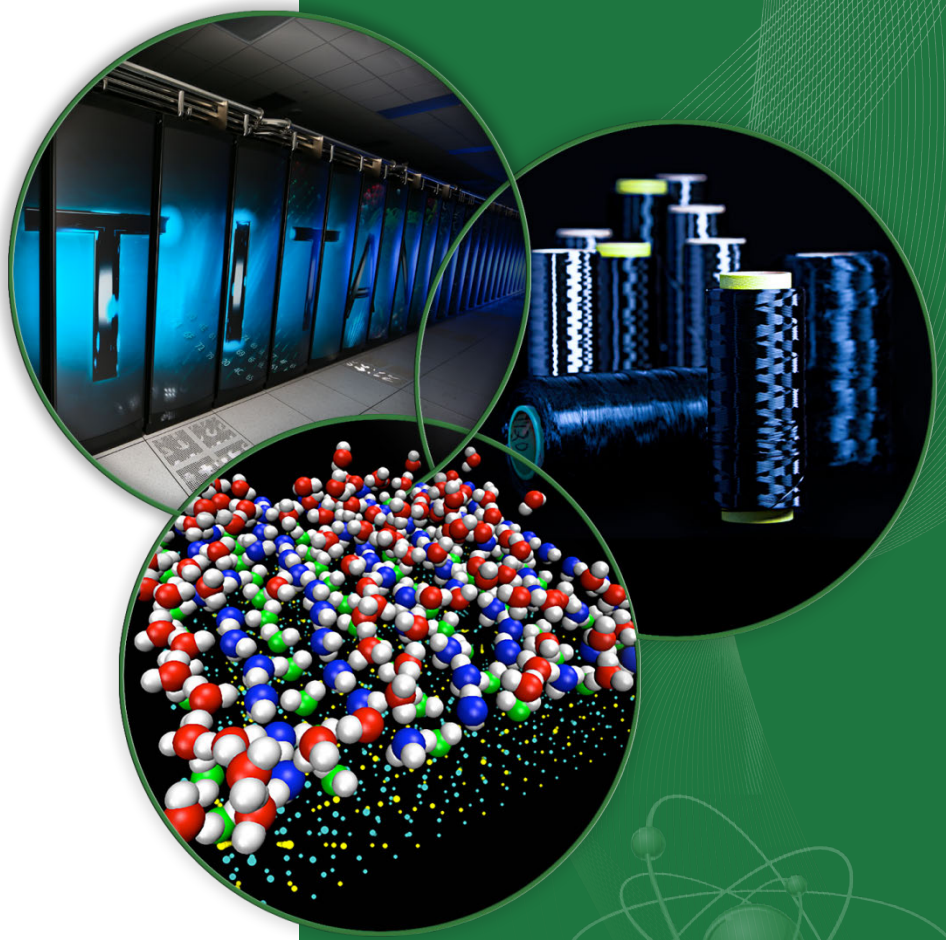
Fuel qualification: Thermodynamic modeling and simulation

Molten Salt Reactor Workshop 2017 – Key Technology and Safety Issues for MSRs

JW McMurray
Oak Ridge National Laboratory

TM Besmann
University of South Carolina



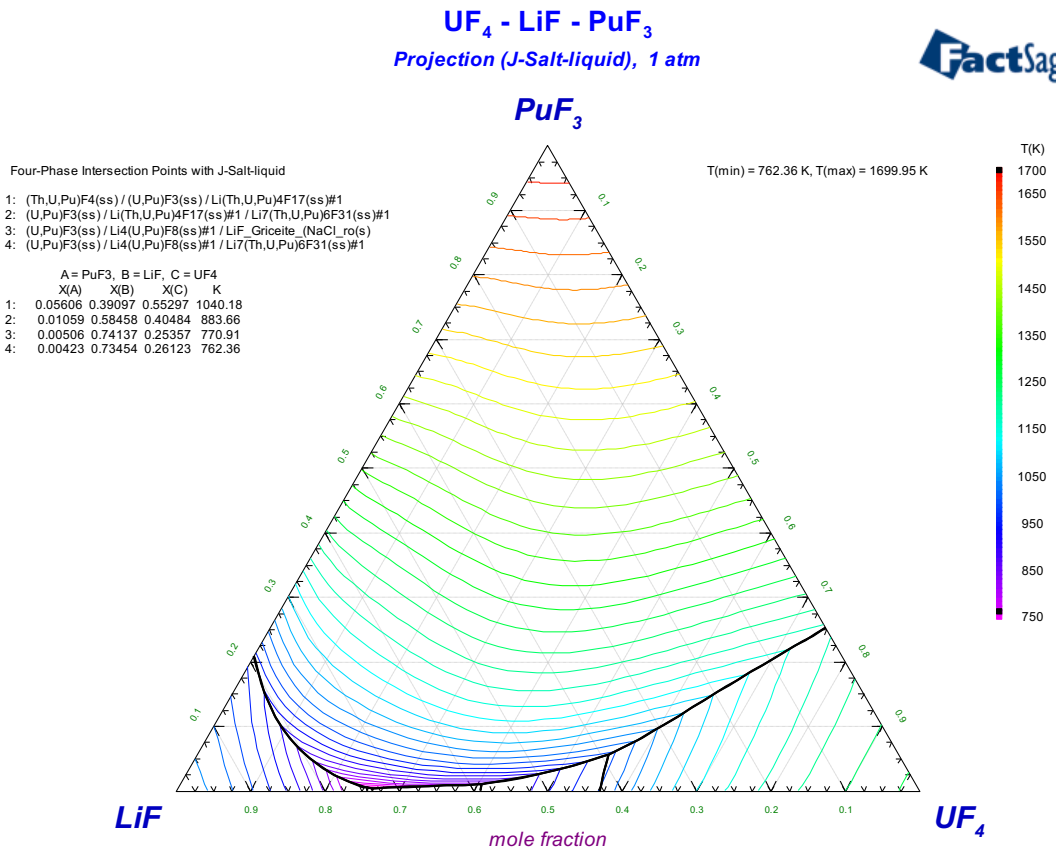
ORNL is managed by UT-Battelle
for the US Department of Energy

Thermochemical and thermophysical models are necessary for reactor design and fuel salt behavior predictions

- Models are developed from thermochemical and physical properties databases provided by measurements or computational representations
- A modeling database is a practical way to retrieve the thermochemical information and provides:
  - Liquid-liquid immiscibilty
  - Melting points/precipitation/volatilization – **allows for tracking of radionuclides which is key for safety and safegaurds**
  - Chemical potential (corrosion, vapor pressure...)
  - Inputs for viscosity models (e.g., Quasichemical model gives NNN pairs in multicomponent silicate melts – Grundy et al.)
  - Heat capacity
- Kinetic phenomena can be simulated by coupling with time dependent behavior for representatig reactor/fuel performance
- Can be incorporated in reactor simulation codes/real-time reactor control
- CALPHAD modeling basis for more reliable prediction of behavior outside empirical data envelope

OAK RIDGE National Laboratory

Development of thermodynamic models



Example of Thermochemical State Calculation in Pseudo-Ternary: Liquidus Projection UF_4-LiF-PuF_3

- The CALPHAD (CALculation of PHase Diagram) method
  - Not just phase diagrams but a *complete* thermodynamic picture
  - Developed with validated data from measurements/calculations
- Semi-empirical physics based Gibbs energy models developed using
  - Quasi-chemical for molten salts
  - Compound energy formalism for crystalline phases
  - Gas law governs vapor phase
  - Phase equilibria and other relevant thermodynamic values mined from the open literature or generated with experiments/calculations
- Base models for the fundamental unary and binary subsystems can be integrated to generate many-element simulations.

OAK RIDGE National Laboratory

Creating practical, qualified many element thermochemical databases is tractable

- For thermochemistry, not necessary to generate cross interactions between all possible constituents
  - Interaction of minor elements with major constituents sufficient
- Experimental efforts would be restricted to
  - Particularly critical systems
  - Where uncertainties are outside acceptable bounds
  - Benchmarking/validation/refining models developed from subsystems
- Can build on existing empirical data and already assessed databases
  - Data mining to collect and curate information on targeted systems
  - International partners can provide already developed data from their efforts
  - NEA *Thermodynamics of Advanced Fuels-International Database* program can add molten salts and be invaluable asset

Validated databases may shorten development & speed regulatory processes

OAK RIDGE National Laboratory

TAF-ID is an international effort to understand fuel and cladding chemistry with fission products

- NEA is developing the Thermodynamics of Advanced Fuels-International Database (TAF-ID)
- Current effort objective: Use the CALPHAD method to develop a unified thermodynamic description of fuel/cladding with fission products from key binary/ternary subsystems
- Current TAF-ID Systems include:
  - Fuel: Oxides, nitrides, carbides, metals, minor actinides and fission products
  - Cladding: Zircaloy, SiC, ODS steels, ferritic steels like FeCrAl, and other advanced materials

OECD
BETTER POLICIES FOR BETTER LIVES

NEA
Nuclear Energy Agency

add molten salt fuel with fission and corrosion products as well as MSR structural materials

Application: The database is to be used to aid design of advanced fuel/cladding systems and for physics based fuel performance simulations.

Status of molten salt fuel thermochemistry: Data exist for multi-element salts, including U, Th, Pu, but more is needed

- Fresh fluoride salt fuel (plus some additional elements) currently represented by existing data/models
  - *LiF-NaF-BeF_2-ThF_4-UF_3-UF_4-PuF_3-PuF_4-CrF_2-CrF_3-NiF_2-MoF_5*
  - **Chloride salt systems have an even more restricted data set**
- More data is needed because fuel compositions evolve due to build up of:
  - Fission and transmutation products as salts or secondary solid or liquid phases
  - Corrosion products as salts/solids
  - Air/moisture contaminants
  - Refueling
  - Salt conditioning (redox adjustment)
  - Mechanical filtering, etc.
- These non-fuel elements can affect the properties and chemistry of the fuel. For example, they can:
  - Alter salt melting point (solidus/liquidus) resulting precipitates
  - Alter vapor pressures (source term!)
  - Create liquid-liquid immiscibility
  - Produce unexpected corrosion mechanisms
  - Modify thermal conductivity, heat capacity, and viscosity

OAK RIDGE National Laboratory

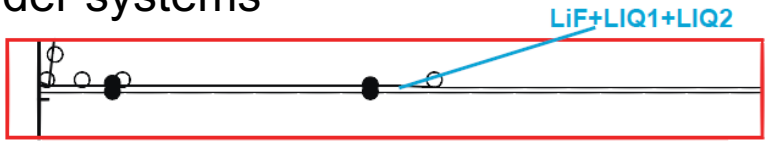
Significant effort on models and data needed for simulating salt thermochemical state with operation

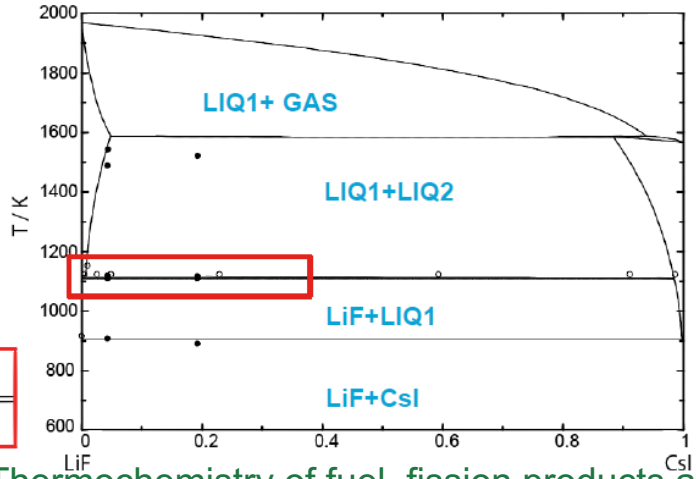
- Liquid and crystalline CALPHAD models for major salt elements are needed
  - This means determining binary through quaternary interaction behavior
- For minor constituents (transuranics, FPs, corrosion products...) only need interaction representations with each of the major constituents
  - Probability of minor constituents interacting and mangitude of the affect is small and can be neglected
- **Experimental and computational efforts will be required to obtain the needed data and models** – collaboration is essential to provide adequate resources to cover all compositional regions of interest
- Uncertainties in values/models can and should be included

OAK RIDGE National Laboratory

Need for thermochemical measurements of MSR fuel with major fission products

- **CsI** is a stable iodide
- CsF can form when Cs is in excess
- Need for thermochemical measurements to define key binary systems and validate models for higher order systems

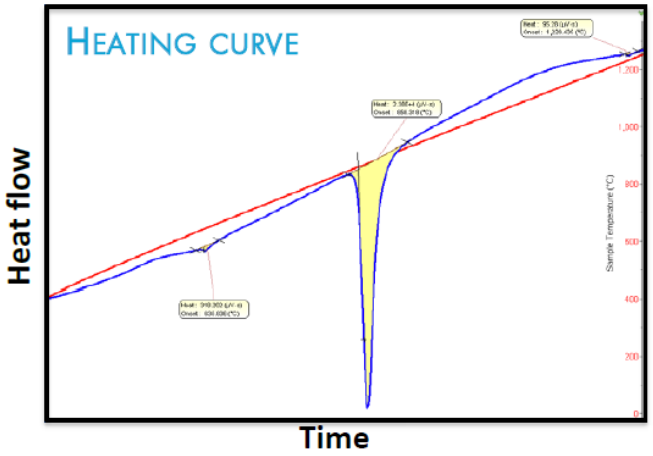




Filled symbols from JRC-Delft Univ. collaboration. Capelli et al. Thermochemistry of fuel, fission products and corrosion products in Molten Salt Reactor

The international experimental thermodynamic community has the tools and techniques to attack this problem

Example DSC data



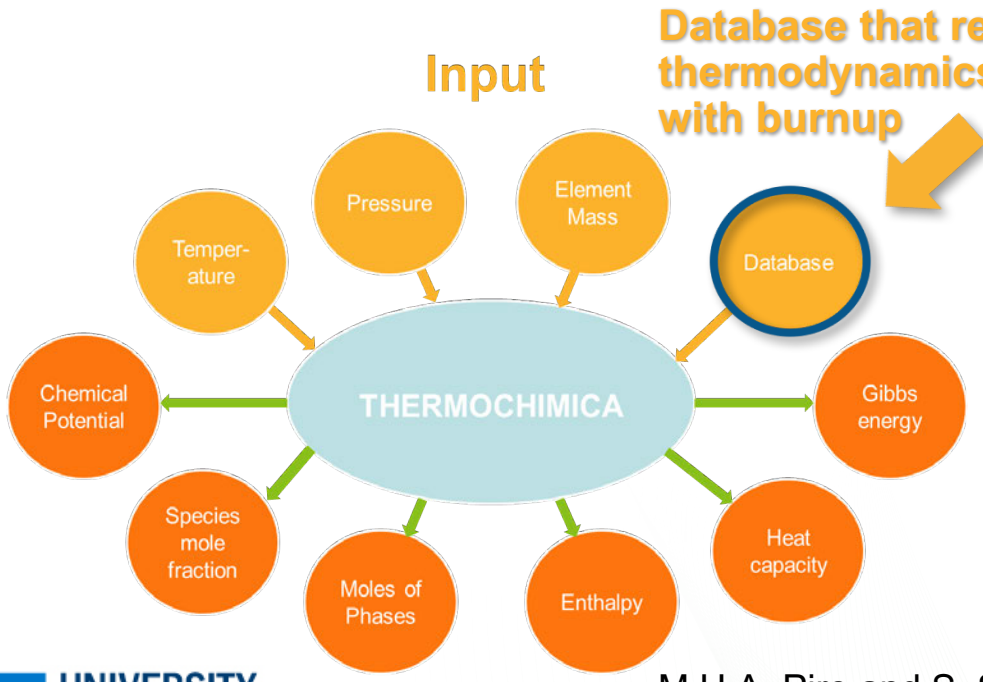
Thermochemical measurement needs	Techniques
Vapor pressures	Knudsen effusion, transpiration
Phase equilibria	Differential Scanning Calorimetry (DSC), Differential Thermal Analysis (DTA) Mass Spectrometry (MS)
Heat capacities	DSC
Heats of fusion	DSC, other calorimetry
Corrosion behavior	Redox potentials, exposure testing, etc

OAK RIDGE National Laboratory

Coupling thermochemistry to kinetic processes: Example for UO_{2+x}

- Thermodynamic inputs were coupled to a Finite Element (FE) transport code
- Thermochimica (similar to ThermoCalc, FactSage, etc.) is an open-source software library for computing thermodynamic equilibria with the primary purpose of direct integration into multi-physics codes.
- The software is written in Fortran and it can be called from a Fortran, C, or C++ Application Programming Interfaces (API) on a desktop workstation or high performance computing environment.
- Software development by M.H.A. Piro is currently being maintained and developed by M.H.A. Piro and S. Simunovic (ORNL).

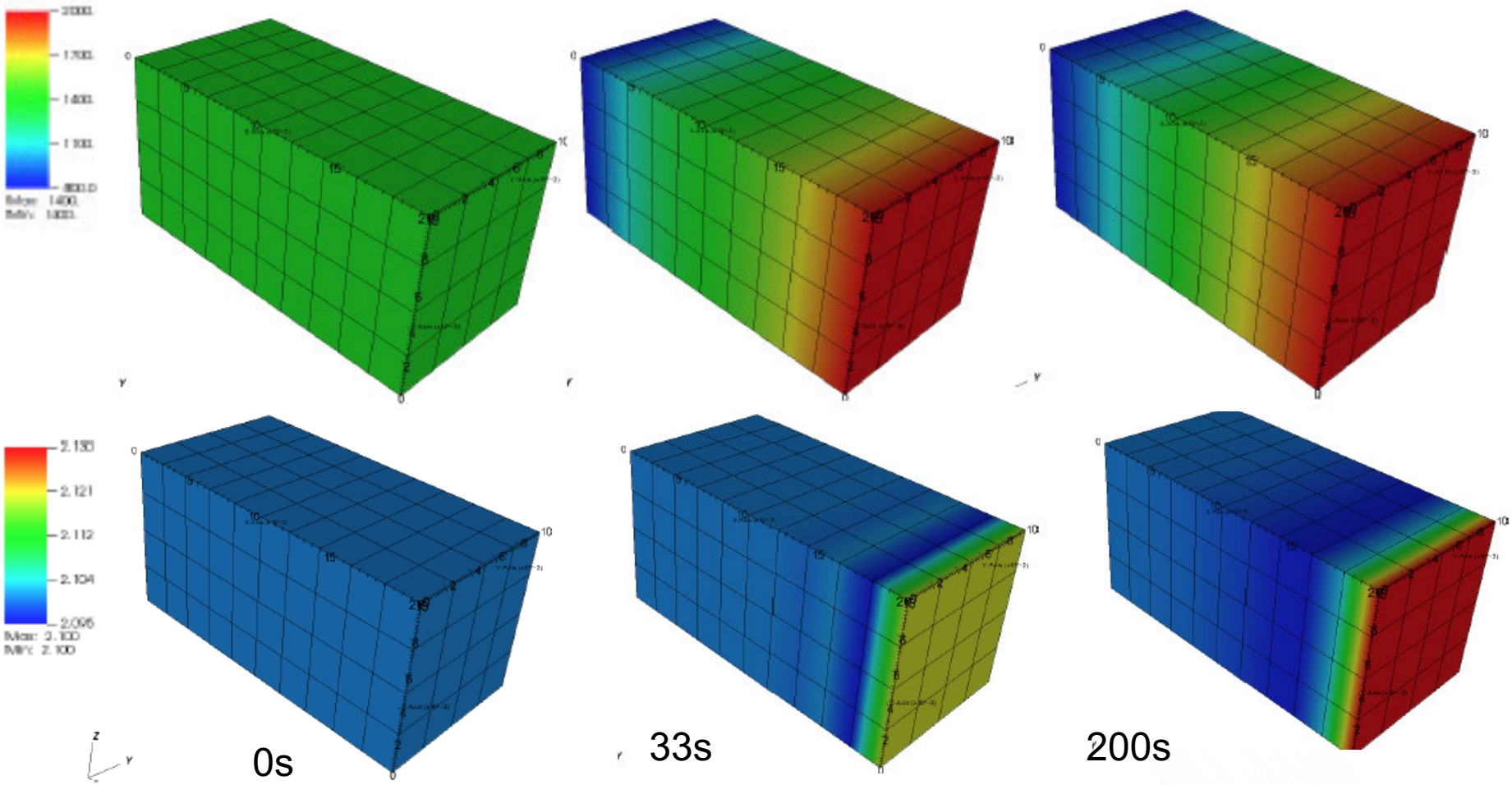
Requires an Efficient Gibbs Energy Minimizer: Thermochimica



M.H.A. Piro and S. Simunovic, CALPHAD, 39 (2012) 104-110.

Outputs become Inputs FEM simulations

Temperature distribution with time



Oxygen concentration distribution with time

Simulation conditions

- Composition 1 mole U, 2.05 moles O
- 1500 and 500 °C boundary conditions
- Single phase fluorite urania test case

OAK RIDGE National Laboratory

Path forward will require collaborations and focused efforts

- Need for measurements of thermochemical/thermophysical properties. They are essential for reactor design and effective, safe unit operation.
- Representing thermochemical/thermophysical properties with models gives us a way to efficiently extract the information:
  - Thermochemical models predict source terms – the chemical state of the radionuclides. Are they in solution, will they plate out, will they volatilize, etc.
  - Thermochemical/thermophysical models give us heat transfer behavior
  - Coupling thermodynamics with kinetic models allows physics based simulations, e.g. predicting heat and mass transport.
- JRC – Karlsruhe and Delft University of Technology developing thermochemical and thermophysical databases for fluoride salts
- INERI proposed between ORNL – JRC – University of South Carolina (T. Besmann)
- We are poised to make rapid progress on essential modeling and simulation capability for MSRs with critical database development

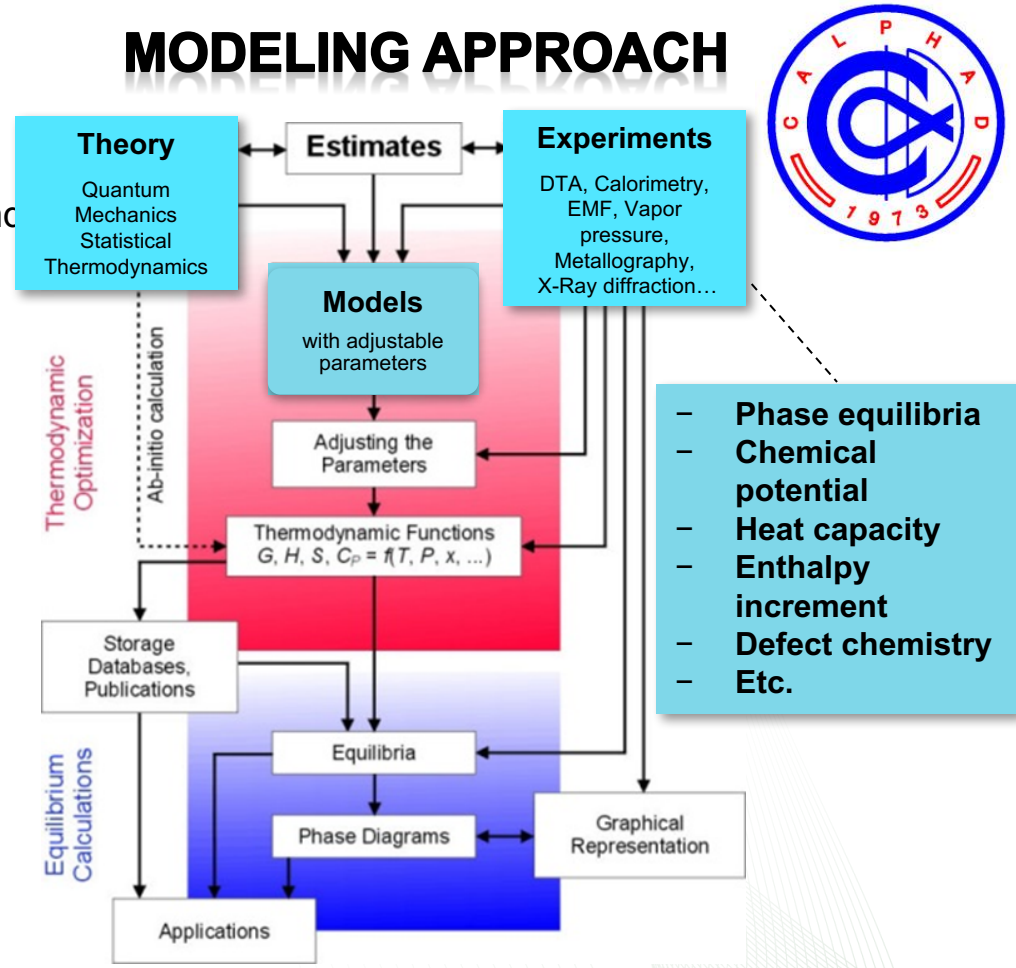
OAK RIDGE National Laboratory

Additional slides

OAK RIDGE National Laboratory

Within the community of materials thermodynamics we use the CALPHAD method

- CALPHAD (CALculation of PHAse Diagrams)
- Gives us a way to perform a thermodynamic assessment: An internally consistent set of Gibbs energy models for all of the phases in a particular system
- Gibbs energy models are based on the physical and chemical properties of the phases they represent.
- All available thermodynamic data is critically reviewed and considered
- Results in models that
  - reproduce the thermodynamic properties and phase relations in a system
  - **and can be extrapolated with higher confidence outside of their range of experimental validation**
- Based on, and consistent with, fundamental unary and binary subsystems – SGTE (Scientific Group Thermodata Europe) is the standard



M. ZINKEVICH, *Doing and Using, Max-Planck-Institut für Metallforschung, Germany*, (2003)

OAK RIDGE National Laboratory

Uncertainty assessment

- Genetic algorithm with Bayesian statistics allows for linking uncertainty in the data to assess the overall predictive credibility of the models.
- From *Stan and Reardon, CALPHAD 27 (2003) 319*

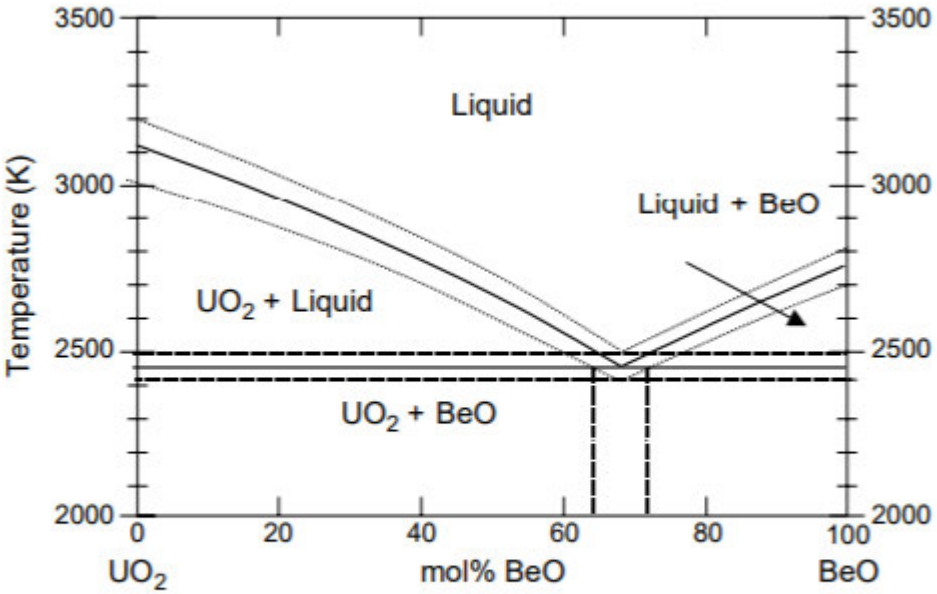


Fig. 2. The calculated UO_2–BeO phase diagram (solid lines) and the uncertainty intervals (dotted lines).

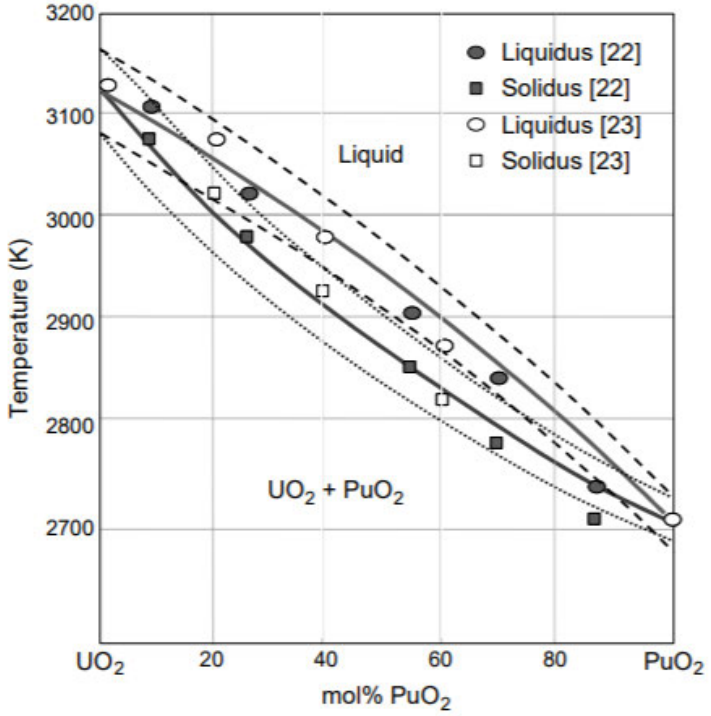


Fig. 1. The calculated UO_2–PuO_2 phase diagram (solid lines) and the uncertainty intervals of the liquidus (dashed lines) and the solidus (dotted lines) curves.

OAK RIDGE National Laboratory