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## Thermodynamics of Moten Salt Reactor Fuel



*Ondřej Beneš*

SAMOFAR – Summer School  
*Lecco, Italy, 2017*

# Outline



- **What is Thermodynamics**
- **Laws of Thermodynamics**
- **Gibbs energy function**
- **Experimental data**
- **Modelling of phase diagrams**
- **Application of Thermodynamic database**
  - **Fuel optimization**
  - **Determination of fuel properties**

# Why is Thermodynamics important?

Thermodynamics = Equilibrium (Stability)

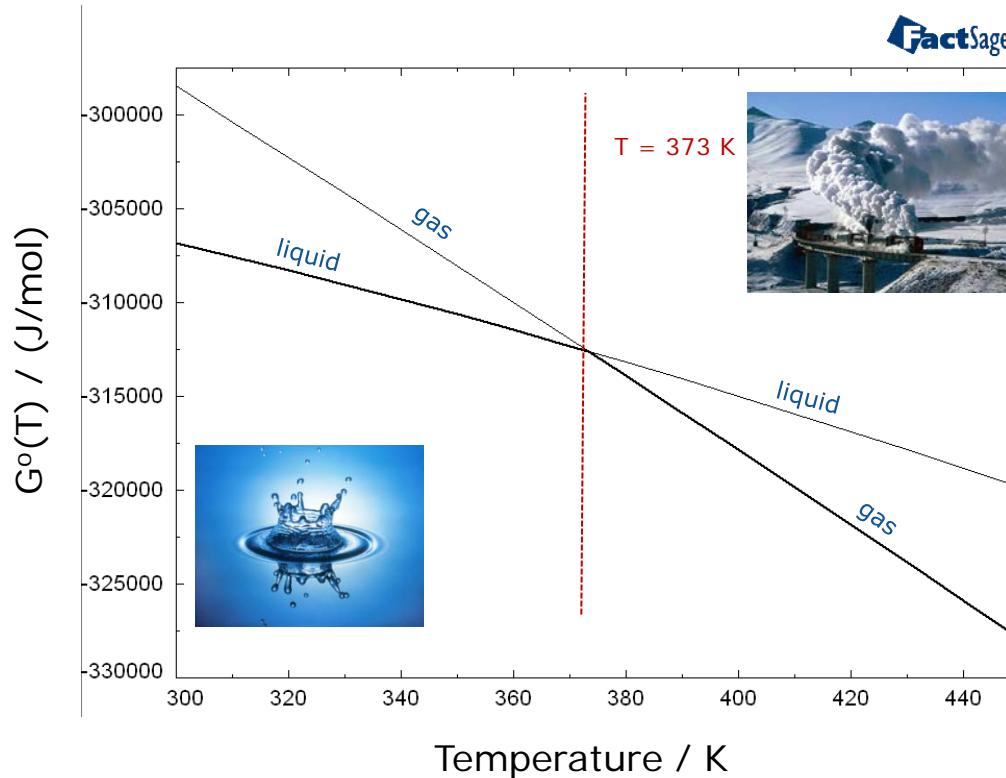


What will be the stable form at given conditions ( $T$ ,  $p$ ,  $p(F_2)$ , etc.)

Stable = Lowest energy (Gibbs energy)

$$G(T) = H(T) - T \cdot S(T)$$

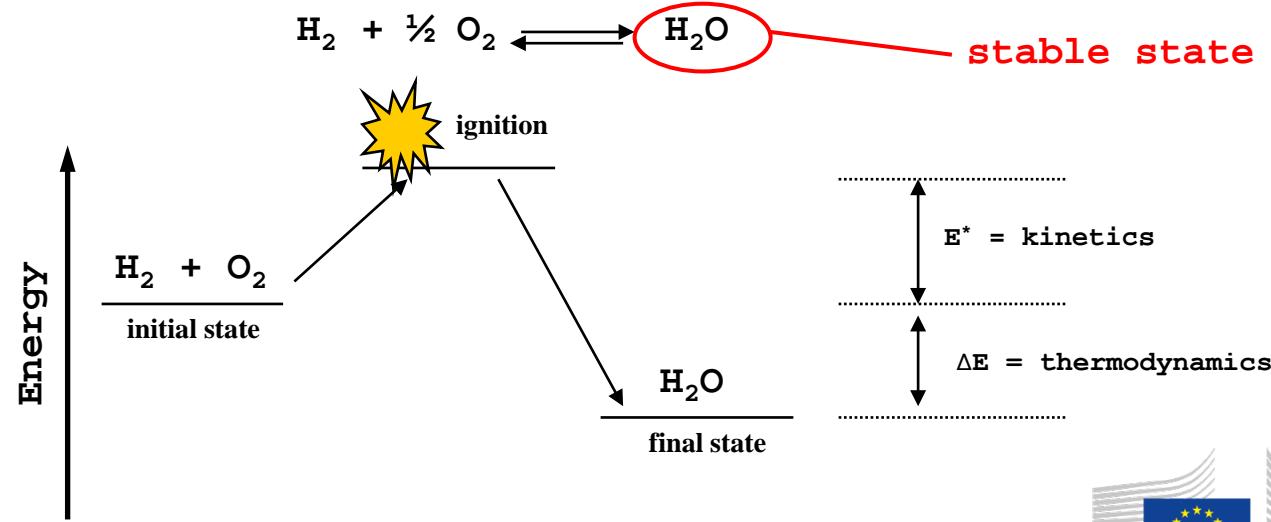
## example of H<sub>2</sub>O



... but be aware !!!

Thermodynamics tells us if a process **CAN** or **CAN NOT** occur  
however

It does not necessarily tell if it **WILL** or **WILL NOT** happen



# The First Law

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Energy cannot be produced or destroyed, and the energy increase  $\Delta U$  of a body or a system equals the sum of the heat absorbed from the environment ( $q$ ) and the work ( $w$ ) done by the environment on the system.

$$\Delta U = q + w$$

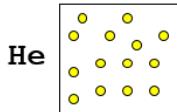
# The Second Law

From the fact that in spontaneous processes heat always 'flows' from higher to lower temperatures and not in the reverse direction, Rudolf Clausius formulated a criterion for the direction in which a process will occur and called this the entropy ***S*** which is defined as:

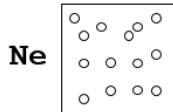
$$(q/T)_{rev} = dS$$

Isolated system evolve towards TD equilibrium  $\sim$  max. entropy

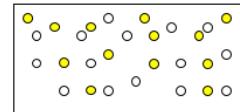
$$S_1 = 151.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$



$$S_2 = 171.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$



$$S_2 = 334.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$



$$S_1 + S_2 = 322.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

He + Ne ideal gas

## The Third Law

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The value of the entropy of a perfect crystalline solid at absolute zero is exactly equal to zero:

$$dS \rightarrow 0 \quad \text{when} \quad T \rightarrow 0$$

[Walther Nernst]

$$S = k_B \ln \Omega$$

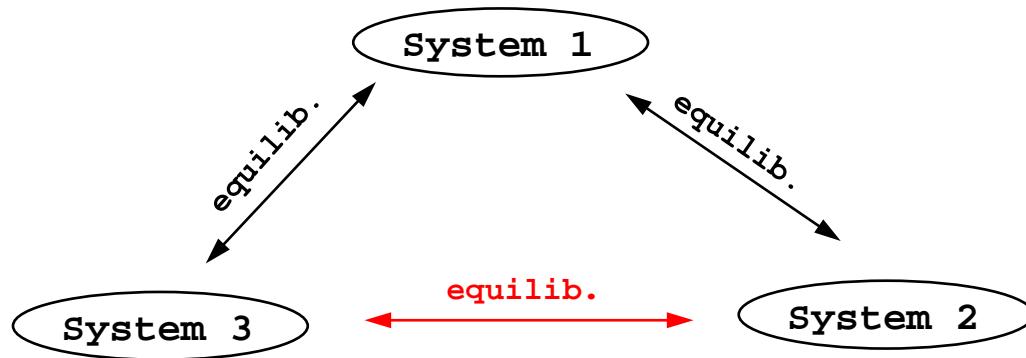
Where

$\Omega$  .... number of microstates

# The Zeroth Law

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When two systems are each in thermal equilibrium with a third system, the systems are in thermal equilibrium with each other.



# Practical info to be taken !!!

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1. Law: You will never WIN you can only DRAW
2. Law: You can draw only at 0 K
3. Law: You will never reach 0 K

which means

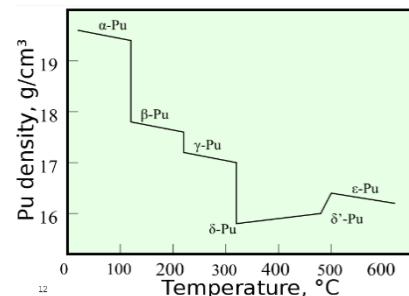
**SORRY, YOU CAN ONLY LOOSE !!!**

# What are Thermodynamic properties – part 1

Melting temperature



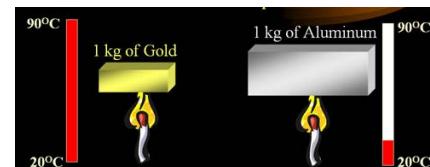
Transition temperature



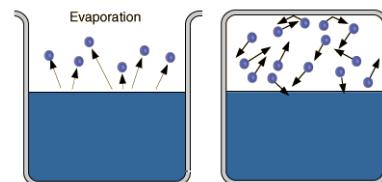
Boiling temperature



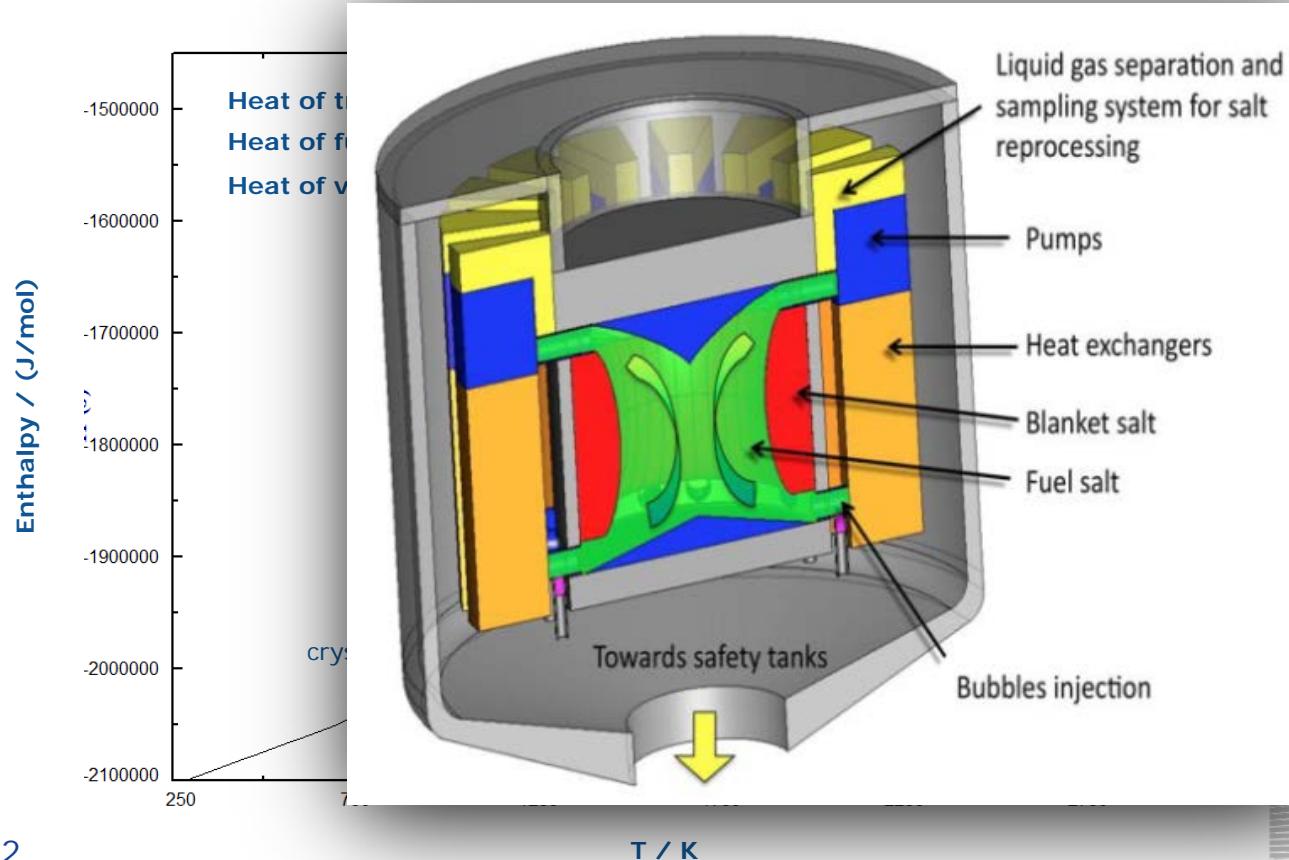
Heat capacity

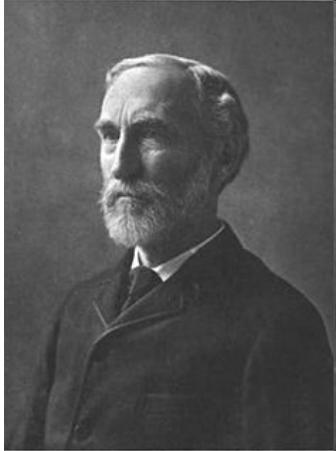


Vapour pressure



# What are Thermodynamic properties – part 2





All these properties linked to

## GIBBS ENERGY

Josiah Williard Gibbs  
(1839-1903)

Or

If we know Gibbs energy  
We know the properties!!!

# How to describe Gibbs energy from experimental data ?



$$G(T) = H(T) - T \cdot S(T)$$

$$H(T) = \Delta_f H_{298}^0 + \int_{298}^T C_p(T) dT$$

$$S(T) = S_{298}^0 + \int_{298}^T \frac{C_p(T)}{T} dT$$

- *formation enthalpy*                       $\Delta_f H^0(298)$
- *absolute entropy*                           $S^0(298)$
- *heat capacity as T*                         $C_p(T)$
- *transition enthalpy*                         $\Delta_{trs.} H + T_{trs.}$

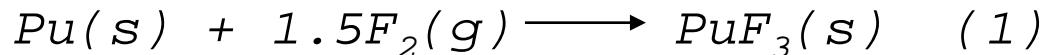
## Experimental determination

# Formation enthalpy $\Delta_f H^0(298)$

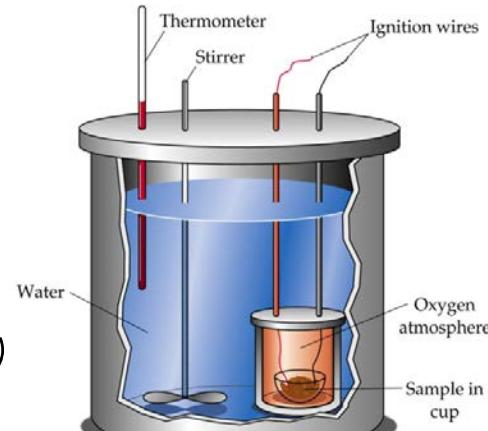


## Combustion calorimetry

**Example of  $PuF_3$ :**



$$\Delta_f H^0 = \Delta_r H^0(1) = -1586.7 \text{ kJ/mol}$$



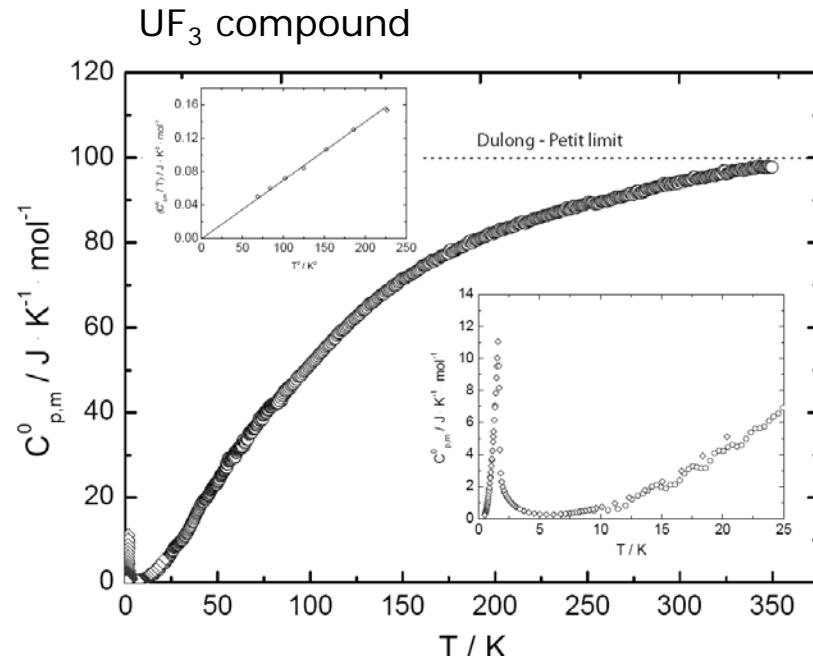
## Solution calorimetry

for mixtures, e.g.  $(Li, Th)F_x$

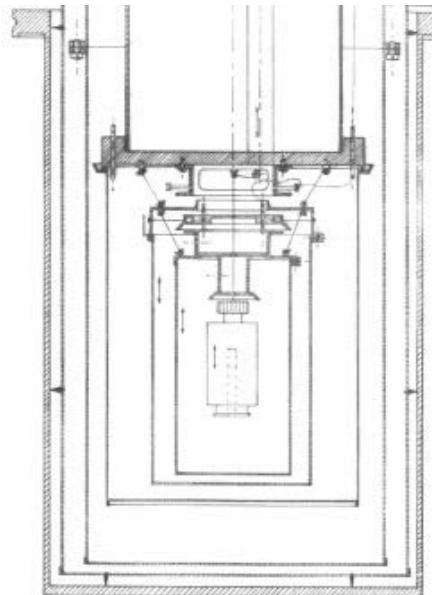
# Absolute entropy $S^0(298)$

## Adiabatic calorimetry, PPMS

- $C_p$  measurement from 0 K (close to)



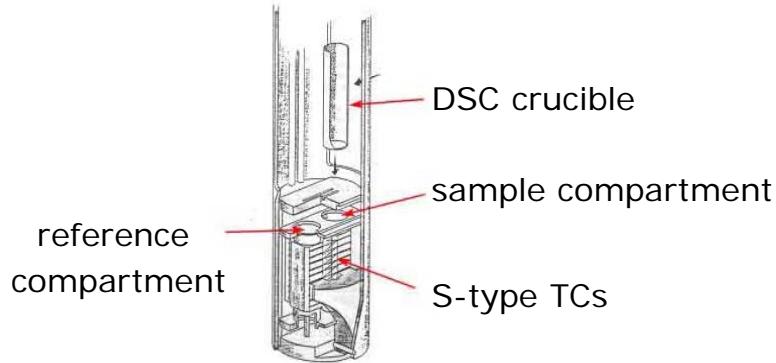
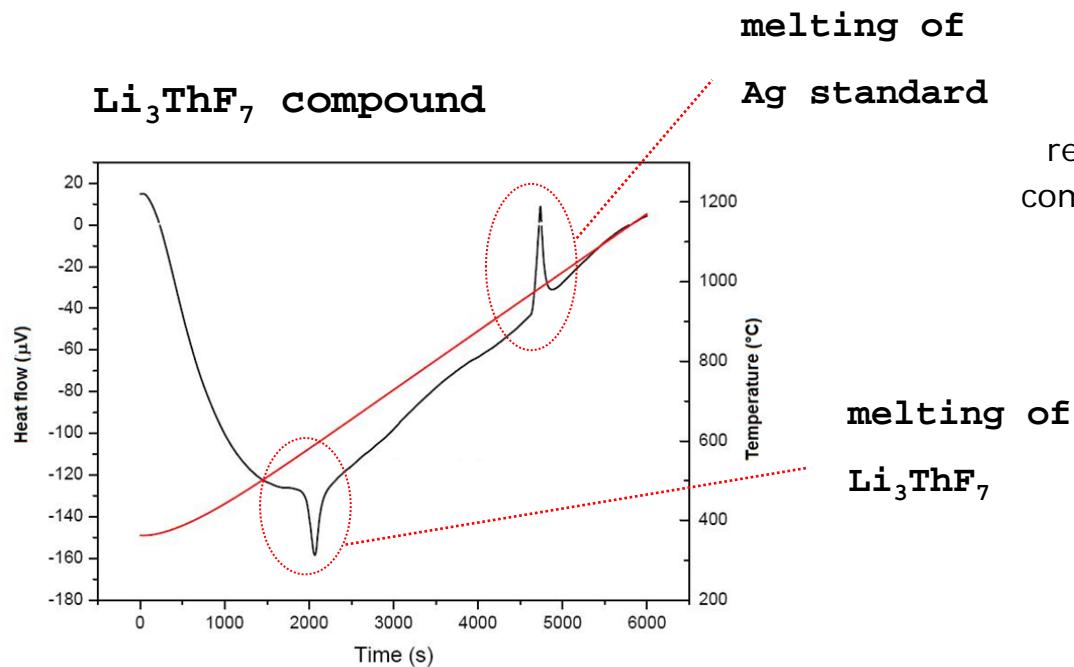
$$S^0(298) = \int_0^{298} \frac{Cp(T)}{T} dT$$



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# Transition enthalpy $\Delta_{trs.}H + T_{trs.}$

## 1. Conventional DSC technique ( $T < \sim 2000$ K)



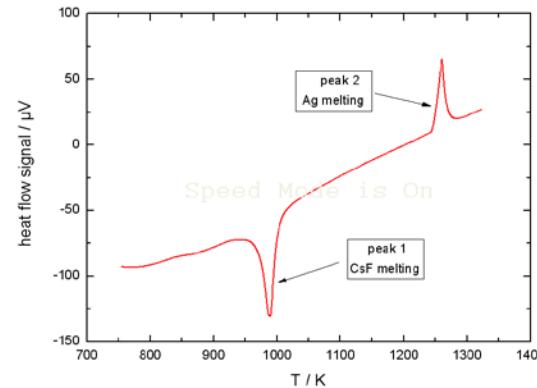
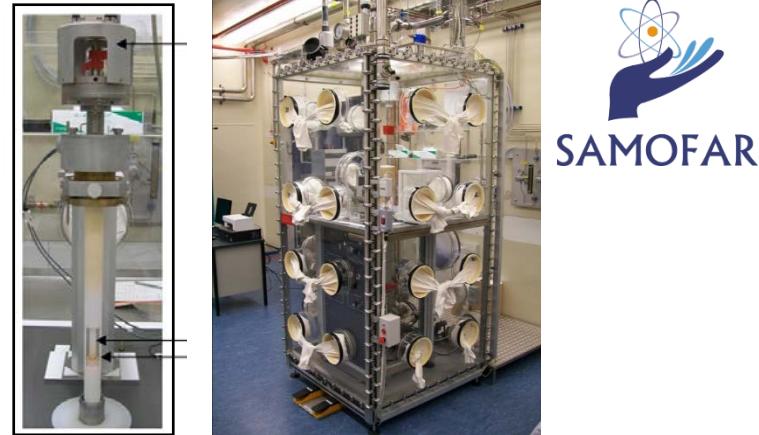
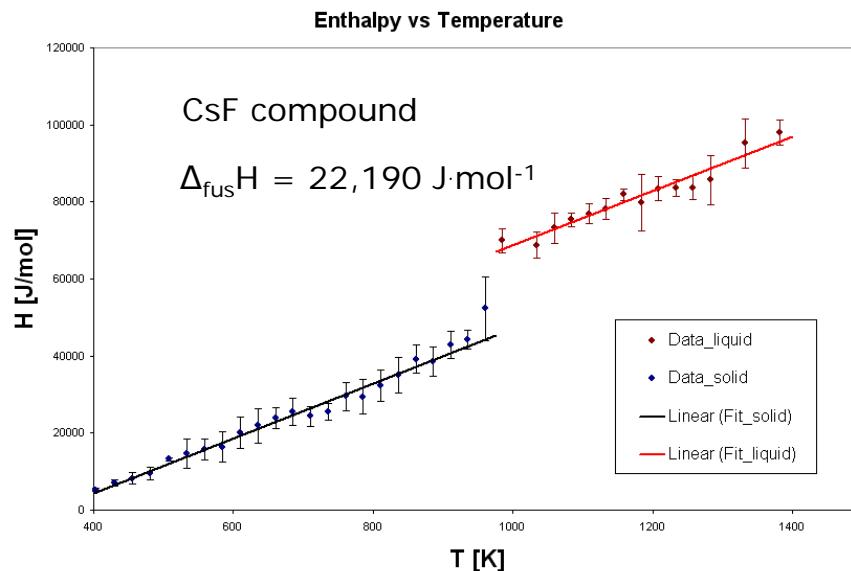
$$\Delta_{fus}H = 13.7 \pm 2 \text{ kJ/mol}$$
$$T_{fus} = 831.3 \text{ K}$$

# Heat capacity as T $C_p(T)$

## Drop calorimeter

1. Enthalpy increments  $\Delta H_{T_a}^T$
2. derivation of  $C_p$

$$C_p = \left( \frac{dH}{dT} \right)_p$$

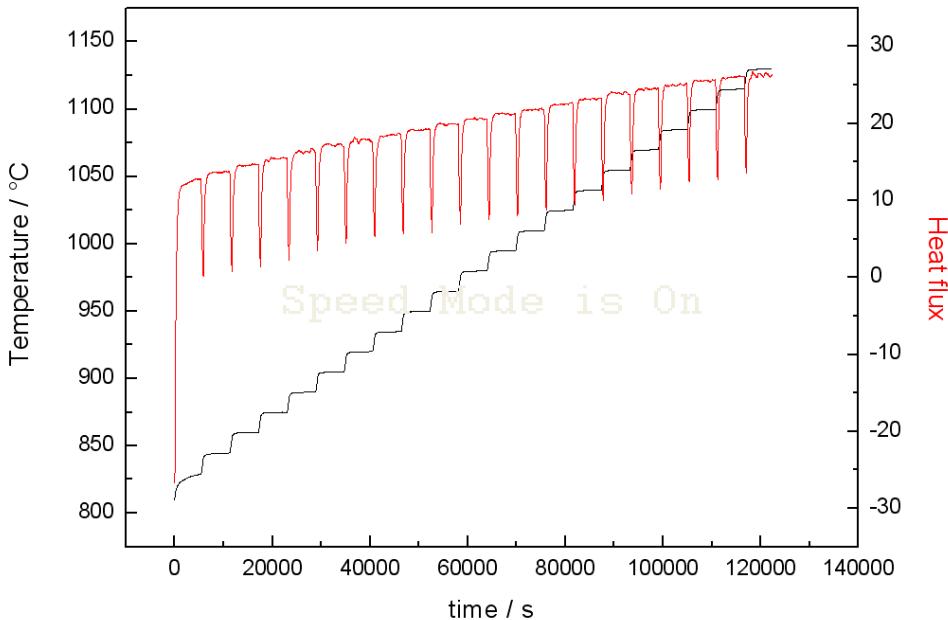


$$\Delta_{\text{fus}}H = 21,550 \text{ J}\cdot\text{mol}^{-1}$$

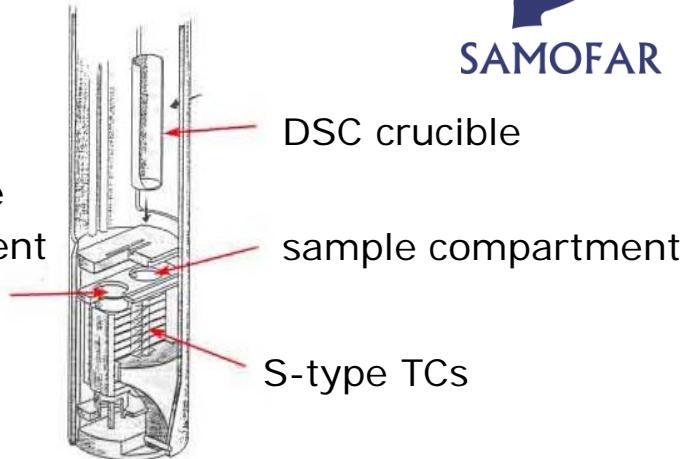
# Heat capacity as $T$ $C_p(T)$



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reference  
compartment



This method requires 3 measurements

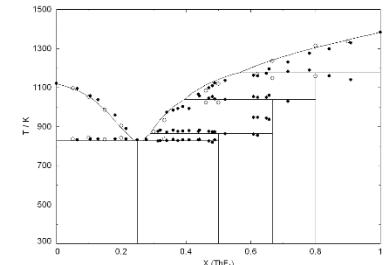
- blank
- reference (sapphire, platinum)
- sample

# Gibbs energy of mixtures

## Compounds:

$$G = H - TS = H^0(298) + \int_{298}^T Cp(T)dT - T \left( S^0(298) + \int_{298}^T \frac{Cp(T)}{T} dT \right)$$

Data required:  $H^0(298)$ ,  $S^0(298)$ ,  $Cp(T)$ ,  $\Delta_{\text{fus.}}H$ ,  $T_{\text{fus.}}$ .



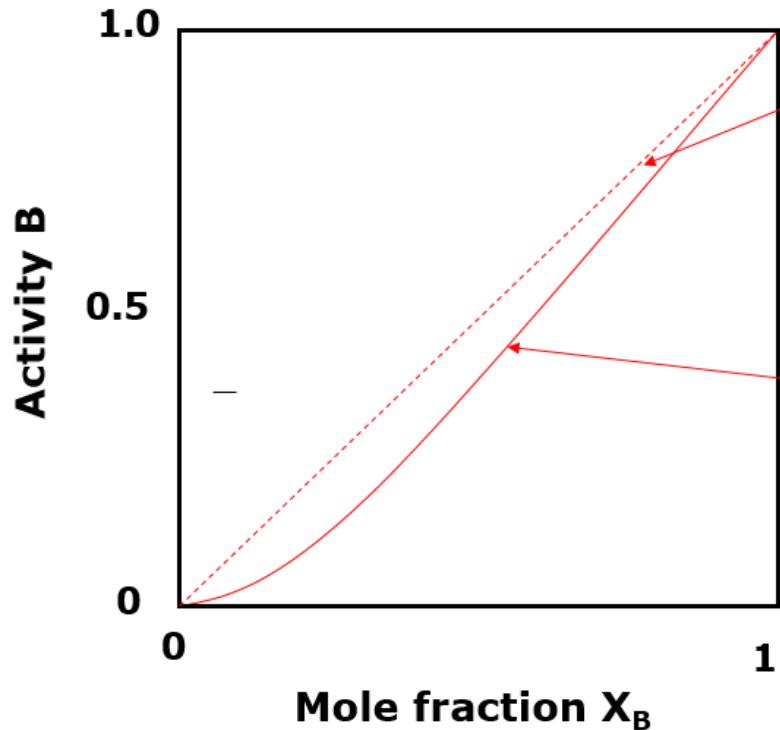
## Binary solutions: $(U, Th) F_4$ liquid solution

$$G_{\text{sol.}} = x_1 G_1 + x_2 G_2 + \Delta G^{\text{mix}}$$

usually unknown energy contribution

$$\Delta G^{\text{mix}} = x_1 RT \ln a_1 + x_2 RT \ln a_2$$

# Gibbs energy of mixtures



Raoult's law

$$a = x$$

$$\Delta G^{mix} = x_1 RT \ln x_1 + x_2 RT \ln x_2$$

Real solution

$$a \neq x, \quad a = \gamma x$$

$$\Delta G^{mix} = x_1 RT \ln a_1 + x_2 RT \ln a_2$$

$$\Delta G^{mix} = x_1 RT \ln x_1 + x_2 RT \ln x_2 + \Delta G^{xs}$$

$$\Delta G^{xs} = \Delta H^{mix} + T\Delta S^{xs}$$

TD models

## Example: Binary LiF - KF system

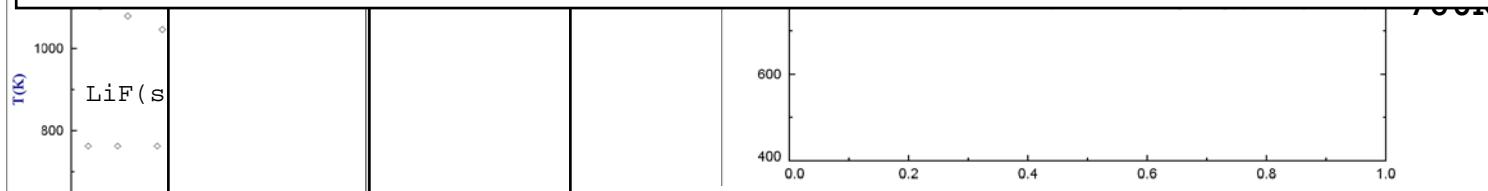
$$G_{sol.} = x_1 G_1 + x_2 G_2 + \Delta G^{mix}$$

$$\Delta G^{mix} = x_1 RT \ln x_1 + x_2 RT \ln x_2 + \Delta G^{xs}$$



4 step -  $\Delta G^{mix}$  optimization

$$1. \quad \Delta G^{mix} = \underbrace{x_1 RT \ln x_1 + x_2 RT \ln x_2}_{\text{ideal mixing}} + \underbrace{x_1 x_2 (-17200 - 0.5T)}_{\text{excess contribution}}$$

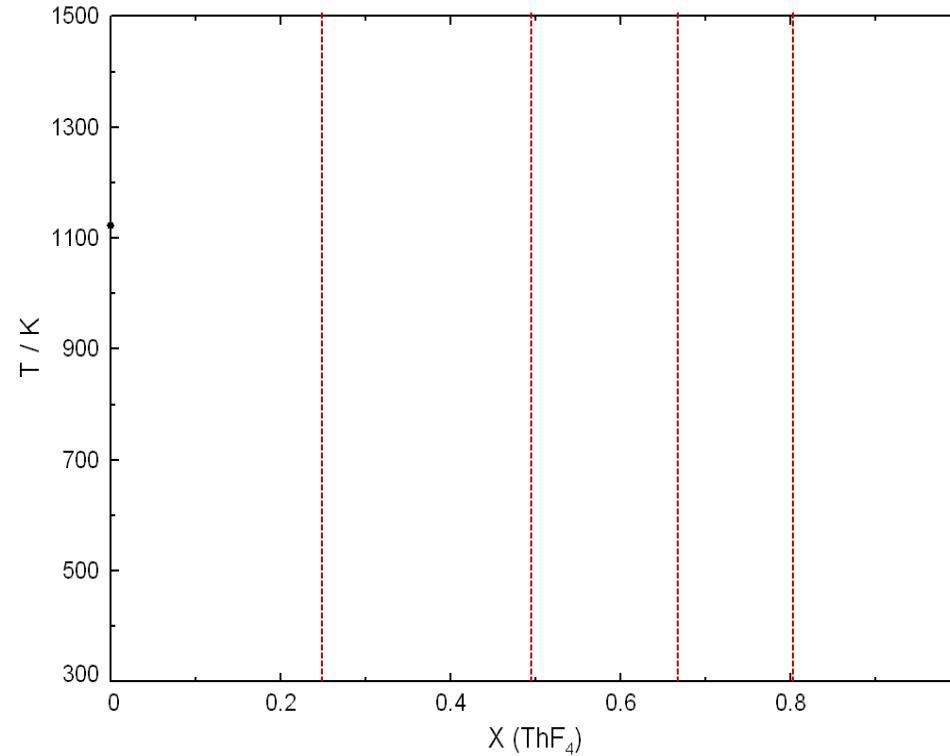


$$\Delta G^{mix} = x_1 RT \ln x_1 + x_2 RT \ln x_2$$

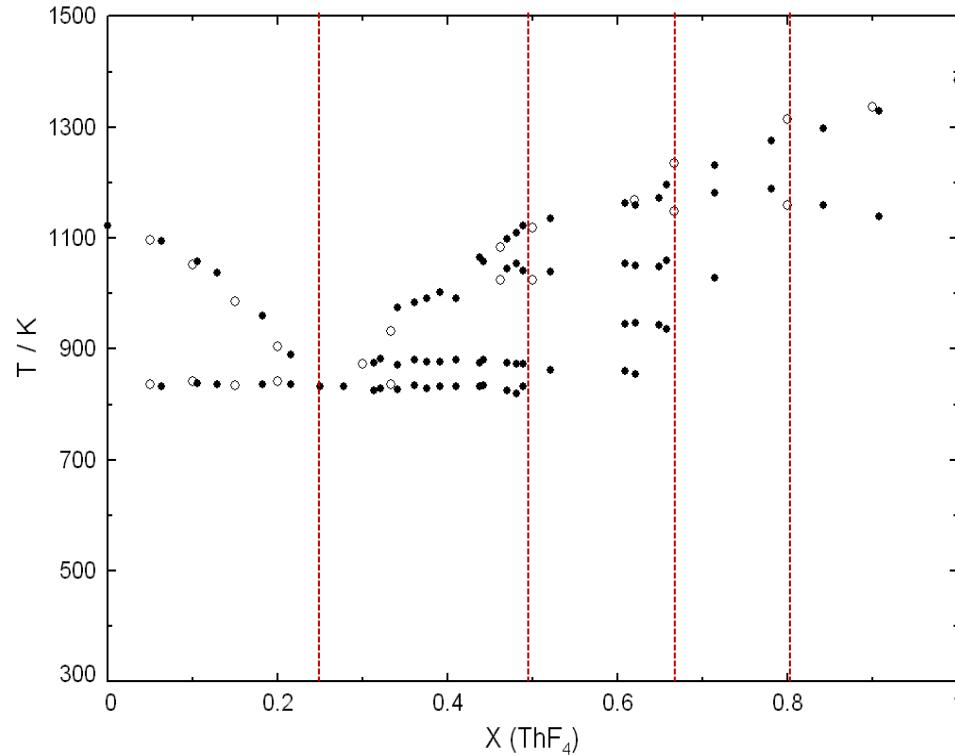
$$\Delta H^{mix} = x_1 x_2 \cdot -17200$$

$$\Delta S^{xs} = x_1 x_2 \cdot -0.5$$

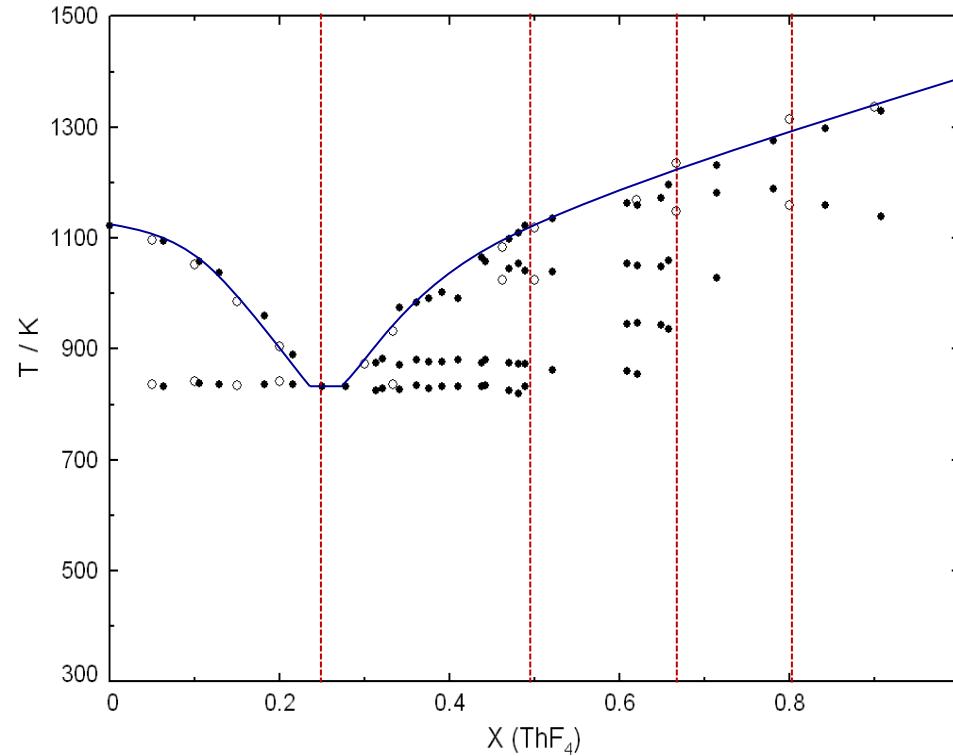
# LiF-ThF<sub>4</sub> phase diagram construction



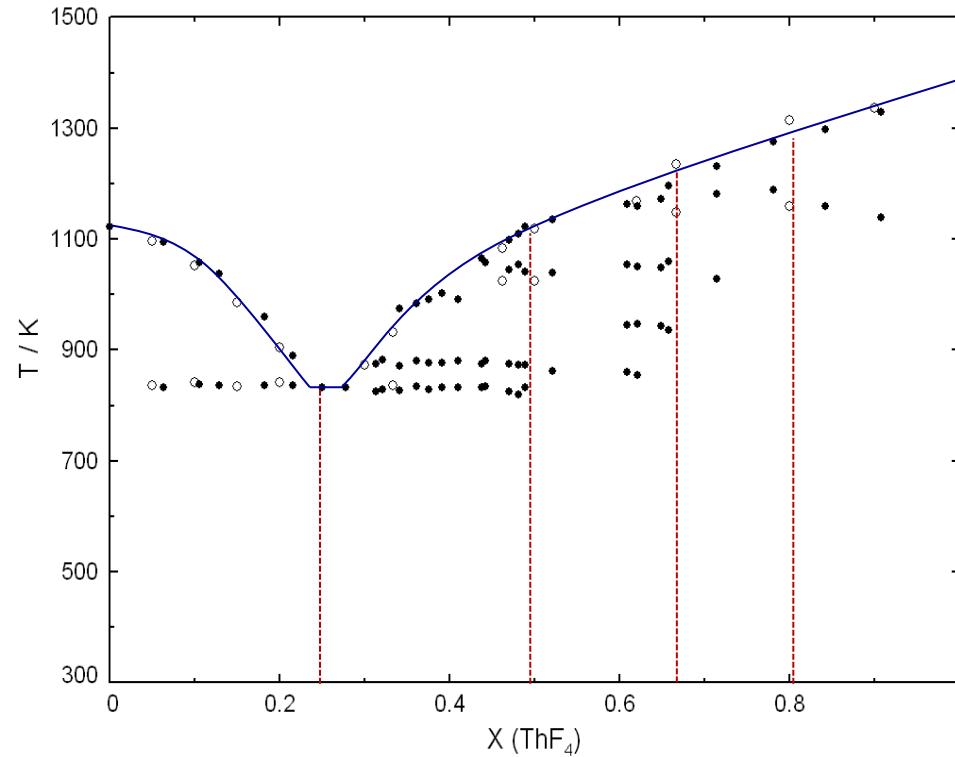
# LiF-ThF<sub>4</sub> phase diagram construction



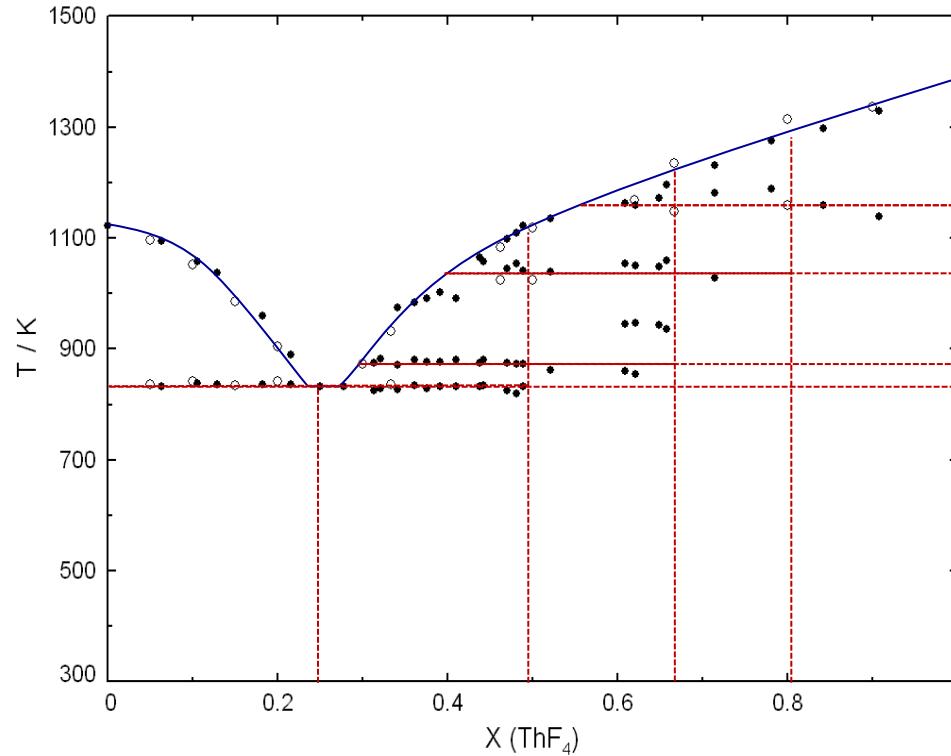
# LiF-ThF<sub>4</sub> phase diagram construction



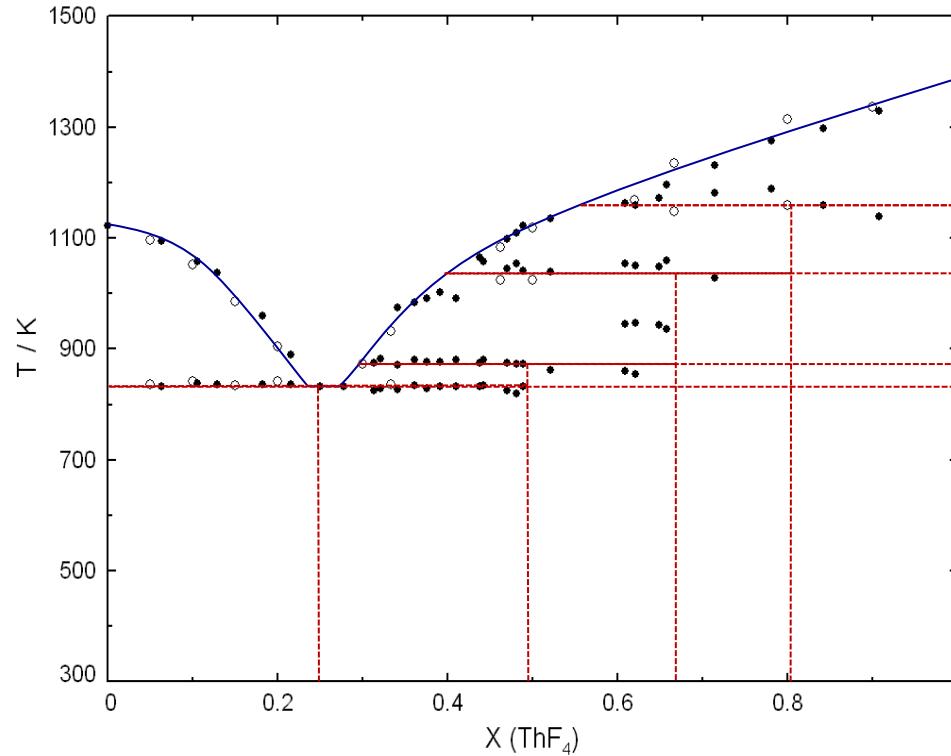
# LiF-ThF<sub>4</sub> phase diagram construction



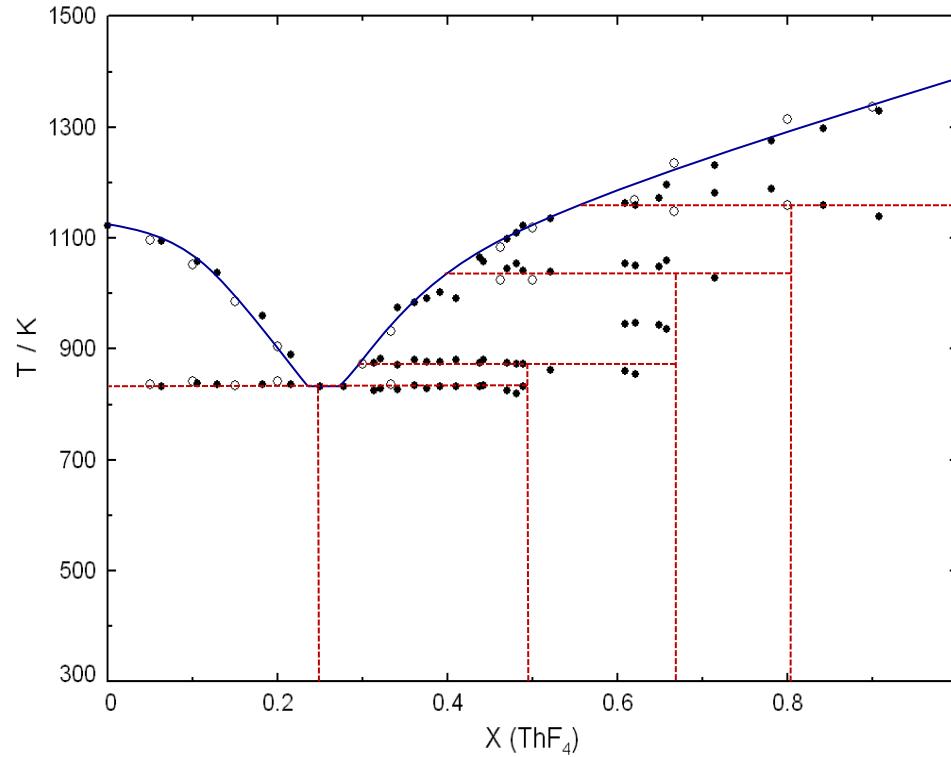
# LiF-ThF<sub>4</sub> phase diagram construction



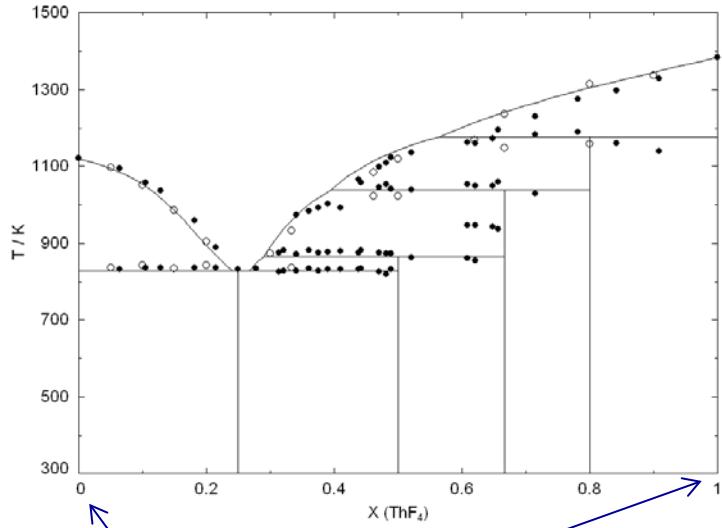
# LiF-ThF<sub>4</sub> phase diagram construction



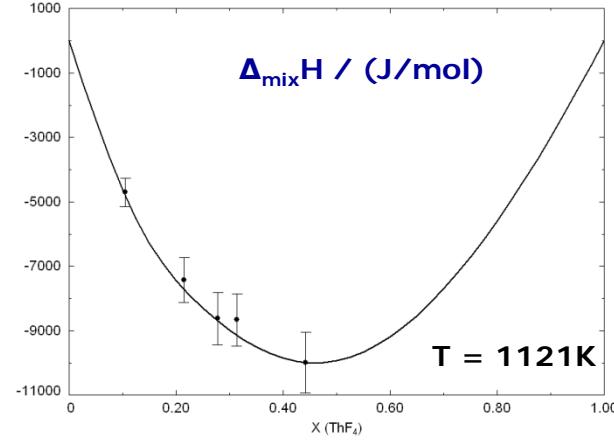
# LiF-ThF<sub>4</sub> phase diagram construction



# LiF-ThF<sub>4</sub> modelling

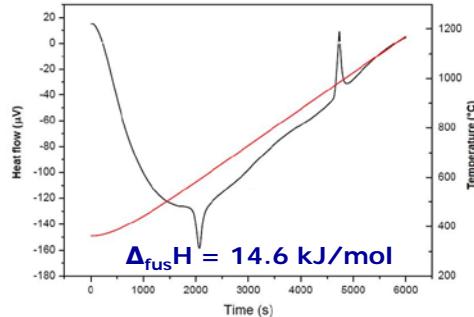


TD of LiF and ThF<sub>4</sub>  
(Literature TD tables)



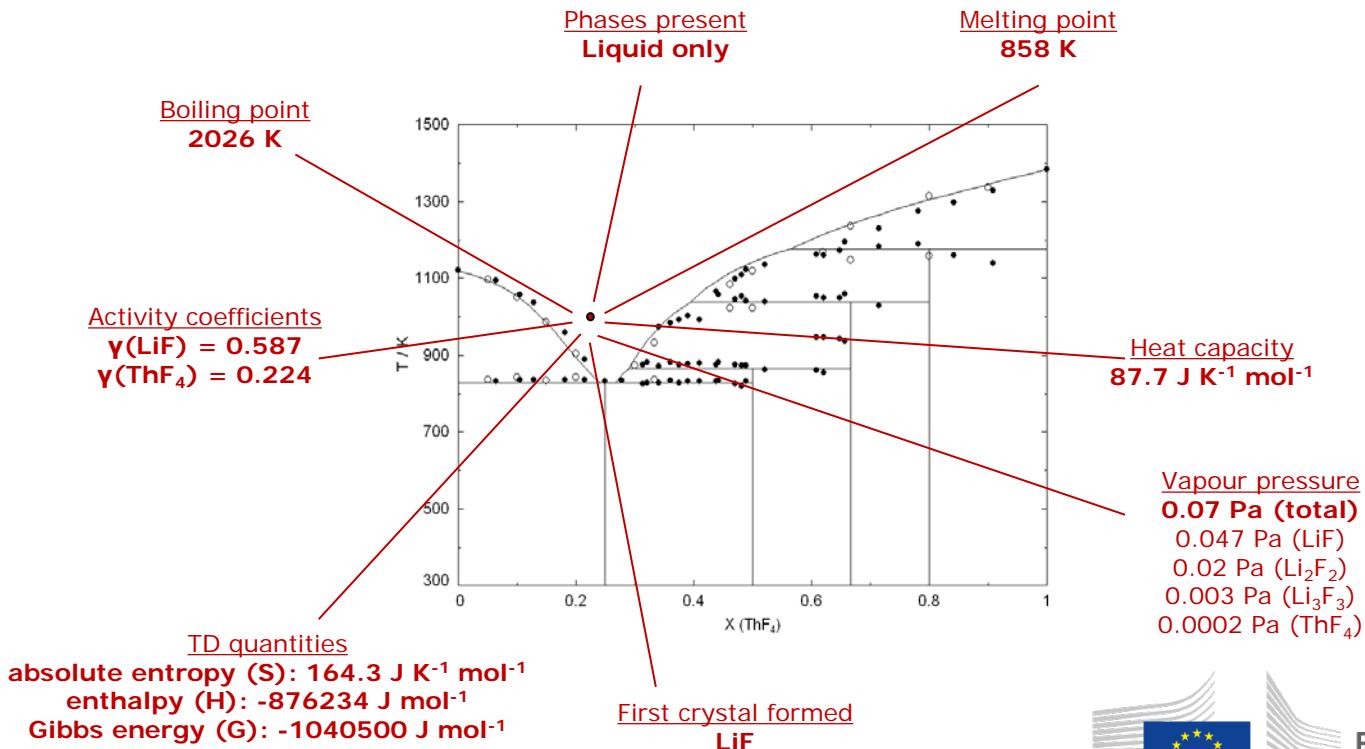
**fusion enthalpy value**  
**our experiment**  
 $\Delta_{\text{fus}}H = 13.7 \pm 2 \text{ kJ/mol}$

**Gilbert 1962**  
 $\Delta_{\text{fus}}H = 14.6 \text{ kJ/mol}$



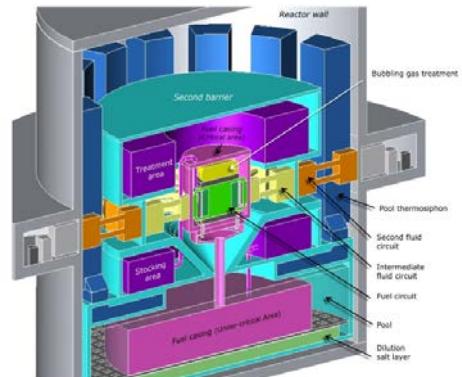
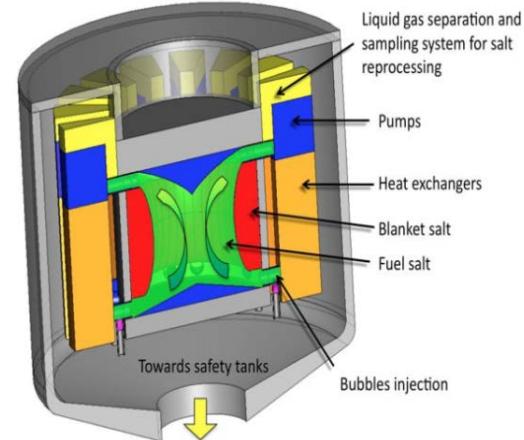
# Phase diagram reading

LiF – ThF<sub>4</sub> (78 – 22) at 1000K



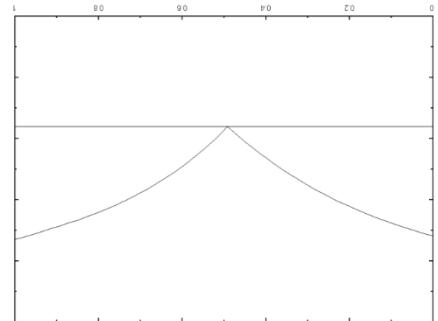
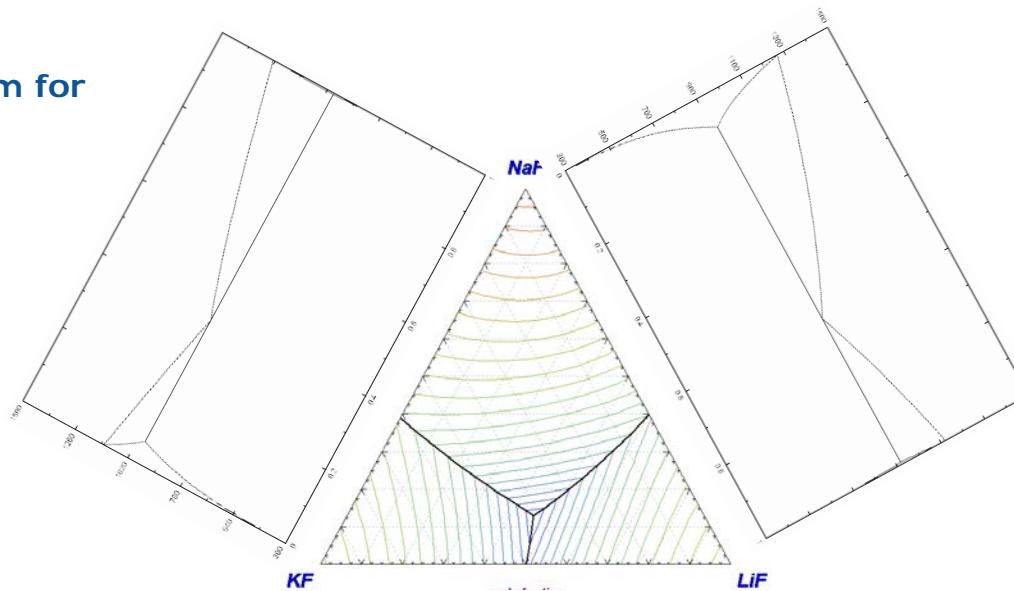
# MSR fuel = multi-component system

Fuel circuit	MSFR (EU)
Fuel salt, mole %	78.0LiF-20.0ThF <sub>4</sub> -2.5UF <sub>4</sub> 77.5LiF-6.6ThF <sub>4</sub> -12.3UF <sub>4</sub> - 3.6TRUF <sub>3</sub>
Temperature, °C	650 - 750
Core radius / height, m	1.13 / 2.26
Core specific power, W/cm <sup>3</sup>	270
Container material in fuel circuit	Ni-W alloy EM 721
Removal time for soluble FPs, yrs	1 - 3



# Higher order systems

- Mathematical formalism for Gibbs energy estimation



- Validation by series of experimental data

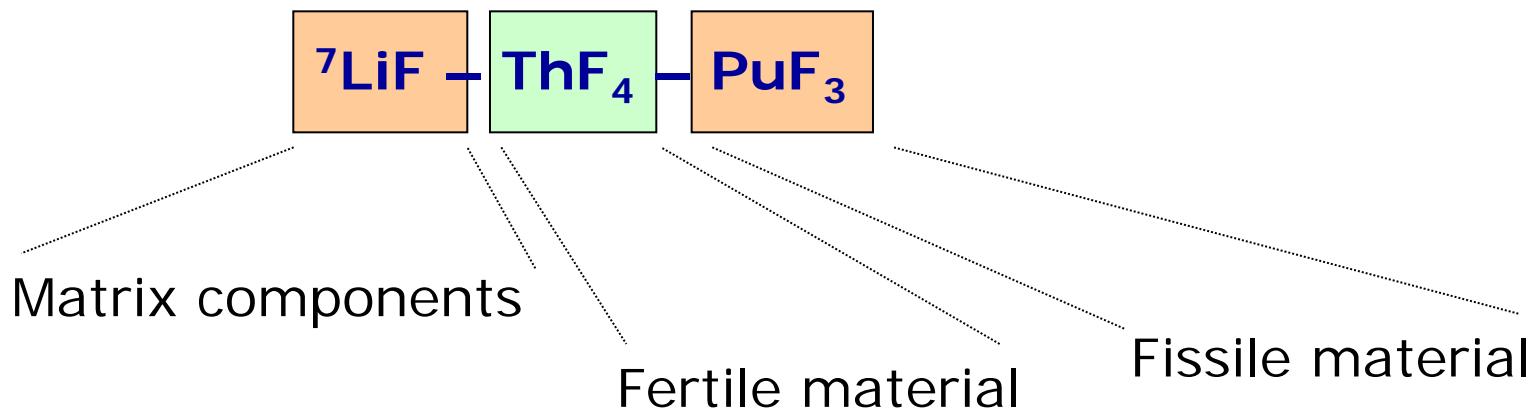


# Use of Thermodynamic Database

## EXAMPLE 1:

Use of thermodynamic database

### Optimization of the Fuel for Molten Salt Fast Reactor (MSFR)

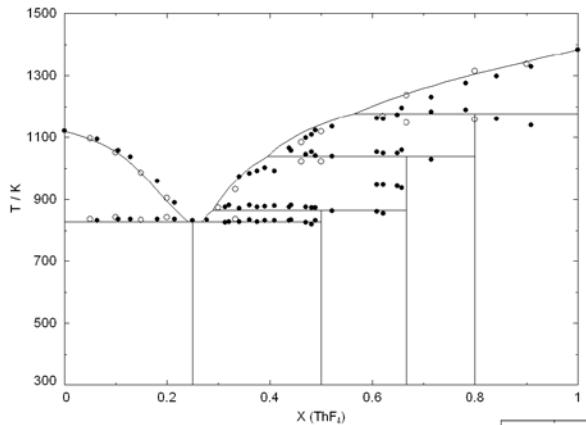


# Binary systems

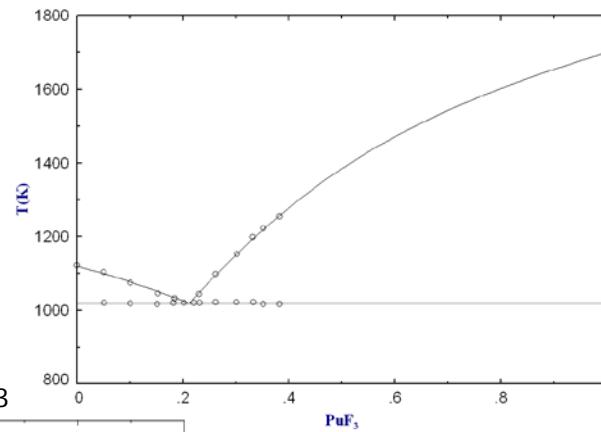


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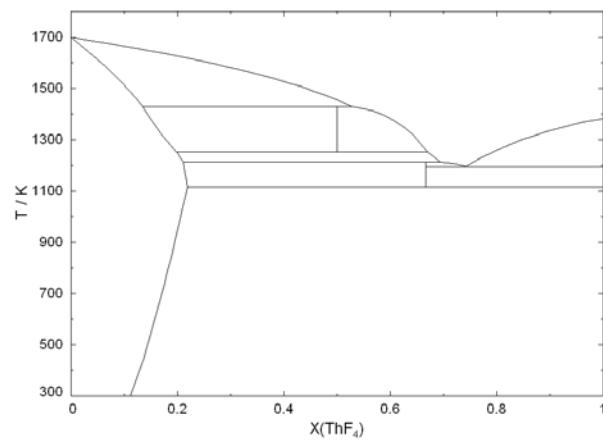
LiF – ThF<sub>4</sub>



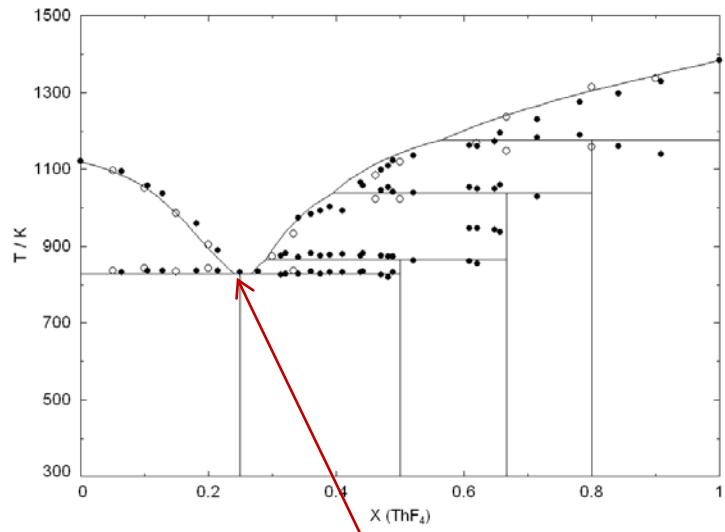
LiF – PuF<sub>3</sub>



ThF<sub>4</sub> – PuF<sub>3</sub>



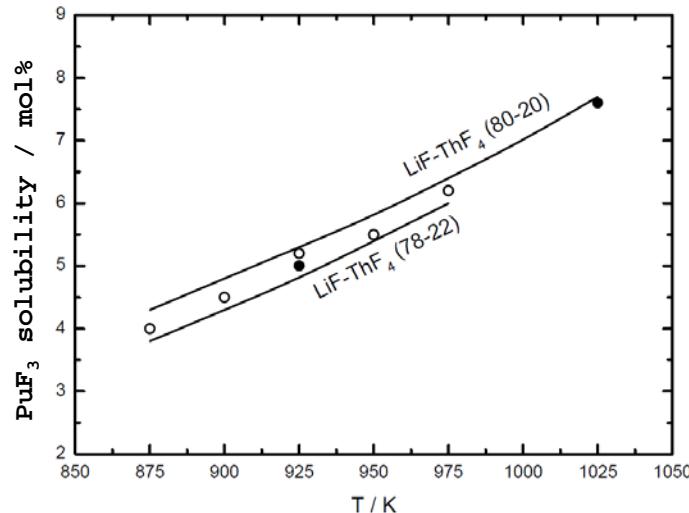
# MSFR concept



LiF-ThF<sub>4</sub> (77.5-22.5)  
m.p. 840 K

## MSFR concept

PuF<sub>3</sub> ~ 5 mol%



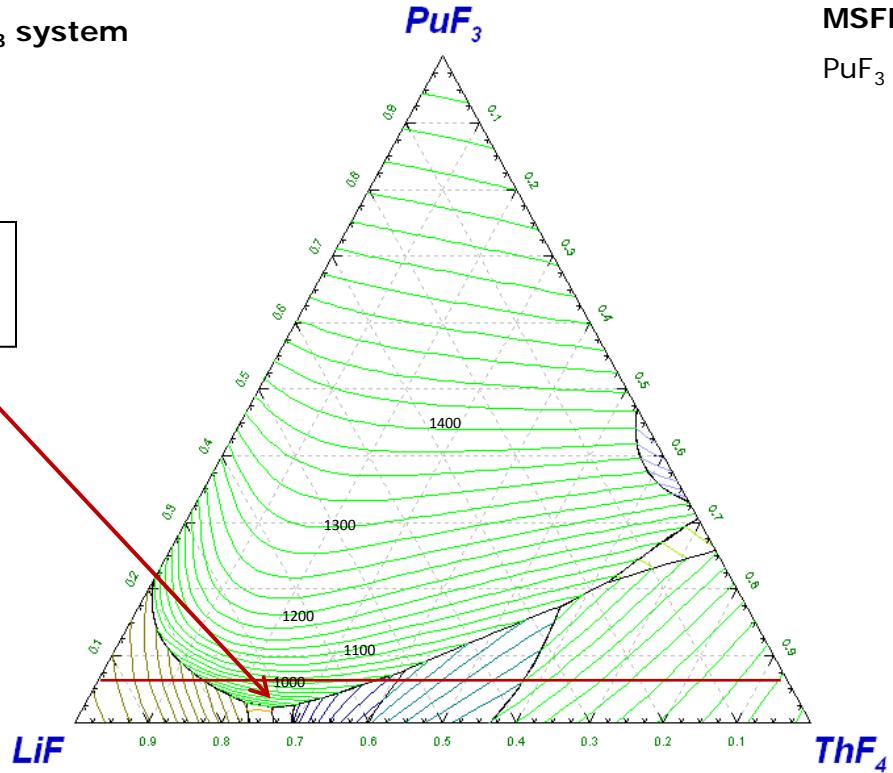
5 mol% PuF<sub>3</sub> ~ 935 K

# MSFR concept



LiF-ThF<sub>4</sub>-PuF<sub>3</sub> system

~820 K  
1.8 mol % PuF<sub>3</sub>



MSFR concept

PuF<sub>3</sub> ~ 5 mol%

# MSFR concept



Reference system of the MSFR

LiF-ThF<sub>4</sub>-PuF<sub>3</sub> (74-21-5 mol%) ... solvent is LiF-ThF<sub>4</sub> (78-22)  
- liquidus point is 935 K (662 °C)

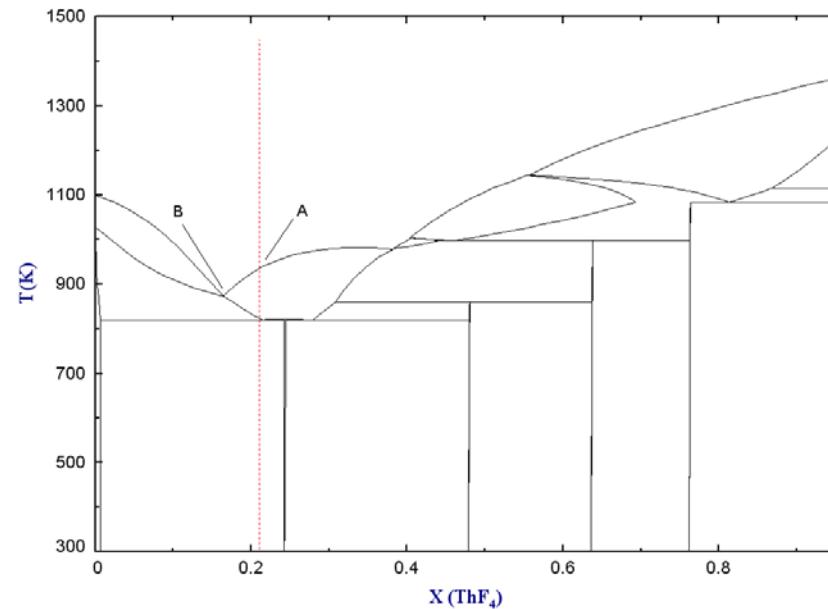
Point A

Point B

LiF-ThF<sub>4</sub>-PuF<sub>3</sub> (78.6-16.4-5 mol%)  
- liquidus point is 873 K (600 °C)



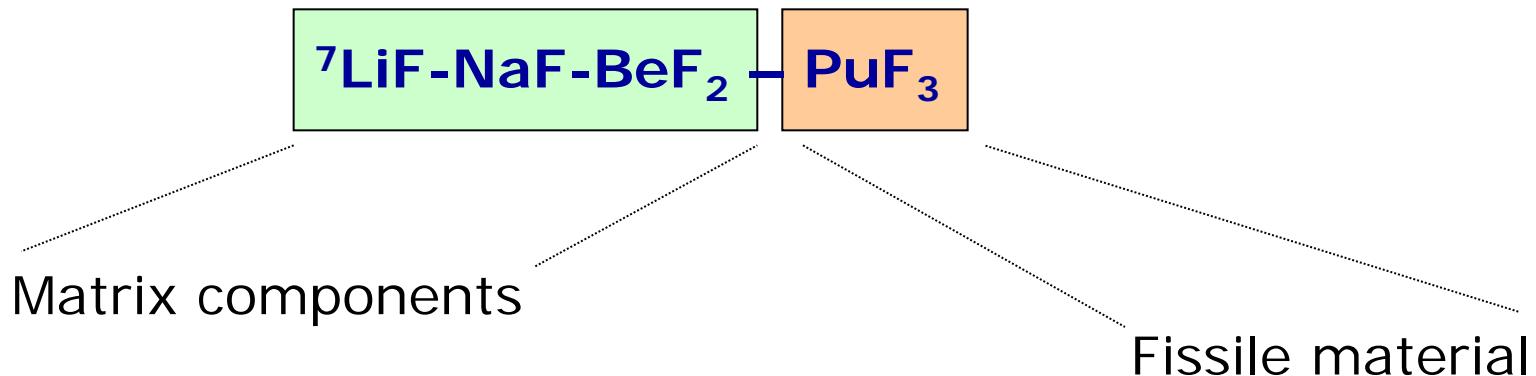
Proposed for MSFR fuel



## EXAMPLE 2:

Use of thermodynamic database

### Optimization of the Fuel for MOSART concept



# MSR concept



## MOSART reactor (Russian concept – ISTC project)

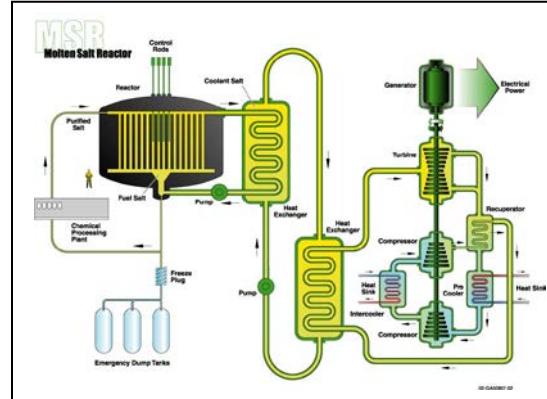
- $T_{\text{inlet}} = 873 \text{ K}$  (melting point of the fuel must be lower than 823 K, 50 K safety margin)
- $T_{\text{outlet}} = 988 \text{ K}$
- $X(\text{PuF}_3) = 1.3 \text{ mol\%}$  (‘An’ is mostly  $^{239}\text{Pu}$ )
- matrix composition: LiF–NaF–BeF<sub>2</sub> (15-58-27)

### Criteria:

$T_{\text{melting}} < 823 \text{ K}$

$X(\text{PuF}_3) = 1.3 \text{ mol\%}$

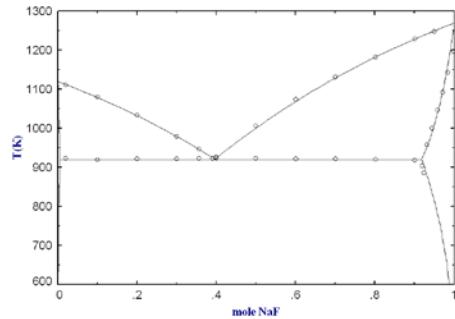
$X(\text{BeF}_2) = \text{low}$



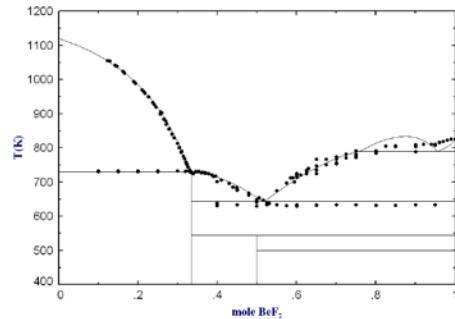
# Binary systems



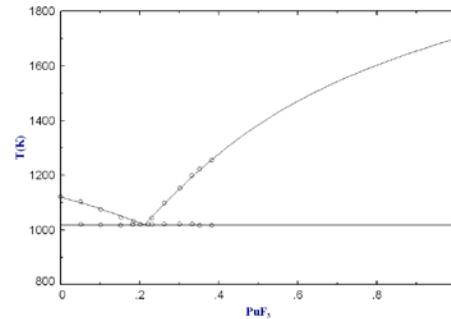
LiF - NaF



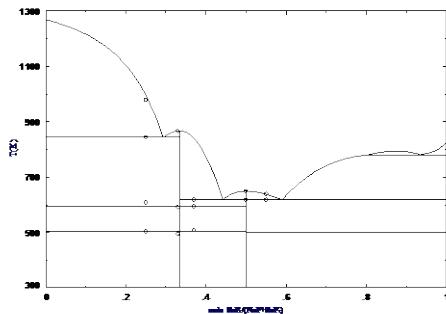
LiF – BeF<sub>2</sub>



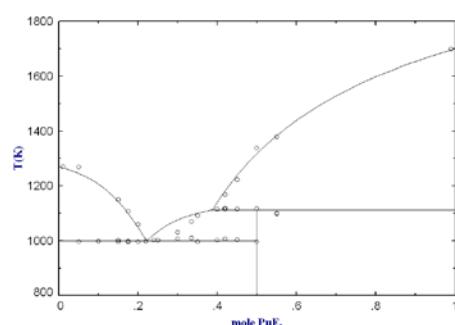
LiF – PuF<sub>3</sub>



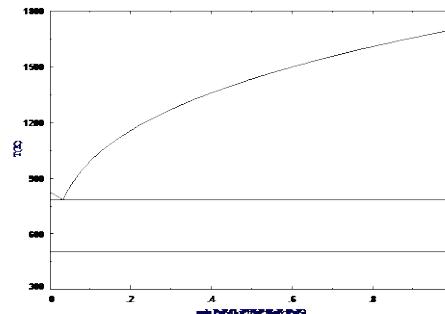
NaF – BeF<sub>2</sub>



NaF – PuF<sub>3</sub>



BeF<sub>2</sub> – PuF<sub>3</sub>



# LiF-NaF-PuF<sub>3</sub> system



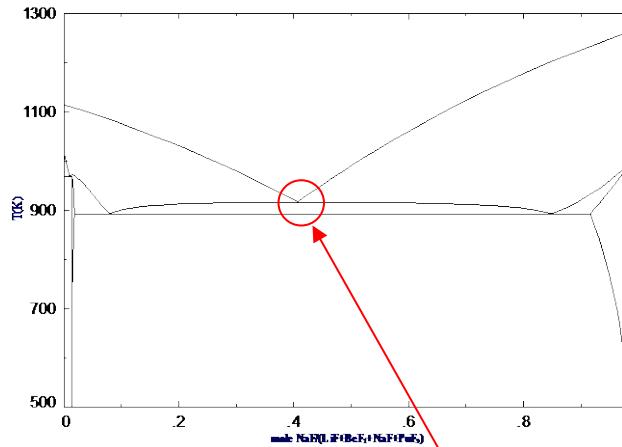
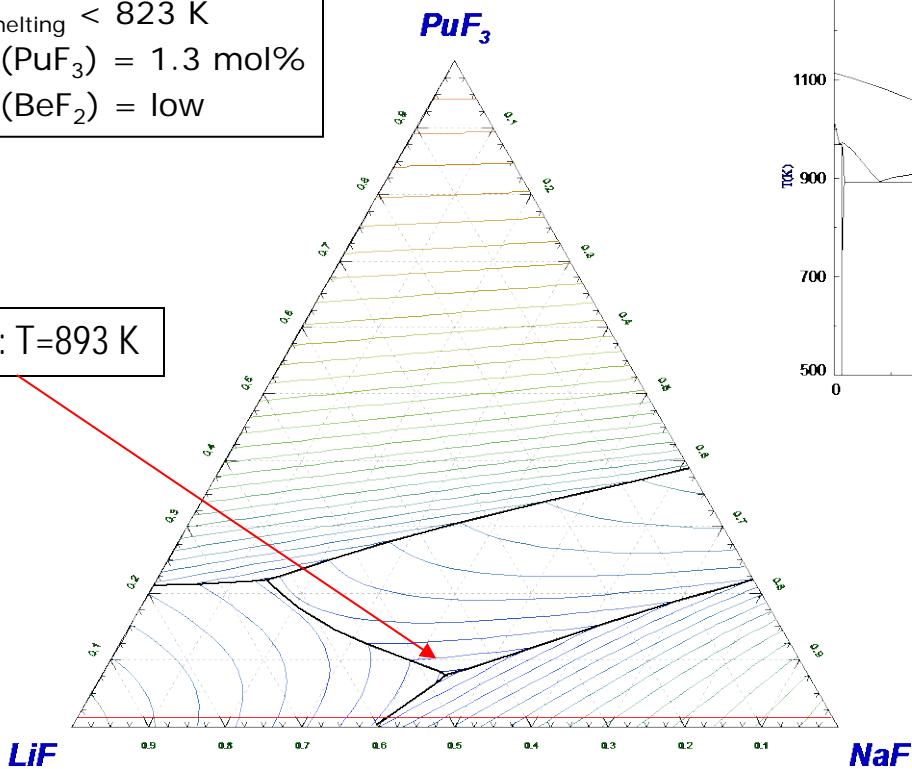
## Criteria:

T<sub>melting</sub> < 823 K

X (PuF<sub>3</sub>) = 1.3 mol%

X (BeF<sub>2</sub>) = low

E<sub>1</sub>: T=893 K



T = 917 K at:  
X(LiF) = 0.580  
X(NaF) = 0.407  
X(PuF<sub>3</sub>) = 0.013

# LiF-BeF<sub>2</sub>-PuF<sub>3</sub> system **Criteria:** $$T_{\text{melting}} < 823 \text{ K}$$ $$X(\text{PuF}_3) = 1.3 \text{ mol\%}$$ $$X(\text{BeF}_2) = \text{low}$$ A ternary phase diagram for the LiF-BeF<sub>2</sub>-PuF<sub>3</sub> system. The vertices are labeled LiF, BeF<sub>2</sub>, and PuF<sub>3</sub>. The axes represent mole fractions: LiF (bottom left), BeF<sub>2</sub> (bottom right), and PuF<sub>3</sub> (top). Activity contours are shown as concentric curves around the PuF<sub>3</sub> vertex. The curves are color-coded: red for low activity (0.1 to 0.2), orange for intermediate activity (0.3 to 0.4), yellow for high activity (0.5 to 0.6), green for very high activity (0.7 to 0.8), and blue for highest activity (0.9 to 1.0). A binary phase diagram for the BeF<sub>2</sub>-PuF<sub>3</sub> system. The y-axis is temperature T(K) from 300 to 1300. The x-axis is the mole fraction of BeF<sub>2</sub> from 0 to 8. Several curves represent melting points for different compositions. A horizontal line at T = 761 K intersects the curves. A red circle highlights a point on the curve for approximately 8.2 mol% BeF<sub>2</sub>, which is labeled with a red arrow. T = 761 K, but too much of BeF<sub>2</sub>

# NaF-BeF<sub>2</sub>-PuF<sub>3</sub> system

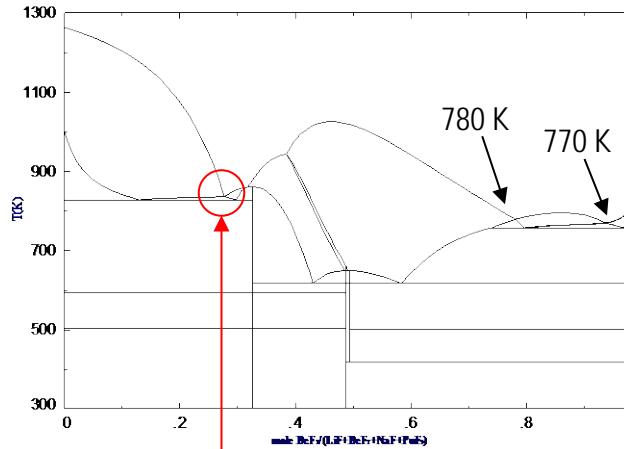
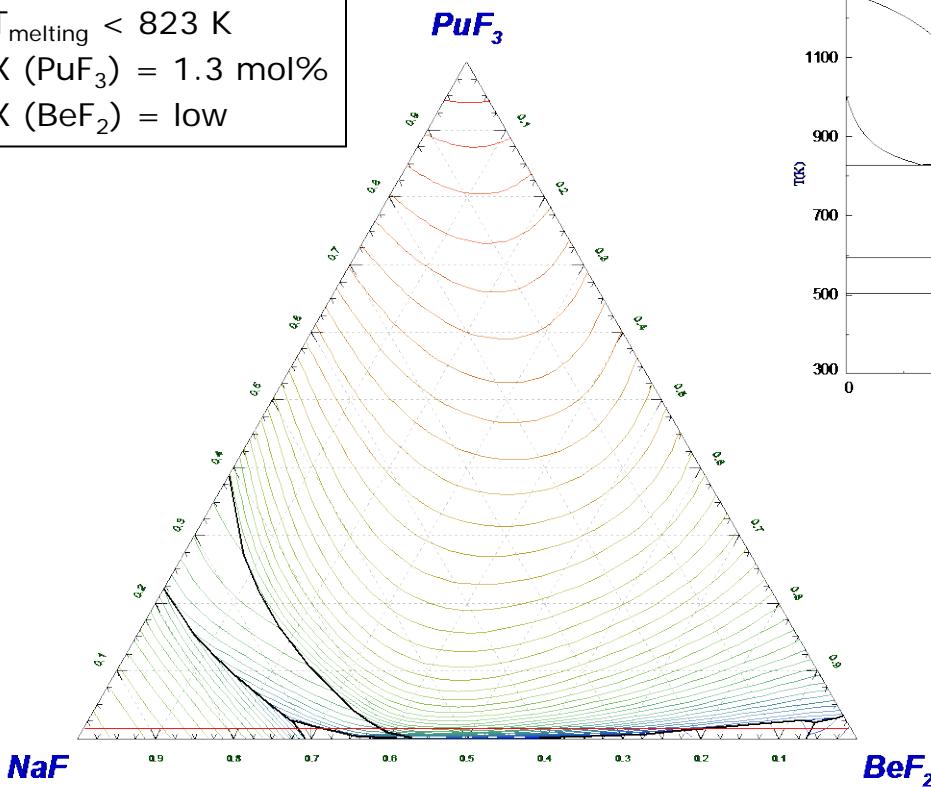


**Criteria:**

$$T_{\text{melting}} < 823 \text{ K}$$

$$X(\text{PuF}_3) = 1.3 \text{ mol\%}$$

$$X(\text{BeF}_2) = \text{low}$$



T = 837 K at:  
X(NaF) = 0.710  
X(BeF<sub>2</sub>) = 0.277  
X(PuF<sub>3</sub>) = 0.013

# **LiF-NaF-BeF<sub>2</sub>-(PuF<sub>3</sub>=1.3 mol%) system**



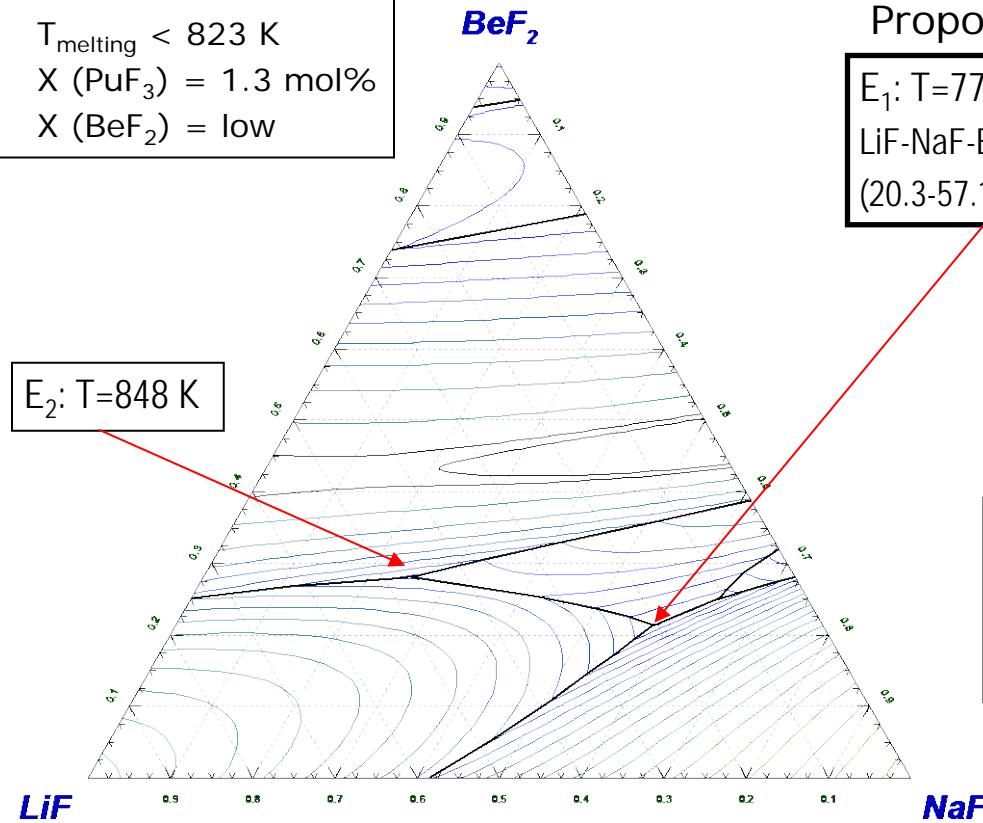
**Criteria:**

$$T_{\text{melting}} < 823 \text{ K}$$

$$X(\text{PuF}_3) = 1.3 \text{ mol\%}$$

X(BeF<sub>2</sub>) = low

E<sub>2</sub>: T=848 K



**Proposed fuel**

$$E_1: T=775 \text{ K}$$

LiF-NaF-BeF<sub>2</sub>-PuF<sub>3</sub>  
(20.3-57.1-21.2-1.3)

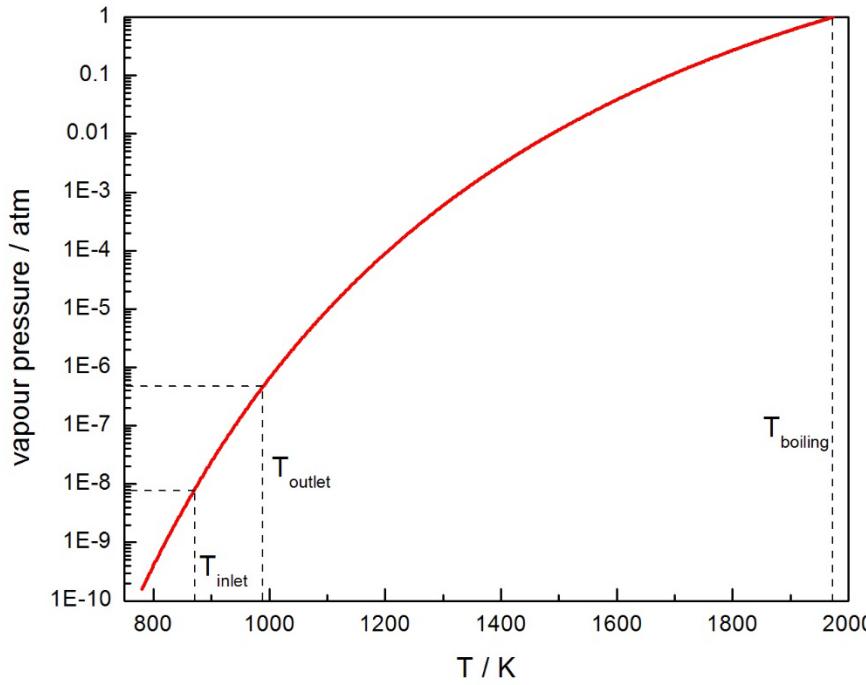
**MOSART composition:**  
LiF-NaF-BeF<sub>2</sub>-PuF<sub>3</sub>  
(14.8-57.2-26.7-1.3)

# Vapour pressure

---

LiF-NaF-BeF<sub>2</sub>-PuF<sub>3</sub> (20.3-57.1-21.2-1.3) composition:

## 4. Example 5



$$T_{\text{inlet}} = 873 \text{ K} \sim 0.001 \text{ Pa}$$
$$T_{\text{outlet}} = 988 \text{ K} \sim 0.046 \text{ Pa}$$

Boiling point: 1973 K



Thank you for your attention  
Questions???

# Stay in touch



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