Uncertainties on Thermodynamic and Physical Property DataBases for Severe Accidents and their Consequences on Safety Calculations.

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Outline

• Introduction
• Uncertainties on phase diagrams
• Uncertainties on Physical Properties
• Application to Severe Accident Calculations
  – Example : Spreading calculations
General procedure for calculation

• Composition and Temperature of corium
• Thermodynamic Modelling
  – Repartition of phases (liquids, solids, vapours)
  – Composition of Each Phase
• Physical Properties estimation
  – Database
  – Mixing Law
• Calculation of corium behaviour using calculated properties
• Determination of new temperature/composition
Some aspects of thermodynamic modelling

- Research of the phases composition and proportions minimizing the system Integral Gibbs Energy
  \[ G = \min \text{ or } dG = 0 \text{ and } d^2G \geq 0 \]
  \[ dG = -SdT + VdP + \sum \mu_i dn_i + \ldots \]

- *Thermodynamic database*
  + *Minimization software*

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- **Experimental thermodynamic properties and phase equilibria**
- Assessment programs
- **Gibbs Energy database**
- Application programs
- Calculations of:
  - Thermodynamic properties
  - Phase equilibria
  - Process simulation

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Augmented by
Estimation techniques based on
- experimental trends
- ab initio calculations
Data in Thermodynamic Databases

- Thermodynamic data for pure elements (compiled by SGTE)
- Thermodynamic data for stoichiometric substances
  - H formation at 298.15K (from pure elements)
  - Entropy at 298.15K
  - Cp(T) from 298.15K to gaseous state
- Thermodynamic data for solutions
  - Mixing laws (excess Gibbs energy)
    \[ G = G_{\text{reference}} + G_{\text{ideal mixing}} + G_{\text{excess}} \]
How is the data produced?

- Assessment of experimental work.
  - Some data (H, Cp) may be directly available
  - Usually, indirect validation on phase diagrams, partial pressures, ...
  - Weighing of different works. *Expert judgement.*
- Choice of modelling (1 or n sub-lattices, order of excess terms, nonstoichiometries, ....)
- Use of an optimizer to determine the dataset which reproduces the best the experimental data.
  - This operation is done for binary interaction terms first, then on ternaries, ....
  - The database is incremented gradually, no global reoptimization.

- **NUCLEA, European Database**
  - 18 elements
  - >300 binary and ternary diagrams
Causes of Uncertainties

- Experimental errors (esp. at high temperatures)
- Exhaustivity of assessed experiments
- Modelling errors
- Optimization errors

- Errors due to the execution of Gibbs Minimizer
  + Poor convergence/divergence problems! (metastability zones or numerical analysis?)
How can we assess the uncertainties?  
(from an end-user standpoint)

- The database has been optimized as a whole.  
  ⇒ It is impossible to study independantly the effect of one term in the DB.
- Expert judgement provided ratings to subsystems (*, **, *** , ****)

Study of the evolution of database results with successive versions
=> order of magnitude of uncertainties at version n-1.
• Differences < 1.2%w => very consistent output.
Typical EPR Concrete

36\%_w \text{SiO}_2, 49\%_w \text{Fe}_2\text{O}_3, 5\%_w \text{CaO}, 6\%_w \text{Al}_2\text{O}_3, 4\% \text{H}_2\text{O}

- Large discrepancies (100-200K) between THMO and TDBCR
- Consistency of TDBCR versions.
- SiO$_2$-Fe$_2$O$_3$ system rated *
Gaseous species over corium-concrete mixture at 2573 K

No large evolutions except appearances of new phases: $\text{UO}_3$, $\text{Al(OH)}_2$,
Disapearance of baryum hydroxides.
Gases over In-vessel corium at 3000K

- Variations can reach factors of 3-10
- New gaseous species appeared in newer versions (ex. BaH, BaOH, HSr, …)
Conclusions on Thermodynamic Uncertainties

• the thermodynamic outputs uncertainties are decreasing with the latest versions of the databases. All the thermodynamic outputs don’t have the same uncertainties,

• for the liquidus and solidus temperatures and for the enthalpy, the uncertainties are getting lower for the successive databases,

• for the liquid, the uncertainties of the compositions are low,

• between solidus and liquidus temperatures, the uncertainties are may be important, especially for less validated systems,

• for the gaseous substances, the uncertainties are mainly due to the absence of some vapours from the bases

• if all the pseudo-binary systems that constitute the corium composition have been well assessed, it’s possible to have a good confidence that uncertainties on temperature will be less than 50K;

• if one or more pseudo-binary systems that constitute the corium composition have a low assessment quality, at least an uncertainty on the temperature of ±100 K could be expected.
Properties of Multiphasic Corium Mixtures

- Database of Pure-Substance Physical properties
- Mixture Physical properties depend on the spatial repartition of phases
  - Thermalhydraulic steady state => phase segregation
  - Rapid cooling => dendrites
  - Bubbling + shear => emulsions/suspensions

- Only one phase

- 2 liquids (Sedimented)

- 2 liquids (Emulsioned)

- Dendritic mushy zone (percolation)

- Semi-solid suspension
Density of Metallic Uranium

- Solid phase data quite consistent
- Large dispersion of liquid phase data
- Critical review by Fischer (FZK) 2000

\[ \rho_{\text{liq}} = 17270 - 1.6010(T-1408) \]  
\( \text{(brown curve)} \)
Mixing laws for solutions (1)

\[ V = \sum y_i V_i + V_{\text{excess}} \]

Hypothesis: Ideal mixing – No excess volume
Applicable to solid and liquid solutions

- Molecules of similar molar volumes (at ±30 %)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Volume (cm³/mol)</th>
<th>Element</th>
<th>Atomic Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>30.5</td>
<td>U</td>
<td>13.8</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>22.3</td>
<td>Zr</td>
<td>14.6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>27</td>
<td>Fe</td>
<td>7.9</td>
</tr>
<tr>
<td>(FeO)₂</td>
<td>26</td>
<td>Cr</td>
<td>8.2</td>
</tr>
</tbody>
</table>

- Excess volumes for metallic alloys (Crawley 74)
  - Maximum: -20 % for Na-In - 15 % for Fe-Si (at 50-50%at)
  - Generally < ± 3 %
- For oxides (slags, natural silicates), Excess volume generally < 1% (Nelson & Carmichael 1974)
Which density for liquids below $T_{\text{fusion}}$?

- Between $T_{\text{fusion}}$ and $T_{\text{sol}}$, the refractory component is still present in the liquid phase.
- Which density to be used below $T_{\text{fusion}}$?
- $\text{UO}_2$ present in corium-concrete oxidic phase for 1000 K below $T_{\text{fusion}}$!!

**Hypothesis #1**

Constant volume

$$V_{\text{molar}}(T<T_{\text{fusion}}) = V_{\text{molar}}(T_{\text{fusion}})$$

**Hypothesis #2**

Constant expansion coefficient

$$V_{\text{molar}}(T) = V_{\text{molar}}(T_{\text{fusion}}) [1 + \alpha(T_{\text{fusion}})(T-T_{\text{fusion}})]$$

![Graph showing temperature vs. percentage composition](image)
The 2 hypotheses below Tfusion

Hypothesis #1

Hypothesis #2

Temperature K

Density kg/m³

JK Fink & Petri 97
JK Fink & Petri 97 (liquid)
liquid hypoth 1
Fink et al. 81
Fink et al 81
Strizhov et al. 95
Chu et al. 95
Espinosa et al 2000
MAAP
Christensen 1962
Influence of these uncertainties to global calculation

Different types of uncertainties are present when calculating a SA experiment or a reactor case.

1. Uncertainties on initial/boundary conditions
2. Uncertainties on physical properties
3. Uncertainties due to modelling approximations

• Development of a methodology
  – n-Parameter analysis
  – 2 values for each parameter => $2^n$ calculations
  – Reduced map

• Example of Application
  – VE-U1 Spreading test
  – Post test calculations with THEMA (CEA Spreading code)
  – 11 parameters 2048 calculations !!
  – 128 calculation performed. Wilk’s quality level > 96%
## Parameters used in the exercises

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low Value</th>
<th>High Value</th>
<th>V2.2mod lc</th>
<th>V2.3mod6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_0$ Shaw correlation coefficient</td>
<td>0.021</td>
<td>0.034</td>
<td>studied</td>
<td>studied</td>
</tr>
<tr>
<td>A Shaw correlation coefficient</td>
<td>0.01</td>
<td>0.024</td>
<td>studied</td>
<td>studied</td>
</tr>
<tr>
<td>Melt liquidus temperature, (K)</td>
<td>2175</td>
<td>2325</td>
<td>studied</td>
<td>2250</td>
</tr>
<tr>
<td>Initial melt temperature (K)</td>
<td>2015</td>
<td>2185</td>
<td>studied</td>
<td>studied</td>
</tr>
<tr>
<td>Assumption for the inlet flow rate</td>
<td>High flow rate</td>
<td>Low flow rate</td>
<td>studied</td>
<td>studied</td>
</tr>
<tr>
<td>Surrounding temperature (K)</td>
<td>300</td>
<td>700</td>
<td>studied</td>
<td>300</td>
</tr>
<tr>
<td>Melt emissivity</td>
<td>0.6</td>
<td>1</td>
<td>0.8</td>
<td>studied</td>
</tr>
<tr>
<td>Solidification model</td>
<td>Bulk freezing</td>
<td>Crust and bulk</td>
<td>studied</td>
<td>Crust and Bulk</td>
</tr>
<tr>
<td>Solidification temperature (K)</td>
<td>1300</td>
<td>2000</td>
<td>1300</td>
<td>studied</td>
</tr>
<tr>
<td>Transport of the upper crust</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>studied</td>
</tr>
<tr>
<td>Melt density (kg/m3)</td>
<td>Std. values ±250 or ±500 (depend. on T)</td>
<td>studied</td>
<td>Std. values</td>
<td></td>
</tr>
<tr>
<td>Melt therm. conduct. (W/m/K)</td>
<td>1</td>
<td>5</td>
<td>studied</td>
<td>studied</td>
</tr>
<tr>
<td>Melt heat capacity</td>
<td>Std. values ±10 %</td>
<td>studied</td>
<td>studied</td>
<td></td>
</tr>
<tr>
<td>Therm. resist. with substratum (K.m²/W)</td>
<td>0</td>
<td>0.006</td>
<td>studied</td>
<td>studied</td>
</tr>
<tr>
<td>Substratum thermal conduct. (W/m/K)</td>
<td>0.8</td>
<td>1.4</td>
<td>1.1</td>
<td>studied</td>
</tr>
</tbody>
</table>
Correlations between parameters and Spreading length

Most correlated parameters
1. Flow rate. Especially at initial instants of spreading
2. Viscosity Law exponent $\mu = \mu^0 e^{A(T-T_{liq})}$
3. Liquidus Temperature
4. Inlet Temperature
Correlations between parameters and substrate temperature

Most correlated parameters
1. Substrate conductivity
2. Thermal contact resistance
3. Melt conductivity
4. Flow rate and Inlet Temperature
Conclusions

• Uncertainties due to uncertainties on Physical Properties and through those to thermodynamic modeling remain important.
• Sensitivity analyses are useful to determine which properties should be prioritized.
• R&D on corium viscosity has been performed for the validation of the EPR spreading concept, reducing these uncertainties.
• Several physical properties are still poorly known, esp. mixing laws
• Phase diagrams (thermodynamic database) must be improved e.g. in the corium-concrete diagram to reduce remaining uncertainties.
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