A Thermodynamic database for Salts Systems in Nuclear applications

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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

ARE \( \text{NaF} - \text{ZrF}_4 - \text{UF}_4 \)

MSR \( ^7\text{LiF} - \text{BeF}_2 - \text{ZrF}_4 - \text{ThF}_4 \)

MSBR \( ^7\text{LiF} - \text{BeF}_2 - \text{ThF}_4 \)
The Molten Salt Reactor - The present

- Moderated breeder based on MSBR (thermal)
  \[ \text{LiF-BeF}_2-\text{ThF}_4-\text{UF}_4 \]
- Non-moderated breeder (fast)
  \[ \text{LiF-ThF}_4 \]
- Actinide burner (fast)
  \[ \text{LiF-BeF}_2-\text{NaF-PuF}_3 \]

- AHTR (USA): coated particle fuel with molten salt (fluoride) cooling
  \[ \text{LiF-BeF}_2 \]
Physical properties needed for design calculations

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

Phase diagram optimisation

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.

$$\Delta_{xs}G = \sum_{p,q} L_{A,B}^{p,q}(T) Y_A \left( \frac{\chi_i}{\chi_i + \chi_j} \right)^p Y_B \left( \frac{\chi_j}{\chi_i + \chi_j} \right)^q$$

Excess parameters

Equivalent fractions

Sum of Equivalent fractions
Quasichemical model with quadruplet approximation by Chartand & Pelton

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

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

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

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$_2$

\[
\frac{dT}{dX} = \frac{R T_{\text{fus}}}{\Delta_{\text{fus}} S^0_{\text{i fus}}} 
\]
The LiF-BeF$_2$ phase diagram

exp. data by Thoma et al. (1968)
LiF-BeF$_2$ re-assessed in SUBG
Our model
by Thoma et al. (1960)
A binary cross-section of LiF-BeF$_2$-ThF$_4$ at ThF$_4$ = 10%
Solubility of ThF₄ in LiF-BeF₂ matrix:

LiF / BeF₂ = 76.6 / 23.3 (lowest melting)
T = T_{inlet (MSBR)} = 839 K (566 °C)
solubility ~ 4.7 – 18.2 mol% of ThF₄

Isothermal section for T = 839K (566 °C)
Vapour pressure of the LiF-BeF$_2$-ThF$_4$ system
Comparison to the experimental liquidus data from ORNL reports
eutectic #1: $T=536$ K at LiF-NaF-BeF$_2$ (36.7-18.5-44.8)
(E1) $T=548$ K (estimated value by Moore et al.)

eutectic #2: $T=599$ K at LiF-NaF-BeF$_2$ (30.3-37.1-32.6)
(E2) $T=601$ K at LiF-NaF-BeF$_2$ (23-41-36)

Quasi-peritectic #1 (U):
$T=722$ K at LiF-NaF-BeF$_2$ (22.9-51.2-25.8)
$T=753$ K at LiF-NaF-BeF$_2$ (15-58-27)

MOSART matrix composition
LiF-NaF-BeF$_2$ (15-58-27)
X (PuF$_3$) = 1.3 mol%

Lowest melting point at: $T = 837$ K

LiF-NaF-BeF$_2$-PuF$_3$ (37.9-45.2-15.6-1.3)

- PuF$_3$ addition has large influence on the melting behaviour
- Inlet temperature at least $T=887$K
- Relatively low content of BeF$_2$
Solubility of PuF$_3$ in 2LiF-BeF$_2$

Our model

Mailen et al.
PuF$_3$ solubility in LiF–NaF–BeF$_2$

**Graph 1:**
- LiF–NaF–BeF$_2$ (17.5–56.5–26)
- LiF–NaF–BeF$_2$ (60.1–2.1–37.8)

**Graph 2:**
- LiF–NaF–BeF$_2$ (15-58-27)
PuF$_3$ solubility in LiF–BeF$_2$ as a function of LiF/BeF$_2$
The UF₄-ThF₄ system

\[ \text{G}^{\text{excess}} = ??? \]

2 \((U,\text{Th})\text{F}_4\) solutions

- liquid solution
- solid solution
Our ab initio (DFT) approach: the CsF-RbF example

2. DFT calculation of these configurations using the CASTEP code

\[ E_{\text{conf.}}^{x} = E(\text{Rb}_{x}\text{Cs}_{(1-x)}\text{F}) - x E(\text{RbF}) - (1-x) E(\text{CsF}) \]

18 different configurations calculated +
the 2 RbF and CsF end-members

3. Limited amount of configurations therefore the analysis of the results was made using the Surrounded Atom Model.

- interprets the excess energies in terms of the nearest neighbors
Excess G function derived based on the DFT calculation of the (Rb,Cs)F solid solution

4. The results of the Surrounded Atom Model for the excess energy of the (Th,U)F₄ solid solution can be interpreted using statistical thermodynamics models:

- Bragg-Williams model
- Guggenheim model
The CsF-RbF system

\[ T(K) \]

\[ \text{mole } \text{RbF}/(\text{RbF}+\text{CsF}) \]

Our DSC data
- liquidus points (cooling curves)
- Solidus points (heating curves)

Experimental studies: calorimetry

Heat flow DSC/DTA
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