ where $v \neq 1$. Note that $01=0$ and $0/0 = 1$; although some may argue that these two special cases are undefined.

Note that Fortran returns $00 = 1$, $0/0 = \text{NaN}$ and $1/0 = \text{inf}$. A simple solution to this problem is to evaluate the following term independently,

(24)

and set

(25)

Therefore, q_a may be infinite if $x_1 = x_2$ and $v = 0$, but q_b

4. Compound Energy Formalism

4.1. Background on CEF

A common source of confusion with those uninitiated with the Compound Energy Formalism (CEF) is the distinction between the terms, “species”, “constituent” and “component”. Following the nomenclature of Hillert [3], the term “species” refers to a molecule, pure element, vacancy or ion, and the term “constituent” refers to a particular species on a particular sublattice. The term “component” is used in the context of the CEF to refer to a unique combination of constituents on each sublattice, or “compound end member”. The total number of components of a CEF phase is the product of the number of constituents on each sublattice.

For example, the solid solution $\text{UO}_{2\pm x}$ phase [4] may be represented by the CEF model with three sublattices, where U^{3+} , U^{4+} and U^{5+} are species on the first sublattice, O^{2-} and Va are species on the second sublattice and O^{2-} and Va are species on the third sublattice. Also, $\text{O}_{(2)}^{2-}$ and $\text{O}_{(3)}^{2-}$ represent the same species but are different constituents because they reside on different sublattices (as identified by the subscripts). Since there are three constituents on the first sublattice, two on the second and two on the third sublattice, the total number of components for this phase is twelve. These constituents can be combined to form the following components $\text{U}^{4+}:\text{O}^{2-}:\text{Va}$ (i.e., UO_2), $\text{U}^{4+}:\text{O}^{2-}:\text{O}^{2-}$ (i.e., UO_3^{2-}), in addition to several others. Continuing with the representation of components from Hillert, the constituents on each sublattice is separated by a colon, “:”. Finally, standard molar Gibbs energy expressions are defined for each component and excess Gibbs energy of mixing parameters are defined between components.

The molar Gibbs energy, g_λ , of solution phase λ based on the CEF model is generally given as,

$$g_\lambda = \sum_{i=1}^{N_\lambda} g_i^\circ(\lambda) \prod_{s=1}^{N_s} y_{i(s)} + RT \left(\sum_{s=1}^{N_s} a_s \sum_{c=1}^{N_c} y_{c(s)} \ln(y_{c(s)}) \right) + g_\lambda^{ex} \quad (38)$$

where $g_i^\circ(\lambda)$ 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} .

Several constraints are applied to a phase modelled by the CEF. First, the sum of site fractions for each sublattice must equal unity,

$$\sum_{c=1}^{N_c} y_{c(s)} = 1 \quad (39)$$

and the sum of mole fractions of all components in a solution phase (recall that the components differ from the constituents) must also equal unity,

$$\sum_{i=1}^{N_\lambda} x_{i(\lambda)} = 1 \quad (40)$$

As a natural consequence of the formulation of components from the constituents, the constraints represented by equation (40) are necessarily satisfied when equation (39) is satisfied, and vice versa. The mole fraction of a component is related to the site fraction of all associated constituents on each sublattice (i.e., a component will be represented by one constituent on every sublattice) through the following relationship,

$$x_{i(\lambda)} = \prod_{s=1}^{N_s} y_{i(s)} \quad (41)$$

As an example, the mole fraction for component $\text{U}^{4+}:\text{O}^{2-}:\text{Va}$ is computed as $x_{\text{U}^{4+}:\text{O}^{2-}:\text{Va}} = y_{\text{U}^{4+}(1)}y_{\text{O}^{2-}(2)}y_{\text{Va}(3)}$. Also, the site fraction of a constituent on a particular sublattice is related to the mole fractions of the components through the following summation relation:

$$y_{c(s)} = \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \delta_{i,c(s)} \quad (42)$$

where $\delta_{i,c(s)}$ is a Kronecker delta term that is equal to unity when constituent c on sublattice s is the same as the corresponding constituent for component i and is otherwise equal to zero. At equilibrium, equations (41)

and (42) must be equivalent. However, from a numerical point of view, equation (42) is insensitive to the mole fractions of dilute components because it is a summation function. On the other hand, equation (41) is sensitive to dilute site fractions because it is a multiplicative function. This must be taken into consideration in the programming to minimize numerical errors.

An analytical derivation of $\mu_{i(\lambda)}$ that is useful for computer calculation for an ideal solution phase will be given in §?? and for a non-ideal solution phase in §??.

4.2. Derivation of Equations for CEF

The chemical potential of component i in solution phase λ represented by a CEF model is generally given as [5],

$$\mu_{i(\lambda)} = g_\lambda + \sum_{s=1}^{N_s} \left(\frac{\partial g_\lambda}{\partial y_{i(s)}} - \sum_{j=1}^{N_\lambda} y_{j(s)} \frac{\partial g_\lambda}{\partial y_{j(s)}} \right) \quad (43)$$

First, one must evaluate the partial derivative of equation (38) with respect to $y_{i(s)}$,

$$\frac{\partial g_\lambda}{\partial y_{i(s)}} = \sum_{j=1}^{N_\lambda} g_j^\circ(\lambda) \left(\frac{\delta_{i,j}}{y_{i(s)}} \right) \prod_{s=1}^{N_s} y_{j(s)} + RT \sum_{s=1}^{N_s} a_s \ln(y_{i(s)} + 1) \quad (44)$$

where $\delta_{i,j}$ is a Kronecker delta term that is equal to unity when the constituents correspond to i and j are the same and is otherwise equal to zero. Substituting equation (44) into equation (43) yields the chemical potential for component i in an *ideal* solution phase represented by the CEF model [5]

$$\mu_{i(\lambda)} = \sum_{j=1}^{N_\lambda} x_j(\lambda) g_j^\circ(\lambda) \left(1 - N_s + \sum_{s=1}^{N_s} \frac{\delta_{i,j}}{y_{j(s)}} \right) + RT \sum_{s=1}^{N_s} a_s \ln(y_{i(s)}) \quad (45)$$

The chemical potential of a component in a phase based on the CEF model therefore includes contributions from the standard molar Gibbs energies of all components in that phase. The ideal mixing contribution to $\mu_{i(\lambda)}$ only considers the constituents associated with component i .

The molar Gibbs energy for a non-ideal solution phase based on the CEF model is represented by equation (38) with a non-zero value for g_λ^{ex} . The molar excess Gibbs energy of mixing is generally represented as

$$g_\lambda^{ex} = \sum_{p=1}^{N_p} \left(\prod_{m=1}^{N_p} y_{m(s)} \right) \sum_{z=0}^{N_z} z L_{j,k} (y_j - y_k)^z \quad (46)$$

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. For example, the molar excess Gibbs energy of mixing for the $\text{UO}_{2\pm x}$ fluorite phase is

$$g_{\text{fluorite}}^{\text{ex}} = y_{\text{U}^{3+}} y_{\text{U}^{4+}} y_{\text{O}^{2-}} y_{\text{Va}} \left({}^0 L_{(\text{U}^{3+}, \text{U}^{4+})(\text{O}^{2-})_2(\text{Va})} + (y_{\text{U}^{3+}} - y_{\text{U}^{4+}}) {}^1 L_{(\text{U}^{3+}, \text{U}^{4+})(\text{O}^{2-})_2(\text{Va})} \right) + y_{\text{U}^{4+}} y_{\text{U}^{5+}} y_{\text{O}^{2-}} y_{\text{O}^{2-}}^0 L_{(\text{U}^{4+}, \text{U}^{5+})(\text{O}^{2-})_2(\text{O}^{2-})} \quad (47)$$

The partial molar excess Gibbs energy of mixing of a component in a CEF phase is derived by Sundman *et al.* [5] for the case of composition independent interaction parameters. Here, the partial molar excess Gibbs energy of mixing allows for composition dependent terms to be considered,

$$g_{i(\lambda)}^{\text{ex}} = \sum_{p=1}^{N_p} \left(\prod_{m=1}^{N_p} y_{m(s)} \right) \sum_{z=0} z L_{j,k} (y_j - y_k)^z \left(-(N_s + z) + \sum_{s=1}^{N_s} \frac{\delta_{i,p}}{y_{i(s)}} \frac{z}{(y_j - y_k)} \right) \quad (48)$$

where $\delta_{i,e}^s$ is a Kronecker delta term which is equal to unity when the constituent associated with component i on sublattice s is the same as the corresponding constituent of mixing parameter p . Unlike the contribution from the reference molar Gibbs energy, the only terms in equation (48) that are component dependent are $\delta_{i,p}$ and y_i . Thus, only component i must be considered in computing the partial molar excess Gibbs energy of mixing of component i . Also, note that the indexing scheme used here differs from that of Sundman *et al.* [5]. Sundman *et al.* use the variables z (where $z > 0$) and b to represent the order of mixing where $z = b + 1$. To minimize confusion, only z is used here (where $z \geq 0$).

As an example, consider computing $g_{i(\lambda)}^{\text{ex}}$ for component $\text{U}^{3+}:\text{O}^{2-}:\text{Va}$ in the $\text{UO}_{2\pm x}$ phase. One of the mixing parameters in this phase considers the mixing between components $\text{U}^{4+}:\text{O}^{2-}:\text{O}^{2-}$ and $\text{U}^{5+}:\text{O}^{2-}:\text{O}^{2-}$, which is commonly written in short hand notation as $(\text{U}^{4+}, \text{U}^{5+})(\text{O}^{2-})(\text{O}^{2-})$. The contribution from this particular mixing parameter to the partial molar excess Gibbs energy of mixing of component $\text{U}^{3+}:\text{O}^{2-}:\text{Va}$ requires evaluation of the Kronecker delta terms for each sublattice. Since the constituent on the first sublattice of this component (i.e., U^{3+}) is not represented by this mixing parameter, the Kronecker delta term for the first sublattice is zero. However, since the constituent on the second sublattice of this component (i.e., O^{2-}) is represented by this mixing parameter, the Kronecker delta for the second sublattice is equal to unity.

The number of components in a CEF phase is equal to the product of the number of sites

5. Modified Quasichemical Model

5.1. Background on MQM

The [Modified Quasichemical Model \(MQM\)](#) in the quadruplet approximation is the most generalized thermodynamic model for treating [Short-Range Ordering \(SRO\)](#). The [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 FNN and 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.* [6, 7, 8, 9]

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:

$$(A - [X] - A) + (B - [X] - B) = 2(A - [X] - B); \Delta g_{AB/X} \quad (49)$$

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:

$$(X - [A] - X) + (Y - [A] - Y) = 2(X - [A] - Y); \Delta g_{A/XY} \quad (50)$$

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:

$$(A - X) + (B - Y) = (A - Y) + (B - X); \Delta g_{A/XY}^{exchange} \quad (51)$$

where $\Delta g_{A/XY}^{exchange}$ 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 [9]

$$Z_A n_A = 2n_{A_2/X_2} + 2n_{A_2/Y_2} + 2n_{A_2/XY} + n_{AB/X_2} + n_{AB/Y_2} + n_{AB/XY} + \dots \quad (52)$$

$$Z_X n_X = 2n_{A_2/X_2} + 2n_{B_2/X_2} + 2n_{AB/X_2} + n_{A_2/XY} + n_{B_2/XY} + n_{AB/XY} + \dots \quad (53)$$

where Z_A and Z_B are the coordination numbers for A and B, respectively. A generic statement for a multi-component system is (fix this equation to be a general equation !!!)

$$Z_i n_i = 2n_{ii} + \sum_{j \neq i} n_{ij} \quad (54)$$

The mole fractions then follow:

$$x_i = \frac{n_i}{\sum n_j} \quad (55)$$

$$x_k = \frac{n_k}{\sum n_l} \quad (56)$$

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:

$$x_{i/k} = \frac{n_{i/k}}{\sum_j \sum_l n_{j/l}} \quad (57)$$

$$x_{ij/kl} = \frac{n_{ij/kl}}{\sum n_{ij/kl}} \quad (58)$$

Another useful term is the coordination equivalent fraction, which is

$$y_i = \frac{Z_i n_i}{\sum Z_j n_j} \quad (59)$$

$$y_k = \frac{Z_k n_k}{\sum Z_l n_l} \quad (60)$$

Since the coordination numbers of the constituents are not equal like in solid solutions and can vary with composition, a composition dependence can be defined. Assuming that all species of a constituent m exist in quadruplets with non-repeating constituents, the SNN coordination number of a species of m , $z_{ij/kl}^m$, are defined such that they result in the following relations

$$n_A = \frac{2n_{A_2/X_2}}{z_{A_2/X_2}^A} + \frac{2n_{A_2/Y_2}}{z_{A_2/Y_2}^A} + \frac{2n_{A_2/XY}}{z_{A_2/XY}^A} \quad (61)$$

The non-configurational Gibbs energy term is given by:

$$\Delta g_{AB} = \Delta g_{AB}^\circ + \sum_{p \geq 1} \sum_{q \geq 1} x_{AA}^p x_{BB}^q g_{AB}^{pq} \quad (62)$$

The integral Gibbs energy of solution is given by

$$G_\lambda = (n_A g_A^\circ + n_B g_B^\circ) - T \Delta S^{config} + \frac{n_{AB} \Delta g_{AB}}{2} \quad (63)$$

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

$$\Delta S^{config} = -R (n_A \ln(x_A) + n_B \ln(x_B) + n_{AA} \ln(x_{AA}/y_A^2) + n_{BB} \ln(x_{BB}/y_B^2) + n_{AB} \ln(x_{AB}/(2y_A y_B))) \quad (64)$$

In this derivation, one defines the quantities of the phase components as the independent variables, namely n_A and n_B . One would then have to compute the quantities of the pair fractions, which are necessarily greater in number. One could compute these quantities; however, it would require an additional iterative cycle to solve a separate system of non-linear equations. Instead, a more productive approach that Pelton *et al* recommend is to reformulate the problem such that the pair fractions are the independent variables [6]. The interested reader is referred to Pelton *et al* [6] for a derivation.

The integral Gibbs energy of a solution phase represented by MQM can be written in an alternate form that differs from equation (63):

$$\begin{aligned}
G_\lambda = & (n_{AA}g_{AA}^\circ + n_{BB}g_{BB}^\circ + n_{AB}g_{AB}^\circ) \\
& + RT \left(n_{AA}\ln(x_{AA}) + n_{BB}\ln(x_{BB}) + n_{AB}\ln(x_{AB}) \right. \\
& \left. + n_A\ln(x_A) + n_B\ln(x_B) - n_{AA}\ln(y_A^2) - n_{BB}\ln(y_B^2) - n_{AB}\ln(2y_Ay_B) \right) \\
& + G_\lambda^{ex}
\end{aligned} \tag{65}$$

where G_λ^{ex} is the integral excess Gibbs energy of mixing, given by:

$$G_\lambda^{ex} = \left(\frac{n_{AA} + n_{BB} + n_{AB}}{2} \right) \left(x_{AA}x_{AB} \sum_{p \geq 1} g_{AB}^p x_{AA}^{p-1} + x_{BB}x_{AB} \sum_{q \geq 1} g_{AB}^q x_{BB}^{q-1} \right) \tag{66}$$

Note that equation (65) is a function of the reference molar Gibbs energies of the pair fractions, not the phase components. One can compute the former as a function of the phase components through the following relationships [6]:

$$g_{AA}^\circ = \frac{2g_A^\circ}{Z_{AA}^A} \quad g_{BB}^\circ = \frac{2g_B^\circ}{Z_{BB}^B} \quad g_{AB}^\circ = \frac{\Delta g_{AB}^\circ}{2} + \frac{g_A^\circ}{Z_{AB}^A} + \frac{g_B^\circ}{Z_{BA}^B} \tag{67}$$

Finally, one will need to compute coordination numbers that may vary with respect to composition, such that:

$$\frac{1}{Z_A} = \frac{1}{Z_{AA}^A} \left(\frac{2n_{AA}}{2n_{AA} + n_{AB}} \right) + \frac{1}{Z_{AB}^A} \left(\frac{n_{AB}}{2n_{AA} + n_{AB}} \right) \tag{68}$$

$$\frac{1}{Z_B} = \frac{1}{Z_{BB}^B} \left(\frac{2n_{BB}}{2n_{BB} + n_{AB}} \right) + \frac{1}{Z_{BA}^B} \left(\frac{n_{AB}}{2n_{BB} + n_{AB}} \right) \tag{69}$$

where Z_A and Z_B are the coordination numbers of A and B, Z_{AA}^A is the value of Z_A when all neighbors of an A are A's, and Z_{AB}^A is when all nearest neighbors of an A are B's.

To summarize, one can represent the integral Gibbs energy of a solution phase represented by the MQM model using equation (65) by treating the independent variables as the molar quantities of the pair fractions using equations (67), (68), and (69). A thermodynamic database would provide values for Z_{ij}^k and equations for the reference molar Gibbs energy of the phase components and excess molar Gibbs energy of mixing terms.

5.2. Derivation of Equations for MQM

MAKE CLEAR THAT ONE SHOULD USE THE APPROACH RECOMMENDED BY PELTON ET AL WHEREBY PAIRS ARE TREATED AS FRACTIONAL “ASSOCIATES”. THIS ALLOWS ONE TO EASILY MODIFY EXISTING GEM CODES...

The preceding section gave a summary of the MQM model and a derivation of integral Gibbs energy equations. This section provides a derivation of equations necessary to compute thermochemical equilibria.

Derivation of the chemical potential of AA gives:

$$\begin{aligned}\mu_{AA} &= \left(\frac{\partial G_\lambda}{\partial n_{AA}} \right)_{T,P,n_j \neq AA} \\ &= g_{AA}^\circ + RT \left(\frac{2\ln(x_A)}{Z_{AA}^A} + \ln \left(\frac{x_{AA}}{y_A^2} \right) \right) + g_{AA}^{ex}\end{aligned}\tag{70}$$

where g_{AA}^{ex} is the partial molar excess Gibbs energy of mixing of AA. Similarly, the chemical potential of BB is:

$$\begin{aligned}\mu_{BB} &= \left(\frac{\partial G_\lambda}{\partial n_{BB}} \right)_{T,P,n_j \neq BB} \\ &= g_{BB}^\circ + RT \left(\frac{2\ln(x_B)}{Z_{BB}^B} + \ln \left(\frac{x_{BB}}{y_B^2} \right) \right) + g_{BB}^{ex}\end{aligned}\tag{71}$$

and the chemical potential of AB is:

$$\begin{aligned}\mu_{AB} &= \left(\frac{\partial G_\lambda}{\partial n_{AB}} \right)_{T,P,n_j \neq AB} \\ &= \frac{g_A^\circ}{Z_{AB}^A} + \frac{g_B^\circ}{Z_{BA}^B} + RT \left(\ln \left(\frac{x_{AB}}{2y_A y_B} \right) + \frac{\ln(x_A)}{Z_{AB}^A} + \frac{\ln(x_B)}{Z_{BA}^B} \right) + g_{AB}^{ex}\end{aligned}\tag{72}$$

Note that equation (62) is written in a familiar form to what is given by Pelton [6, 7]. This equation can be reformulated in a more amenable form for programming such that:

$$\Delta g_{AB} = \sum_{p \geq 0} \sum_{q \geq 0} x_{AA}^p x_{BB}^q g_{AB}^{pq}\tag{73}$$

where one may interpret Δg_{AB}° as g_{AB}^{ij} with $i = 0$ and $j = 0$. One should be conscientious of the removal of Δg_{AB}° from equation (67), which is noticeable in equation (72) and is naturally included in equation (77) below. With this term, one can therefore compute the excess Gibbs energy of mixing in a simpler form.

$$G_\lambda^{ex} = \frac{n_{AB}}{2} \Delta g_{AB}\tag{74}$$

Solving for the partial molar excess Gibbs energy of mixing of AA gives:

$$\begin{aligned} g_{AA}^{ex} &= \left(\frac{\partial G_\lambda^{ex}}{\partial n_{AA}} \right)_{T,P,n_j \neq AA} \\ &= \left(\frac{x_{AB}x_{AA}^{p-1}x_{BB}^q(p(x_{BB} + x_{AB}) - qx_{AA})}{2} \right) g_{AB}^{pq} \end{aligned} \quad (75)$$

Similarly, the partial molar excess Gibbs energy of mixing of BB is:

$$\begin{aligned} g_{BB}^{ex} &= \left(\frac{\partial G_\lambda^{ex}}{\partial n_{BB}} \right)_{T,P,n_j \neq BB} \\ &= \left(\frac{x_{AB}x_{AA}^{p+1}x_{BB}^q(q(x_{AA} + x_{AB}) - px_{BB})}{2x_{AA}x_{BB}} \right) g_{AB}^{pq} \end{aligned} \quad (76)$$

Finally, the partial molar excess Gibbs energy of mixing of AB is:

$$\begin{aligned} g_{AB}^{ex} &= \left(\frac{\partial G_\lambda^{ex}}{\partial n_{AB}} \right)_{T,P,n_j \neq AB} \\ &= \left(\frac{x_{AA}^{p+1}x_{BB}^q(x_{AB}(1-p-q) + x_{AA} + x_{BB})}{2x_{AA}} \right) g_{AB}^{pq} \end{aligned} \quad (77)$$

I've found that a concern with the MQM phase is that many times the Hessian has a nearly inconsistent row and is difficult to solve the system of linear equations. Why is that exactly? I need to really wrap my head around this but in a way the system is represented by two species, but not really...why is this happening? I took some example calculations of the LiF-BeF₂ system and solved the system of linear equations in Excel in simultaneously from Thermochimica at three different iterations near one another. The molar quantities of the pairs did not change very much at all and therefore the Hessian did not change much either. Solving the system of equations in both Thermochimic and Excel yielded wildly different values for the Lagrangian multipliers for all three iterations. One would expect that they would be somewhat close – at the very least the same order of magnitude and sign – but that was not the case. I should think about how to tackle this problem. To temporarily solve this problem, I increased the maximum # of iterations to 5000 (from 3000). This seemed to solve the problem at least in the interim.

5.2.1. Special Cases for MQM

Talk about how by definition of the model one creates an under-determined Hessian matrix. Take the LiF-BeF₂ pseudo-binary system as an example. In this case, A = LiF and B = BeF₂. Therefore, one deals with AA = LiF-LiF, BB = BeF₂-BeF₂, and AB = LiF-BeF₂. In this case, the system components are taken as the chemical elements (i.e., Li, F, Be) and the independent variables are associated with the species AA,

BB, and AB. However, one cannot uniquely define a Gibbs plane by these three points because they are coincident in composition space. See figure below. *This about creating a 3D plot with the ternary as a base to demonstrate that it's not a 3D surface but rather a curve.*

It looks like Thermochimica can solve this problem just fine...small imprecisions in the stoichiometries and co-ordination numbers appear to help prevent the Hessian from having a true inconsistent row. I believe that the analogy of defining a plane by three colinear points needs to be used whereby the plane is wobbling about this line. Despite the plane wobbling about this line, the functional norm can still make great progress because the functional norm doesn't care about how much Gamma F changes – it cares about how much the Gibbs Criteria is respected. For that reason, I relaxed the constraint that dMaxGamma is set to 100 (instead of between 1 and 5). As a result, now only does it converge, but it also converges in a small number of iteraitons (e.g., 10-50).

6. Conclusion

7. Acknowledgements

The authors thank P. Chartrand (Ecole Polytechnique) for stimulating discussions. This research was undertaken, in part, thanks to funding from the Canada Research Chairs program and the Discovery Grant Program of the Natural Sciences and Engineering Research Council of Canada.

References

- [1] P. Chartrand and A. Pelton, “On the choice of geometric thermodynamic models,” *Journal of Phase Equilibria*, vol. 21, no. 2, pp. 141–147, 2000.
- [2] G. Eriksson and K. Hack, “Chemsage – a computer program for the calculation of complex chemical equilibria,” *Metallurgical and Materials Transactions B*, vol. 21B, pp. 1013–1023, 1990.
- [3] M. Hillert, “The compound energy formalism,” *Journal of Alloys and Compounds*, vol. 320, no. 2, pp. 161 – 176, 2001.
- [4] C. Guéneau, N. Dupin, B. Sundman, C. Martial, J.-C. Dumas, S. Gossé, S. Chatain, F. D. Bruycker, D. Manara, and R. J. Konings, “Thermodynamic modelling of advanced oxide and carbide nuclear fuels: Description of the U-Pu-O-C systems,” *Journal of Nuclear Materials*, vol. 419, no. 1-3, pp. 145–167, 2011.

- [5] B. Sundman and J. Ågren, “A regular solution model for phases with several components and sublattices, suitable for computer applications,” *Journal of Physics and Chemistry of Solids*, vol. 42, pp. 297–301, 1981.
- [6] A. Pelton, S. Degterov, G. Eriksson, C. Robelin, and Y. Dessureault, “The modified quasichemical model I – binary solutions,” *Metallurgical and Materials Transactions B*, vol. 31B, pp. 651–659, 2000.
- [7] A. Pelton and P. Chartrand, “The modified quasichemical model II – multicomponent solutions,” *Metallurgical and Materials Transactions A*, vol. 32A, pp. 1355–1360, 2001.
- [8] P. Chartrand and A. Pelton, “The modified quasichemical model III – two sublattices,” *Metallurgical and Materials Transactions A*, vol. 32, pp. 1397–1407, 2001.
- [9] A. Pelton, P. Chartrand, and G. Eriksson, “The modified quasichemical model IV – two-sublattice quadruplet approximation,” *Metallurgical and Materials Transactions A*, vol. 32, pp. 1409–1416, 2001.

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. [Accepted]

Development of a New Thermochemistry Solver for Multiphysics Simulations of Nuclear Materials

Parikshit Bajpai, Max Poschmann, David Andrš, Chaitanya Bhave, Michael Tonks, and Markus Piro

Abstract Nuclear materials are highly complex multiscale, multiphysics systems and an effective prediction of nuclear reactor performance and safety requires simulation capabilities that tightly couple different physical phenomena. The Idaho National Laboratory's **Multiphysics Object Oriented Simulation Environment (MOOSE)** provides the computational foundation for performing such simulations and currently consists of the continuum scale fuel performance code **Bison** and the mesoscale phase field code **Marmot**. With the move towards advanced reactors that employ higher temperature fluids than conventional reactors, corrosion has become a problem of great interest. A new application called **Yellowjacket** is under development to directly couple thermodynamic equilibrium and kinetics to model corrosion in advanced reactors. As part of **Yellowjacket**, a thermochemistry code is being developed to perform thermochemical equilibrium calculations for a range of different materials, which is currently in its infancy. This paper describes the recent progress towards development of **Yellowjacket** and presents the plans for developing capabilities of practical interest to the nuclear industry.

Parikshit Bajpai
Ontario Tech University, Oshawa, ON, Canada e-mail: parikshit.bajpai@ontariotechu.net

Max Poschmann
Ontario Tech University, Oshawa, ON, Canada e-mail: max.poschmann@ontariotechu.ca

David Andrš
Idaho National Laboratory, Idaho Falls, ID, USA e-mail: david.andrs@inl.gov

Chaitanya Bhave
University of Florida, Gainesville, FL, USA e-mail: chaitanya.bhave@ufl.edu

Michael Tonks
University of Florida, Gainesville, FL, USA e-mail: michael.tonks@ufl.edu

Markus Piro
Ontario Tech University, Oshawa, ON, Canada e-mail: markus.piro@ontariotechu.ca

1 Introduction

With the rapid advancement of high-performance computing capabilities over the past decade, computational models and simulations have become ubiquitous tools for design and development of nuclear systems. Nuclear materials are highly complex multiscale, multiphysics systems and simulations help scientists and engineers overcome the experimental challenges in terms of handling radioactive materials, operating conditions, large costs, safety mitigation, etc. Furthermore, material behaviour is influenced by many different physics, such as mechanics (e.g., dislocations, cracking, stress-driven diffusion), chemistry (e.g., corrosion, oxidation, reactive transport), heat transfer (e.g. convection, melting, precipitation), etc.

As shown in fig. 1, a comprehensive understanding of nuclear materials requires models that span extremely large ranges of length and time scales [1]. By using the information from smaller scales to inform the models at larger length scales, multiscale simulation tools help in exploring phenomena which would be inaccessible using only experimental methods [2]. These tools also serve the purpose of augmenting and guiding experimental characterisation techniques, helping save both time and costs.

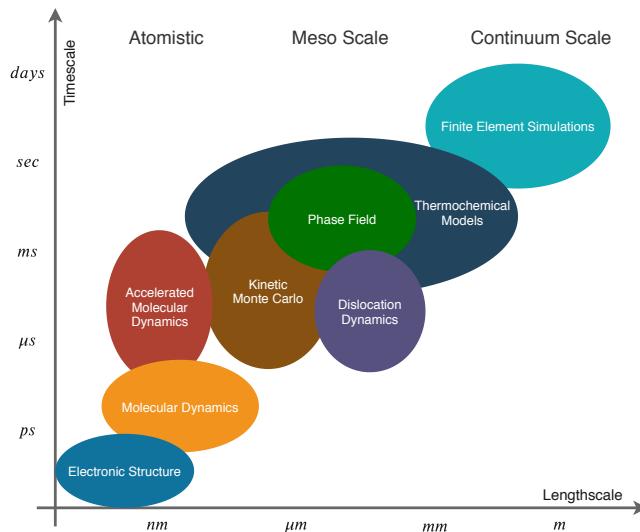


Fig. 1 Multiscale theoretical and computational methods used for materials model development and computer simulations [1].

Many emerging nuclear technologies, such as the Molten Salt Reactor (MSR), use high temperature fluids such as molten fluoride/chloride salts, which lead to increased susceptibility to corrosion of the metal containment leading to problematic behaviour during reactor operation. Corrosion is an electrochemical process composed of ox-

idation and reduction reactions, which are defined by the thermodynamics and kinetics of the reactions. While thermodynamics determines whether or not a material can corrode, kinetics controls 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. The Multiphysics Object Oriented Simulation Environment (MOOSE) [3, 4], developed by the Idaho National Laboratory, provides a framework for multiphysics simulations but lacks the tools for predicting corrosion at the microstructure scale. A new MOOSE-based tool, *Yellowjacket*, is currently being developed to perform thermodynamics based mesoscale corrosion simulations to predict the rate of material loss, corrosion product production, and precipitate production in advanced reactors.

Since the phase and chemical behaviour of nuclear materials is governed by the thermochemical equilibrium state, coupling thermochemistry with multiphysics codes provides various material properties, source terms and boundary conditions such as the chemical potentials that act as the driving force for corrosion. Moreover, it provides the quantitative capability for predicting phase evolution as the chemical composition changes due to irradiation. It is for this reason that a thermochemical equilibrium solver is being developed as part of *Yellowjacket* and this paper describes the recent progress made in this direction.

As shown in fig. 2, by relying on the fundamental laws of thermodynamics, equilibrium computations use the system information, namely, Gibbs energy functions of the species that can be present in the system, temperature, pressure and system composition to provide quantities such as the stable phases and species, Gibbs energy of the system, chemical potentials of the species and can be used to provide information such as the enthalpy, heat capacity, etc.

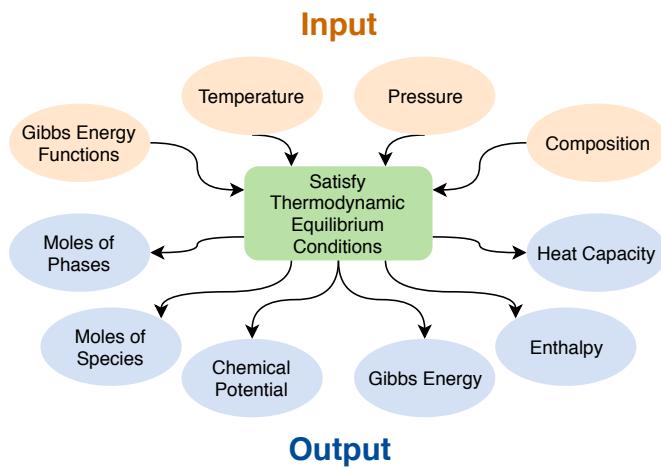


Fig. 2 Input and output parameters of thermodynamic equilibrium calculations.

2 Thermochemical Equilibrium

Thermochemical equilibrium calculations are based on minimising the integral Gibbs energy of a closed system at constant temperature and hydrostatic pressure. From a numerical point of view, the objective of computing thermochemical equilibrium is to determine a unique combination of phases and their composition that yields a global minimum in the integral Gibbs energy subject to various linear and non-linear equality constraints.

2.1 Gibbs energy

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

$$\frac{G}{RT} = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \tilde{g}_{\lambda} + \sum_{\omega=1}^{\Omega} n_{\omega} \tilde{g}_{\omega} \quad (1)$$

where, R [$\text{J mol}^{-1} \text{ K}^{-1}$] is the ideal gas constant and T [K] is the absolute temperature. 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. Finally, \tilde{g}_{λ} and \tilde{g}_{ω} represent the dimensionless form of Gibbs energy of solution phase λ and stoichiometric phase ω respectively.

In a less prevalent but computationally more feasible form, the integral Gibbs energy can be expressed in terms of dimensionless chemical potentials¹ as follows

$$G = RT \left(\sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \tilde{\mu}_i + \sum_{\omega=1}^{\Omega} n_{\omega} \tilde{\mu}_{\omega} \right) \quad (2)$$

where, N_{λ} denotes the number of species in the solution phase λ and $x_{i(\lambda)}$ represents the mole fraction of species i in solution phase λ . $\tilde{\mu}_i$ and $\tilde{\mu}_{\omega}$ represent the dimensionless chemical potential of species i in solution phase λ and stoichiometric phase ω respectively.

The chemical potential is a measure of the change of the Gibbs energy of a system by the introduction of a substance. Mathematically, the chemical potential of a species i is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j \neq i} \quad (3)$$

¹ From a computational perspective, the method of Lagrange multipliers used to compute thermochemical equilibrium results in an objective function where the linear combinations of Lagrange multipliers give the chemical potential of elements. Furthermore, the dimensionless form of chemical potentials helps reduce the computational costs.

and for the species of an ideal phase, the chemical potential incorporates the reference Gibbs energy of pure species, $g_{i(\lambda)}^0$, and the entropic contribution due to mixing as a function of its mole fraction.

$$\tilde{\mu}_i = \tilde{g}_{i(\lambda)}^0 + \ln x_{i(\lambda)} \quad (4)$$

For non-ideal solution phases, the chemical potential also includes the partial molar excess Gibbs energy of mixing, $\tilde{g}_{i(\lambda)}^{ex}$, to account for non-ideal mixing

$$\tilde{\mu}_i = \tilde{g}_{i(\lambda)}^0 + \ln x_{i(\lambda)} + \tilde{g}_{i(\lambda)}^{ex} \quad (5)$$

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 e.g. the Modified Quasichemical Model [5, 6, 7, 8, 9], the Compound Energy Formalism [10], etc.

2.2 Conditions for thermochemical equilibrium

Achieving thermochemical equilibrium in a system requires satisfaction of both necessary and sufficient conditions which are described below.

2.2.1 Necessary conditions

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

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} v_{i,j} + \sum_{\omega=1}^{\Omega} n_{\omega} v_{\omega} \quad (6)$$

where, $v_{i,j}$ and v_{ω} represent the stoichiometric coefficients of element j in solution phase species j and stoichiometric phase ω respectively and the constraints require that the mole fractions must be positive, i.e., $x_{i(\lambda)}$

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

$$F = C - \Phi + 2 + \Xi \quad (7)$$

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 electrochemical terms.

3. *Gibbs' criteria* for equilibrium requires that the Gibbs energy of a system be at a local minimum. In equivalent terms, the chemical potential for each system component must have the same value in all stable phases within the system [11],

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 [12]

$$\mu_i = \sum_{j=1}^C v_{i,j} \Gamma_j \quad (8)$$

2.2.2 Sufficient conditions

The necessary conditions for thermodynamic equilibrium require that the chemical potentials of all stable solution phase species and stoichiometric phases abide by the equality given by eqn. 8, which is equivalent to the 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 [13]

$$\pi_\lambda = \min_\lambda \sum_{i=1}^{N_\lambda} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C v_{i,j} \Gamma_j \right) \quad (9)$$

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

$$\begin{aligned} \sum_{i=1}^{N_\lambda} x_{i(\lambda)} &= 1 \\ x_{i(\lambda)} &> 0 \quad \forall i \end{aligned} \quad (10)$$

i.e., the sum of mole fraction of all the species in a phase λ must be unity and that the individual mole fractions must be greater than or equal to zero. These constraints also apply to ionic species but an additional charge balance must also be respected in such a case.

The aforementioned conditions are used in the Gibbs energy minimiser to find a unique combination of phases that are stable in the system. The computational structure of the code has been presented in the following section.

3 Gibbs Energy Minimiser

A top-level overview of the Gibbs energy minimisation code is shown in fig. 3. Calculation of thermodynamic equilibrium requires a thermodynamic database, which provides reference Gibbs energy terms of different species in addition to models

representing non-ideal behaviour. These thermodynamic databases are developed using the well established Calphad method [14]. The data file parser in Yellowjacket supports the ChemSage format data files generated by FactSage [15]. Parsing is followed by passing the system information such as temperature, pressure and elemental composition to the thermochemistry solver and at each time step, MOOSE provides these inputs for every element of the mesh.

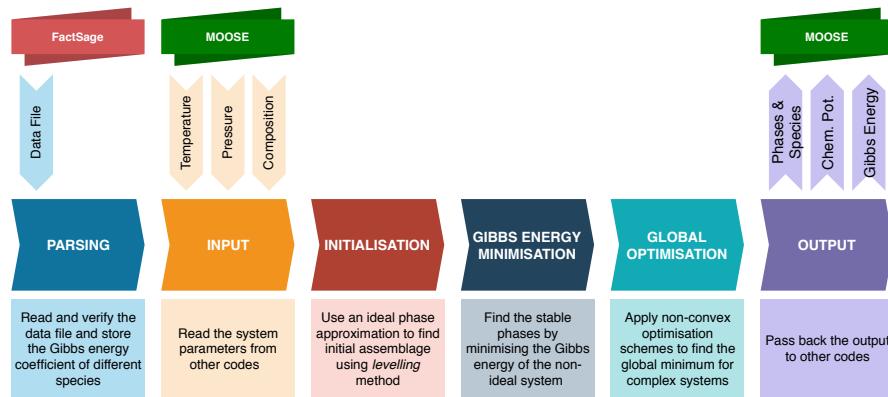


Fig. 3 Computational structure of the Gibbs energy minimisation program

The computation stage of the thermochemistry solver consists of *initialisation*, *Gibbs energy minimisation* and *global optimisation*. Thermodynamic solvers require an initial estimate of molar quantities of species and phases. To this aim, a general estimating procedure called *levelling* was developed by Eriksson and Thompson [16]. Levelling temporarily converts the non-linear optimisation problem into a linear optimisation problem with the objective of systematically adjusting fixed combinations of phases, subject to linear equality and inequality constraints, to progressively make the Gibbs energy of the system more negative, thus, convergence is accelerated by providing an estimated phase assemblage that focuses on only the dominant species. While levelling provides a great initial assemblage for further consideration, in many cases, such as the time dependent problems, other initialisation methods can be used to further reduce the computational time required by the non-linear solver [17]. A couple of these techniques have been studied by Piro [18] and include the use of assemblage from the preceding time step or from the neighbouring elements based on the principle of continuum. In future, such methods will be of significant interest to Yellowjacket and will provide significant speed gains compared to re-initialisation using levelling at each time step.

The linear solver, though an excellent initialisation algorithm, rarely provides the final assemblage of the system under consideration. Gibbs energy minimisation introduced by White *et al.* [19] is the universally used algorithm to perform the non-linear optimisation for obtaining thermochemical equilibrium in complex systems. In mathematical terms, Gibbs energy minimisation is widely performed using the

method of Lagrange multipliers that simultaneously minimises the integral Gibbs energy and the residuals of mass balance equations. This results in a system of linearised equations that can be written in matrix form as [20]

$$\mathbf{H} \cdot \boldsymbol{\pi} = \boldsymbol{\zeta} \quad (11)$$

where $\boldsymbol{\pi}$ and $\boldsymbol{\zeta}$ denote the unknown and constraint vectors respectively, and the Hessian matrix (\mathbf{H}) can be written as [19, 20]

$$\mathbf{H} = \begin{bmatrix} r_{j=1,k=1} & \dots & r_{j=1,k=C} & \phi_{j=1,\lambda=1} & \dots & \phi_{j=1,\lambda=\Lambda} & v_{j=1,\omega=1} & \dots & v_{j=1,\omega=\Omega} \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ r_{j=C,k=1} & \dots & r_{j=C,k=C} & \phi_{j=C,\lambda=1} & \dots & \phi_{j=C,\lambda=\Lambda} & v_{j=C,\omega=1} & \dots & v_{j=C,\omega=\Omega} \\ \phi_{\lambda=1,j=1} & \dots & \phi_{\lambda=1,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ \phi_{\lambda=\Lambda,j=1} & \dots & \phi_{\lambda=\Lambda,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ v_{\omega=1,j=1} & \dots & v_{\omega=1,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \\ \vdots & \ddots & \vdots & \vdots & \ddots & \vdots & \vdots & \ddots & \vdots \\ v_{\omega=\Omega,j=1} & \dots & v_{\omega=\Omega,j=C} & 0 & \dots & 0 & 0 & \dots & 0 \end{bmatrix} \quad (12)$$

where $r_{j,k}$ and $\phi_{j,\lambda}$ can be expressed as follows

$$r_{j,k} = \sum_{\lambda=1}^{\Lambda} \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)} v_{i,j} v_{i,k} \quad (13)$$

$$\phi_{j,\lambda} = \sum_{i=1}^{N_{\lambda}} n_{i(\lambda)} v_{i,j} \quad (14)$$

Clearly, $r_{j,k} = r_{k,j}$ and $\phi_{j,\lambda} = \phi_{\lambda,j}$, which yields a symmetric positive semidefinite matrix for \mathbf{H} .

While finding a solution to eqn. 11 is relatively easy, the challenge arises due to the change in the size of Hessian \mathbf{H} within a computation cycle. This change in size results from the addition/removal of phases in the system and requires the implementation of numerical strategies such as the ones discussed by Piro [18]. In addition, care must be taken in implementing an effective line search algorithm and proper use of Wolfe/Armijo conditions for choosing the step length can significantly improve the convergence and stability of the non-linear solver. However, for the modified quasichemical model, a hitherto unseen situation can also arise when using the chemical elements to define the system components. As shown by Piro *et al.* [21], in such systems, certain compositions can result in a rank-deficient Hessian that ultimately results in chemical potentials that might not be uniquely defined, thus, potentially misleading the users.

The Gibbs energy functions of non-ideal phases are often non-convex, yielding multiple local minima after Gibbs energy minimisation. These local minima correspond to different compositions of phases that may be believed to be stable (e.g., a

miscibility gap), which may not necessarily correspond to the true equilibrium composition. Finding the global minimum of this function among the many local minima within the domain space can be a daunting challenge, especially in large complex thermodynamic systems containing many highly non-ideal solution phases. Consequently, inadequate numerical approaches might result in false positives of thermodynamic equilibrium with little possibility identifying the divergence from the true equilibrium state [13].

While a large number of deterministic (e.g. branch and bound) and stochastic (e.g. particle swarm optimisation) methods are available in literature, none of them guarantees the ability of finding a global extremum of a non-convex function. Moreover, the computational effort associated with this task can increase very rapidly with the size of the system (i.e. the total number of species in the system). The global optimisation module is one of the thrust areas of this work and will explore various strategies to ensure that the final phase assemblage corresponds to the global minimum.

Finally, the outputs produced include the moles of the different phases present in the system, the mole fraction of the species in each phase, Gibbs energy of the system, chemical potentials, etc. and these outputs are passed to the electrochemistry module for corrosion or can be passed back to MOOSE.

4 Demonstration Problem

In this section, the current progress towards the development of the thermochemistry solver has been demonstrated through a demonstration problem. The reference fuel and coolant proposed for the different MSR concepts are fluoride salts due to their advantageous neutronic and physico-chemical properties [22]. LiF–BeF₂ and LiF–NaF–KF are amongst the various salt compositions under study for the primary and secondary coolant and their suitability with respect to their corrosion properties for the structural material is an essential requirement for reactor safety and operation. Since Ni is the main element for prospective alloys in structural materials, and the rate of corrosion is defined by the redox potential of the molten salt, the phase equilibrium of the salt with potential corrosion products must be studied as a function of temperature and pressure [23]. Therefore, the initial focus is on Ni alloys interacting with molten LiF–KF salts and for the present demonstration the KF–NiF₂ binary system has been selected. This system is not only relevant to the MSR but has also been studied experimentally and the required thermodynamic data is available in literature [23].

For the demonstration problem, a bar with molar composition 0.8 KF + 0.2 NiF₂ under a linear temperature gradient has been solved for thermodynamic equilibrium using the linear levelling solver. The predicted stable phases and the Gibbs energies²

² Though the Gibbs energy profile shown in fig. 4 is continuous, the actual results on the finite element mesh are discretised due to a step change in the temperature as we move from one element to the other. The continuous profile has been plotted by interpolation during post processing and is

are shown in fig. 4. As expected from the phase diagram, a transition from a solid phase to a mixture of solid and liquid phase is observed around 1100 °C and a transition from mixed phase to pure liquid phase around 1200 °C.

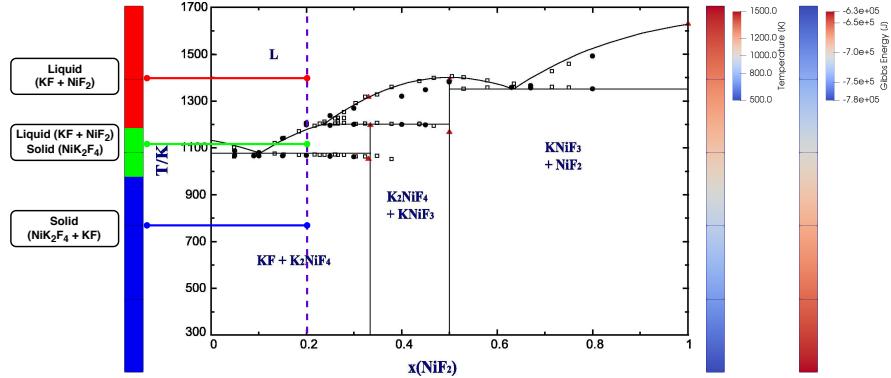


Fig. 4 Stable phases and Gibbs energies predicted by the linear solver.

5 Applications

Within **Yellowjacket**, the thermochemistry solver will be used for predicting microstructure evolution using phase field. **Yellowjacket** will use **MOOSE** to solve phase-field equations to describe the evolution of the chemical components and phases. The chemical components in the system are represented by conserved variables that evolve based on the Cahn-Hilliard equation as follows

$$\frac{dc}{dt} = \nabla M(c_i) \nabla \frac{\delta F}{\delta c_i} \quad (15)$$

where M is the mobility of the component, c_i represents the concentration of the component i , F denotes the free energy density of the system, and the $\frac{\delta F}{\delta c_i}$ denotes chemical potential of species i . The phases are represented as non-conserved order parameters, and are evolved using the Allen-Cahn equation

$$\frac{d\eta_j}{dt} = -L \frac{\delta F}{\delta \eta_j} \quad (16)$$

a better representation of the physical conditions where we expect no step changes if a temperature gradient is applied.

where η_j denotes the order parameter for the phase j , and L is the Allen-Cahn mobility of the interface. The order parameters are used to interpolate between the thermodynamic model for each phase.

Thus, the primary thermodynamic inputs required to the evolution equations are the Gibbs free energy of the system and chemical potentials of the species as a function of the concentrations of components and the phase order parameters. Typically, the free energy functions for each phase are obtained for the given system of components using a Calphad thermodynamic assessment before running the simulation. However, for multicomponent metal alloy systems, the free energy functions can be very complex. In such systems, having a coupled thermodynamic solver that directly provides the values from the database could help to simplify the development of the phase field models. It can simplify the complex coupled problem into two simpler problems. Values for certain derivatives within the simulation can be directly obtained from the thermodynamic solver. Eventually, coupling a thermodynamic solver with MOOSE will also allow phase-field to be operated as a black box with its own material properties database.

6 Conclusion

In summary, recent progress towards development of a new thermochemical equilibrium solver for multiphysics simulations in *Yellowjacket* has been presented. As shown through the initial demonstration problem, the thermochemistry code has been partly integrated with MOOSE and thermochemical equilibrium can now be performed on a MOOSE mesh using the linear levelling solver. While currently only the ideal mixture phases and the Modified Quasichemical Model for molten salts are supported, development is underway to expand support to other thermodynamic models. The ongoing research is now moving towards the implementation of the non-linear Gibbs energy minimiser which can provide more realistic estimates of the phase assemblage and will be followed by the implementation of various optimisation strategies to ensure convergence.

References

1. M. Stan, Materials Today **12**(11), 20 (2009). DOI [https://doi.org/10.1016/S1369-7021\(09\)70295-0](https://doi.org/10.1016/S1369-7021(09)70295-0)
2. R. Devanathan, L. Van Brutzel, A. Chartier, C. Guéneau, A.E. Mattsson, V. Tikare, T. Barret, T. Besmann, M. Stan, P. Van Uffelen, Energy Environ. Sci. **3**, 1406 (2010). DOI <http://dx.doi.org/10.1039/C0EE00028K>
3. D.R. Gaston, C.J. Permann, J.W. Peterson, A.E. Slaughter, D. Andrš, Y. Wang, M.P. Short, D.M. Perez, M.R. Tonks, J. Ortensi, L. Zou, R.C. Martineau, Annals of Nuclear Energy **84**, 45 (2015)

4. B. Alger, D. Andrš, R.W. Carlsen, D.R. Gaston, F. Kong, A.D. Lindsay, J.M. Miller, C.J. Permann, J.W. Peterson, A.E. Slaughter, R. Stogner. MOOSE Web page (2019). URL <https://mooseframework.org>
5. A. Pelton, S. Degterov, G. Eriksson, C. Robelin, Y. Dessureault, Metallurgical and Materials Transactions B **31B**, 651 (2000)
6. A. Pelton, P. Chartrand, Metallurgical and Materials Transactions A **32A**, 1355 (2001)
7. P. Chartrand, A. Pelton, Metallurgical and Materials Transactions A **32**, 1397 (2001)
8. A. Pelton, P. Chartrand, G. Eriksson, Metallurgical and Materials Transactions A **32**, 1409 (2001)
9. G. Lambotte, P. Chartrand, Journal of Chemical Thermodynamics **43**, 1678 (2011). DOI [10.1016/j.jct.2011.05.038](https://doi.org/10.1016/j.jct.2011.05.038)
10. M. Hillert, Journal of Alloys and Compounds **320**(2), 161 (2001)
11. M. Hillert, Physica B+C **103**(1), 31 (1981). DOI [https://doi.org/10.1016/0378-4363\(81\)91000-7](https://doi.org/10.1016/0378-4363(81)91000-7)
12. M. Piro, T. Besmann, S. Simunovic, B. Lewis, W. Thompson, Journal of Nuclear Materials **414**(3), 399 (2011). DOI <https://doi.org/10.1016/j.jnucmat.2011.05.012>
13. M. Piro, S. Simunovic, Computational Materials Science **118**, 87 (2016)
14. Z.K. Liu, Y. Wang, *Computational Thermodynamics of Materials* (Cambridge University Press, 2016)
15. C. Bale, E. Belisle, P. Chartrand, S. Dechterov, G. Eriksson, A. Gheribi, K. Hack, I.H. Jung, Y.B. Kang, J. Melancon, A. Pelton, S. Petersen, C. Robelin, J. Sangster, P. Spencer, M.A.V. Ende, Calphad **54**, 35 (2016). DOI <https://doi.org/10.1016/j.calphad.2016.05.002>
16. G. Eriksson, W. Thompson, Calphad **13**(4), 389 (1989). DOI [https://doi.org/10.1016/0364-5916\(89\)90027-8](https://doi.org/10.1016/0364-5916(89)90027-8)
17. M. Poschmann, M. Piro, S. Simunovic, Acceleration of Thermochemical calculations in Bison. Tech. rep., Oak Ridge National Laboratory (2019). In review
18. M. Piro, Calphad **58**, 115 (2017)
19. W.B. White, S.M. Johnson, G.B. Dantzig, The Journal of Chemical Physics **28**(5), 751 (1958). DOI <https://doi.org/10.1063/1.1744264>
20. M. Piro, Computation of thermodynamic equilibria pertinent to nuclear materials in multi-physics codes. Ph.D. thesis, Royal Military College of Canada (2011)
21. M. Piro, M. Poschmann, P. Bajpai, Journal of Nuclear Materials **526**, 151756 (2019). DOI <https://doi.org/10.1016/j.jnucmat.2019.151756>
22. O. Beneš, R. Konings, in *Comprehensive Nuclear Materials*, ed. by R.J. Konings (Elsevier, Oxford, 2012), pp. 359 – 389. DOI <https://doi.org/10.1016/B978-0-08-056033-5.00062-8>
23. J. Ocadiz-Flores, E. Capelli, P. Raison, R. Konings, A. Smith, Journal of Chemical Thermodynamics **121**, 17 (2018). DOI <https://doi.org/10.1016/j.jct.2018.01.023>

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.

DEVELOPMENT OF A NEW THERMOCHEMISTRY CODE FOR MULTIPHYSICS SIMULATIONS OF NUCLEAR MATERIALS

Parikshit Bajpai¹, Max Poschmann¹, David Andrs², Markus Piro¹

¹ Nuclear Fuels and Materials Group, Ontario Tech University, Oshawa, Canada

² Modeling and Simulation Group, Idaho National Lab, Idaho Falls, USA

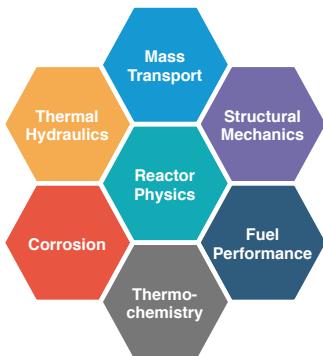
✉ parikshit.bajpai@uoit.net ⚡ <https://nuclear.uoit.ca/piro>

OBJECTIVES

Recently, there has been an increasing interest in direct coupling of thermodynamic computations with multiphysics codes such as INL's MOOSE. A new thermochemistry code is being developed to provide rapid access to thermodynamic databases and perform thermochemical calculations for a range of different materials including nuclear fuels. This poster describes the preliminary work done in this direction and plans for developing capabilities of practical interest to the nuclear industry.

INTRODUCTION

Nuclear reactors are highly complex multiscale, multiphysics systems with strong coupling between various phenomena such as temperature, creep, fission gas release etc.



Idaho National Laboratory's Multiphysics Object Oriented Simulation Environment (MOOSE) provides the computational foundation for performing multiphysics simulations suitable in such problems and a new MOOSE-based application called **Yellowjacket** is under development to model corrosion and fuel problems.

The thermochemistry solver within Yellowjacket will use **Gibbs Energy Minimisation** to provide material properties and boundary conditions such as the phase distribution and chemical potentials in molten salts.

THERMODYNAMIC EQUILIBRIUM

Thermocatalytic equilibrium calculations are based on minimising the integral Gibbs energy of a closed system at constant temperature and hydrostatic pressure.

- Integral Gibbs energy of the system

$$G = RT \left(\sum_{\lambda=1}^A n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \bar{\mu}_i + \sum_{\omega=1}^{\Omega} n_{\omega} \bar{\mu}_{\omega} \right)$$

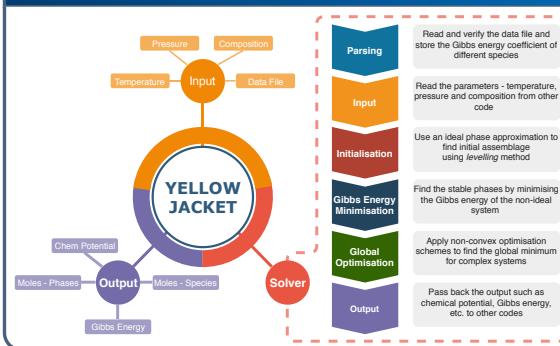
- Chemical potential of ideal phase species

$$\bar{\mu}_i = \tilde{g}_{i(\lambda)}^0 + \ln(x_{i(\lambda)})$$

- Chemical potential of non-ideal phase species

$$\bar{\mu}_i = \tilde{g}_{i(\lambda)}^0 + \tilde{g}_{i(\lambda)}^{ex} + \ln(x_{i(\lambda)})$$

COMPUTATIONAL FRAMEWORK

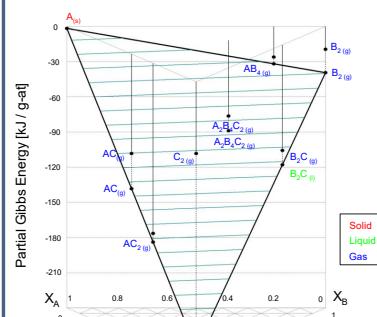


Coding Tools

- Environment: MOOSE
- Language: C++
- Data File Format: ChemSage (*.dat)
- Library: PETSc/Tao, LAPACK
- Documentation: MooseDocs
- Testing: CIVET

GIBBS ENERGY MINIMISATION

From a numerical point of view, the objective of computing thermochemical equilibria is to determine a unique combination of phases and their composition that yields a global minimum in the integral Gibbs energy subject to various linear and non-linear equality and inequality constraints.



Necessary conditions

- Conservation of mass

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

- Gibbs' phase rule

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

- Gibbs' criterion

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

Sufficient condition

- Integral Gibbs energy at global minimum

$$\pi_{\lambda} = \min \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} \left(\mu_{i(\lambda)} - \sum_{j=1}^C a_{i,j} \Gamma_j \right)$$

REFERENCES

- [1] W. B. White, S. M. Johnson, and G. B. Dantzig. Chemical equilibrium in complex mixtures. *Journal of Chemical Physics*, 28(5):751–755, 1958.
- [2] M. H. A. Piro, T. M. Besmann, S. Simunovic, B. J. Lewis, and W. T. Thompson. Numerical verification of equilibrium thermodynamic computations in nuclear fuel performance codes. *Journal of Nuclear Materials*, 414(3):399–407, 2011.

CONCLUSION

The new MOOSE based app, **Yellowjacket**, is aimed at developing corrosion modelling capability for advanced reactors and will help in improving multiphysics simulations for nuclear reactor materials by coupling thermochemistry computations with continuum and meso-scales models.

ACKNOWLEDGEMENT

This work was funded by the Department of Energy Nuclear Energy Advanced Modeling and Simulation program. This manuscript has been authored under Contract No. DE-AC07-05ID14517 with the US Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a nonexclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

This research made use of the resources of the High-Performance Computing Center at Idaho National Laboratory, which is supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities under Contract No. DE-AC07-05ID14517.

PROGRESS IN DEVELOPING A NEW THERMOCHEMISTRY CODE FOR CORROSION MODELLING AND MULTIPHYSICS SIMULATION OF NUCLEAR FUELS

P. Bajpai^{1,*}, M. Poschmann¹, D. Andrs², M.H.A. Piro¹

¹ University of Ontario Institute of Technology, Oshawa, Ontario, Canada

² Idaho National Laboratory, Idaho Falls, Idaho, United States

* Corresponding author (parikshit.bajpai@uoit.ca)

A PhD Level Submission

Nuclear materials are highly complex multiscale, multiphysics systems and an effective prediction of nuclear reactor performance and safety requires simulation capabilities that exhibit a very tight coupling between different physical phenomena. The Idaho National Laboratory's Multiphysics Object Oriented Simulation Environment (MOOSE) provides the computational foundation for performing such simulations. The simulation platform currently consists of the continuum scale fuel performance code BISON, the mesoscale phase field code MARMOT, and a new application called YELLOWJACKET is under development to directly couple thermodynamic equilibrium and kinetics in order to model corrosion and fuel problems. As part of YELLOWJACKET, a thermochemistry code is being developed to provide rapid access to thermodynamic databases and perform thermochemical calculations for a range of different materials, which is currently in its infancy. This paper describes preliminary work in YELLOWJACKET development and plans for developing capabilities of practical interest to the nuclear industry.

1. Introduction

Nuclear fuels exhibit complex behaviour with strong coupling between various physical phenomena on multiple scales, such as temperature, creep, fission gas release, etc. The fuel composition and other fuel materials, such as the cladding, affect these phenomena and play an important role in nuclear fuel performance. As a result, the evolving composition of nuclear materials during irradiation significantly affects nuclear reactor performance and safety. An effective prediction of nuclear reactor performance benefits from simulation of coupled multiphysics, multi-scale problems [1]. Recently, there has been an increasing interest in direct coupling of thermodynamic computations with INL's Multi-physics Object Oriented Simulation Environment (MOOSE), which is a massively parallel finite element framework and provides the computational foundation for numerous scientific and engineering codes for multi-scale, multiphysics modelling and simulation [2].

Many emerging nuclear technologies, such as the Liquid Metal cooled Fast Breeder Reactor and Molten Salt Reactor (MSR), involve high temperature fluids, such as sodium, lead and molten fluoride or chloride salts, which can lead to corrosion of the metal containment structure leading to problematic behaviours during reactor operation. However, the current MOOSE-BISON-MARMOT (MBM) toolkit is not capable of modelling this sort of corrosion behaviour due to direct access to thermodynamic calculations. YELLOWJACKET is a new MOOSE-based

application currently being developed with the intent to directly couple thermodynamic equilibrium and kinetics, which is important to numerous corrosion problems (among others).

YELLOWJACKET will be capable of predicting the rate of material loss, corrosion product production, and precipitate production in liquids by coupling quantitative electrochemistry models of corrosion and chemical reactions with thermochemical equilibrium solvers that can directly access thermodynamic and kinetic databases.

An essential part of YELLOWJACKET is a thermochemistry code to provide rapid access to thermodynamic databases and perform thermochemical calculations for a range of different materials. The thermochemistry code will be capable of providing material properties and boundary conditions such as the phase distribution in high burnup UO₂ fuel pellet and will rely on the Gibbs Energy Minimization (GEM) approach originally proposed by White et al. [3]. The thermochemistry solver is being developed within the MOOSE framework using the same language (C++), libraries, standards, documentation, etc. Furthermore, it will leverage the experience gained during the development of Thermochimica [4], a stand-alone Fortran thermochemistry code developed for coupling with multiphysics codes.

2. Thermodynamic equilibrium in multicomponent systems

Thermochemical equilibrium calculations are based on minimizing the integral Gibbs energy of a closed system at constant temperature and hydrostatic pressure. From a numerical point of view, the objective of computing thermochemical equilibria is to determine a unique combination of phases and their composition that yields a global minimum in the integral Gibbs energy subject to various linear and non-linear equality and inequality constraints. The integral Gibbs energy of a closed system, G [J], is given by the following equation

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

where, R [J mol⁻¹ K⁻¹] is the ideal gas constant, T [K] is the absolute temperature, N_{λ} denotes the number of species in solution phase λ , and, Λ and Ω represent the total number of stable solution phases and stoichiometric phases, respectively. $x_{i(\lambda)}$ [unitless] represents the mole fraction of species i in solution phase λ and the number of moles of the solution phase λ and the stoichiometric phase ω are denoted by n_{λ} and n_{ω} [mol], respectively. Finally, $\tilde{\mu}_i$ and $\tilde{\mu}_{\omega}$ [unitless] represent the dimensionless chemical potential of species i in solution phase λ and stoichiometric phase ω , respectively.

For the species of an ideal phase, the chemical potential can be expressed in terms of the reference Gibbs energy of the pure species, $\tilde{g}_{i(\lambda)}^0$, and mole fraction, $x_{i(\lambda)}$, as follows¹

$$\tilde{\mu}_i = \tilde{g}_{i(\lambda)}^0 + \ln(x_{i(\lambda)}) \quad (2)$$

where the natural logarithmic term accounts for the entropy distribution due to mixing [5]. However, for the species of non-ideal phases, as shown in Equation (3), the chemical potential

¹ The dimensionless quantities, $\tilde{\Omega}_i$, are the same as the dimensional quantities Ω_i divided by RT , i.e., $\tilde{\Omega}_i = \Omega_i / RT$.

must also contain a mixing term, $\tilde{g}_{i(\lambda)}^{ex}$ [unitless], to account for the change in Gibbs energy associated with non-ideal mixing.

$$\tilde{\mu}_i = \tilde{g}_{i(\lambda)}^0 + \tilde{g}_{i(\lambda)}^{ex} + \ln(x_{i(\lambda)}) \quad (3)$$

While the chemical potential of stoichiometric phases, ω , does not include a composition dependent term, the partial molar excess Gibbs energy of mixing for non-ideal solution models (e.g., regular solution model, compound energy formalism, modified quasi-chemical model) depend on the mixing model employed some of which have been presented in the works of Pelton and Bale [6] and Sundman and Ågren [7].

2.1. Conditions for thermodynamic equilibrium

Thermodynamic equilibrium in a system is subject to multiple constraints, such as conservation of mass and Gibbs phase rule. The total mass of element j , b_j , must satisfy the following mass balance equation

$$b_j = \sum_{\lambda=1}^{\Lambda} n_{\lambda} \sum_{i=1}^{N_{\lambda}} x_{i(\lambda)} a_{i,j} + \sum_{\omega}^{\Omega} n_{\omega} a_{\omega,j} \quad (4)$$

where, $a_{i,j}$ and $a_{\omega,j}$ [g-at mol⁻¹] are the stoichiometric coefficients of element j in the solution phase species i and the stoichiometric phase ω , respectively. Furthermore, the sum of mole fractions of all species of solution phase, x_{λ} [unitless], must be positive and equal to unity if phase λ is stable at equilibrium.

The equilibrium conditions must also comply with the Gibbs phase rule, which relates the thermodynamic degree of freedom of the system, F , with the number of system components, C , and the number of phases predicted to be stable in the system, Φ (i.e. $\Phi = \Lambda + \Omega$), as shown in the following equation²

$$F = C - \Phi + 2 \quad (5)$$

Finally, the Gibbs' criterion for equilibrium requires that the integral Gibbs energy of a closed system be at a global minimum at constant temperature and pressure. An equivalent statement states that the chemical potential for each system component must have the same value in all stable phases within the system [8], where the chemical potential of any constituent in a stable phase can be defined in terms of a linear function of the element potentials as the following

$$\mu_i = \sum_{j=1}^C a_{i,j} \Gamma_j \quad (7)$$

In summary, the necessary conditions for thermodynamic equilibrium require that the chemical potentials of all stable solution phase species and stoichiometric phases abide by the above linear equality, which is equivalent to Gibbs energy of the system being at a local minimum [9], and that the conservation of mass and the Gibbs phase rule are satisfied. The sufficient condition requires that all metastable phases abide by the following inequality:

² It must be noted that imposing isothermal and isobaric conditions reduces the thermodynamic degree of freedom by 2 and Equation (5) reduces to $F = C - \Phi$.

$$\pi_\lambda = \min_{\lambda} \sum_{i=1}^{N_\lambda} x_{i(\lambda)} (\mu_{i(\lambda)} - \sum_{j=1}^C a_{i,j} \Gamma_j) \quad (8)$$

The conditions of thermodynamic equilibrium are used in the Gibbs Energy Minimization method to find a unique combination of phases that are stable in a closed isothermal-isobaric system.

3. Plans for computational framework development involving thermodynamics

The objective of this work is to directly implement a GEM solver within the finite element framework MOOSE to facilitate direct coupling with the fuel performance code BISON and mesoscale phase field code MARMOT without any approximations or limitations associated with data transfer of thermodynamic calculations.

Calculation of thermodynamic equilibrium requires a thermodynamic database, which includes Gibbs energy parameters of pure species in addition to models to capture non-ideal behaviour. This is needed to compute the stable phases at given input conditions by minimizing the Gibbs energy of the system. These thermodynamic databases are developed using the well-established CALPHAD method [5] and are available in different formats, the most commonly used in practice being ThermoCalc (*.tdb) and FactSage (*.dat) data file formats, which are generated by the commercial software ThermoCalc and FactSage, respectively. A data file parser would allow the extraction of Gibbs energy expressions from *.dat thermodynamic database files (FactSage format) and export a list of Gibbs energy terms for each phase (or a user specified subset of phases).

Data parsing will be followed by computing an initial estimate of molar quantities of species and phases. To this aim, a general estimating procedure called '*Levelling*' was developed by Eriksson and Thompson [10], which will be leveraged in this work. At every iteration, the levelling algorithm helps accelerate convergence by providing an estimated phase assemblage that focuses on only the dominant species. These are typically not equivalent to the final equilibrium state, but a good initial approximation. From a computational point of view, an advantage of the levelling algorithm is that the number of iterations required to achieve convergence does not increase rapidly with the number of system components. Moreover, the initialization of the non-linear solver using the phase assemblage calculated by the Levelling solver can greatly improve the rate of convergence.

In many circumstances, the levelling solver would only provide an estimated assemblage and will require the final assemblage to be determined using the GEM method. The GEM solver would be capable of handling the frequent changes to the active set of constraints. Furthermore, the Gibbs energy function of non-ideal phases may be non-convex, yielding multiple local minima, which correspond to different compositions of phases that may be believed to be stable (e.g., a miscibility gap), but may not necessarily correspond to the true equilibrium composition. Finding the global minimum in large thermodynamic systems makes the development of GEM solver a daunting challenge and will require the application of global optimization techniques, as developed by Piro and Simunovic [11].

The thermochemistry solver will be useful in applications such as predicting the equilibrium concentrations of a Uranium-Oxygen binary system for a range of O/U ratio [12] and a range of temperatures in addition to corrosion for MSR applications.

4. Conclusions

A new MOOSE based app called YELLOWJACKET is being developed to simulate and predict corrosion in advanced nuclear reactors with the aim of improving the multiphysics simulations for nuclear reactor fuels and structural materials. Within YELLOWJACKET, a thermochemistry solver is being developed that would systematically alter the molar concentrations of numerous species of interest to yield a solution that has the lowest Gibb's energy for a particular temperature and pressure. The new application will fulfill the increasing desire to directly couple thermochemistry computations with continuum and meso-scales and help in improving nuclear fuel performance modelling. For example, the code could capture the local oxygen chemical potential and, together with temperature and diffusion relations, allow for prediction of oxygen redistribution within nuclear fuel.

5. Acknowledgements

This research made use of the resources of the High-Performance Computing Center at Idaho National Laboratory, which is supported by the Office of Nuclear Energy of the U.S. Department of Energy and the Nuclear Science User Facilities under Contract No. DE-AC07-05ID14517.

6. References

- [1] M. Stan, "Discovery and design of nuclear fuels", Materials Today, Vol. 12, No.11, 2009, pp. 20-28.
- [2] D.R. Gaston, C.J. Permann, J.W. Peterson, A.E. Slaughter, D. Andrs, Y. Wang, M.P. Short, D.M. Perez, M.R. Tonks, J. Ortensi, and R.C. Martineau, "Physics-based multiscale coupling for full core nuclear reactor simulation", Annals of Nuclear Energy, Vol. 84, 2015, pp. 45-54.
- [3] W.B. White, S.M. Johnson, and G.B. Dantzig, "Chemical Equilibrium in Complex Mixtures", The Journal of Chemical Physics, Vol. 28, No. 5, 1958, pp. 751-755.
- [4] M.H.A. Piro, S. Simunovic, T.M. Besmann, B.J. Lewis and W.T. Thompson, "The thermochemistry library Thermochimica", Computational Materials Science, Vol. 67, 2013, pp. 266-272.
- [5] Z.K. Liu and Y. Wang, "Computational thermodynamics of materials", Cambridge University Press, Cambridge, 2009.
- [6] A.D. Pelton and C.W. Bale, "Computational techniques for the treatment of thermodynamic data in multicomponent systems and the calculation of phase equilibria", Calphad, Vol. 1, No. 3, 1977, pp. 253-273.
- [7] B. Sundman and J. Ågren, "A regular solution model for phases with several components and sublattices, suitable for computer applications", Journal of Physics and Chemistry of Solids, Vol. 42, No. 4, 1981, pp. 297-301.
- [8] M. Hillert, "Some viewpoints on the use of a computer for calculating phase diagrams" Physica B+C, Vol. 103, No. 1, 1981, pp. 31-40.
- [9] M.H.A. Piro, T.M. Besmann, S. Simunovic, B.J. Lewis and W.T. Thompson, "Numerical verification of equilibrium thermodynamic computations in nuclear fuel performance codes", Journal of Nuclear Materials, Vol. 414, No. 3, 2011, pp. 399-407.
- [10] G. Eriksson and W.T. Thompson, "A procedure to estimate equilibrium concentrations in multicomponent systems and related applications", Calphad, Vol. 13, No. 4, 1989, pp. 389-400.
- [11] M.H.A. Piro and S. Simunovic, "Global optimization algorithms to compute thermodynamic equilibria in large complex systems with performance considerations" Computational Materials Science, Vol. 118, 2016 pp. 87-96.
- [12] S. Simunovic, J.W. McMurray, T.M. Besmann, E.E. Moore and M.H.A. Piro, "Coupled Mass and Heat Transport Models for Nuclear Fuels using Thermodynamic Calculations", Oak Ridge National Laboratory, ORNL/TM-2018/2, 2017.