Molten Salt Reactor Fuel: experiments and assessments on metal fluoride fluoride phase diagrams

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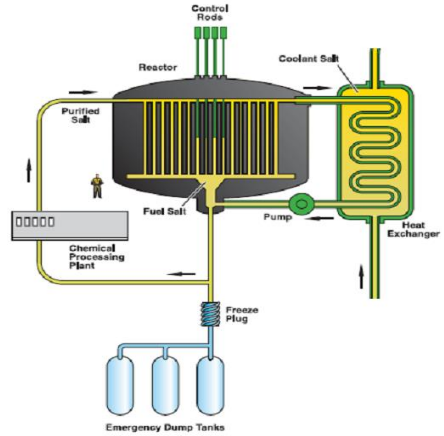

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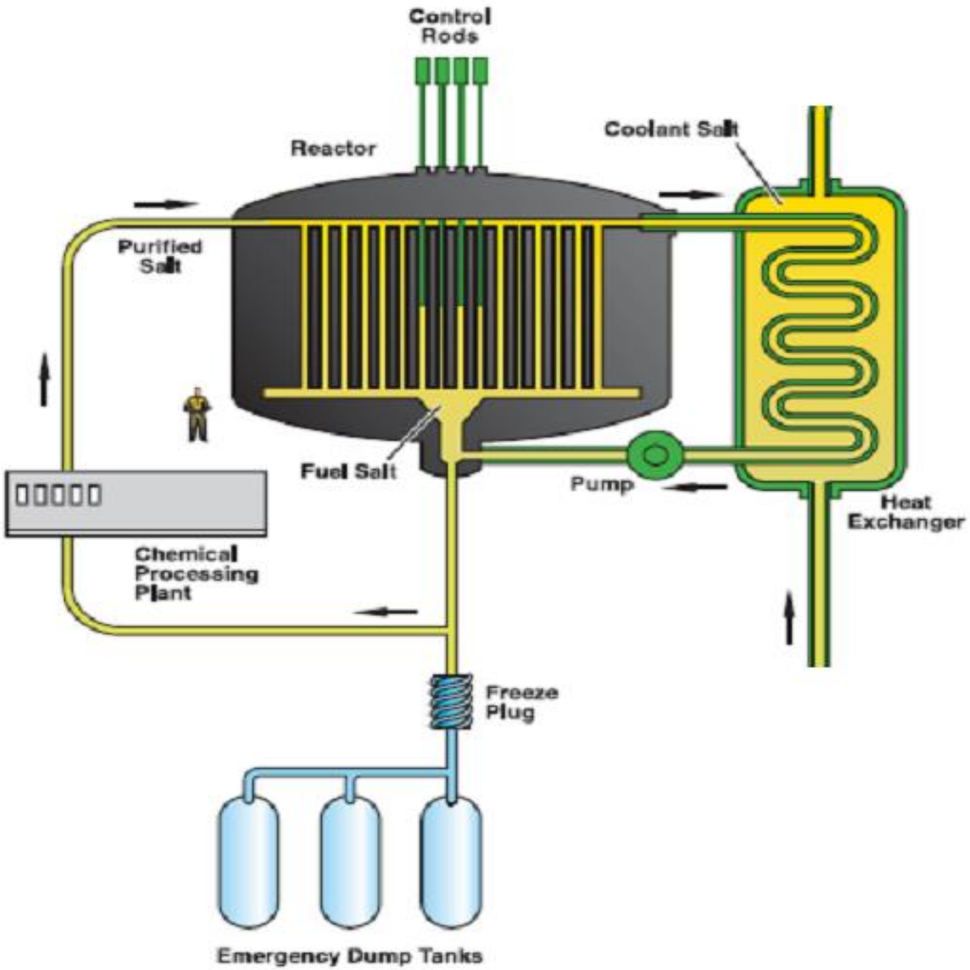
Control
Rods
Reactor
Coolant Salt
Purified
Salt
Fuel Salt
Pump
Heat
Exchanger
Chemical
Processing
Plant
Freeze
Plug
Emergency Dump Tanks

Materials requirements for solvents for the MSR

Only a limited number of metals is suitable from neutronic considerations

- ✓ 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
- ✓ Compatible with the reprocessing techology

ARE	$NaF - ZrF_4 - UF_4$
MSRE	$^7LiF - BeF_2 - ZrF_4 - ThF_4 - UF_4$
MSBR	$^7LiF - BeF_2 - ThF_4 - UF_4$
MSFR	$^7LiF - ThF_4 - UF_4$

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Some of the questions to be addressed

- ✓ Do we have a sufficient understanding of the ^{7}LiF-ThF_4-UF_4 salt ?
- ✓ Are there alternative solvent components that could be considered ?
- ✓ Can UF_4 be replaced by PuF_3 as fissile source?
- ✓ How do the physical properties vary in the multicomponent systems ?

↓

Thermochemical approach:

- CALPHAD modelling
- Experimental studies

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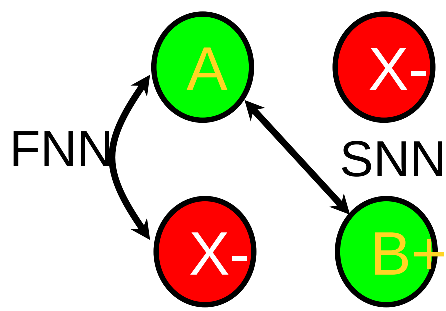
Relevant physical properties to be considered

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

Phase diagram optimisation

Quasichemical model with quadruplet approximation (Chartand & Pelton)



$$(A \cdots X) + (B \cdots Y) = (A \cdots Y) + (B \cdots X) \qquad \Delta g_{AB/XY}^{exchange}$$

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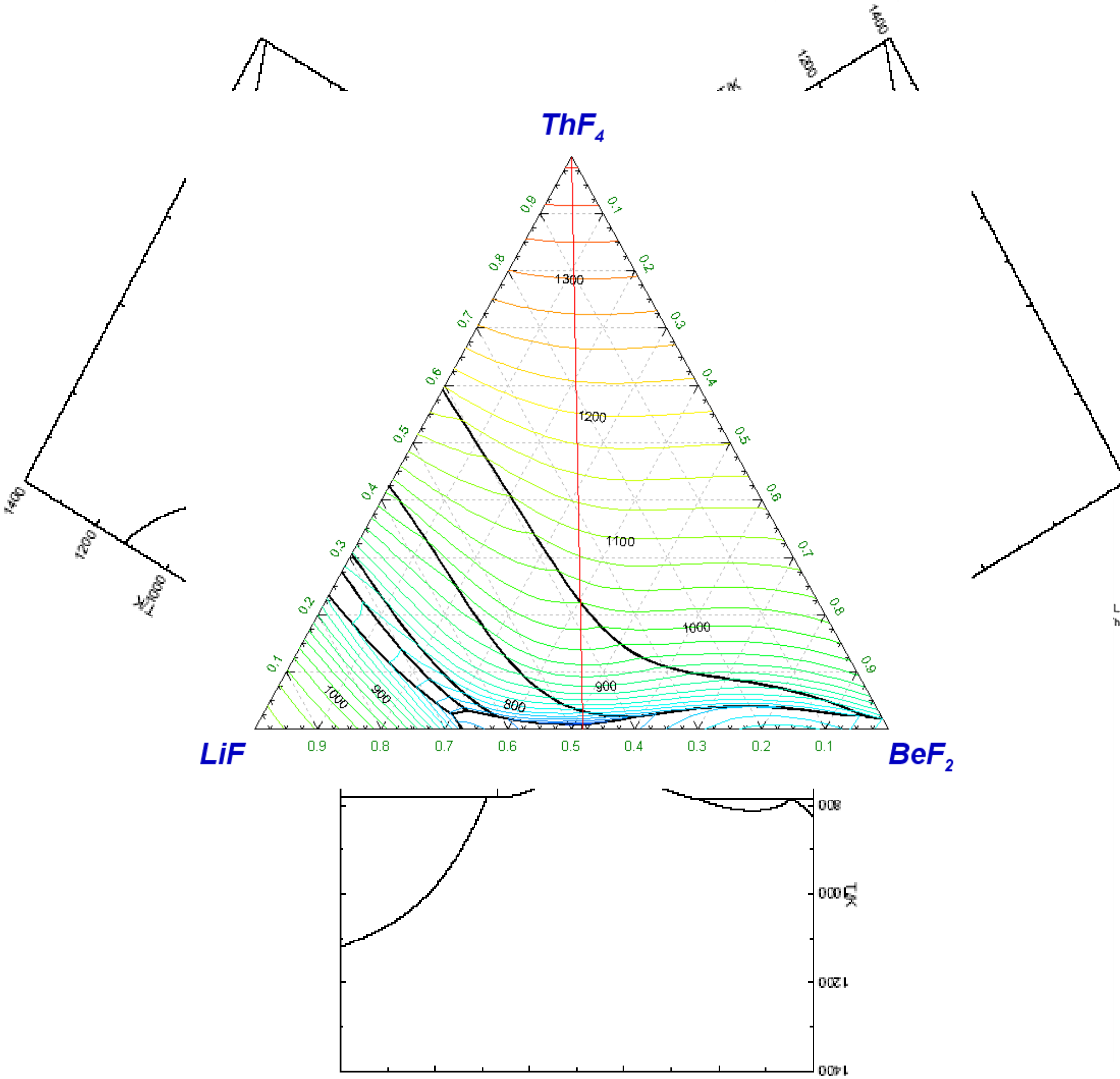


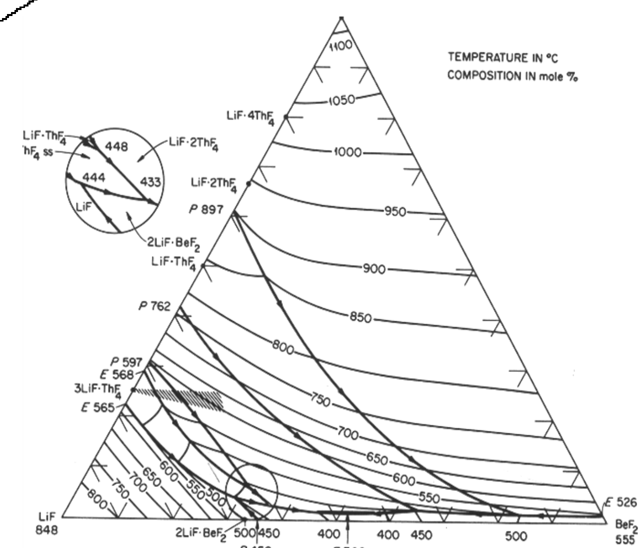
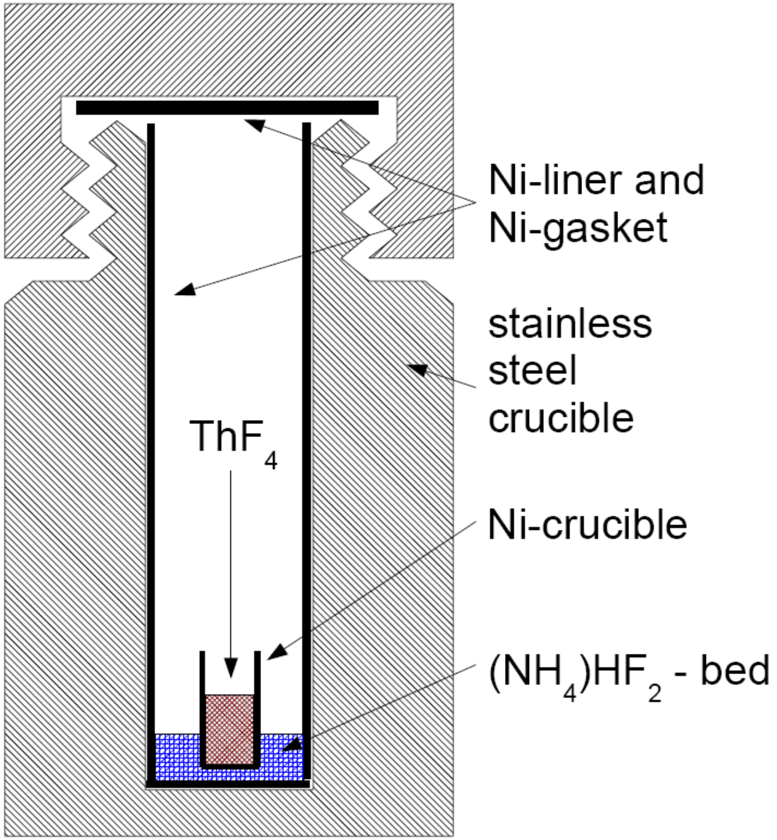
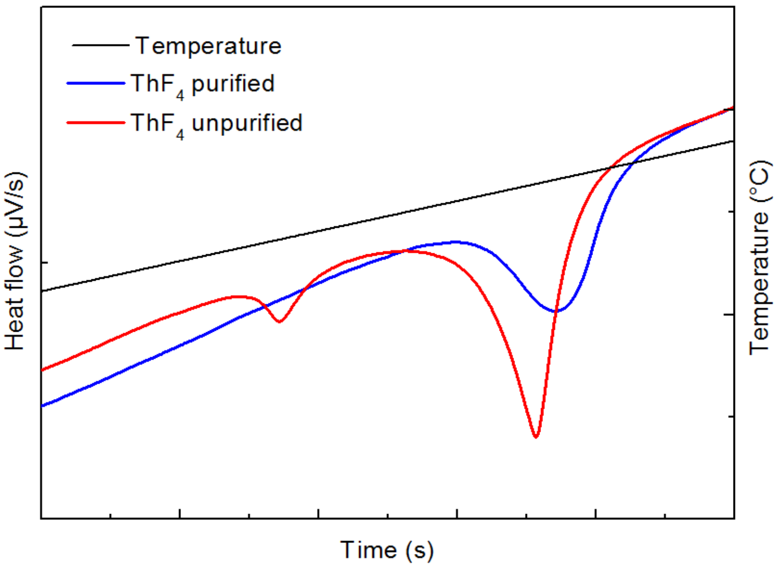


Fig. 218. The system $LiF–BeF_2–ThF_4$.

Purification of ThF_4





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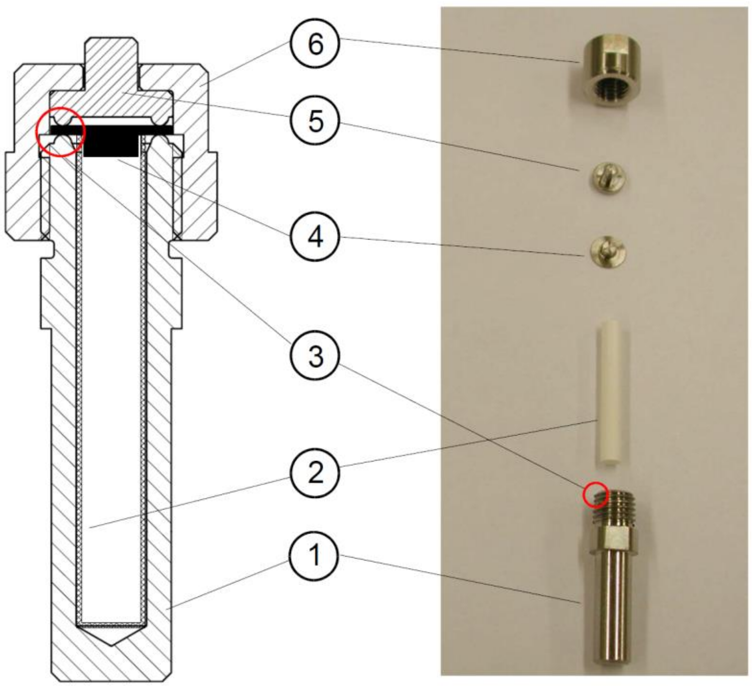
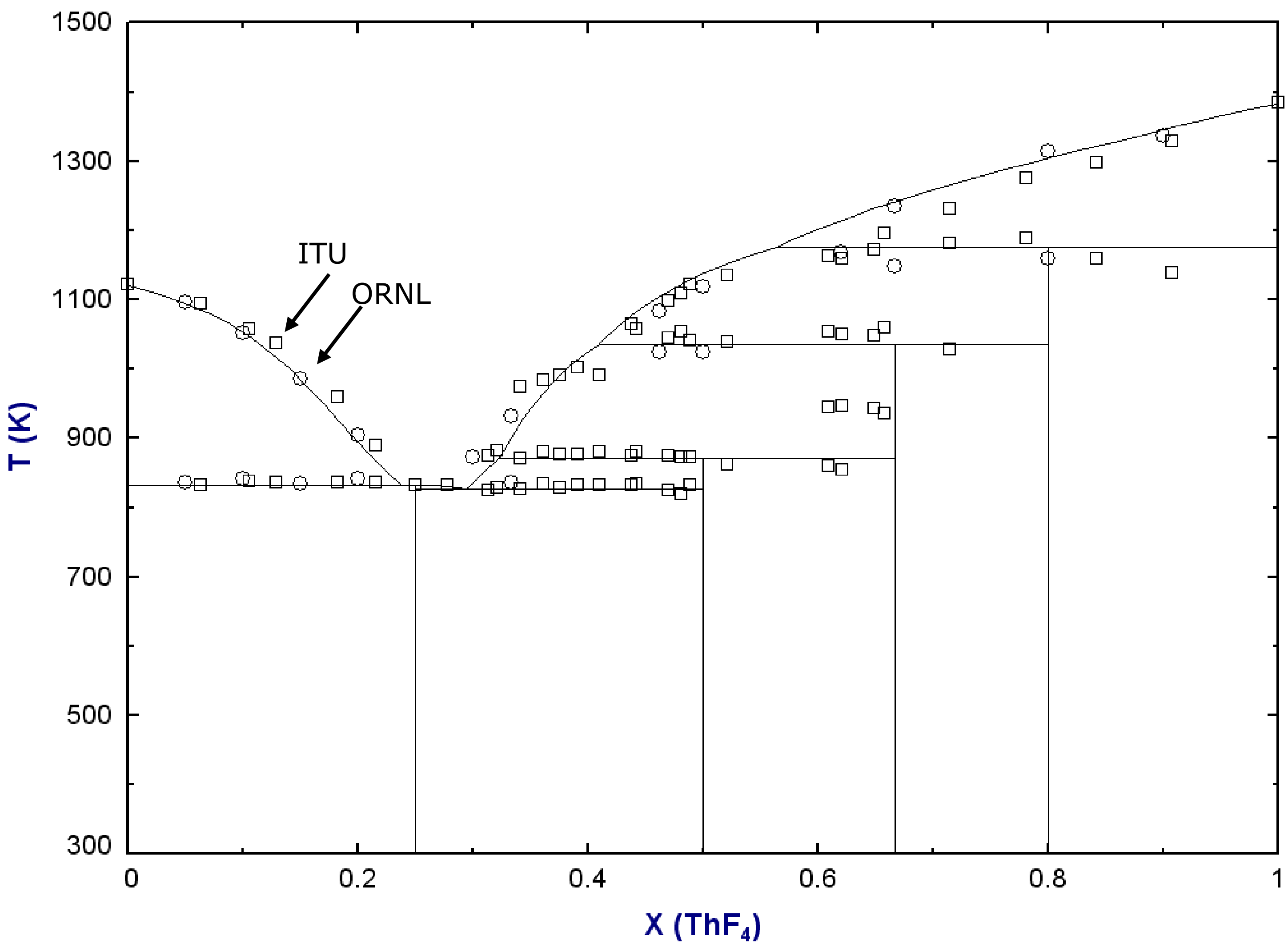
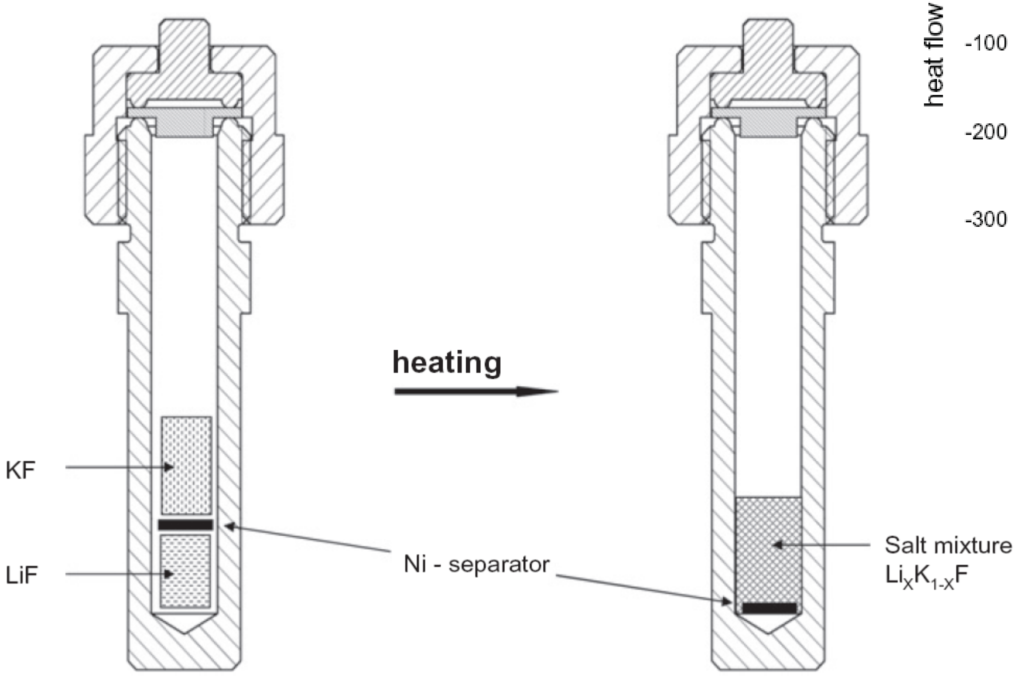
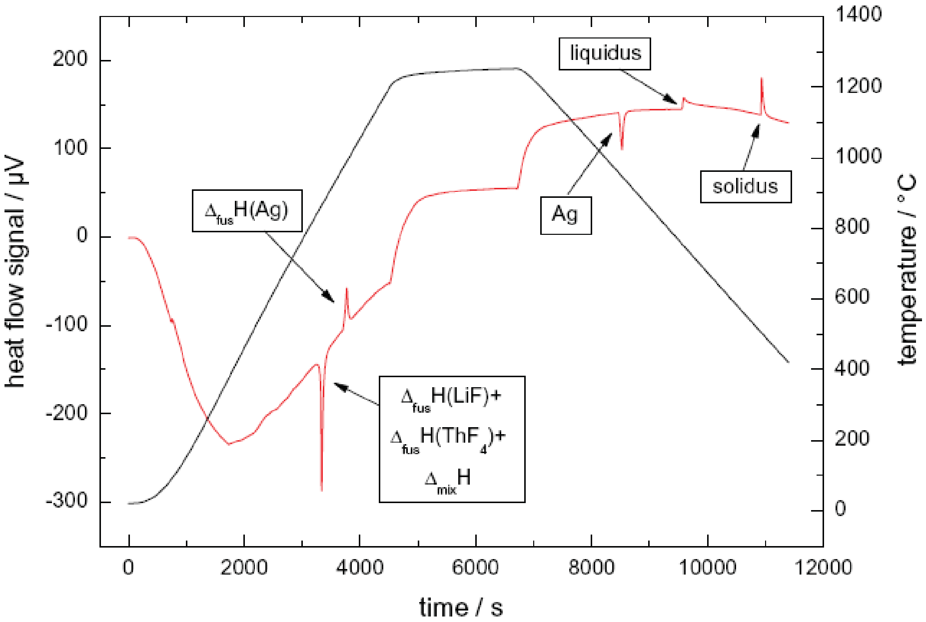
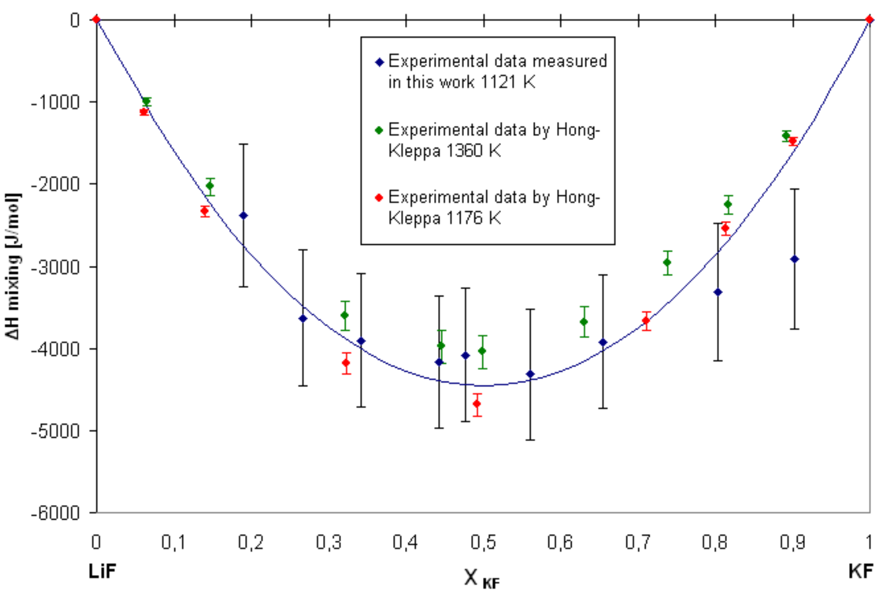
The experimental approach for the LiF-ThF_4 phase diagram

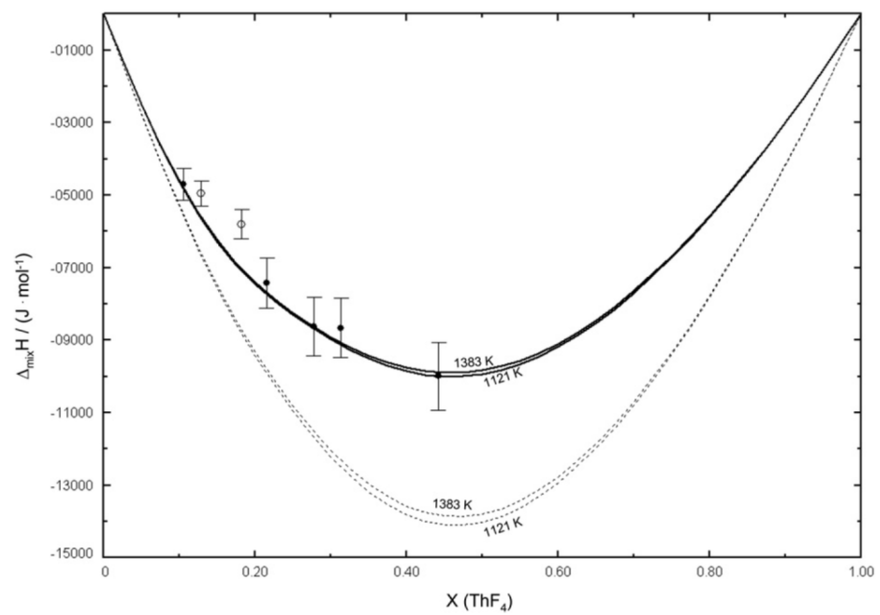



1500
1300
1100
900
700
500
300
T (K)
0
0.2
0.4
0.6
0.8
1
X (ThF_4)
ITU
ORNL


heating
KF
LiF
Ni - separator
Salt mixture
$Li_xK_{1-x}F$

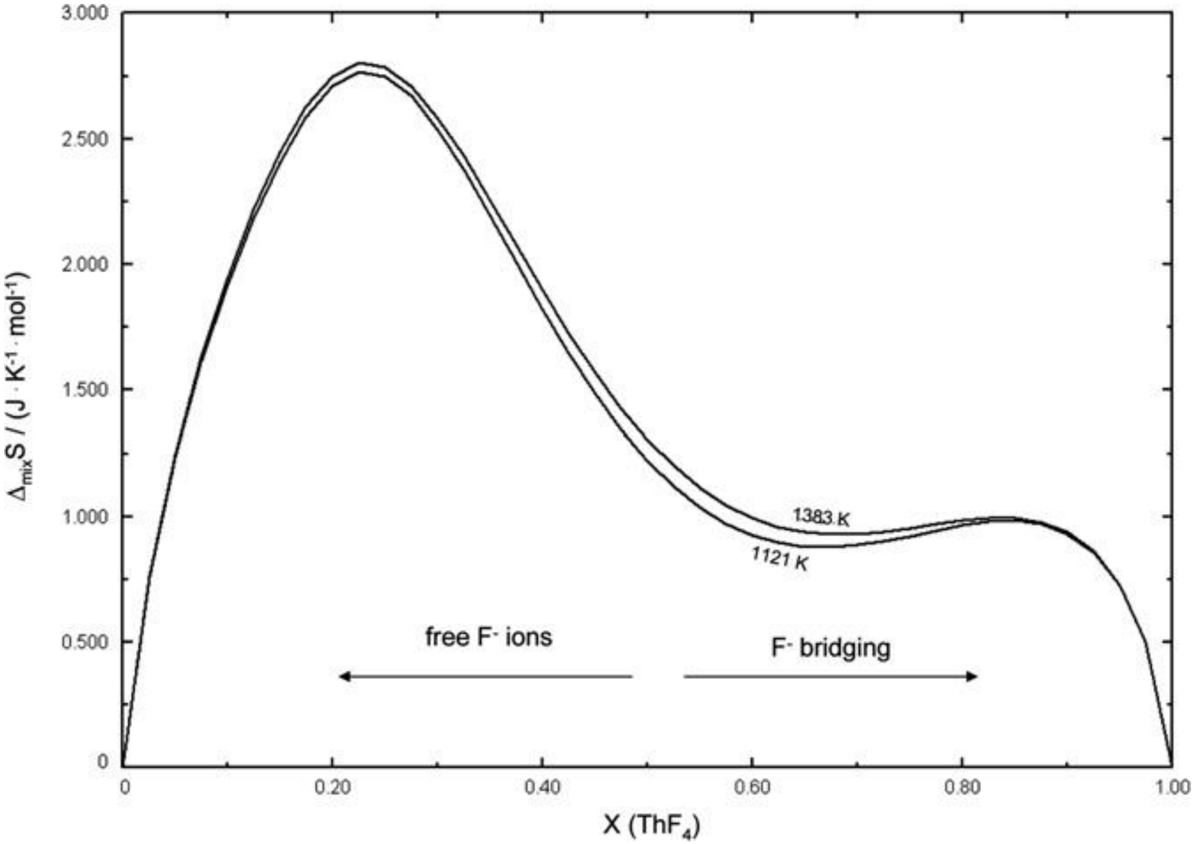

heat flow signal / µV
temperature / °C
time / s
liquidus
solidus
Ag
$\Delta_{fus}H(Ag)$
$\Delta_{fus}H(LiF)+$
$\Delta_{fus}H(ThF_4)+$
$\Delta_{mix}H$





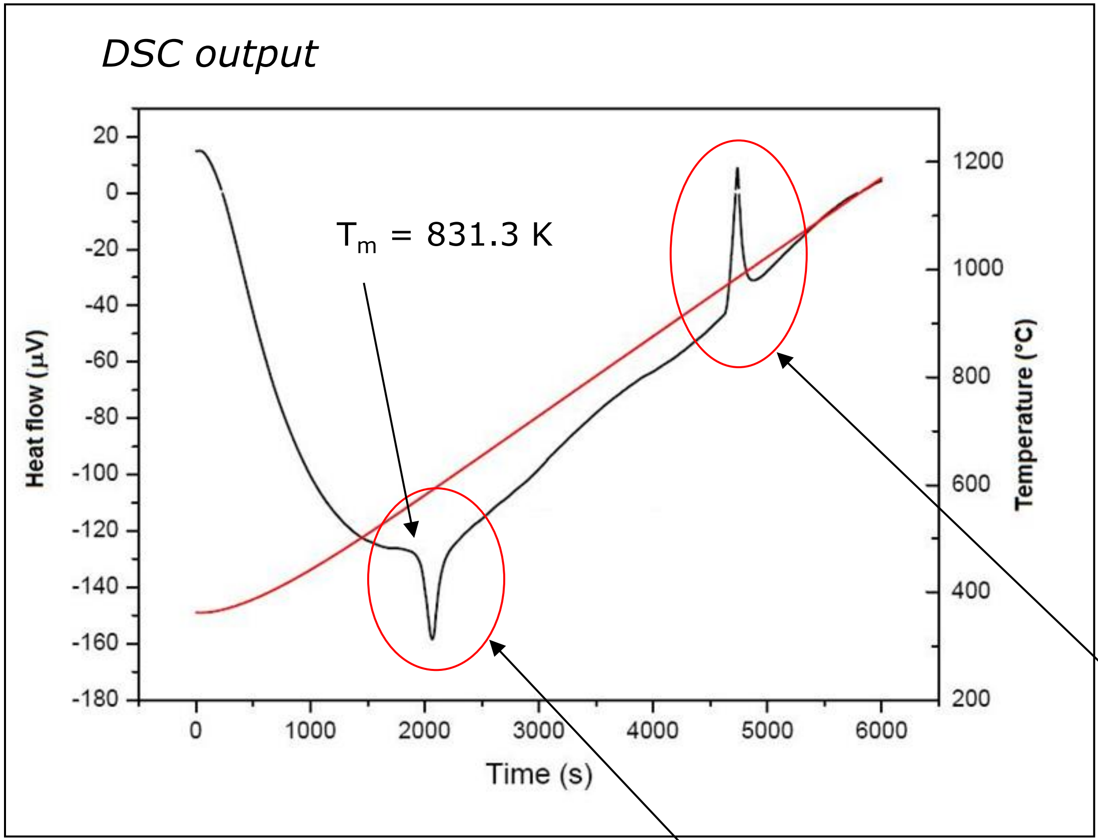
Enthalpy of mixing of the LiF–KF system. (●) this study at T = 1121 K. (▲▼) Hong and Kleppa at T = 1176 K and T = 1360 K.

Enthalpy of mixing of the LiF–ThF4 system. (○, ●) Data obtained in this study at T = 1121 K and T = 1383 K. Solid line: Calculated enthalpy of mixing from the assessment performed in this work. Dashed line: Calculated enthalpy of mixing from the previous assessment.



$\Delta_{mix}S$ / (J · K^{-1} · mol^{-1})
3.000
2.500
2.000
1.500
1.000
0.500
0
0
0.20
0.40
0.60
0.80
1.00
X (ThF_4)
1383 K
1121 K
free F^- ions
F^- bridging

DSC analysis of Li_3ThF_7



melting of Ag standard

congruent melting of Li_3ThF_7

Fusion enthalpy values

<u>our experiment</u>

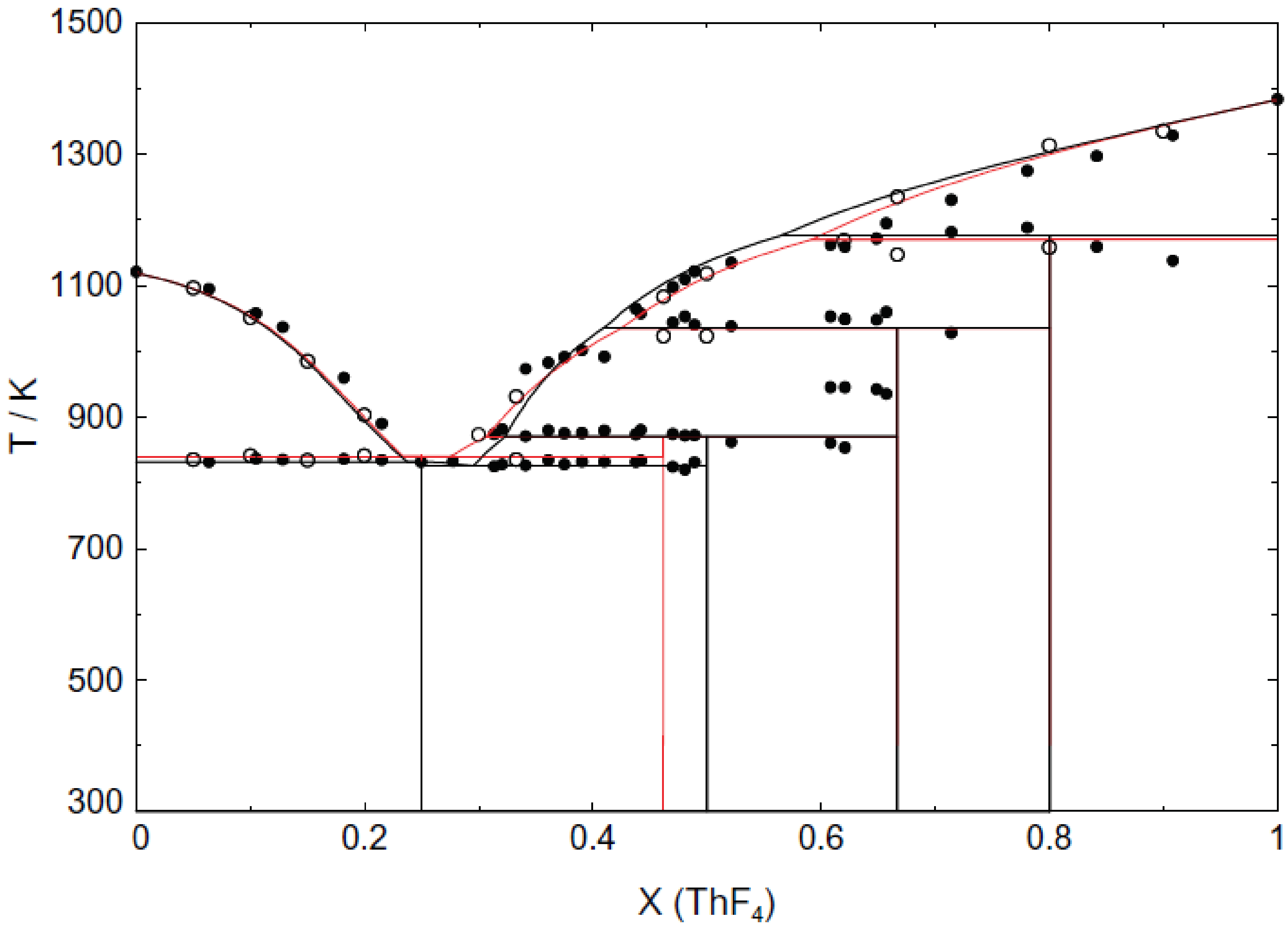
$\Delta_{fus}H$ = 13.7 ± 2 kJ/mol

<u>Gilbert 1962</u>

$\Delta_{fus}H$ = 14.6 kJ/mol

<u>our LiF-ThF$_4$ assessment</u>

$\Delta_{fus}H$ = 14.6 kJ/mol



1500
1300
1100
900
700
500
300
T / K
0
0.2
0.4
0.6
0.8
1
X (ThF_4)

Thermodynamic assessment of LiF-ThF_4-UF_4-PuF_3 system

- CeF_3 is considered as proxy compound to PuF_3.

Binary sub-systems:

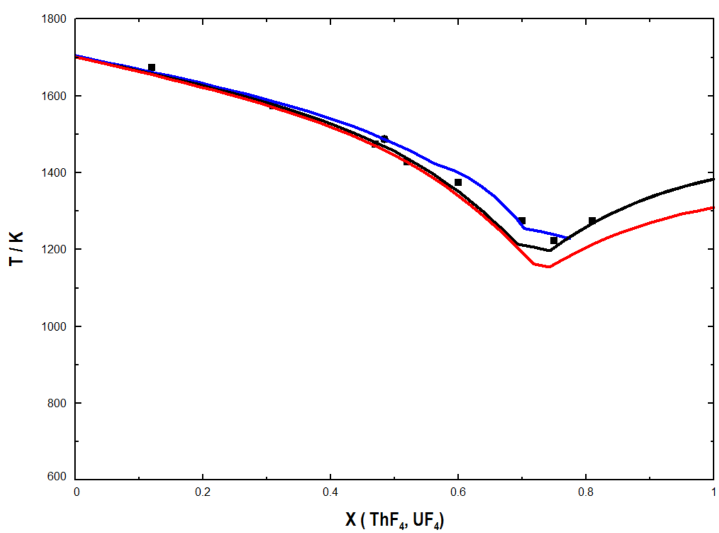
- LiF-ThF_4
- LiF-PuF_3
- ThF_4-PuF_3
- UF_4-PuF_3
- LiF-UF_4
- ThF_4-UF_4

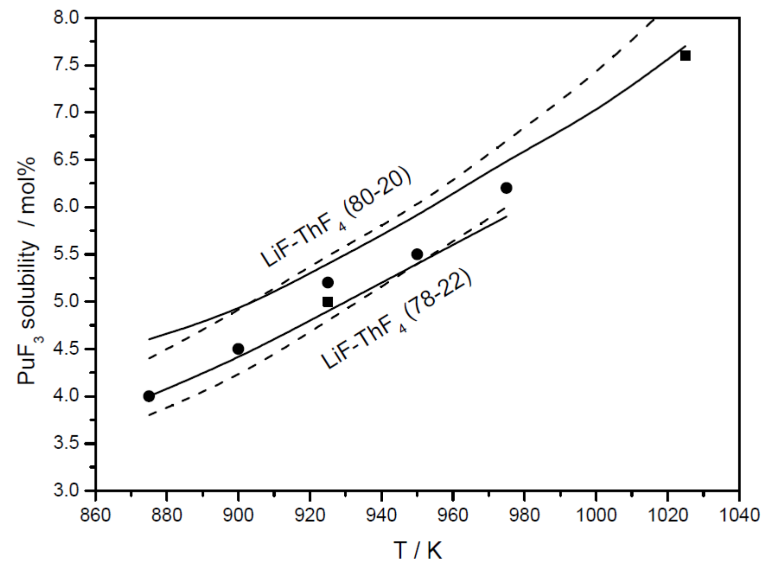
Optimized based on the ThF_4-CeF_3 system

Ternary sub-systems:

- LiF-ThF_4-UF_4
- LiF-ThF_4-PuF_3
- LiF-UF_4-PuF_3
- ThF_4-UF_4-PuF_3

Optimized based on the exp. data



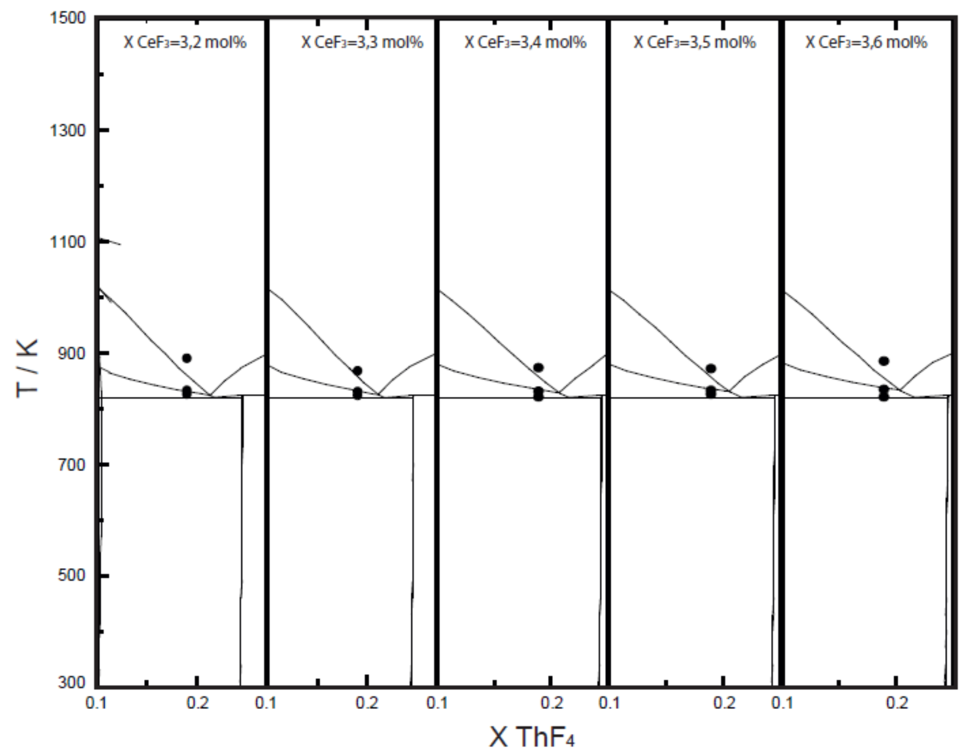


Experimental measurements

- Five compositions have been measured using the DSC technique.
- Fixed LiF/ThF_4 ratio and different CeF_3 concentrations:

  - LiF-ThF_4-CeF_3 (77.5-18.9-3.6)
  - LiF-ThF_4-CeF_3 (77.6-18.9-3.5)
  - LiF-ThF_4-CeF_3 (77.7-18.9-3.4)
  - LiF-ThF_4-CeF_3 (77.7-19.0-3.3)
  - LiF-ThF_4-CeF_3 (77.8-19.0-3.2)

X (LiF)	X (ThF_4)	X (CeF_3)	T_{trans} [K]
0.775	0.189	0.036	883.87
0.776	0.189	0.035	869.93
0.777	0.189	0.034	871.65
0.777	0.19	0.033	867.28
0.778	0.19	0.032	889.31



Application of the database: Fuel Optimization

Criteria:

- The fuel composition is optimized based on the **melting point** of the salt mixture.
- A low melting point decreases the risk of freezing and reduces corrosion problem.
- In order to keep sufficient safety margin, the inlet temperature of the reactor must be at least 50 K higher than the melting point.

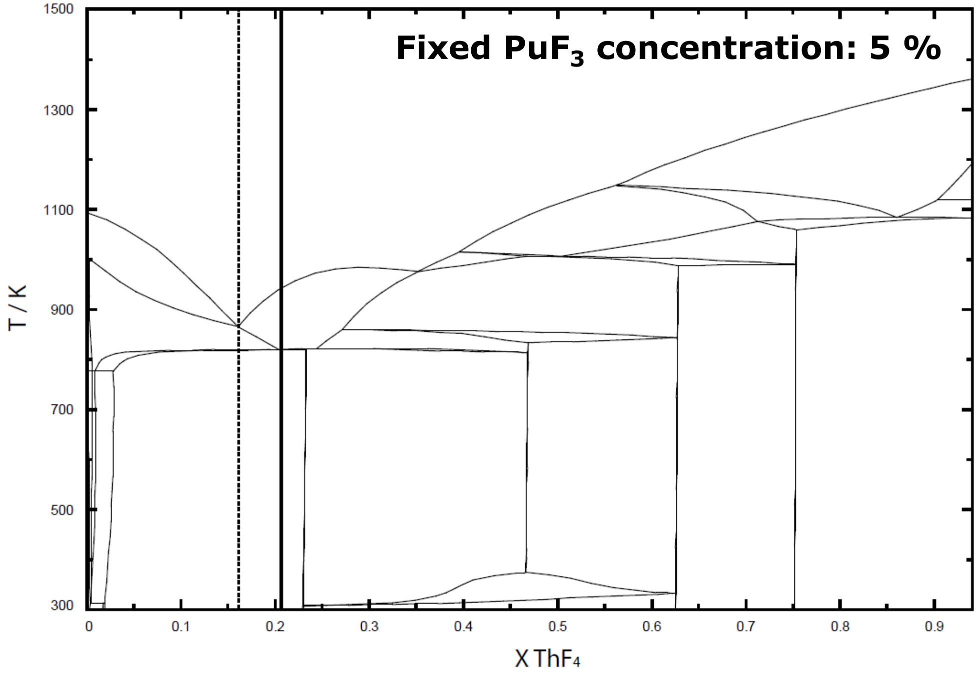
Fuel constrains:

- The minimum concentration of fissile material is fixed at 5 mol%.
- In order to control the redox potential of the salt (via UF_4/UF_3 ratio), a minimum concentration of UF_4 of 1 mol% is needed.
- Due to non-proliferation issues, the enrichment of UF_4 must not exceed 20%

Fuel Optimization

- **<u>Initial MSFR fuel composition</u>**: Eutectic composition LiF-ThF_4 (78-22) with addition of 5% PuF_3 and 1 % UF_4 (**T=941.5 K**)
- **<u>Optimized composition having fixed concentration of UF_4 and PuF_3</u>** (**T=865.8 K**)

Fuel constrain:
Minimum concentration of fissile material: 5%
Minimum concentration of UF_4: 1%
Maximum enrichment UF_4: 20%



Fuel Optimization

- **<u>Initial MSFR fuel composition</u>**: Eutectic composition LiF-ThF_4 (78-22) with addition of 5% PuF_3 and 1 % UF_4 (**T=941.5 K**)

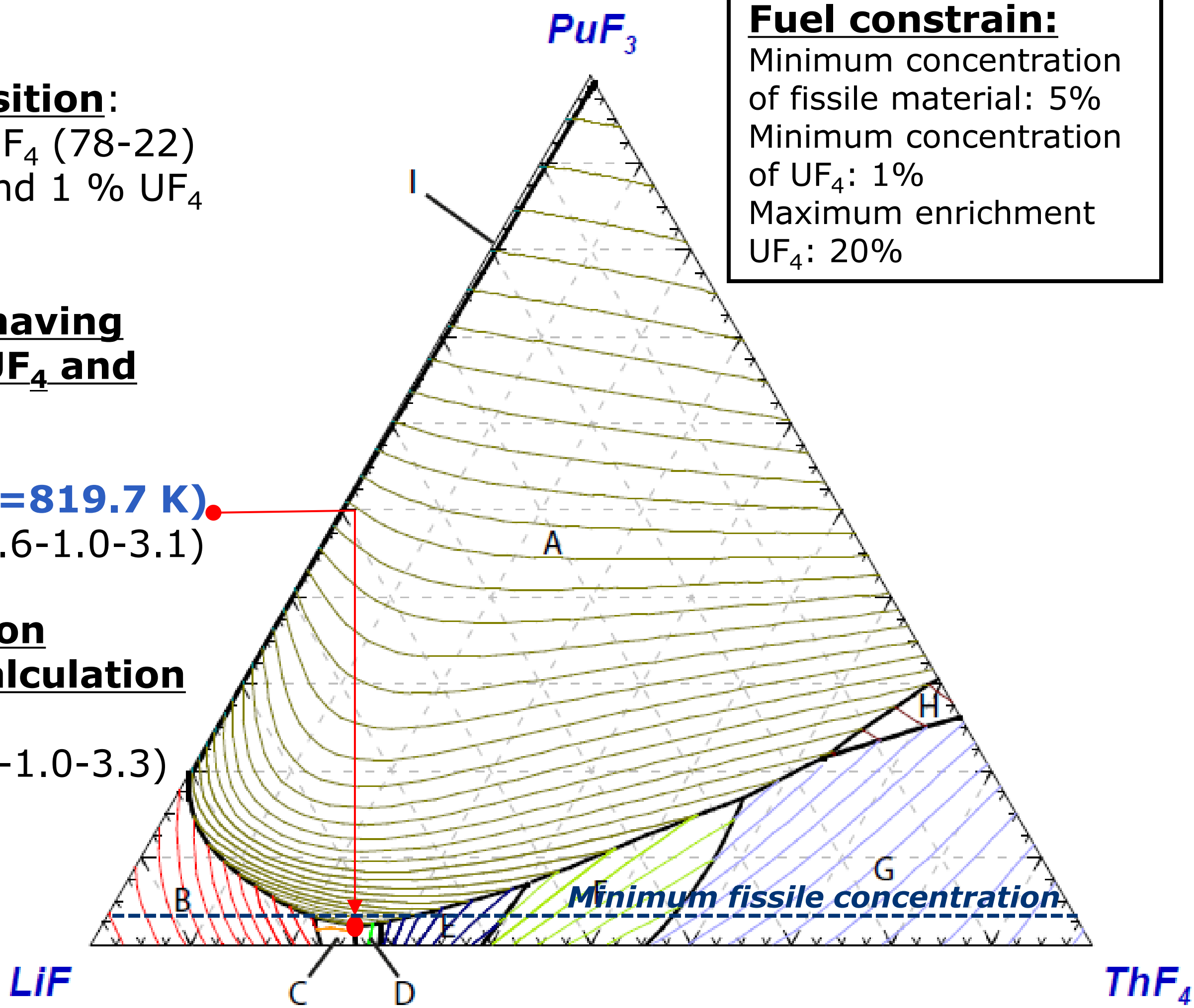
- **<u>Optimized composition having fixed concentration of UF_4 and PuF_3</u>** (**T=865.8 K**)

- **<u>Lowest liquidus point</u> (T=819.7 K)**
LiF-ThF_4-UF_4-PuF_3 (75.3-20.6-1.0-3.1)

- **<u>Proposed fuel composition considering neutronic calculation and exp. results</u>**
LiF-ThF_4-UF_4-PuF_3 (77.7-18-1.0-3.3)

(T=867 K)

<u>Fuel constrain:</u>
Minimum concentration of fissile material: 5%
Minimum concentration of UF_4: 1%
Maximum enrichment UF_4: 20%



Thermodynamic calculations

- **Thermodynamic properties of the identified compositions:**

Composition	T melting (K)	T boiling (K)	P at T_{oper}(Pa)
$LiF-ThF_4-UF_4-PuF_3$ (73.3-20.7-1.0-5.0)	943.9 K	2035 K	$4.62 \cdot 10^{-2}$
$LiF-ThF_4-UF_4-PuF_3$ (78.0-16.0-1.0-5.0)	866.8 K	2035 K	$5.33 \cdot 10^{-3}$
$LiF-ThF_4-UF_4-PuF_3$ (75.3-20.6-1.0-3.1)	819.3 K	2032 K	$7.26 \cdot 10^{-4}$
$LiF-ThF_4-UF_4-PuF_3$ (77.7-18.0-1.0-3.3)	856.4 K	2033 K	$3.58 \cdot 10^{-3}$

- **Influence of partial substitution of ThF_4 with UF_4**

Composition	T melting (K)	T boiling (K)	P at T_{oper}(Pa)
$LiF-ThF_4-UF_4-PuF_3$ (77.7-18.0-1.0-3.3)	856.4 K	2033 K	$3.58 \cdot 10^{-3}$
$LiF-UF_4-PuF_3$ (77.7-19.0-3.3)	855 K	2007 K	$3.7 \cdot 10^{-3}$

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Conclusions

- The combination of assessments and experiments is of key importance to develop the database for molten salt reactor fuel
- We master now the complex handling of these materials for experiments
- Thermochemical modelling has shown to be a useful in teh fuel optimisation
- Work with PuF_3 is the logic next step to improve/verify the database

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