

**The European Commission's
science and knowledge service**

Joint Research Centre

Thermodynamic aspects of nuclear fuels

Rudy Konings

Chemical Thermodynamics

Chemical thermodynamics describe the relation between heat and

- properties of materials
- physical changes
- chemical reactions

Heat

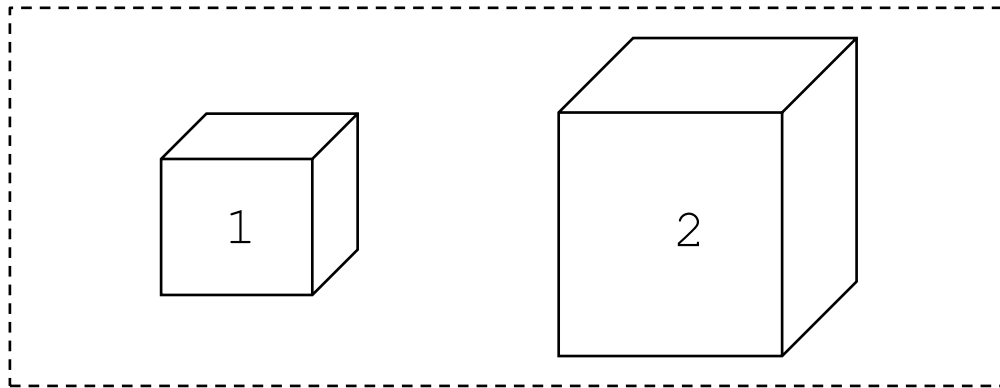
- Heat (Q) is a transfer of energy (U), other than work (W)

$$dU = dQ + dW \quad (1^{\text{st}} \text{ Law})$$

- Heat corresponds to the total energy of molecular motion in a substance
- Heat gains or losses result in
 - changes in temperature
 - changes in state
 - performance of work

Temperature

- Heat (J) = Energy (J) \neq Temperature (K)



$$T_1 = T_2$$

$$E_1 \neq E_2$$

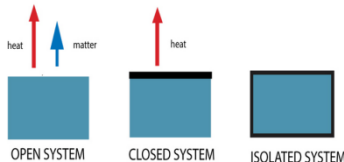
- Temperature correspond to the average kinetic energy of the particles within the object

Chemical Thermodynamics

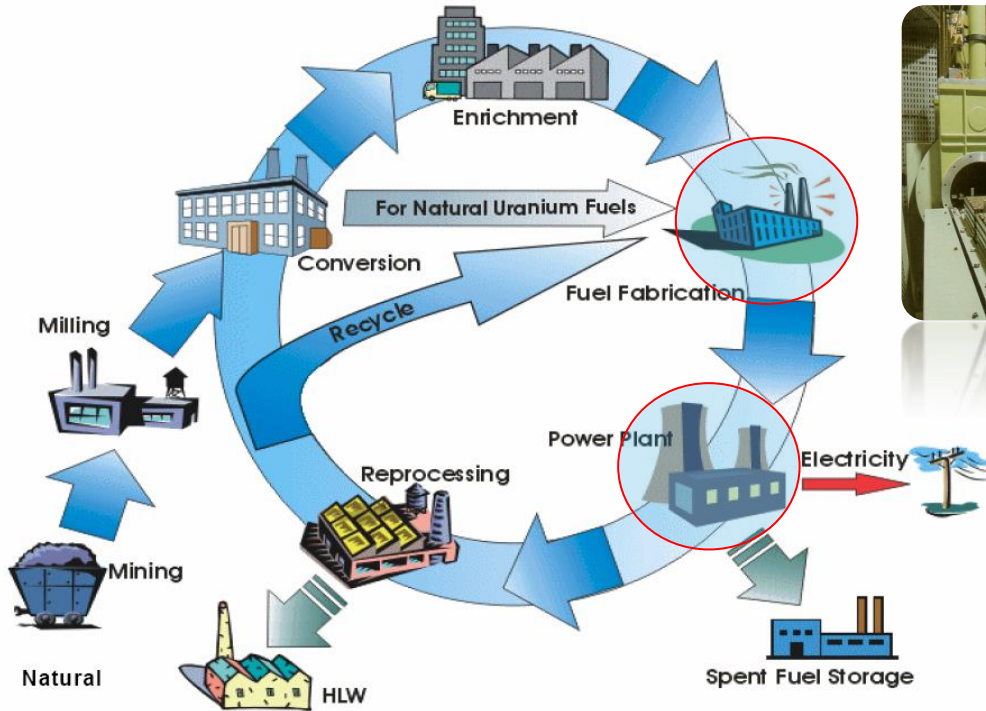
can be applied to systems

- in chemical equilibrium
- with fast reaction kinetics
- closed/isolated

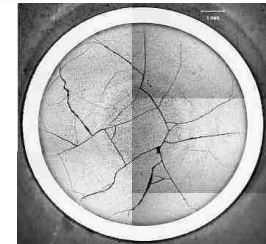
- ✓ High temperatures
- ✓ Solutions
- ✓ Gaseous phases
- ✓ Geological times



Thermodynamics and nuclear fuel

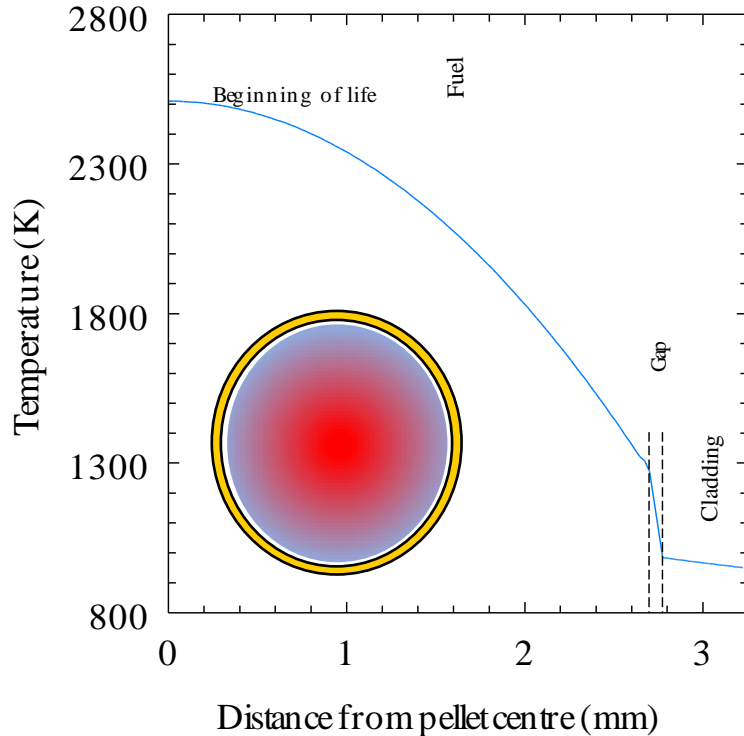


- **Sintering temperature:**
1600-1700 °C
- **Sintering atmosphere:**
Ar+H₂
- **Sintering time:**
6 h



- **See next slide**

Thermodynamics and nuclear fuel



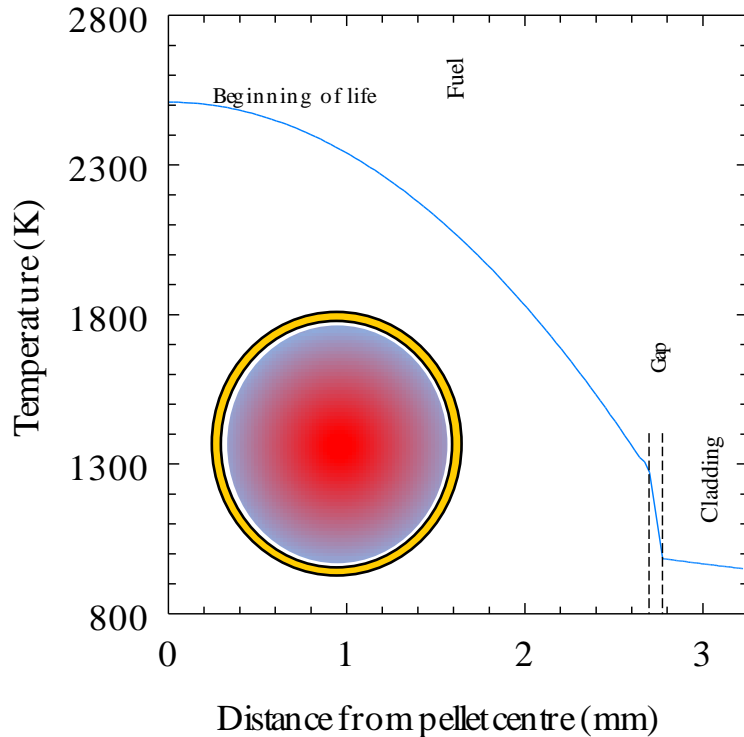
$$\Delta T(r) = T(R) - T(r) = \frac{\chi}{4\pi\lambda R^2} (R^2 - r^2)$$

χ = linear heating rate (W cm^{-1})

R = pellet radius (cm)

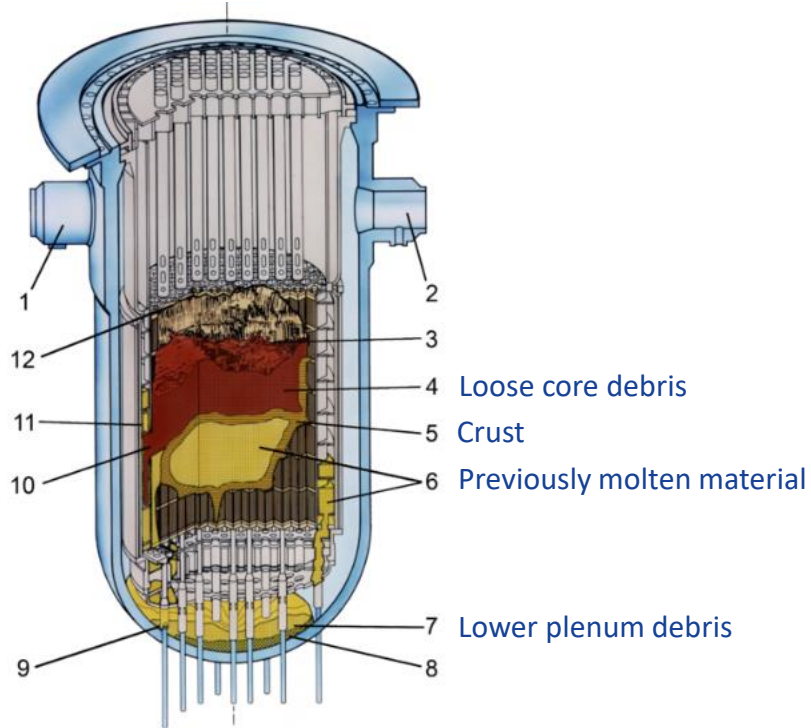
λ = Thermal conductivity ($\text{W cm}^{-1} \text{K}^{-1}$)

Thermodynamics and nuclear fuel



- **Temperature:**
1600-1700 °C
- **Atmosphere:**
He – O₂ imposed by the fuel
- **Time:**
several years

Thermodynamics and nuclear fuel



- **Temperature beyond the $\text{UO}_2\text{-Zr(O)}$ eutectic**
1600-1700 °C
- **Varying atmospheres, depending on the degree of oxidation of metal components**
 $\text{H}_2\text{O}+\text{H}_2$
- **Time**
Weeks

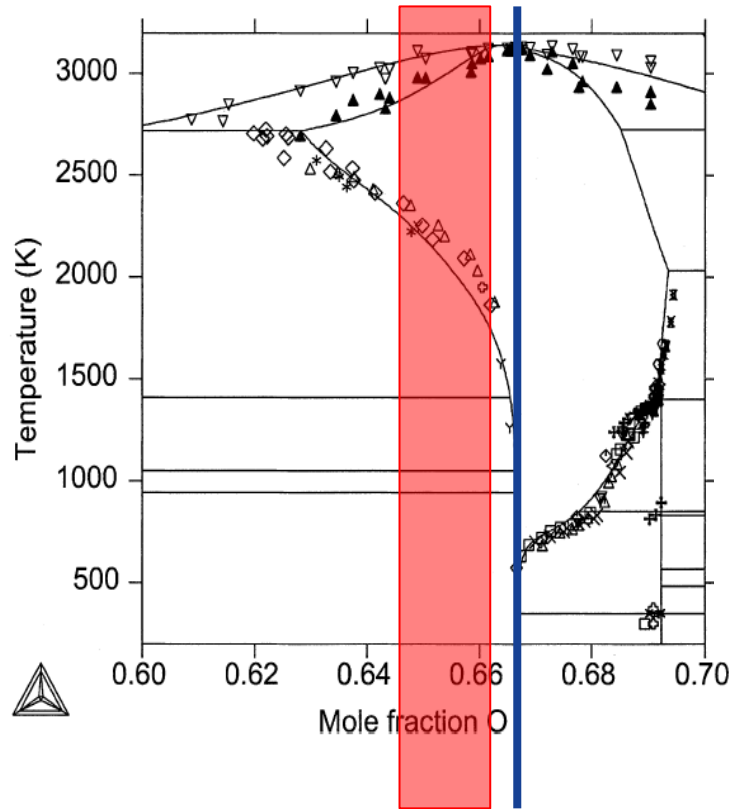
What do we want to know:

- Thermodynamic properties of fuel materials (UO_2 , $(\text{U,Pu})\text{O}_2$, $(\text{U,Am})\text{O}_2$, ...) as a function of temperature and composition
- Phase transformations (melting, vaporisation)
- Chemical reactions (fuel-coolant-fission-products)

Examples to be discussed in this lecture:

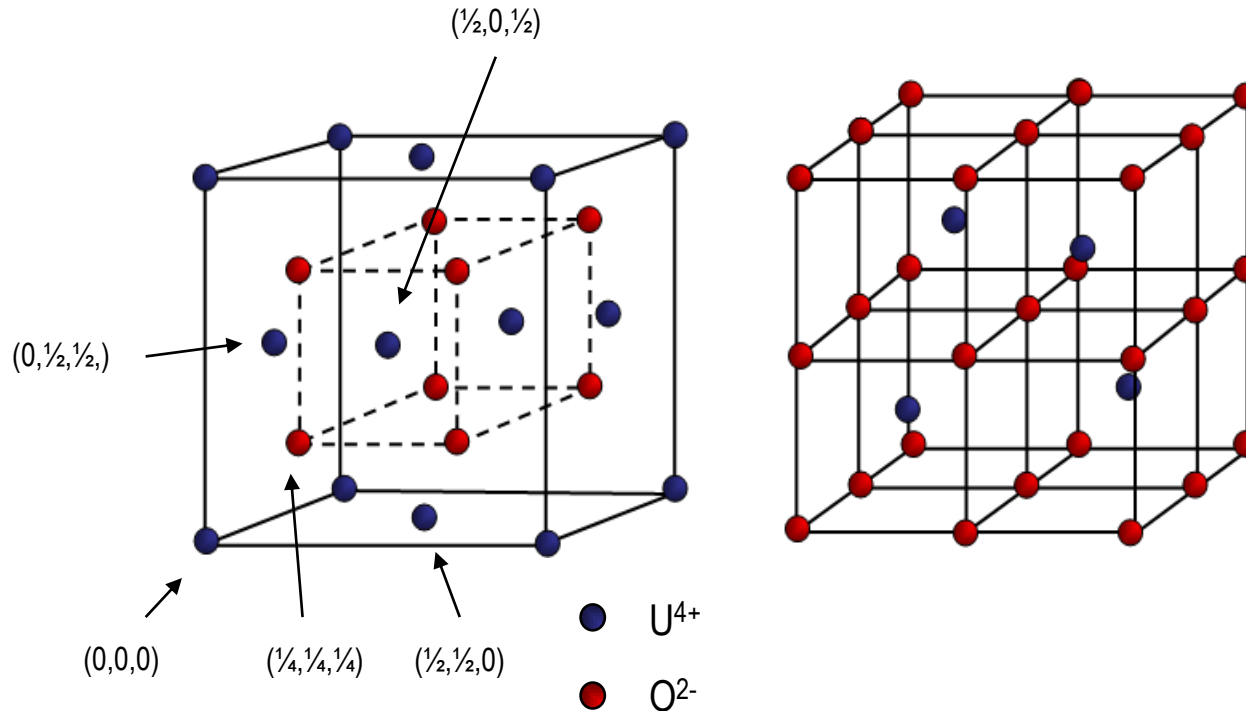
- Oxygen potential
- Heat capacity of UO_2
- Melting transition in $(\text{U,Pu})\text{O}_2$
- Reaction of $(\text{U,Pu})\text{O}_2$ with sodium

Oxygen potential of UO_2



- **LWR** fuel has a composition of $\text{O}/\text{M} = 2$
- In **fast reactor fuel** $\text{O}/\text{M} < 2$, typically 1.93-1.99
 - Avoid inner cladding corrosion

Oxygen potential of UO_2

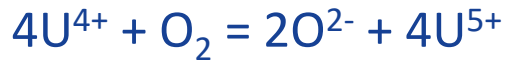


Fluorite-type face-centered cubic structure

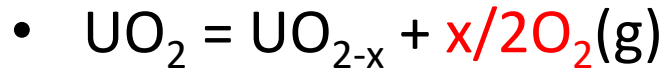
Oxygen potential of UO_2



O occupying "hole" positions in the fcc lattice



"Weakly" bonded O

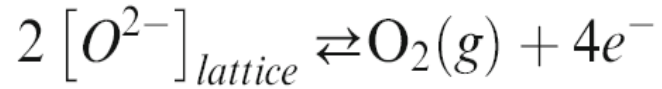


creating O vacancies

Leaves strongly bonded O



Oxygen potential of UO_2

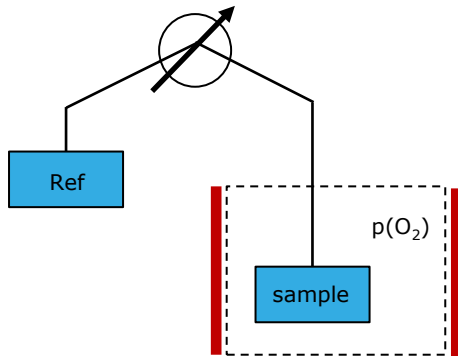


$$\Delta \bar{G}(\text{O}_2) = RT \ln p(\text{O}_2) \longrightarrow \text{Measure } p(\text{O}_2) \text{ as a function of } x$$

- Thermogravimetry (TGA)
- Electromotive force (EMF)

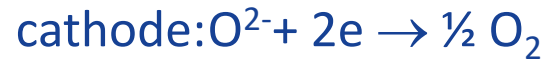
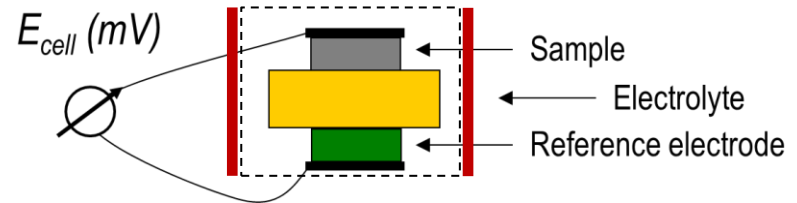
Oxygen potential of UO_2

Thermogravimetry (TGA)



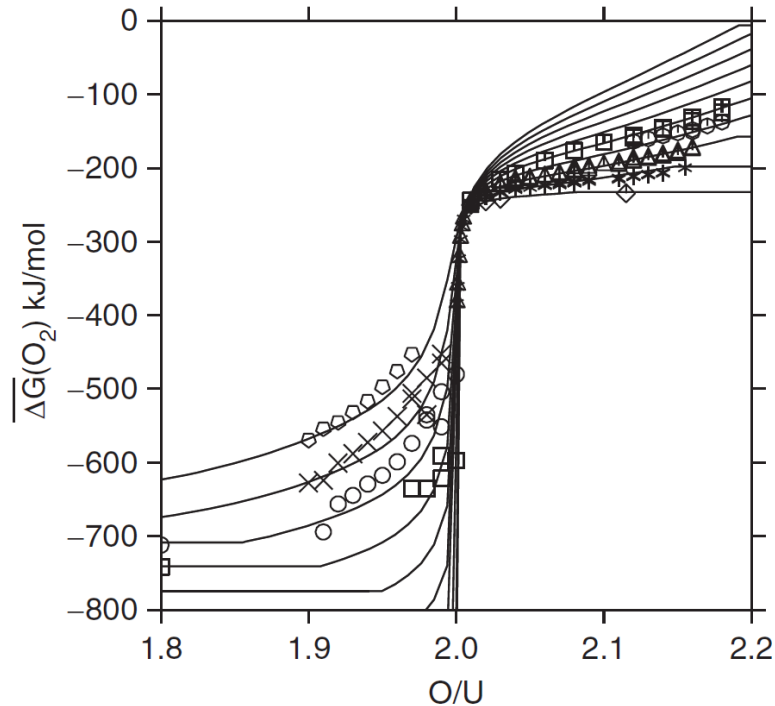
- Measure at fixed $p(\text{O}_2)$ the Δm as a function of T

Electromotive force (EMF)

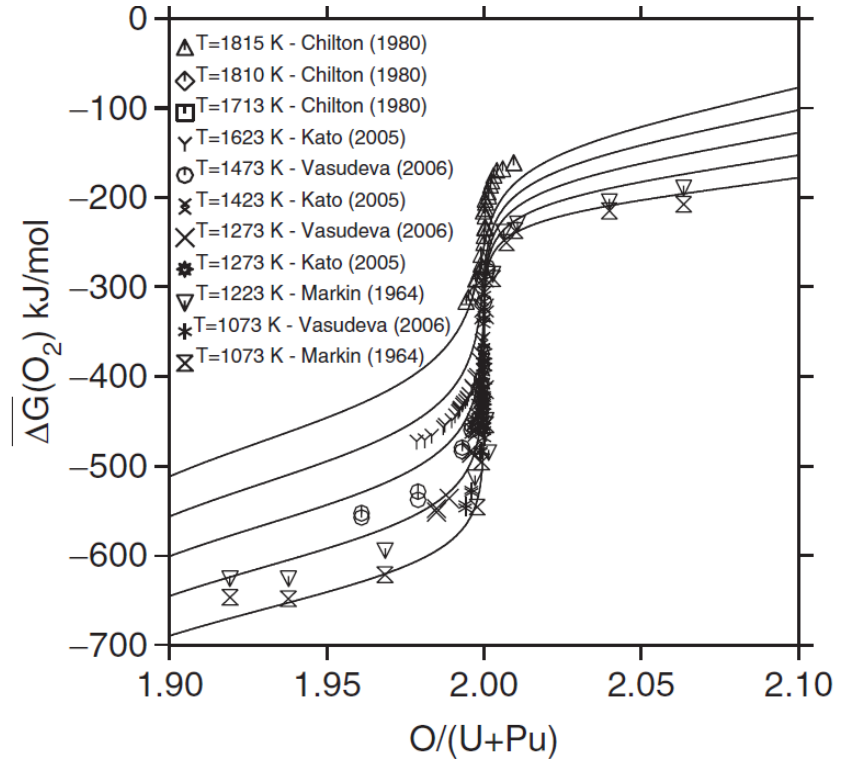


$$\Delta_r G^\circ(T) = -NF \cdot E_{\text{cell}}$$

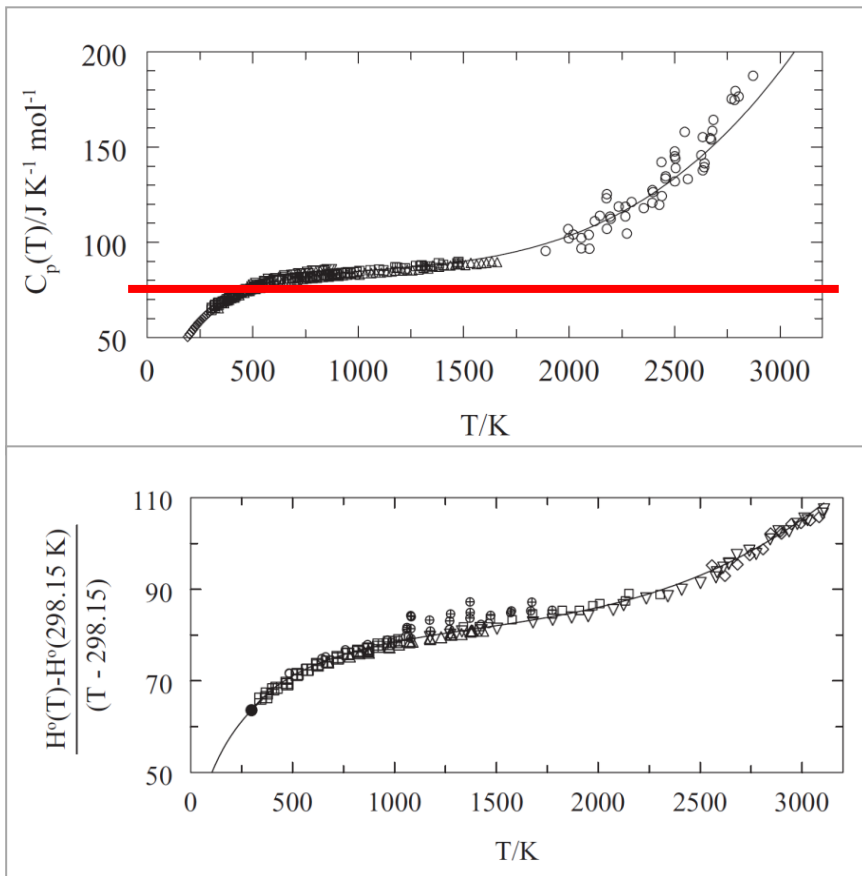
Oxygen potential of UO_2 and $(\text{U}_{0.70}\text{Pu}_{0.30})\text{O}_2$



- ◇ T=2600 K
- × T=2400 K
- T=2200 K
- T=2000 K
- ▽ T=1800 K
- ▣ T=1600 K
- ⊙ T=1400 K
- △ T=1200 K
- * T=1000 K
- ◇ T=800 K

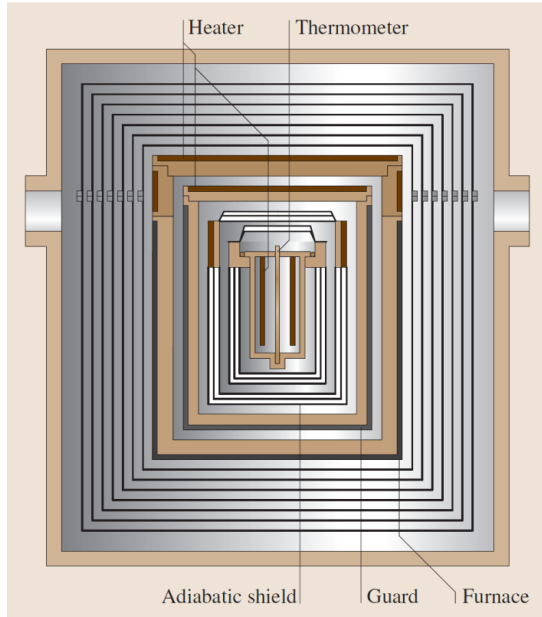


Heat capacity of UO_2



- Exceeds the Neumann-Kopp rule ($3nR$) significantly
- Confirmed by heat capacity and enthalpy increment measurements

Heat capacity (solids/liquids)



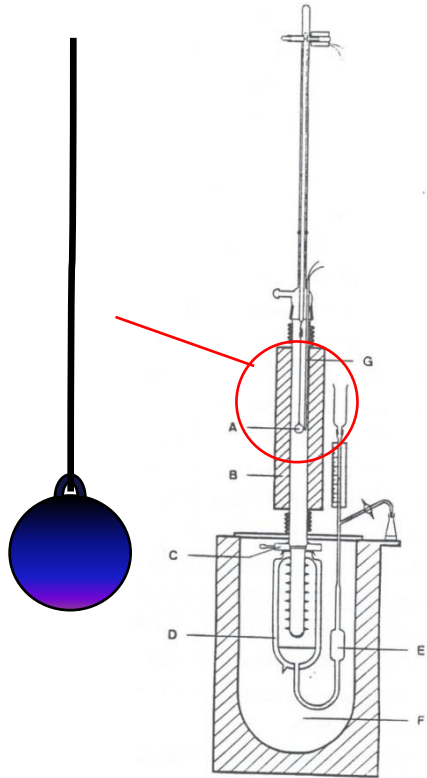
Buck and Rutsch, in: Springer Handbook of Materials Measurement Methods

Under adiabatic conditions $Q = dH$, the enthalpy increment, is equal to the supplied heat:

$$c_p = \frac{Q}{m \Delta T} = \frac{P_{el} t}{m \Delta T}$$

P_{el} is the electric power and t is the time

Heat capacity (solids/liquids)



- Displacement method: measurement of the enthalpy effect by displacement of a liquid metal (mercury)
- Sensitivity determined with a standard (sapphire)

A sample

E Mercury

B furnace

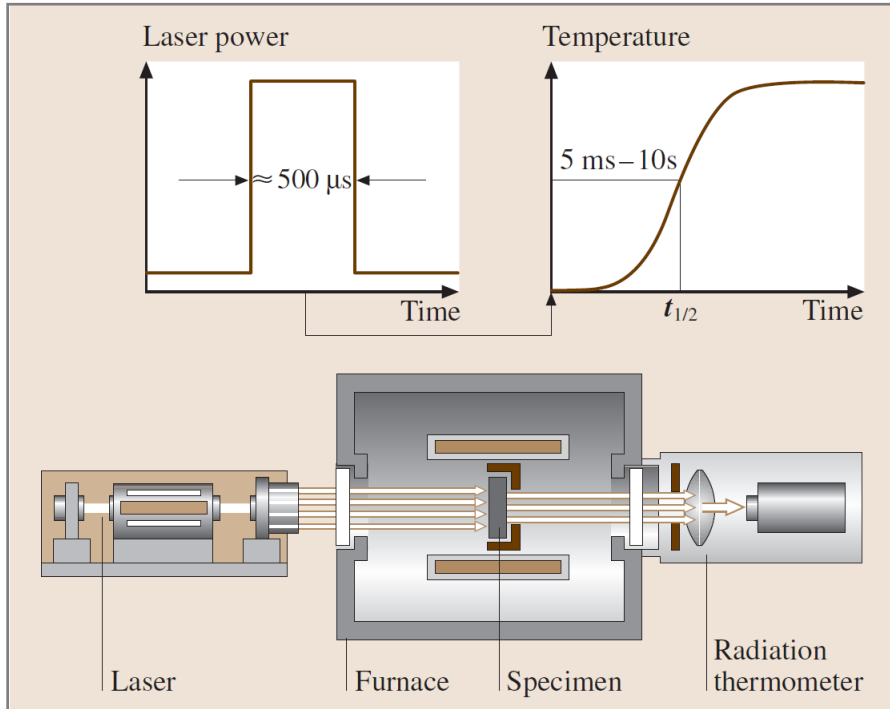
F Thermal jacket

C Diaphragm

G Thermocouple

D Calorimeter vessel

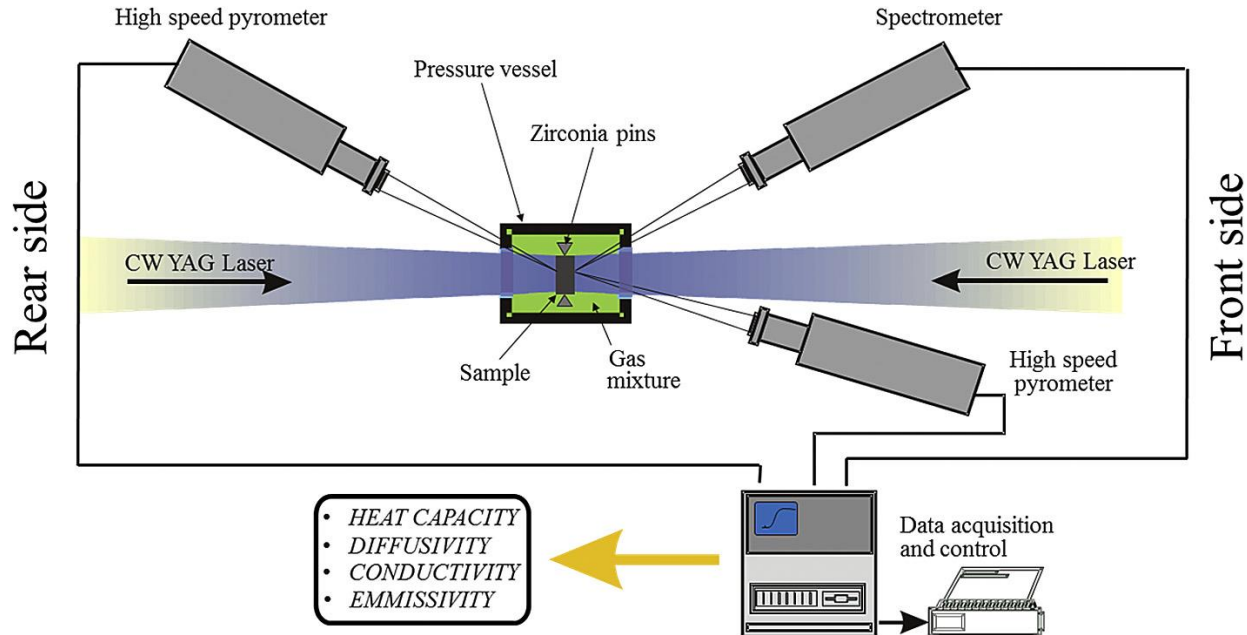
Heat capacity (solids/liquids)



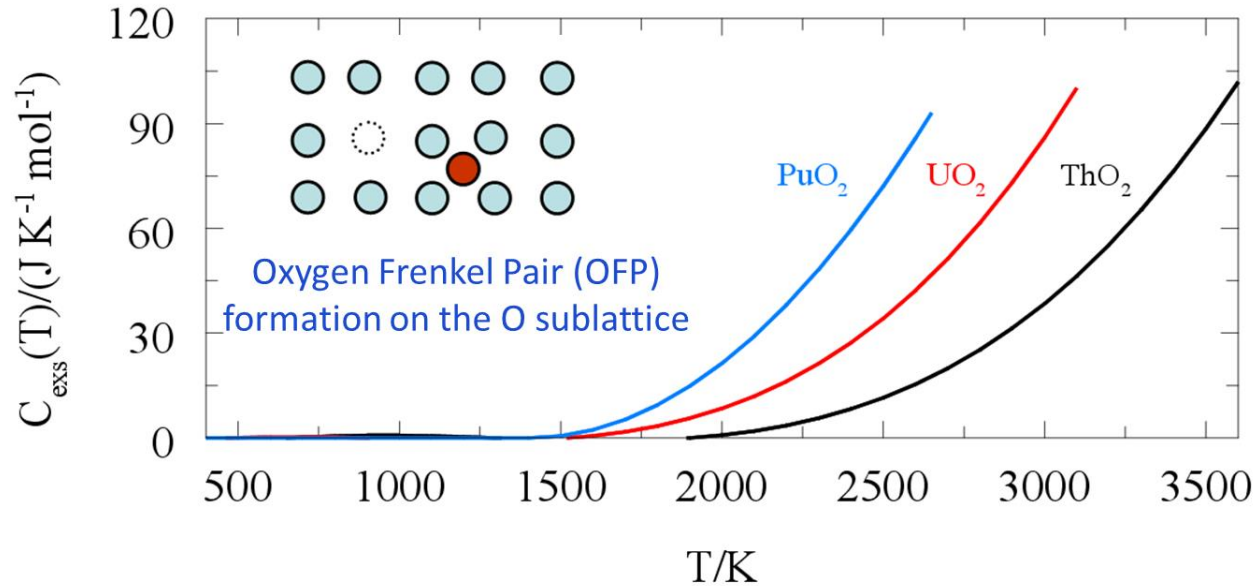
- Fast advanced pyrometry to measure the rear face temperature increase
- Precise analysis technique taking into account all relevant experimental parameters (heat loss, sample shape, ...)
- The heat capacity can be derived from the **deposited energy** as

$$C_p = Q/\Delta T_{\max}$$

Heat capacity (solids/liquids)



Heat capacity of UO_2



Heat capacity of UO_2

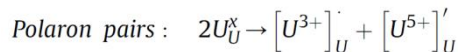
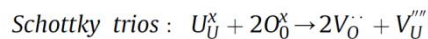
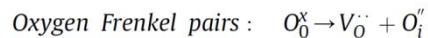
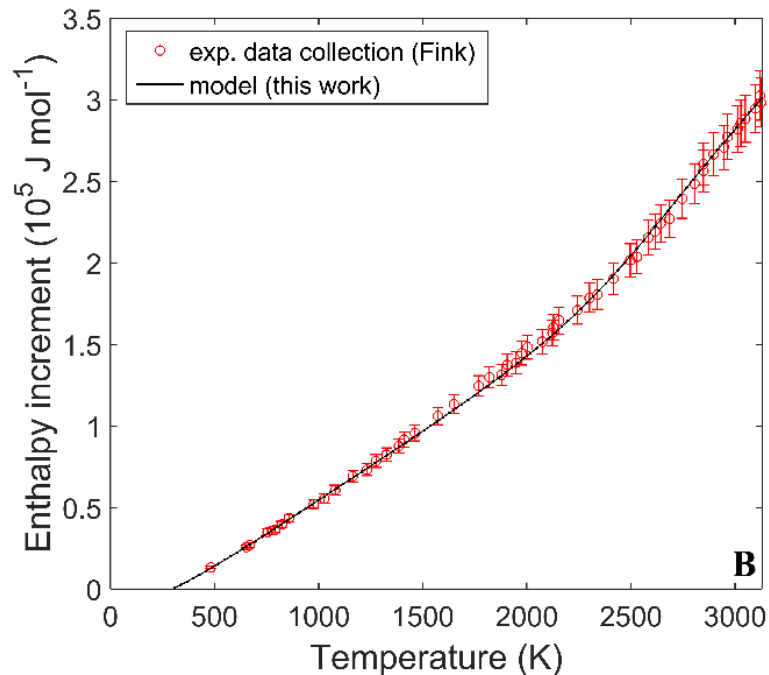
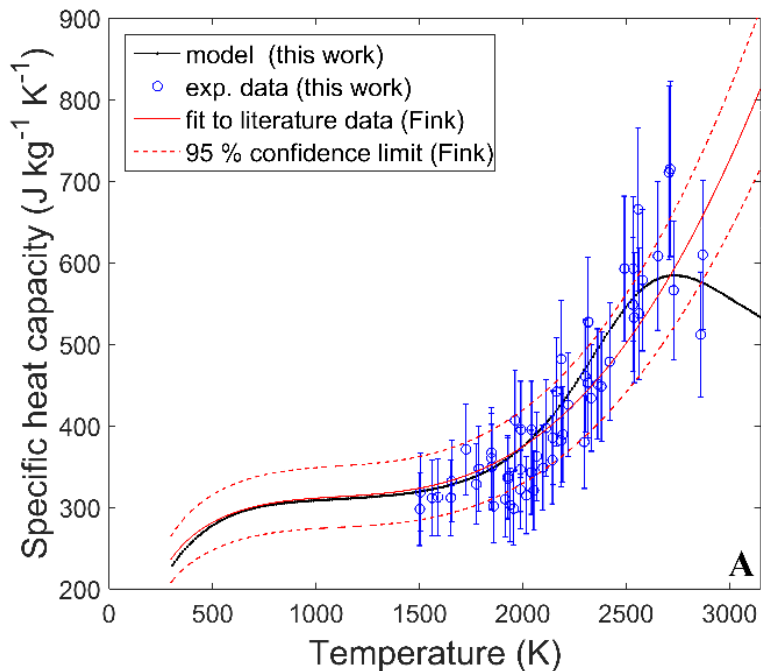
OFP concentration

$$x = \sqrt{2} \exp\left(\frac{-\Delta G_{OFP}}{2\mathbf{R}T}\right) = \sqrt{2} \exp\left(\frac{-\Delta H_{OFP}}{2\mathbf{R}T}\right) \exp\left(\frac{\Delta S_{OFP}}{2\mathbf{R}}\right) \quad (1)$$

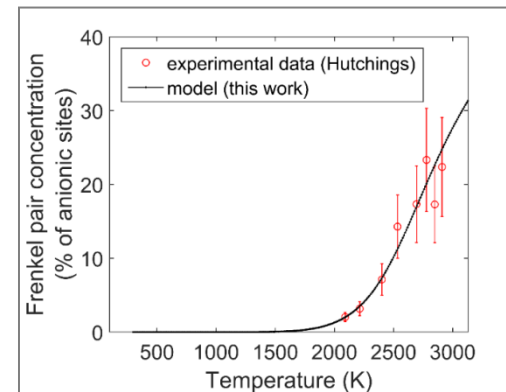
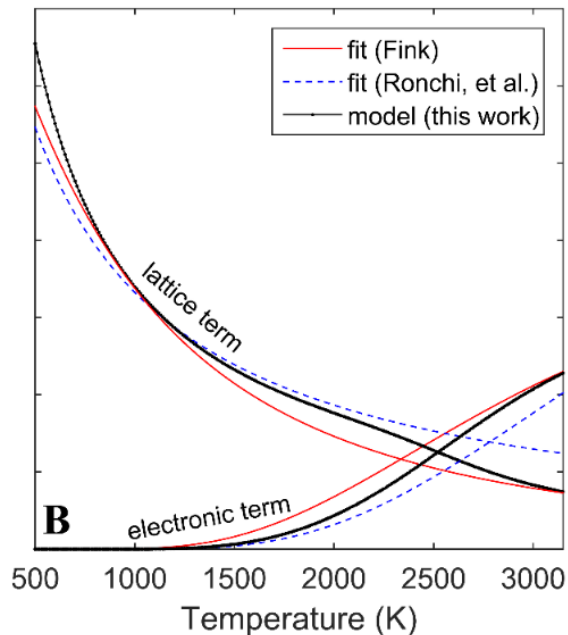
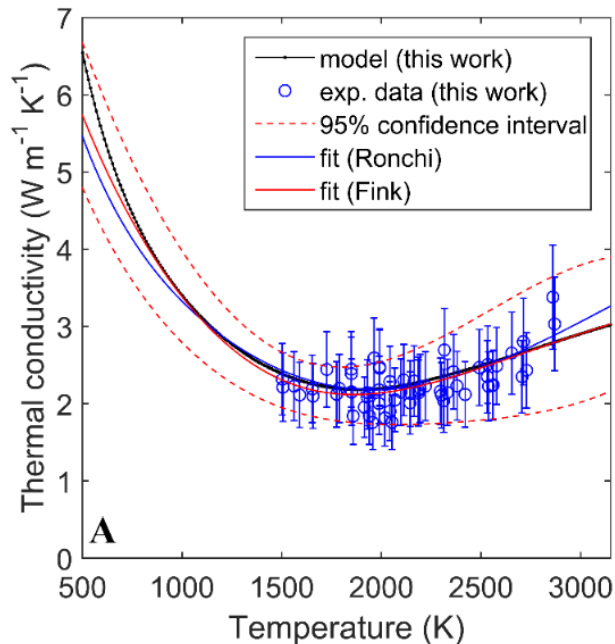
$$C_{p,exc} = \frac{d(x\Delta H_{OFP})}{dT} \quad (2)$$

$$C_{p,exc} = \frac{\Delta H_{OFP}^2}{\sqrt{2}\mathbf{R}T^2} \sqrt{2} \exp\left(\frac{-\Delta H_{OFP}}{2\mathbf{R}T}\right) \exp\left(\frac{\Delta S_{OFP}}{2\mathbf{R}}\right). \quad (3)$$

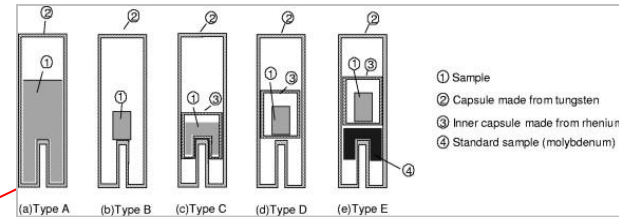
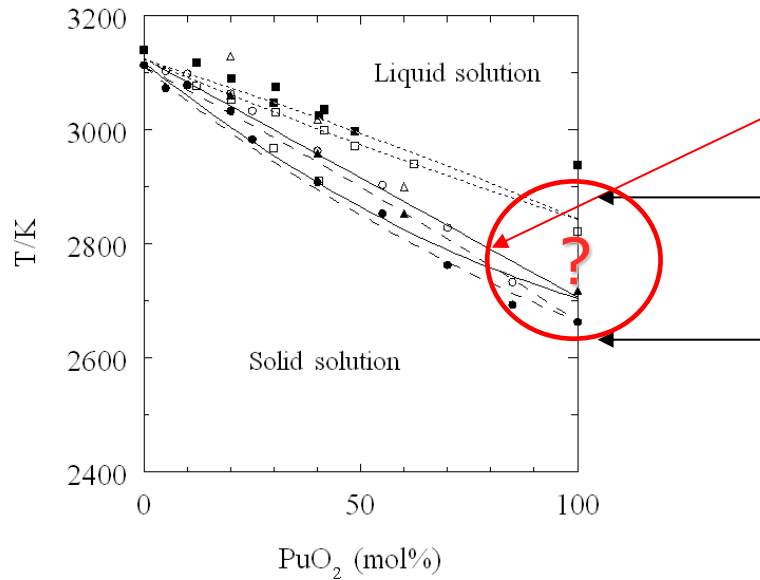
Heat capacity of UO_2



Heat capacity of UO_2



Melting point of $(U,Pu)O_2$



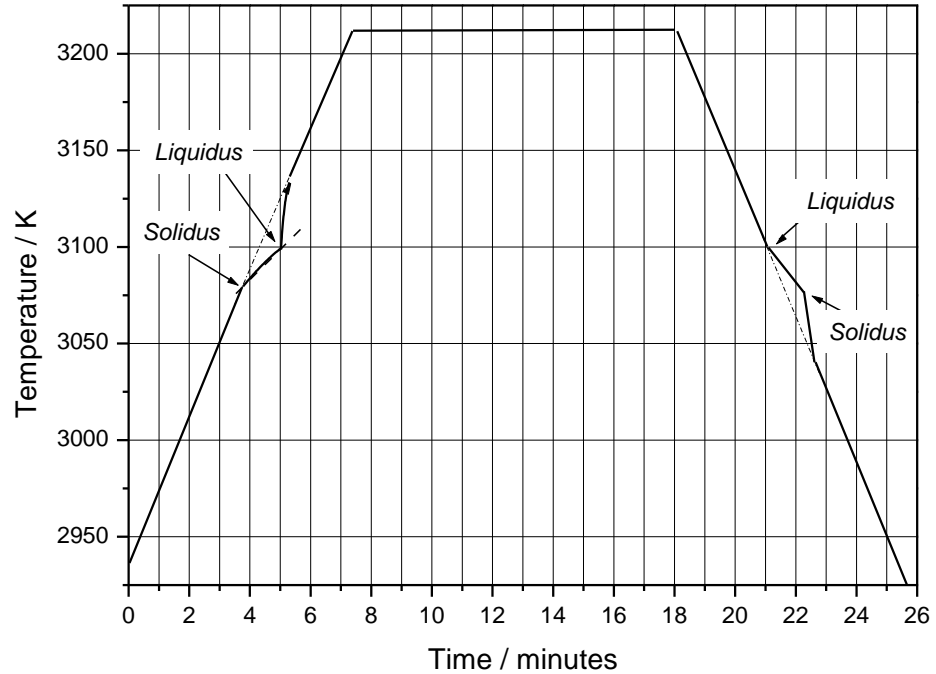
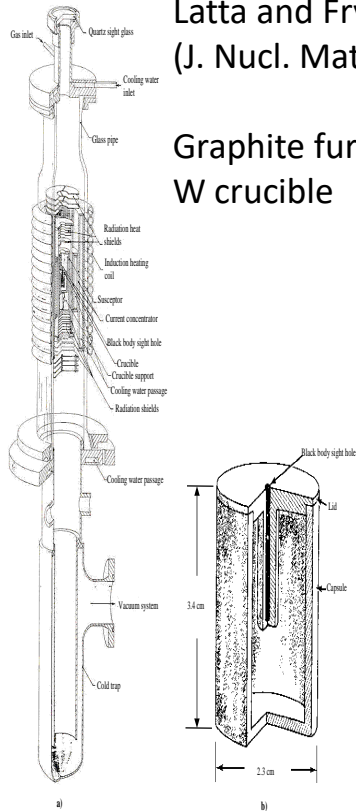
Value suggested by Kato et al.¹ based on study of the $(U,Pu)O_2$ phase diagram

Generally accepted melting temperature based on measurements from the 1960s

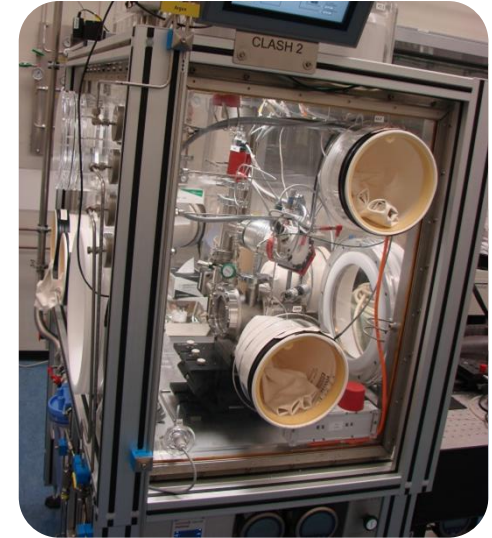
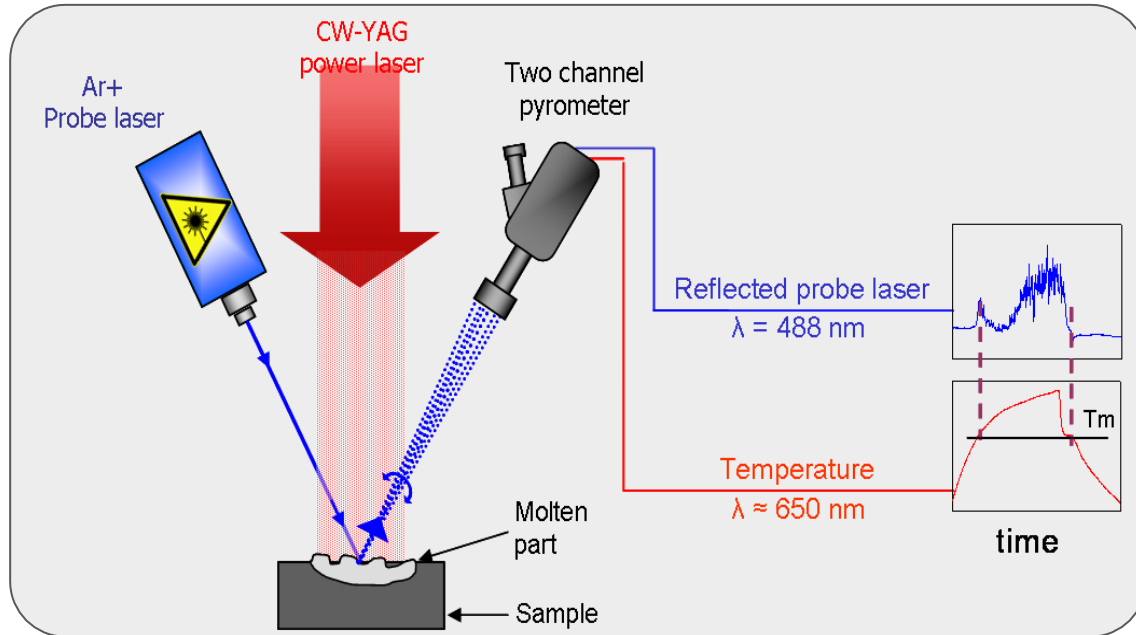
Melting point of $(U,Pu)O_2$

Latta and Fryxell
(J. Nucl. Mater. 1970)

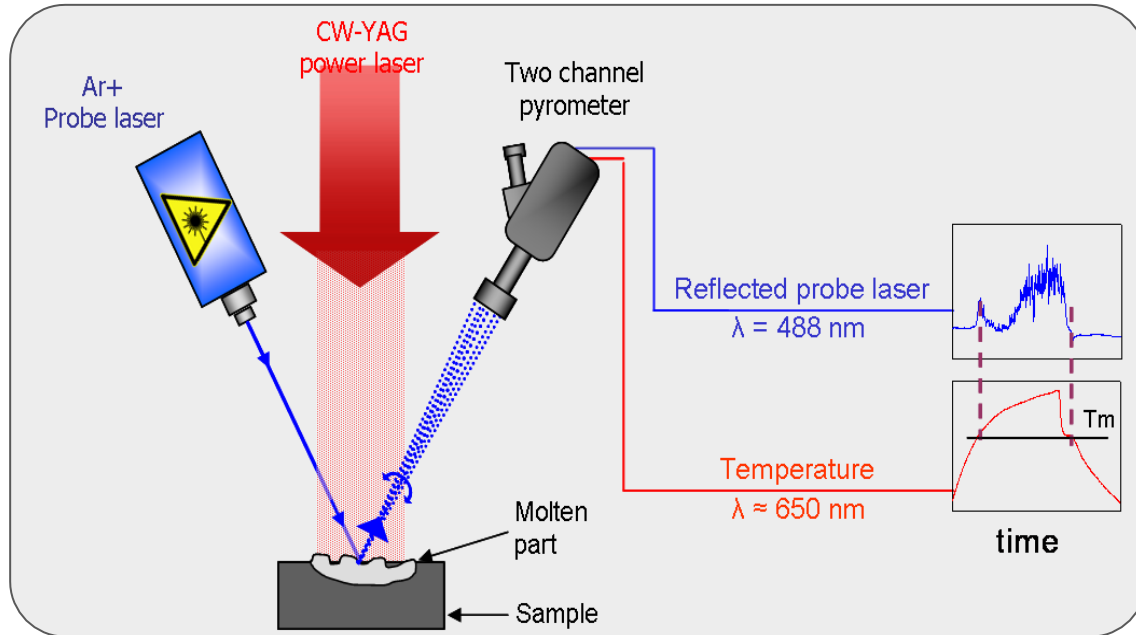
Graphite furnace with
W crucible



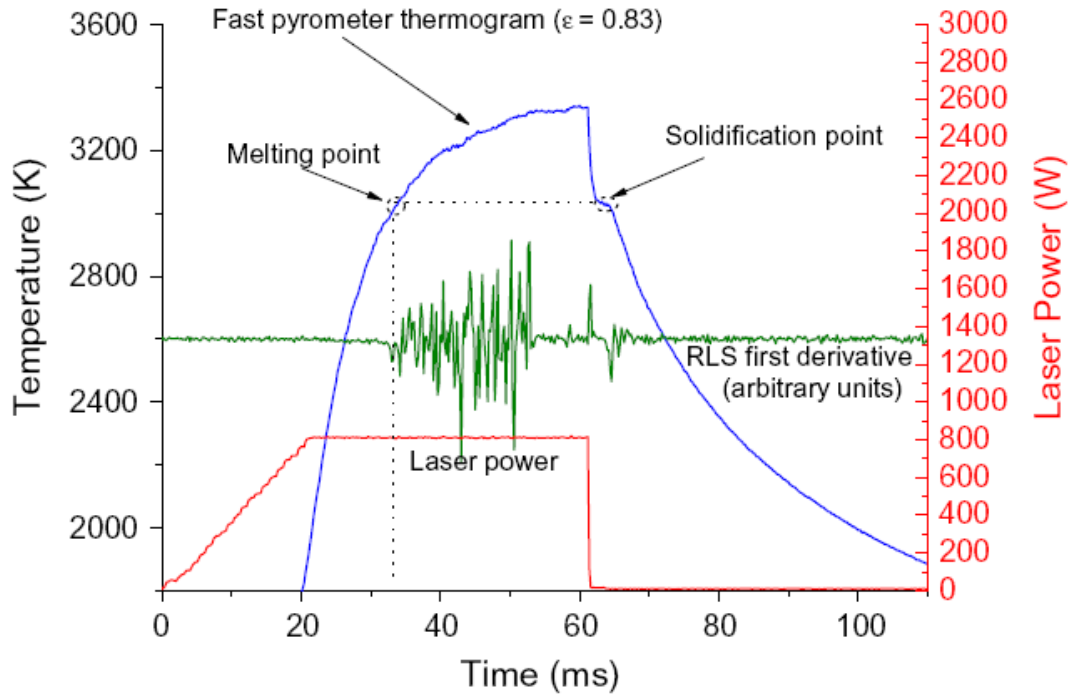
Melting point of $(U,Pu)O_2$



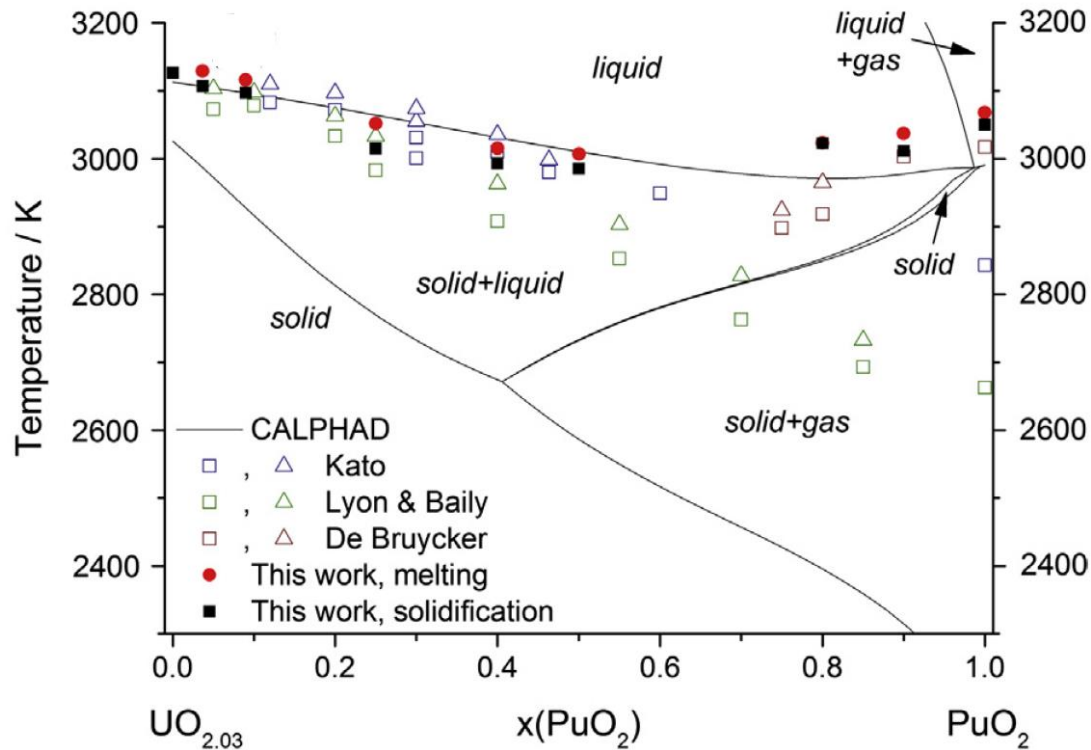
Melting point of $(U,Pu)O_2$



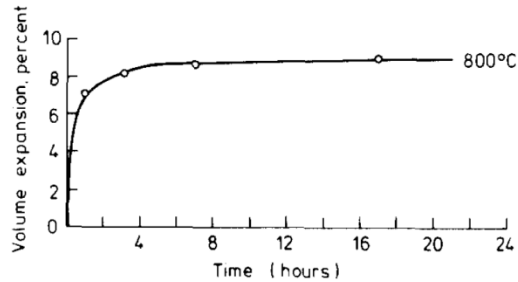
Melting point of $(U,Pu)O_2$



Melting point of $(U,Pu)O_2$

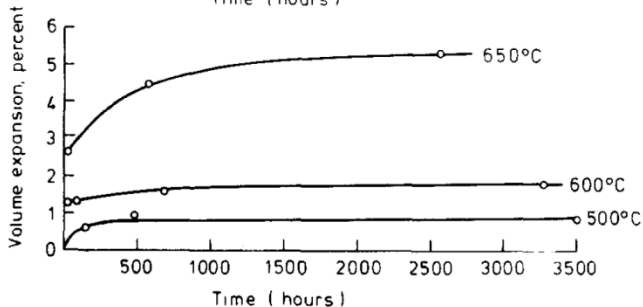
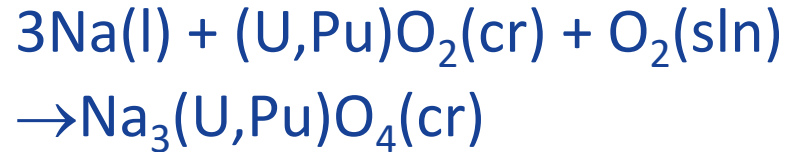
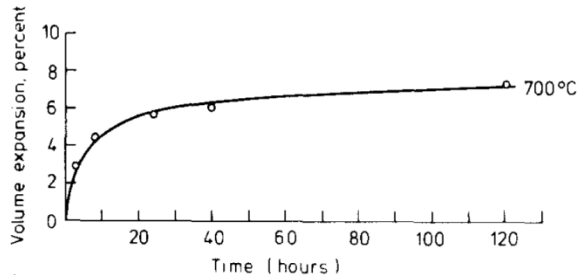


Interaction of (U,Pu)O₂ and sodium

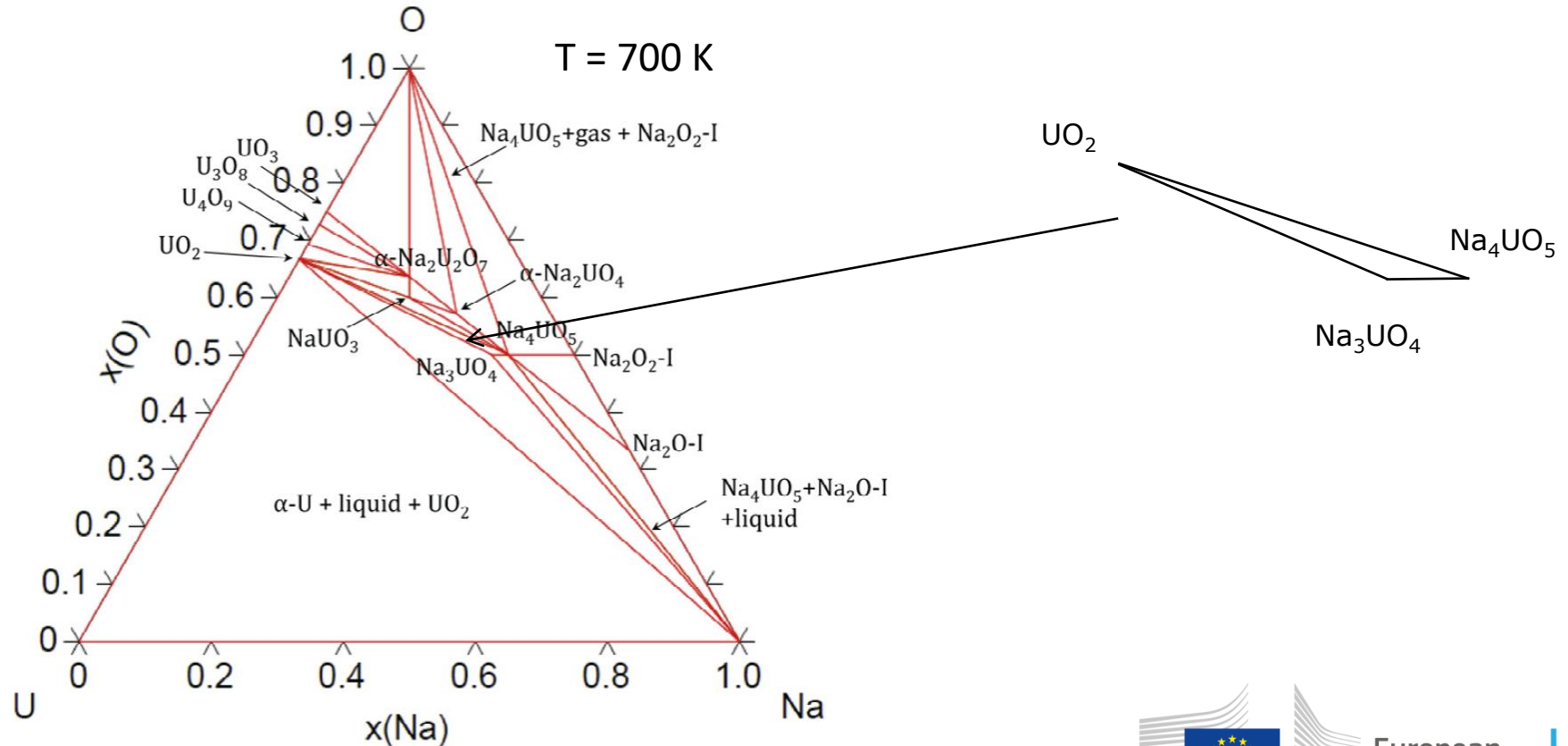


Volume expansion ($\Delta V/V$) of (U_{0.70}Pu_{0.30})O₂ with liquid sodium at various temperatures

Mignanelli and Potter, JNM, 125:182



Interaction of (U,Pu)O₂ and sodium



Interaction of (U,Pu)O₂ and sodium



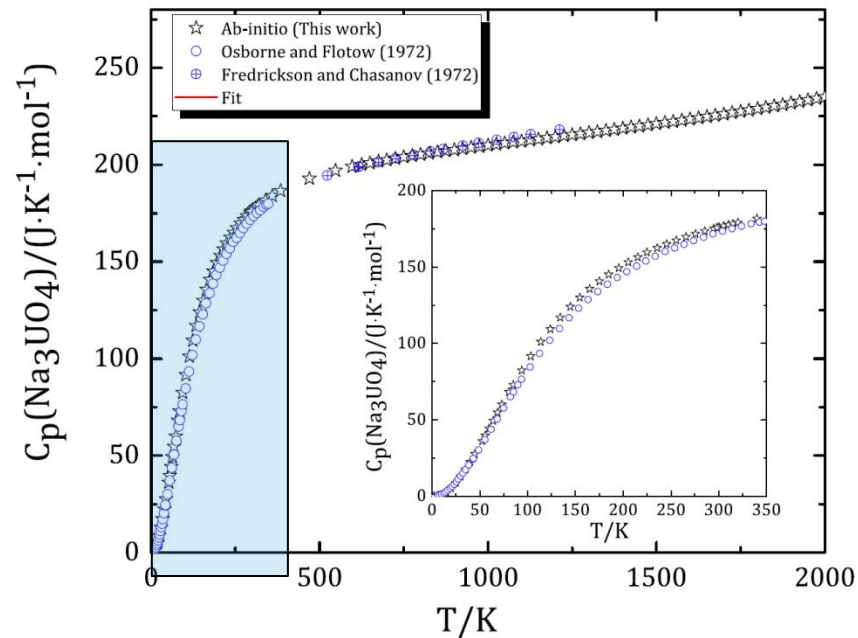
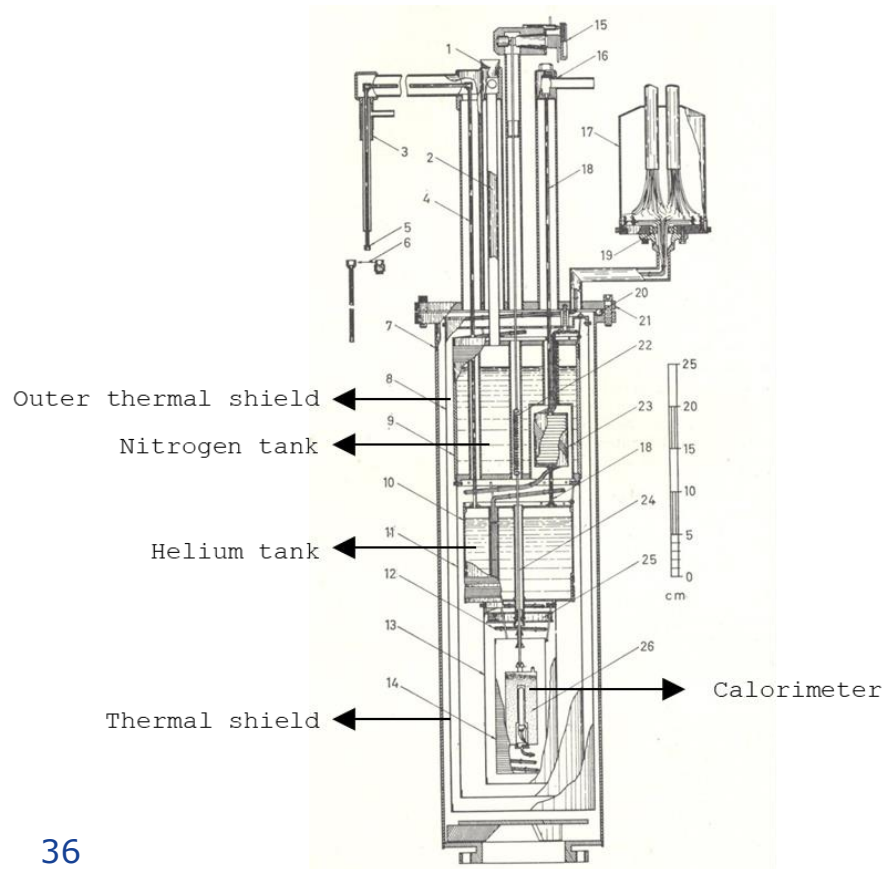
$$\Delta_r G(T) = \underbrace{\Delta_f G(\text{Na}_3\text{UO}_4) - \Delta_f G(\text{UO}_2)} - \Delta_f G(\text{Na}) - \Delta_f G(\text{O}_2, \text{sln})$$

$$\Delta_f G(T) = \Delta_f H(T) - T \times \Delta_f S(T)$$

$$= \Delta_f H(298.15 \text{ K}) + \Delta \{H(T) - H(298.15 \text{ K})\}$$

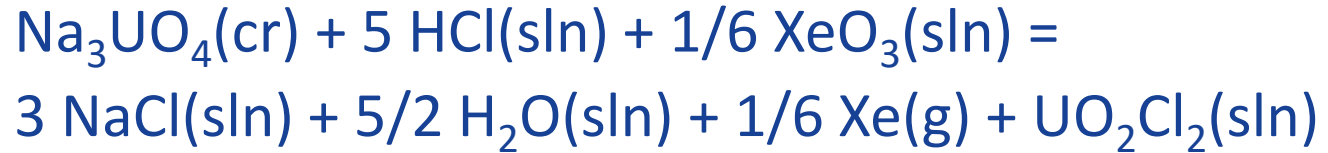
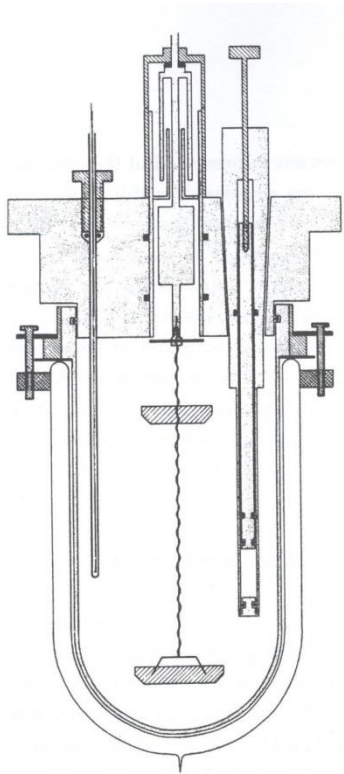
$$= \Delta_f S(298.15 \text{ K}) + \Delta \{S(T) - S(298.15 \text{ K})\}$$

Interaction of (U,Pu)O₂ and sodium



$$S^\circ(298.15 \text{ K}) = (198.20 \pm 0.42) \text{ J K}^{-1} \text{ mol}^{-1}$$

Interaction of (U,Pu)O₂ and sodium

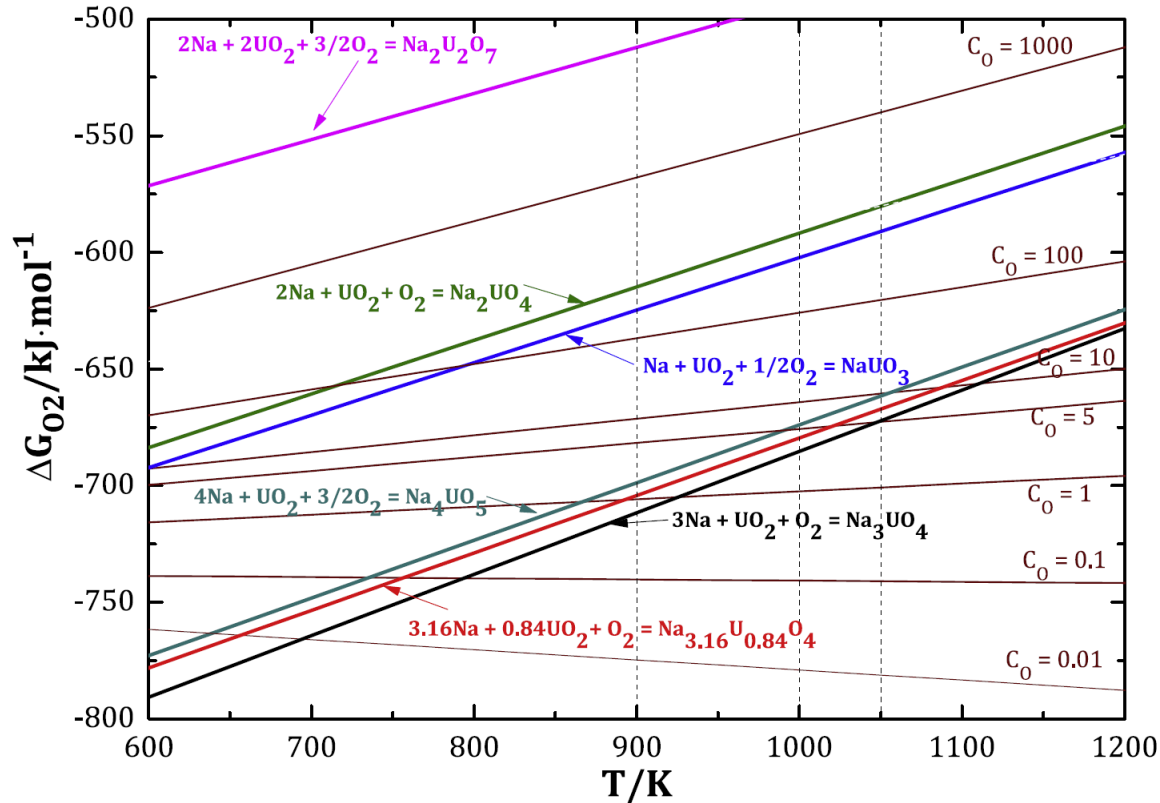


$$\Delta_r H^\circ(298.15 \text{ K}) = -(495.85 \pm 1.04) \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(298.15 \text{ K}) = -(2022.1 \pm 2.5) \text{ kJ mol}^{-1}$$

O'Hare et al., (1978)

Interaction of (U,Pu)O₂ and sodium



Summary:

- Thermodynamics is key for the description of the fuel properties
- Thermodynamics of fuel requires very dedicated facilities to work at high temperatures
- Defect chemistry plays an important role, eventually induced by radioactive decay

Stay in touch



EU Science Hub: [**ec.europa.eu/jrc**](https://ec.europa.eu/jrc)



Twitter: [**@EU_ScienceHub**](https://twitter.com/EU_ScienceHub)



Facebook: [**EU Science Hub - Joint Research Centre**](https://www.facebook.com/EU_Science_Hub_-_Joint_Research_Centre)



LinkedIn: [**Joint Research Centre**](https://www.linkedin.com/company/joint-research-centre)



YouTube: [**EU Science Hub**](https://www.youtube.com/EU_Science_Hub)