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THE CALPHAD (CALculation of PHAsE Diagrams) APPROACH APPLIED TO THE FLUORIDES COMPOUNDS

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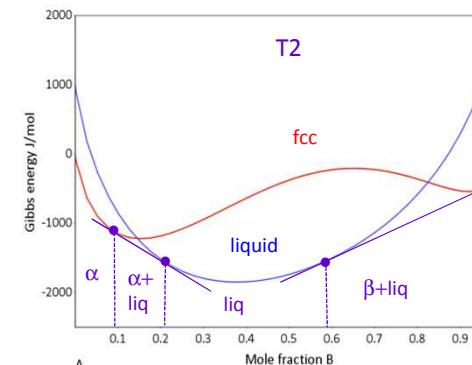
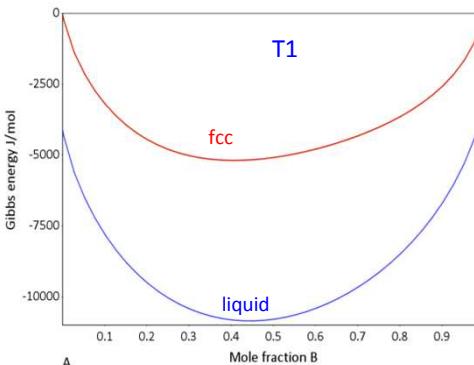
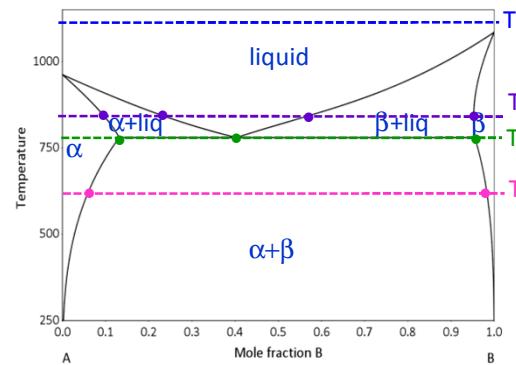


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CALPHAD METHOD

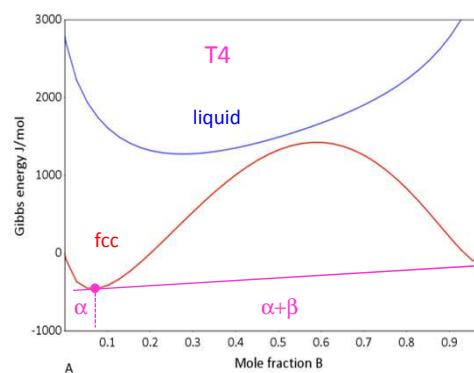
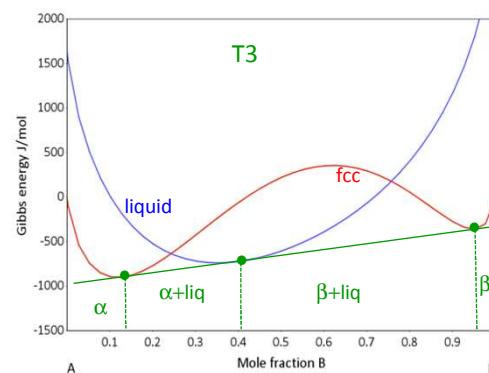
Principle

- Computational method for calculating multicomponent phase diagrams
- Phase diagram = graphical representation of thermodynamic properties
 - ↳ Combination of **thermodynamics (Gibbs energies)** and **phase diagrams** data
- Thermodynamic equilibrium at T, p, N_i is calculated by **minimizing the total Gibbs energy G of the system**



$$G = \sum_{\alpha} n^{\alpha} \cdot G_m^{\alpha}$$

$$x_i = \sum_{\alpha} n^{\alpha} \cdot x_i^{\alpha}$$



$$\min(G) = \min(n^{\alpha} G_m^{\alpha}(T, p, x_i^{\alpha}))$$

Modelling

■ Phases with a fixed composition (pure elements, stoichiometric compounds)

$$G_m^\varphi - b_i H_i^{SER} = a_0 + a_1 T + a_2 T \ln(T) + a_3 T^2 + a_4 T^{-1} + a_5 T^3 + \dots \quad T_1 < T < T_2$$

Enthalpy of the element i in its reference state (298.15 K, 1 bar, denoted SER)

$$H = G - T \left(\frac{\partial G_m}{\partial T} \right)_{p,N_i} \rightarrow H_m^\varphi - b_i H_i^{SER} = a_0 - a_2 T - a_3 T^2 + 2a_4 T^{-1} - 2a_5 T^3 \dots$$

$$S = - \left(\frac{\partial G_m}{\partial T} \right)_{p,N_i} \rightarrow S_m^\varphi = -a_1 - a_2 - a_2 \ln(T) - 2a_3 T + a_4 T^{-2} - 3a_5 T^2 \dots$$

$$C_p = -T \left(\frac{\partial^2 G_m}{\partial T^2} \right)_{p,N_i} \rightarrow C_p = -a_2 - 2a_3 T - 2a_4 T^{-2} - 6a_5 T^2 \dots$$

a_i coefficients are the model parameters assessed when experimental data are available : $C_p=f(T)$, $H_T-H_{298.15K}$, $S^0(298.15K)$, $\Delta H_f^0 \dots$

Modelling

■ Phases with variable composition (solid and liquid solutions)

Gibbs energy
$$G_m = \sum_{i=1}^n x_i G_i^\circ + RT \sum_{i=1}^n x_i \ln(x_i) + G_m^{xs}$$

reference ideal excess

Redlich-Kister *Binary* *Ternary*

$$G_m^{xs} = \sum_i \sum_{j>i} x_i x_j L_{ij} + \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^n x_i x_j x_k L_{ijk}$$

$$L_{ij} = \sum_{v=0}^k (x_i - x_j)^v v L_{ij} = {}^0 L_{ij} + (x_i - x_j) {}^1 L_{ij}$$

$$v L_{ij} = v a_{ij} + v b_{ij} T$$

$$L_{ijk} = v_i {}^i L_{ijk} + v_j {}^j L_{ijk} + v_k {}^k L_{ijk}$$

$$v L_{ijk} = v a_{ijk} + v b_{ijk} T$$

$$v_{i,j,k} = x_{i,j,k} + (1 - x_i - x_j - x_k)/3$$

Modelling

■ Phases with variable composition (solid and liquid solutions)

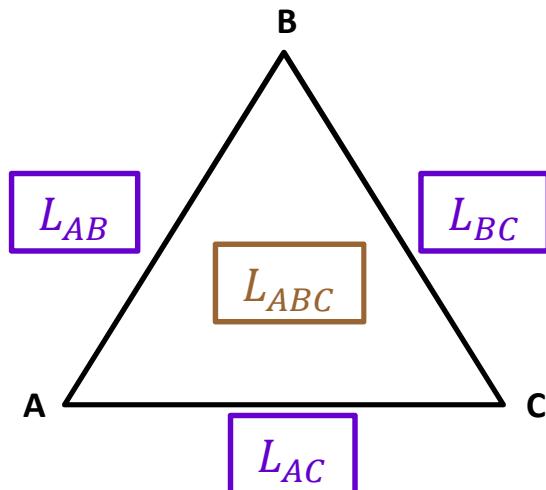
Gibbs energy

$$G_m = \sum_{i=1}^n x_i G_i^\circ + RT \sum_{i=1}^n x_i \ln(x_i) + G_m^{xs}$$

reference ideal excess

$$G_m^{xs} = \sum_i \sum_{j>i} x_i x_j L_{ij} + \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^n x_i x_j x_k L_{ijk}$$

Binary Ternary



Interaction parameters L_{ij} and L_{ijk} are assessed on experimental data

Modelling

■ Gas phase

- Usually described as an ideal mixture of species

$$G_m^{gas} = \sum_i y_i \left[{}^\circ G_i^{gas} - \sum_j b_{ij} H_j^{SER} + RT \ln(y_i) \right] + RT \ln\left(\frac{p}{p_0}\right)$$

- y_i = constituent fractions
- b_{ij} = number of atoms j in species i
- p_0 = standard pressure (1 bar)

Optimization

- In the Gibbs energy functions, the parameters are adjusted to fit the available experimental data using a least-squares method
- When data are scattered or missing
 - New experimental works can be carried out
 - First-principles calculations support can be used

First-principles calculations

Gas molecules

- **1st step:** Optimization of the molecule geometry (E_{cohesive}) and calculation of the vibrational frequencies (ν_i)
- **2nd step:** Thermodynamic properties calculation enthalpy (H), entropy (S), Gibbs energy (G), and heat capacity at constant pressure (Cp) versus temperature

$$H(T) = E_{\text{coh}}(\vec{r}_i) + E_{\text{vib}}(T) + E_{\text{rot}}(T) + E_{\text{trans}}(T) + PV$$

$$H(T) = E_{\text{coh}}(\vec{r}_i) + \frac{R}{k} \frac{1}{2} \sum_i h\nu_i + \frac{R}{k} \sum_i \frac{h\nu_i \exp(-h\nu_i/kT)}{[1 - \exp(-h\nu_i/kT)]} + \frac{3}{2} RT + PV$$

$$\begin{aligned} S(T) &= R \sum_i \frac{h\nu_i / kT \exp(-h\nu_i/kT)}{1 - \exp(-h\nu_i/kT)} - R \sum_i \ln[1 - \exp(-h\nu_i/kT)] \\ &+ S_{\text{rot}} + \frac{5}{2} R \ln T + \frac{3}{2} R \ln M - R \ln P - 2.31482 \\ S_{\text{rot}} (\text{non linear}) &= \frac{R}{2} \ln \left[\frac{\pi}{\sqrt{\sigma}} \frac{8\pi^2 c I_A}{h} \frac{8\pi^2 c I_B}{h} \frac{8\pi^2 c I_C}{h} \left(\frac{kT}{hc} \right)^3 \right] + \frac{3}{2} R \end{aligned}$$

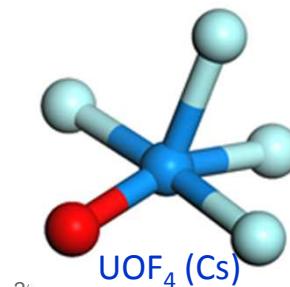
$$C_p = R \sum_i \frac{(h\nu_i/kT)^2 \exp(-h\nu_i/kT)}{[1 - \exp(-h\nu_i/kT)]^2} + \frac{3}{2} R + \frac{5}{2} R$$

M : molecular weight

σ : symmetry number

I_A , I_B and I_C , moment of inertia about principal axis

	Calculation	Measurement
$\Delta H_f^\circ, 298.15K$ (kJ/mol)	-1752	-1762
$S^\circ, 298.15K$ (J/K/mol)	401.7	363
$C_p, 298.15K$ (J/K/mol)	114.4	108
E_{cohesion} (kJ/mol)	2859.2	2861.7



First-principles calculations**Solid compounds**

$$-\left(\frac{\partial F}{\partial T}\right)_V = S \Rightarrow U = F + TS \Rightarrow Cv = \boxed{\left(\frac{\partial U}{\partial T}\right)_V}$$

[J.L. Flèche, Phys. Rev. B, 65 (2002) 245116]

$F = -E_{cohesive}(V) + Nk_B T \left\{ \frac{9}{8} x_D + 3 \ln(1 - e^{-x_D}) - D(x_D) + \sum_{j=1}^{3n-3} \left[\frac{x_j}{2} + \ln(1 - e^{-x_j}) \right] \right\}$

$x_D = \frac{\hbar \bar{v}}{k_B T} k_{max} = \frac{T_D}{T}$

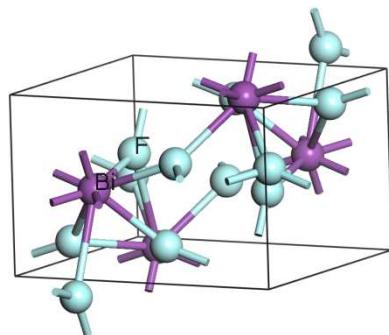
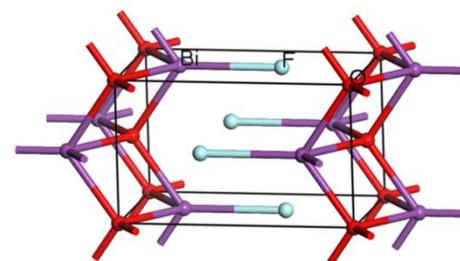
$D(x_D) = \frac{3}{x_D^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx$

$pV = -V \left(\frac{\partial F}{\partial V}\right)_T = V \frac{dE_{cohesive}}{dV} + Nk_B T \left\{ \gamma_{acoustic} \left[\frac{9}{8} x_D + 3D(x_D) \right] + \gamma_{optic} \sum_{j=1}^{3n-3} \left[\frac{x_j}{2} + \frac{x_j}{e^{x_{j-1}}} \right] \right\}$

$x_j = \frac{h v_j(0)}{k_B T}$

$-V \left(\frac{\partial p}{\partial V}\right)_T = B_T \Rightarrow \boxed{\alpha_p = \frac{1}{B_T} \left(\frac{\partial p}{\partial T}\right)_V} \rightarrow \boxed{Cp = Cv + TVB_T \alpha_p^2}$

Unknown: $E_{cohesive}(V)$, $v_j(0)$, \bar{V} or T_D , $\gamma_{optical}$ and $\gamma_{acoustical}$
deduced from first-principles calculations (CASTEP code)

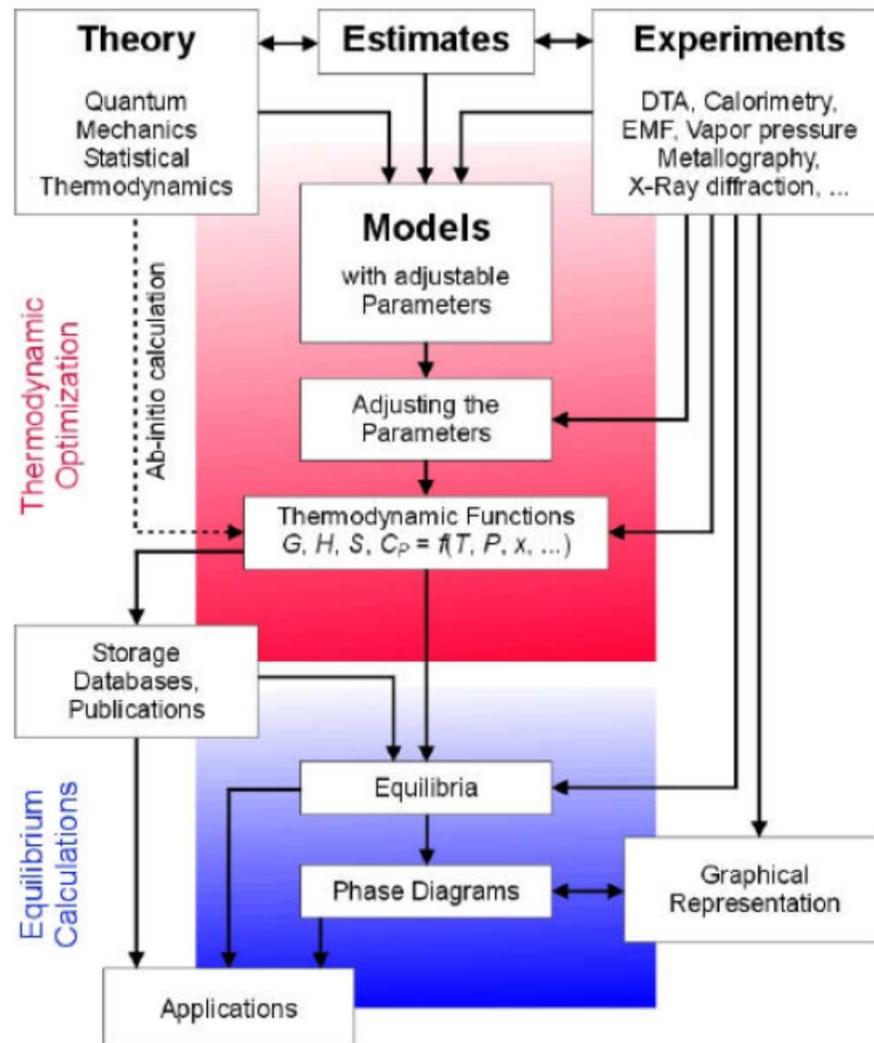
First-principles calculations**Solid compounds** BiF_3  BiOF 

	Calculation
$\Delta H^\circ_{\text{f}, 298.15\text{K}} (\text{kJ/mol})$	-1086.5
$S^\circ_{298.15\text{K}} (\text{J/K/mol})$	127.1
$C_p, 298.15\text{K} (\text{J/K/mol})$	93.0

	Calculation
$\Delta H^\circ_{\text{f}, 298.15\text{K}} (\text{kJ/mol})$	-659.0
$S^\circ_{298.15\text{K}} (\text{J/K/mol})$	77.3
$C_p, 298.15\text{K} (\text{J/K/mol})$	114.4

CALPHAD method

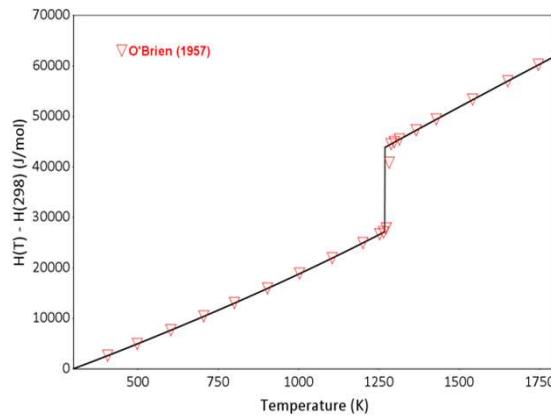
Flowchart



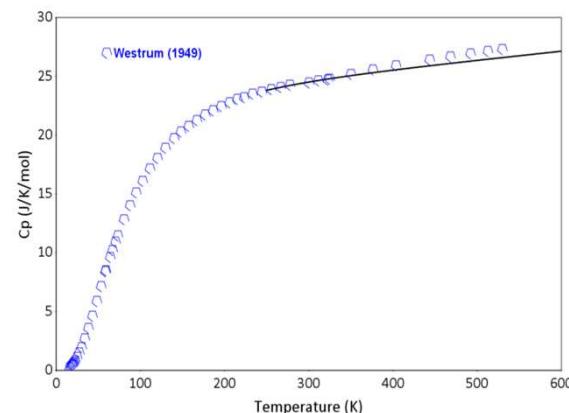
Applications

Thermodynamic properties calculations

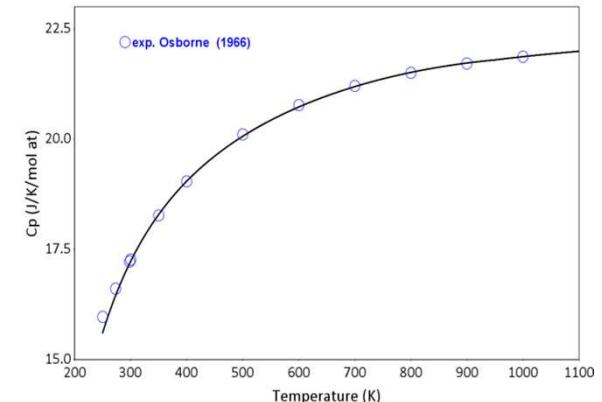
NaF enthalpy increment



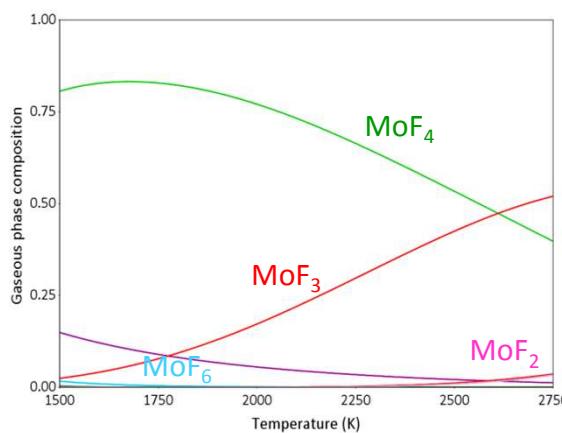
KF heat capacity



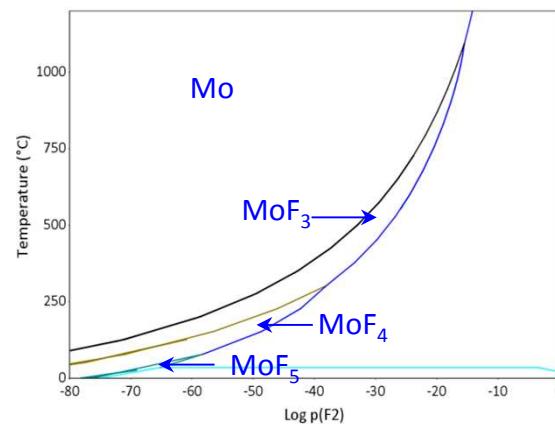
MoF_6 gas heat capacity



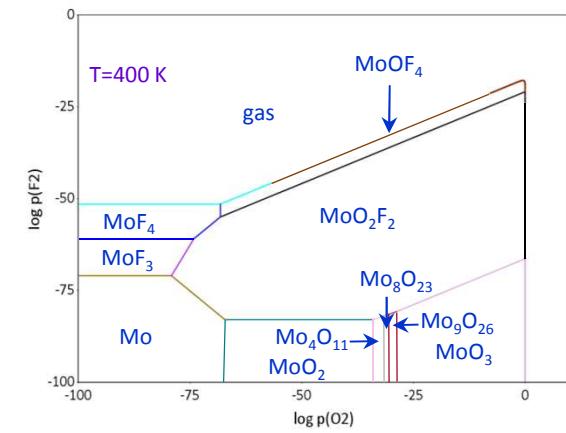
Vapor composition (Mo-F)



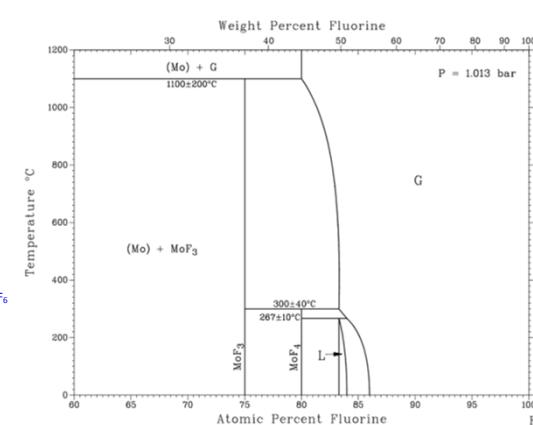
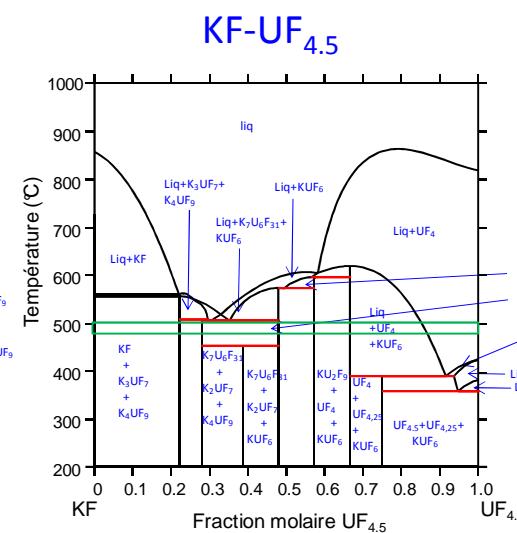
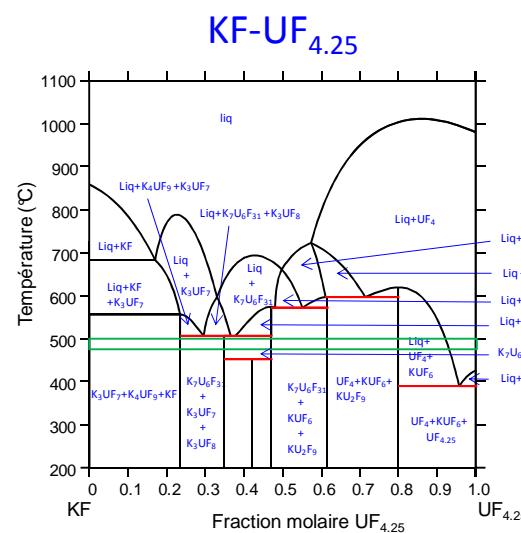
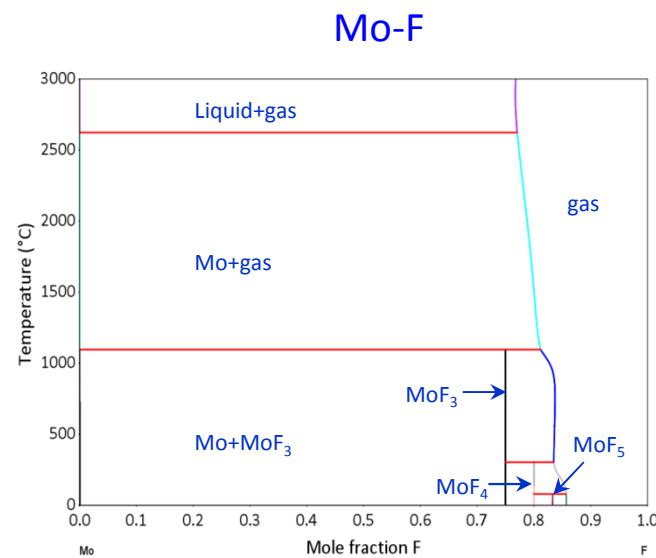
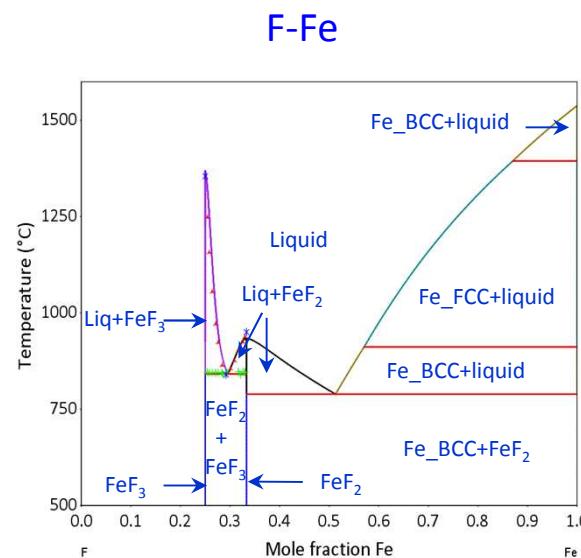
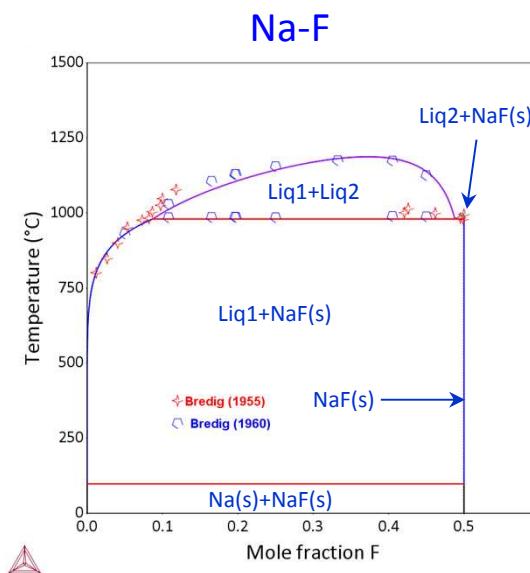
Potential diagram (Mo-F)



Potential diagram (Mo-O-F)



Phase diagrams calculations



Conclusions and perspectives

Conclusions

- CALPHAD is a suitable computational method to accurately model the thermodynamic and phase diagram data for multicomponent systems (ex: TAF with 40 elements)
- BUT reliable experimental data (phase diagram and thermodynamic properties) are absolutely necessary
- Lack of data on fluoride and oxyfluoride compounds
 - ⇒ first-principles calculations
 - ⇒ experimental program
- Databases are useful to interpret or predict results on complex chemical systems

Perspectives

- Thermodynamic databases can be coupled with kinetic databases to solve diffusion equations (1 D) (assessment of mobility parameters)
- Development of nano-CALPHAD to deal with thermodynamics and phase diagrams for nanoparticles

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Thank you for your attention

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