A Thermodynamic database for Salts Systems in Nuclear applications

O. Beneš, R.J.M. Konings

European Commission, Joint Research Centre, Institute for Transuranium Elements, Karlsruhe

rudy.konings@ec.europa.eu
http://itu.jrc.cec.eu.int/
A technological Roadmap for Generation IV Nuclear Energy Systems

- Generation I: Early Prototype Reactors
  - Shippingport
  - Dresden, Fermi I
  - Magnox

- Generation II: Commercial Power Reactors
  - LWR-PWR, BWR
  - CANDU
  - AGR

- Generation III: Advanced LWRs
  - ABWR, System 80+, AP600, EPR

- Generation III+
  - Evolutionary Designs Offering Improved Economics for Near-Term Deployment

- Generation IV
  - Highly Economical
  - Enhanced Safety
  - Minimal Waste
  - Proliferation Resistant

Timeline:
- 1950
- 1960
- 1970
- 1980
- 1990
- 2000
- 2010
- 2020
- 2030

Source: A technological Roadmap for Generation IV Nuclear Energy Systems
The Six GENIV reactor types

- Gas-cooled Fast Reactor (GFR)
- Very high temperature reactor (VHTR)
- Supercritical-water-cooled reactor (SCWR)
- Sodium-cooled Fast Reactor (SFR)
- Lead-cooled Fast Reactor (LFR)
- Molten Salt Reactor (MSR)
The Molten Salt Reactor - The past

Concept: circulating system with fuel dissolved in molten salt developed at ORNL (USA)

1950’s: Aircraft propulsion programme (ARE)

1965-1969: Molten Salt Reactor Experiment (MSRE) & Molten Salt Breeder Reactor (MSBR)
The MSR fuel and its solvent

- Wide range of solubility for actinides
- Thermodynamically stable up to high temperatures
- Stable to radiation (no radiolytic decomposition)
- Low vapour pressure at the operating temperature of the reactor
- Compatible with nickel-based structural materials

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARE</td>
<td>NaF – ZrF$_4$ - UF$_4$</td>
</tr>
<tr>
<td>MSR</td>
<td>$^7$LiF - BeF$_2$ - ZrF$_4$ - ThF$_4$</td>
</tr>
<tr>
<td>MSBR</td>
<td>$^7$LiF - BeF$_2$ - ThF$_4$</td>
</tr>
</tbody>
</table>
The Molten Salt Reactor - The present

- Moderated breeder based on MSBR (thermal)
  LiF-BeF$_2$-ThF$_4$-UF$_4$
- Non-moderated breeder (fast)
  LiF-ThF$_4$
- Actinide burner (fast)
  LiF-BeF$_2$-NaF-PuF$_3$

- AHTR (USA): coated particle fuel with molten salt (fluoride) cooling
  LiF-BeF$_2$
Physical properties needed for design calculations

- Melting point
- Actinide solubility
- Vapour pressure
- Density
- Viscosity
- Heat capacity
- Thermal conductivity

Extensive database available from US (ORNL) and USSR research in the period 1950-1970
Databases compiled

- **LiF-BeF$_2$-ThF$_4$-UF$_4$**
  - QKTO polynomial model in FactSage™
  - Re-assessment in SUBG quasichemical model underway

- **LiF-NaF-KF-RbF-CsF-BeF$_2$-LaF$_3$-PuF$_3$**
  - SUBG quasichemical model in FactSage™

- **NaCl-UCl$_3$-PuCl$_3$**
  - SUBG quasichemical model in FactSage™
Quasichemical model by Blander & Pelton

Symmetry group numbers $i$ and $j$ are attributed to the components A and B, allowing $i$ and $j$ particles to mix substitutionally on a quasi-lattice. In this formalism, general polynomials can be used to describe the excess Gibbs energy coefficients.

\[
\Delta_{xs} G = \sum_{p,q} L_{A,B}^{p,q}(T) Y_A \left( \frac{\chi_i}{\chi_i + \chi_j} \right)^p Y_B \left( \frac{\chi_j}{\chi_i + \chi_j} \right)^q
\]
Quasichemical model with quadruplet approximation by Chartand & Pelton

\[(A \cdots X) + (B \cdots Y) = (A \cdots Y) + (B \cdots X)\]

\[\Delta g_{AB/XY}^{\text{exchange}}\]

\[\Delta g_{AB/X_2} = \Delta g_{AB/X_2}^0 + \sum_{(i+j) \geq 1} \chi_{AB/X_2}^{i} \chi_{BA/X_2}^{j} \chi_{AB/X}^{ij}\]

Two sublattices, which reduces to pair approximation for \(X = Y = F\)
The LiF-BeF$_2$ phase diagram (QKTO)

Region of demixing (ROD)
- “Induced” by the small entropy of fusion of BeF$_2$

$$\frac{dT}{dX} = \frac{R}{\Delta_fus S^0_i} T_{fus}$$
The LiF-BeF$_2$ phase diagram
LiF-BeF$_2$ re-assessed in SUBG
by Thoma et al. (1960)
A binary cross-section of LiF-BeF$_2$-ThF$_4$ at ThF$_4$ = 10%
Solubility of ThF$_4$ in LiF-BeF$_2$ matrix:

LiF / BeF$_2$ = 76.6 / 23.3 (lowest melting)

T = $T_{\text{inlet (MSBR)}}$ = 839 K (566 °C)

solubility $\sim 4.7 - 18.2$ mol% of ThF$_4$

Isothermal section for $T = 839$K (566 °C)
Vapour pressure of the LiF-BeF$_2$-ThF$_4$ system
Comparison to the experimental liquidus data from ORNL reports
X (PuF$_3$) = 1.3 mol%

- PuF$_3$ addition has large influence on the melting behaviour
- Inlet temperature at least T=887K
- Relatively low content of BeF$_2$

Lowest melting point at: $T = 837$ K
LiF-NaF-BeF$_2$-PuF$_3$ (37.9-45.2-15.6-1.3)
Solubility of PuF$_3$ in 2LiF-BeF$_2$

![Graph showing solubility of PuF$_3$ against temperature](image)
Summary & Conclusions

- Two databases for fluoride salts for Molten Salt Reactors have been compiled
- The Quasichemical model with quadruplet interactions proved to be very useful and versatile
- The QKTO model also gave reasonable results and is of more universal use as it can be used in other software packages also
- The models describe melting behaviour, actinide solubility and vapour pressure of the fuel salts well, but some dedicated experiments are needed, especially for plutonium salts