

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

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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 multi-physics, 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, multi-physics 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 Thermochemica [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{O}_i , are the same as the dimensional quantities O_i divided by RT , i.e., $\tilde{O}_i = O_i/RT$.

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.

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