Pyrochemical methods for fuel salt reprocessing

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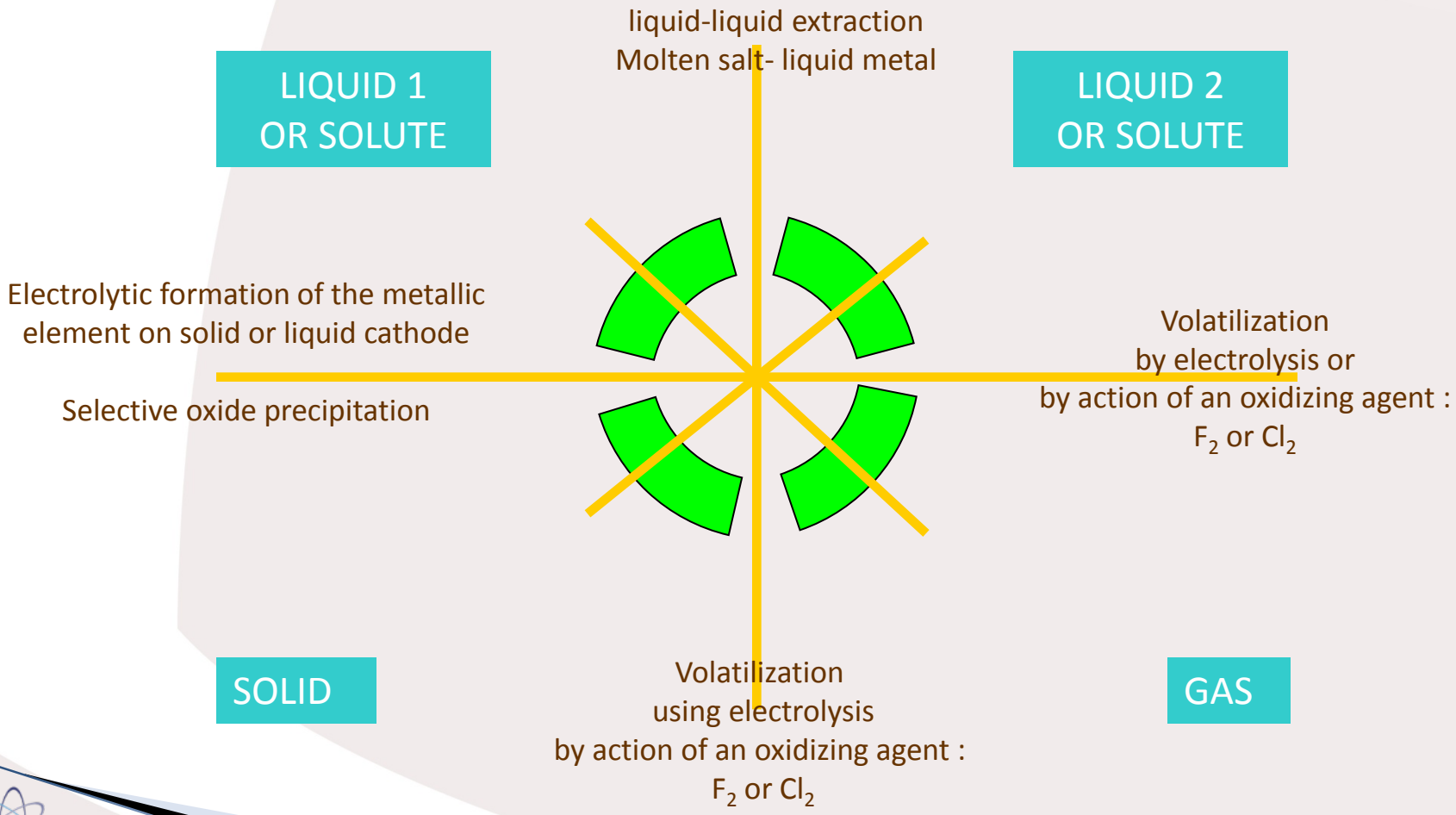
Separation techniques in pyrochemistry



Separation techniques in pyrochemistry

REAGENT STATE	USED EFFECT	METHODS		PRODUCT STATE
SOLUTE (in fluoride or chloride media) (M^{n+})	**A- REDOX** (oxidation state modification)	A1- Action of an oxidizing agent F_2, Cl_2		**GAS** (MF_x)
		A2- Action of an oxidizing electrical current		
		A3- Action of a reducing agent e.g. Li	**METAL** (M)	**SOLID**
		A4- Action of a reducing electrical current		**SOLUTE** (in liquid metal solvent)
	B- ACIDO-BASICITY (oxide precipitation solubilization)	B1- Action of oxide ions donors (e.g. Li_2O)		**SOLID** (MO_x)
		B2- Action of gaseous mixtures $H_2O/HF/H_2$		

- ***Thermodynamic approach / experimental studies***

  - Oxoacidity concept (Lux (1939) and Flood (1947)) in molten salts equivalent to acidity in aqueous solution

  - O^{2-} : abundant ion, high stability with metallic cations, redox system O_2/O^{2-}

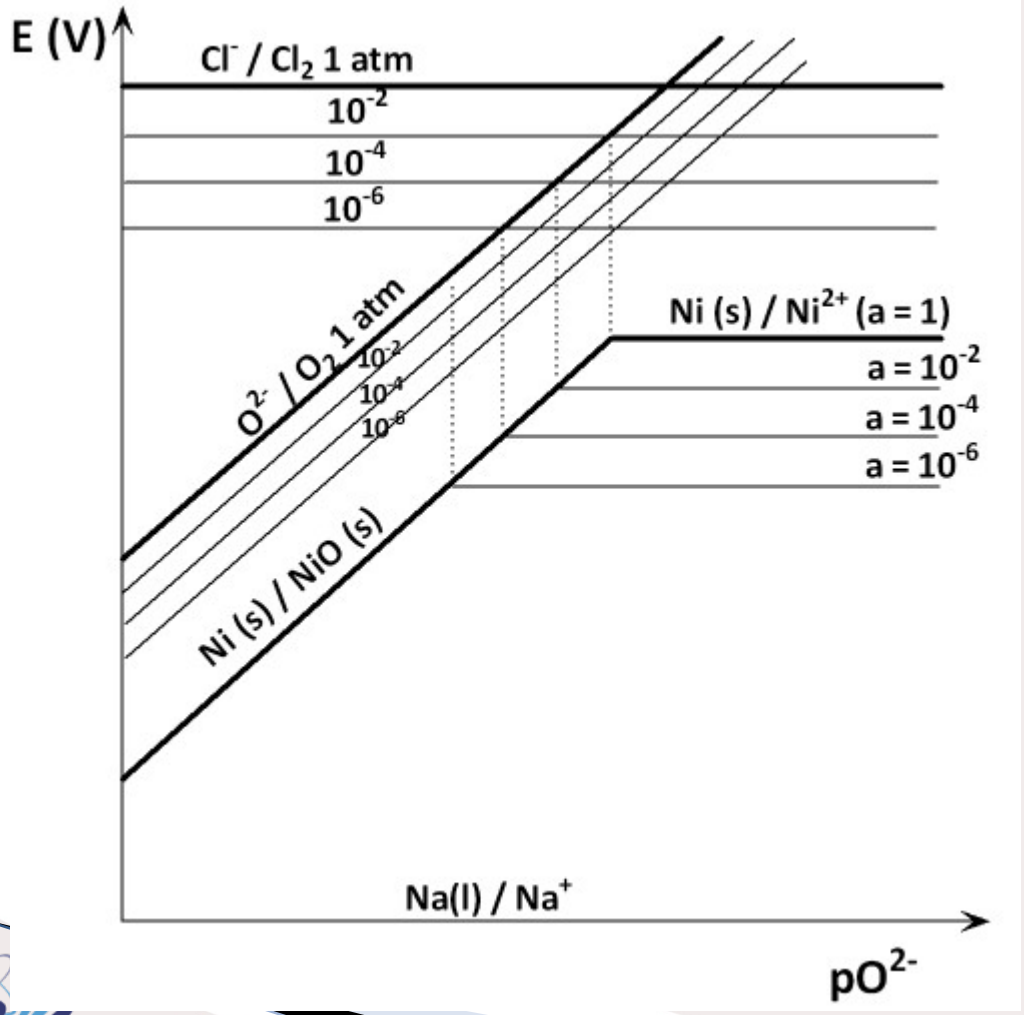
    - $H_2O + F^- (Cl^-) \rightarrow 2HF (HCl) + O^{2-}$

Oxobase/oxoacid systems:

$$\text{oxobase} = \text{oxoacid} + O^{2-}$$

Oxoacidity : $pO^{2-} = - \log a(O^{2-})$

- ***Calculation of E – pO^{2-} diagrams (similar to E-pH diagrams)***
  - Example : Ni stability diagram in NaCl molten salt



½ O_2 (g) + 2Cl^- = ½ Cl_2 (g) + O^{2-}

A gaseous mixture of Cl_2 and O_2 control potential and acidity of the molten salt

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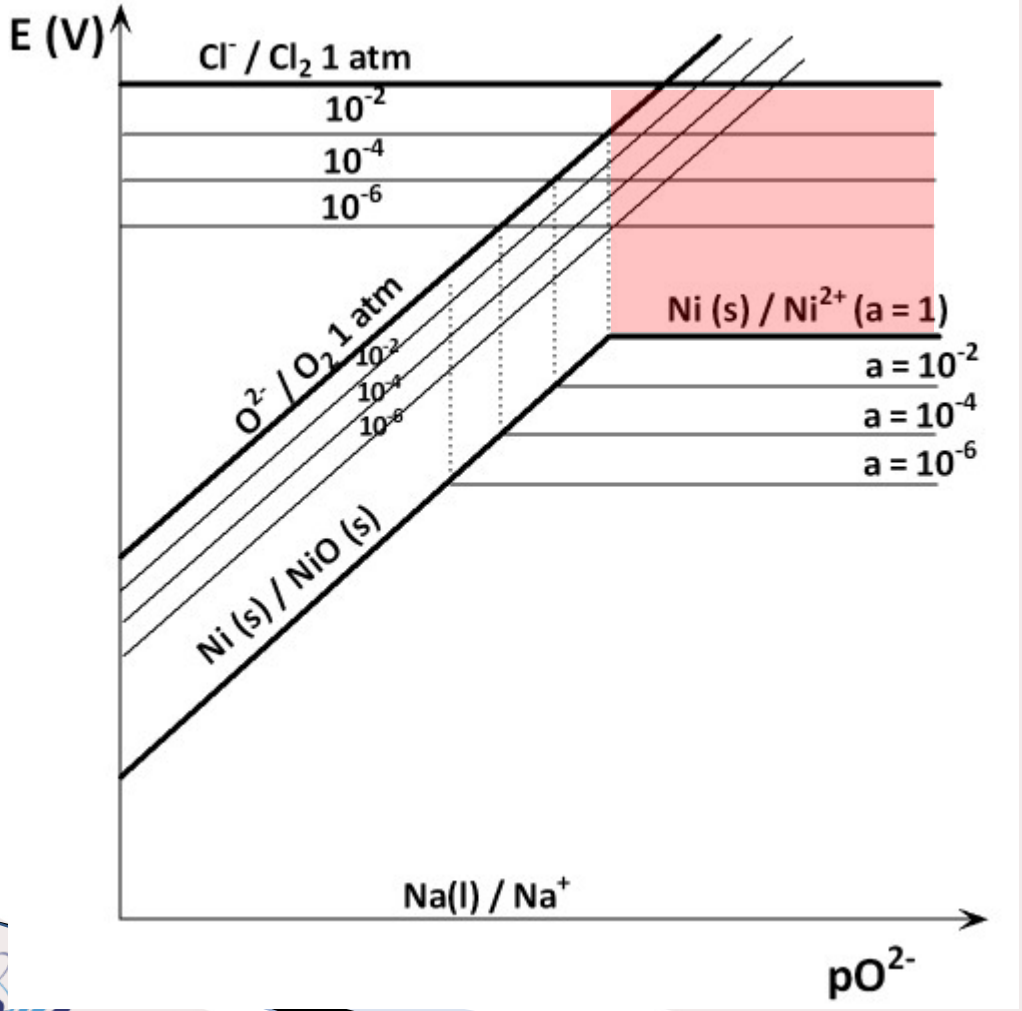

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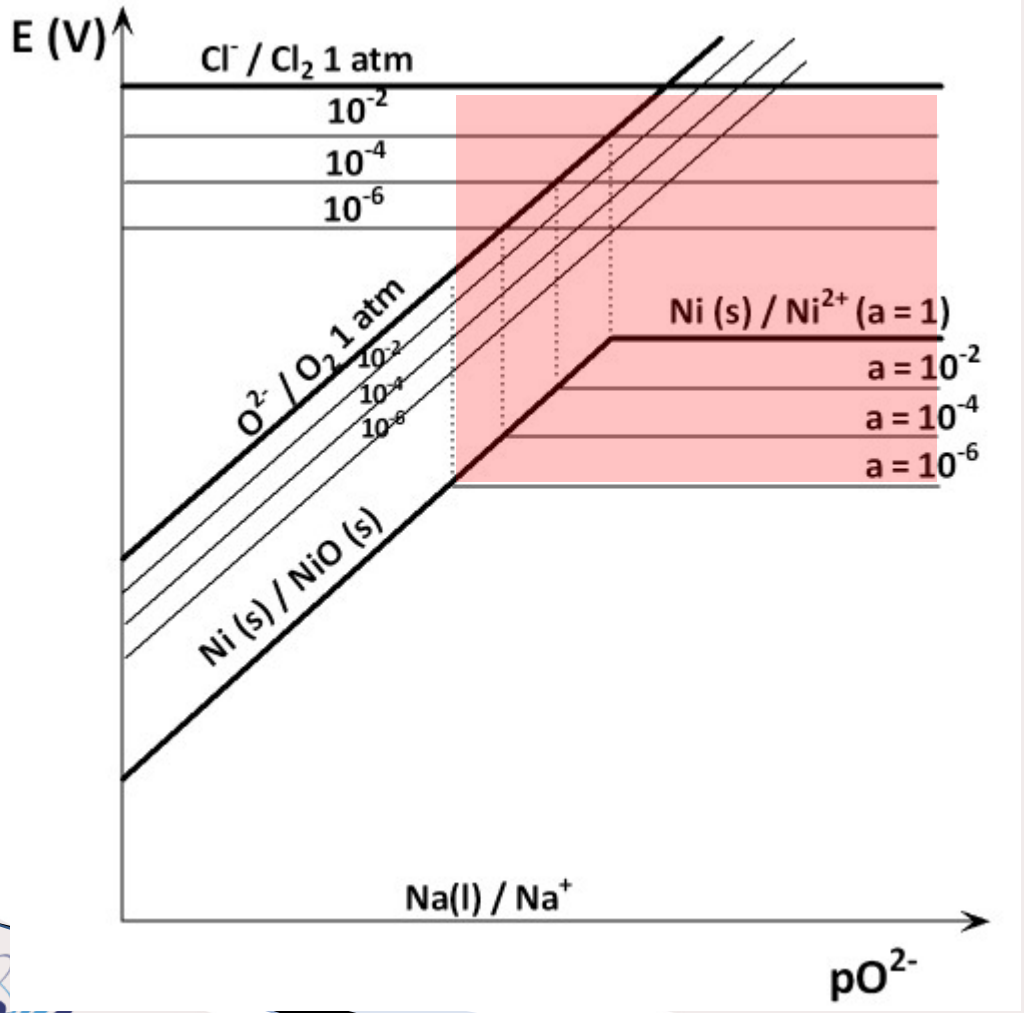

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A gaseous mixture of Cl_2 and O_2 control potential and acidity of the molten salt

- ***Calculation of E – pO^{2-} diagrams***

  - Influence of activity coefficients

    - a (M) = x(M) * γ (M)

    - γ (M) represents the affinity of an element for the solvent
      γ (M) = 1 : no affinity
      Affinity increases = γ (M) decreases

      = Increase of the stability range of the element

Chemistry in molten salts

- Dissociation of the salts:
  - $(Li, Na, K)(F, Cl) \rightarrow (Li, Na, K)^{+} + (F, Cl)^{-}$
    - **MX is a basic salt**
  - $(Be, Mg, Ca, Ba, Th)(F, Cl)_2 + x(F, Cl)^{-} \rightarrow (Be, Mg, Ca, Ba, Th)(F, Cl)_{x+2}^{x-}$
    - **MX_2 is an acidic salt**
- In a molten salt constituted of MX and MX_2, the amount of free X^{-} depends on the ratio of MX over MX_2.
- The activity of solutes introduced in the molten salt depends on the acidity (fluoro- or chloroacidity) of the salt.

Thermodynamic diagrams

Comparison Fe in aqueous solution and in LiCl-KCl (1)

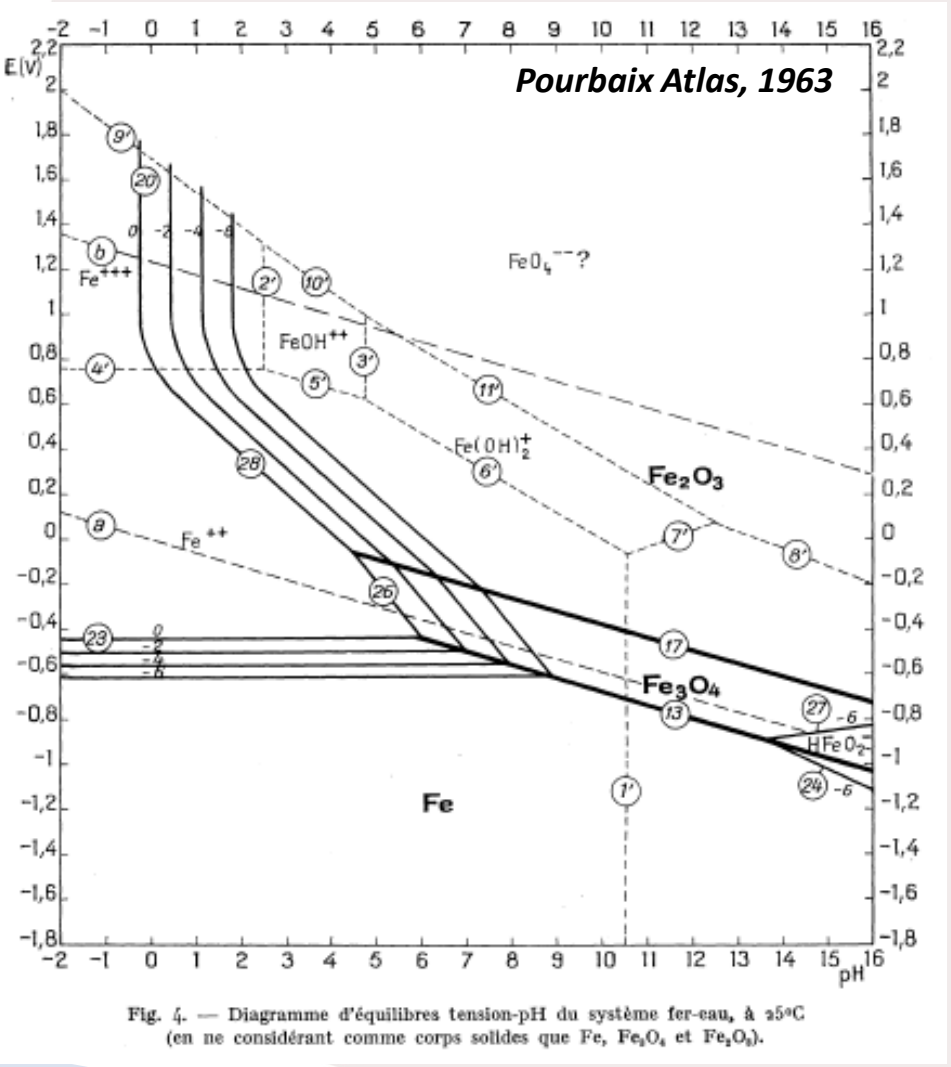
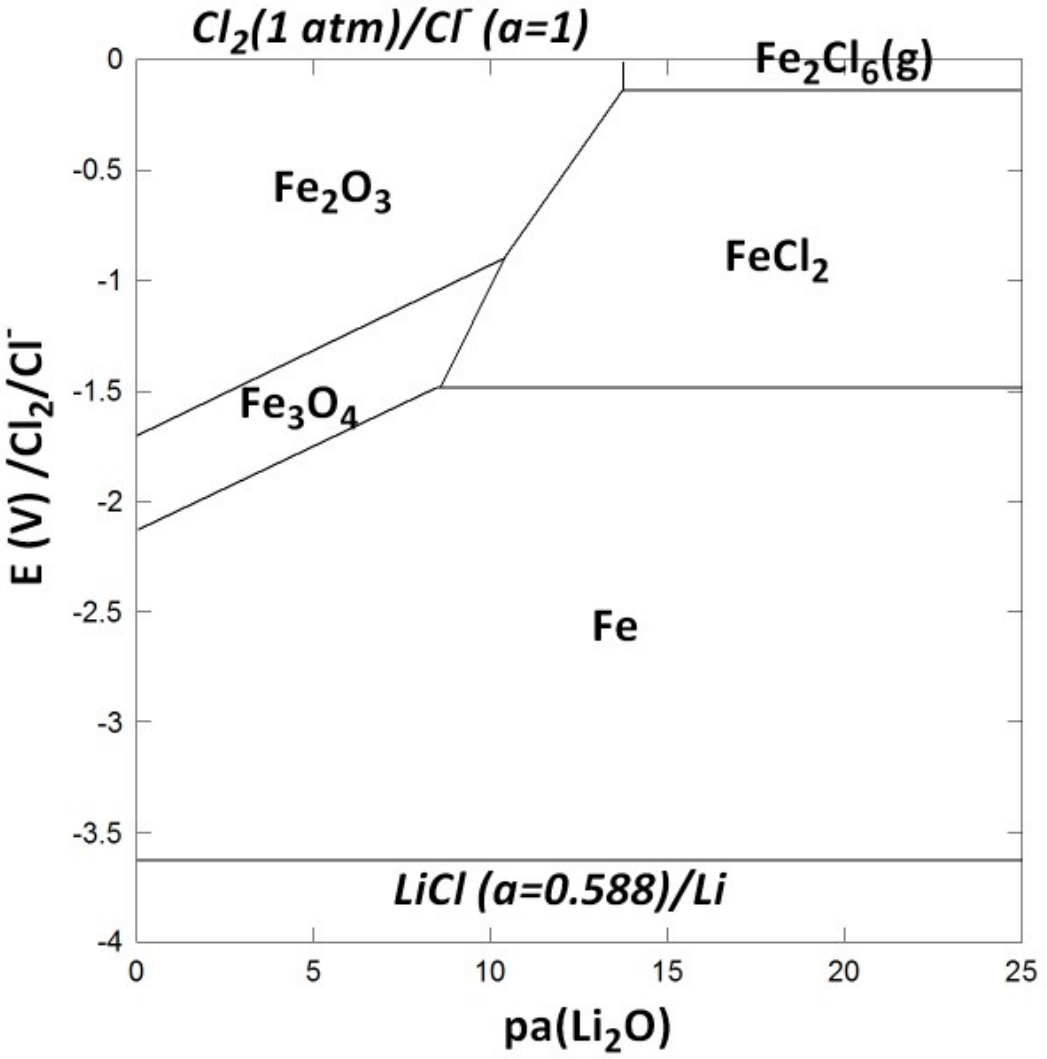


Fig. 4. — Diagramme d'équilibres tension-pH du système fer-eau, à 25°C (en ne considérant comme corps solides que Fe, Fe_3O_4 et Fe_2O_3).

Thermodynamic diagrams

Comparison Fe in aqueous solution and in LiCl-KCl (2)



$pa(Li_2O) = - \log a(Li_2O)$

Li_2O represents the amount of oxide ions dissolved in the salt

Thermodynamic diagrams

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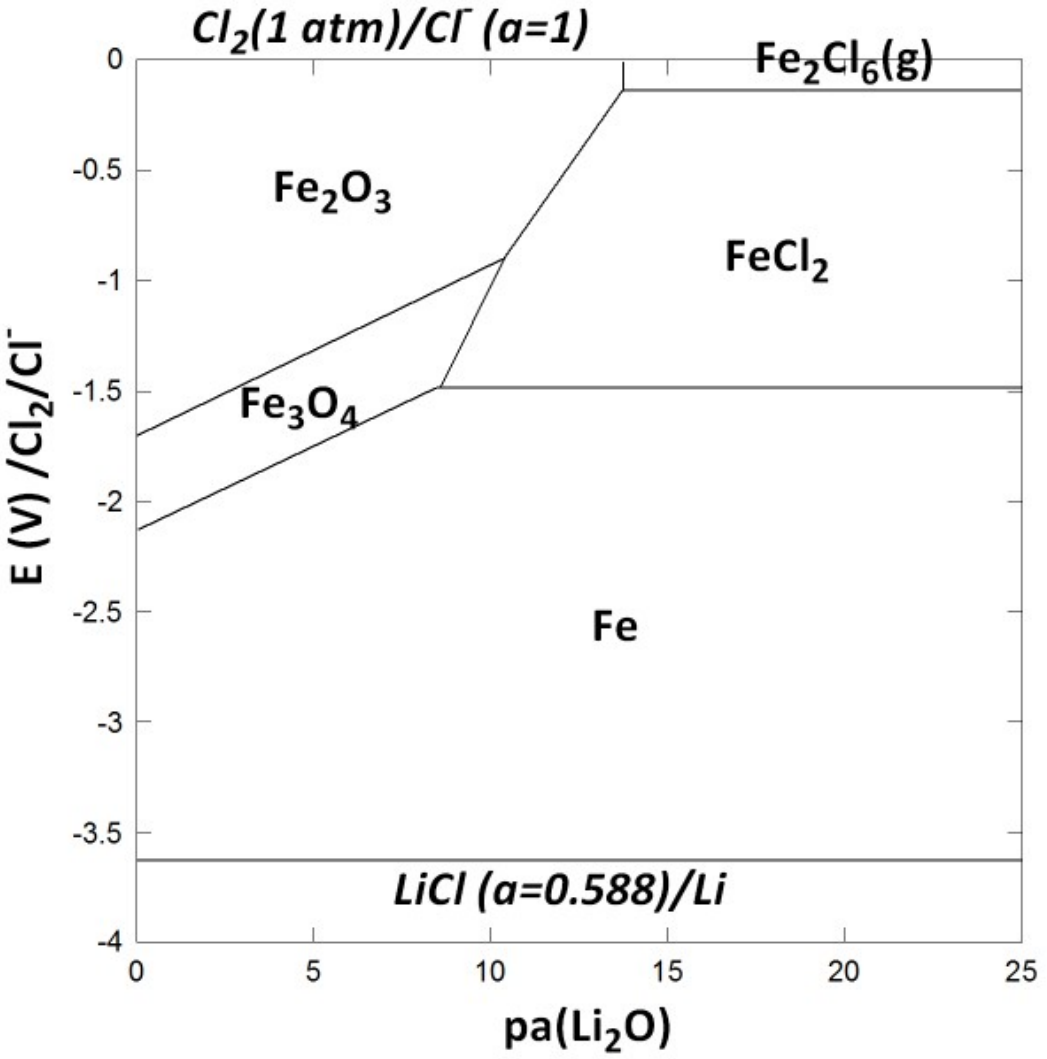

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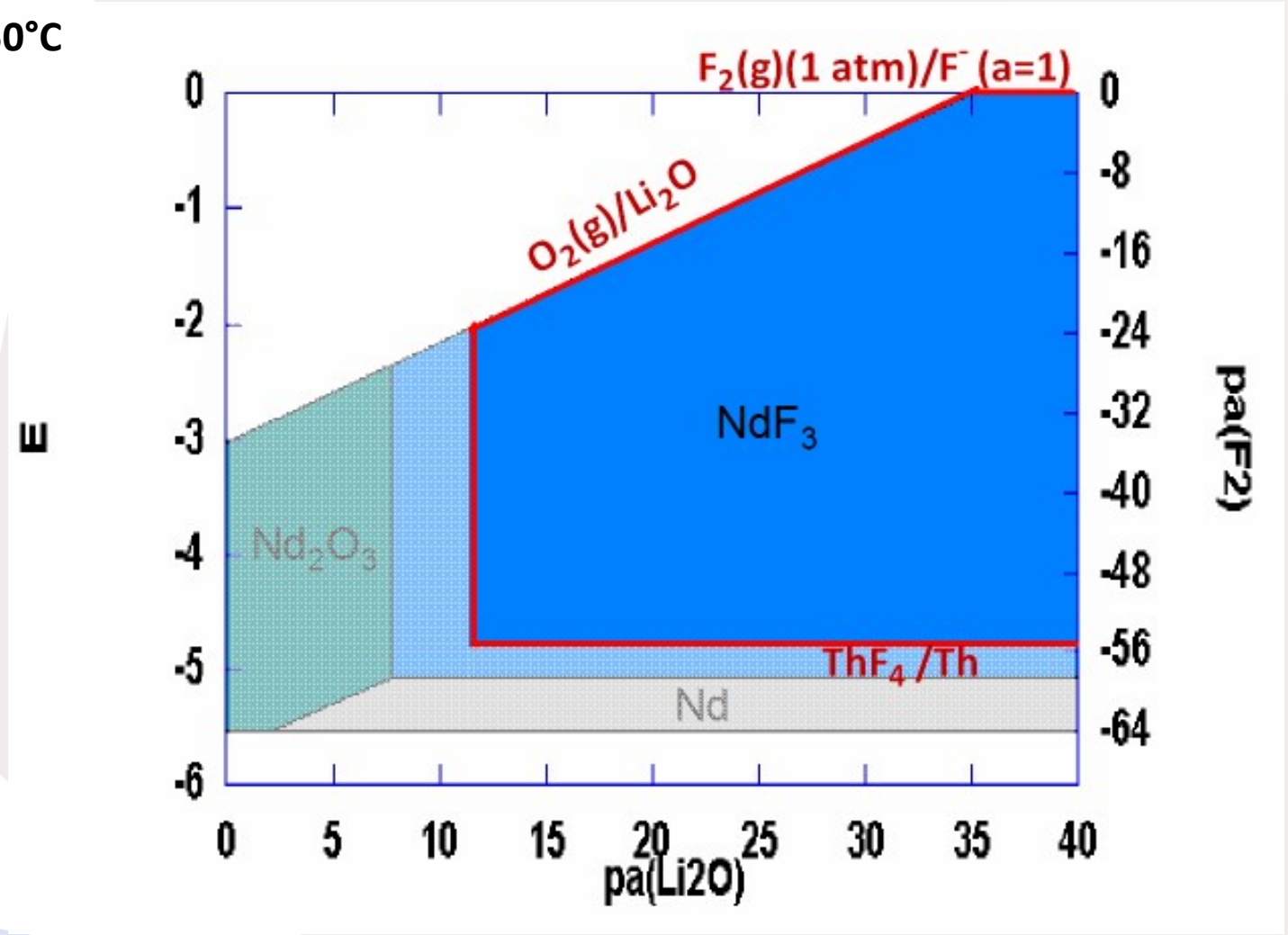
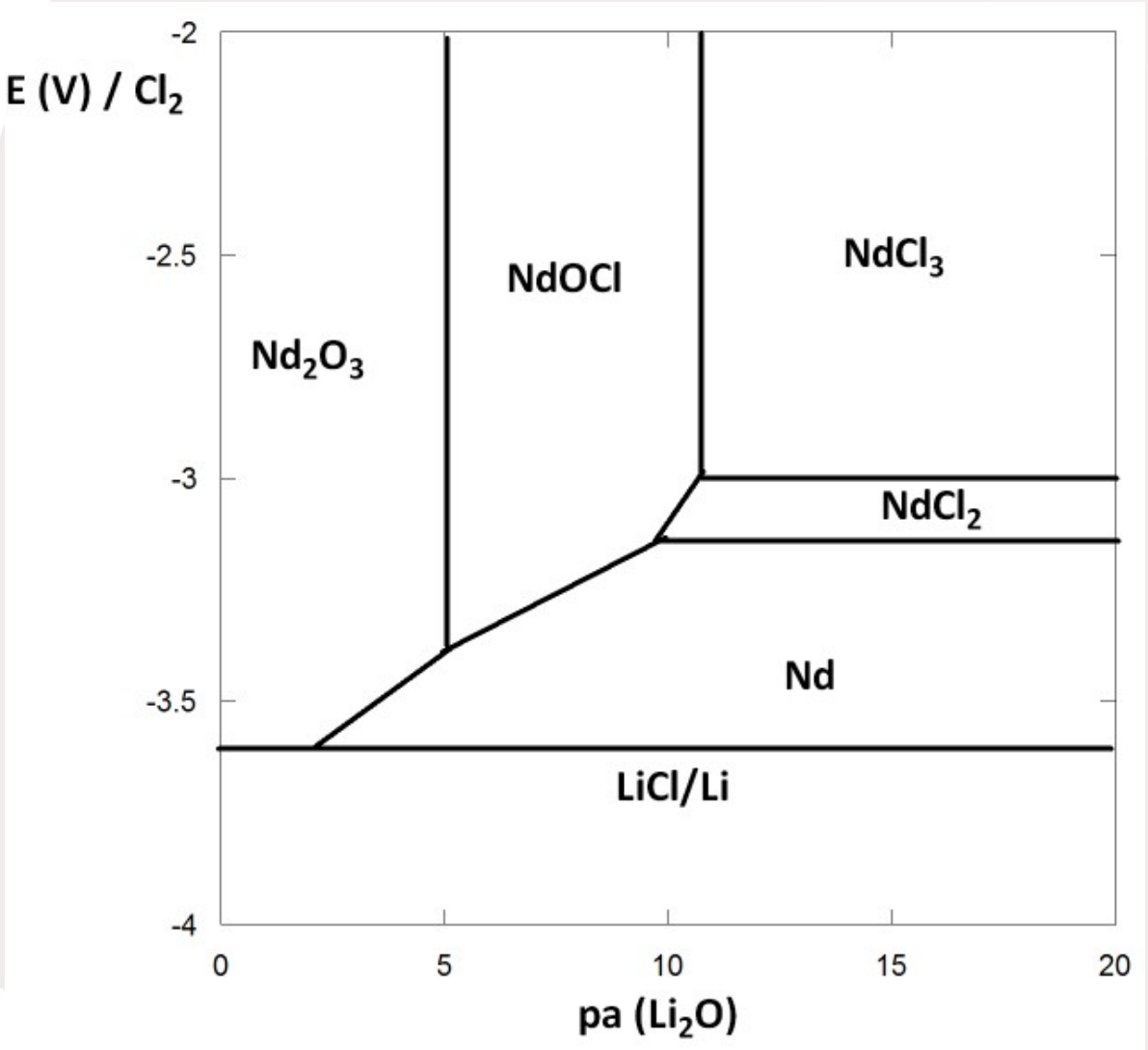
LiF – ThF_4 650°C



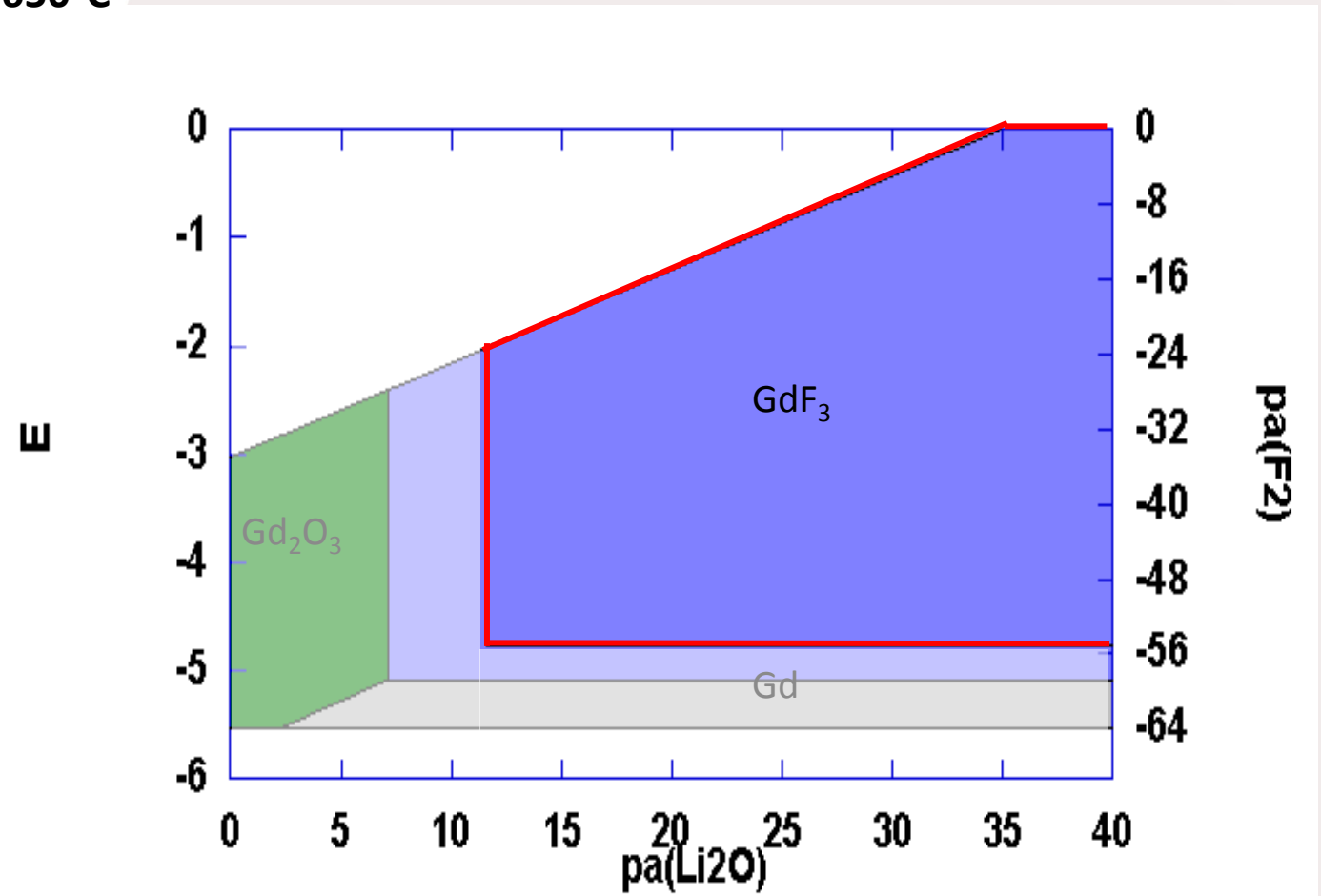
Thermodynamic diagrams

LiCl-KCl 500°C

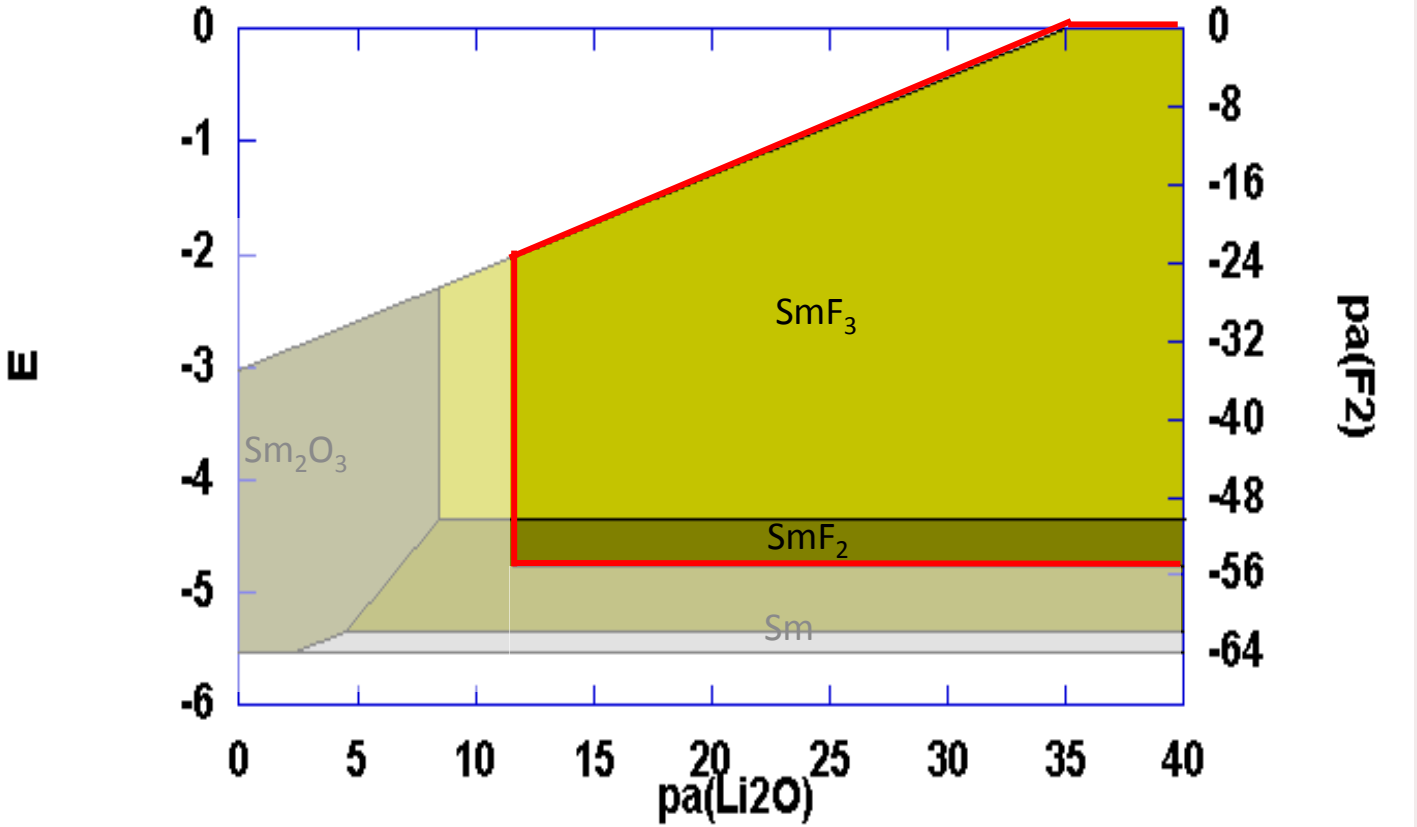


Thermodynamic diagrams

LiF – ThF_4 650°C

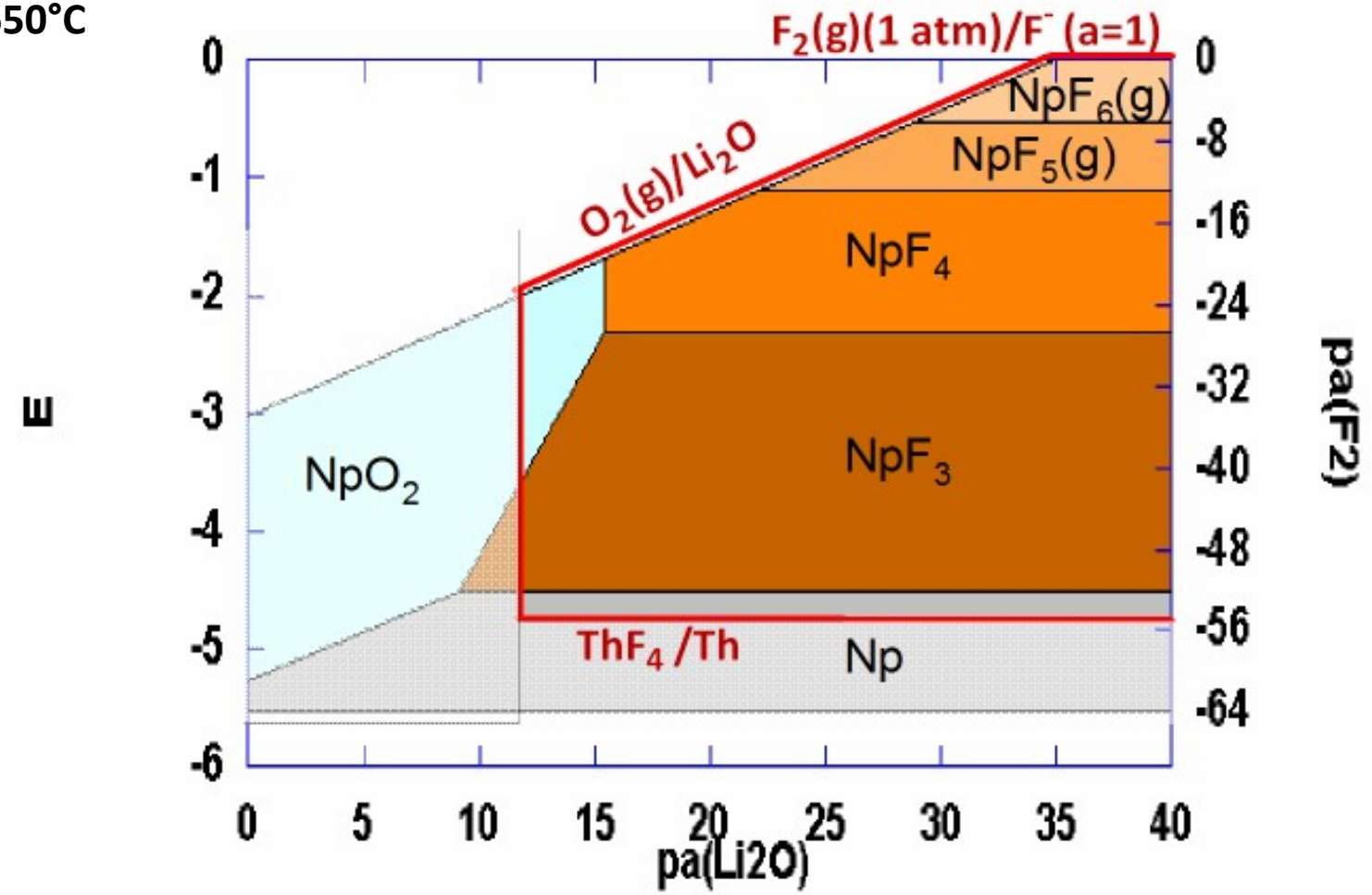


LiF – ThF_4 650°C



Thermodynamic diagrams

LiF – ThF_4 650°C



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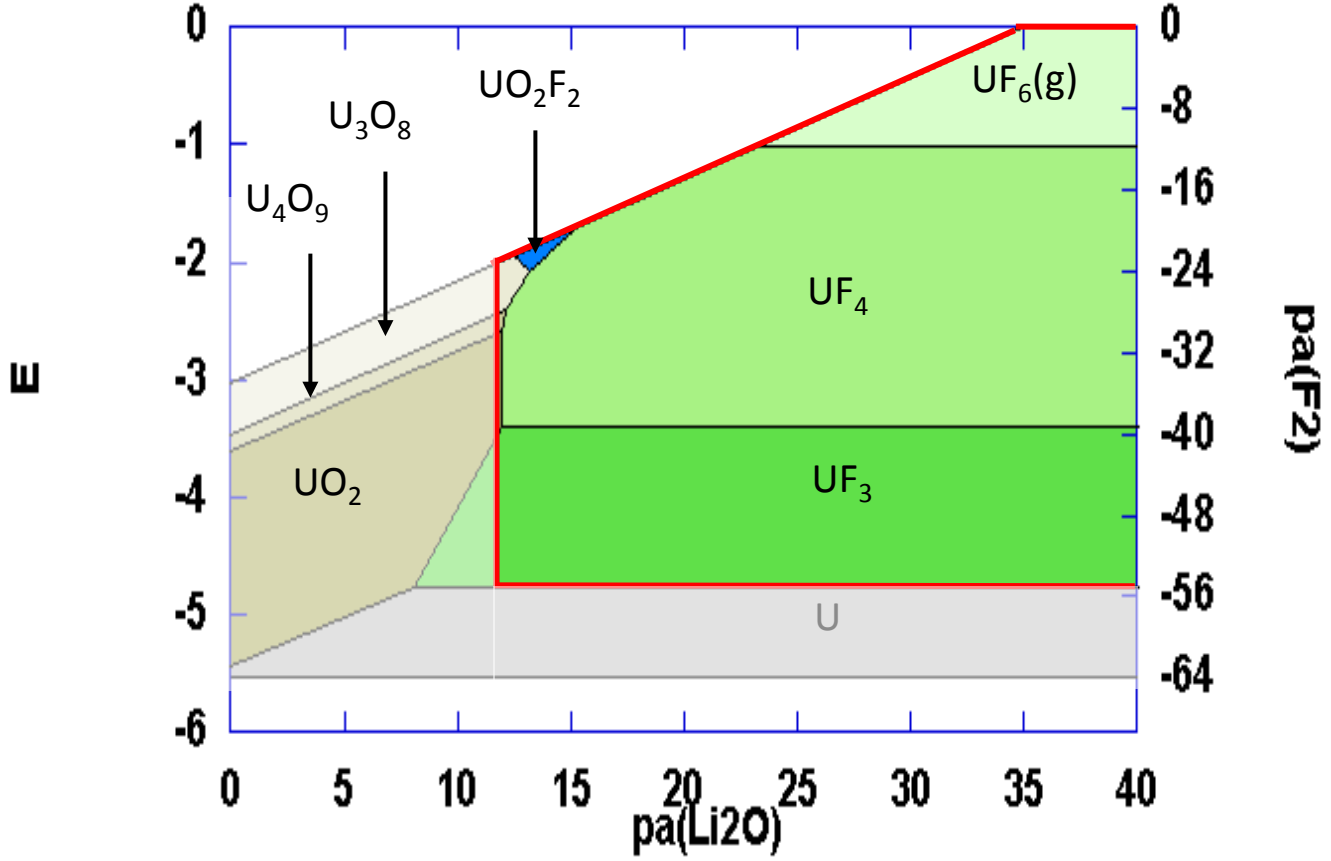
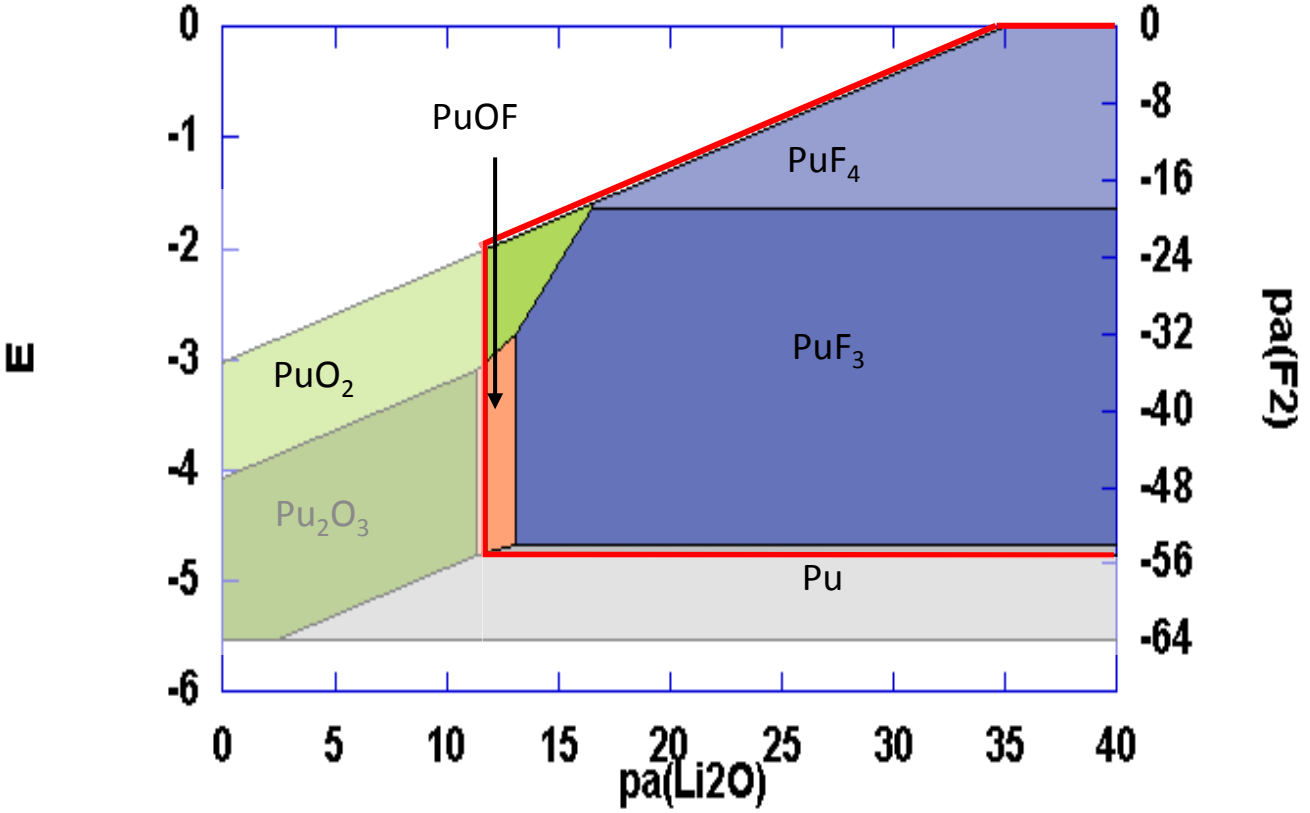


Thermodynamic diagrams

LiF – ThF_4 650°C



Thermodynamic diagrams

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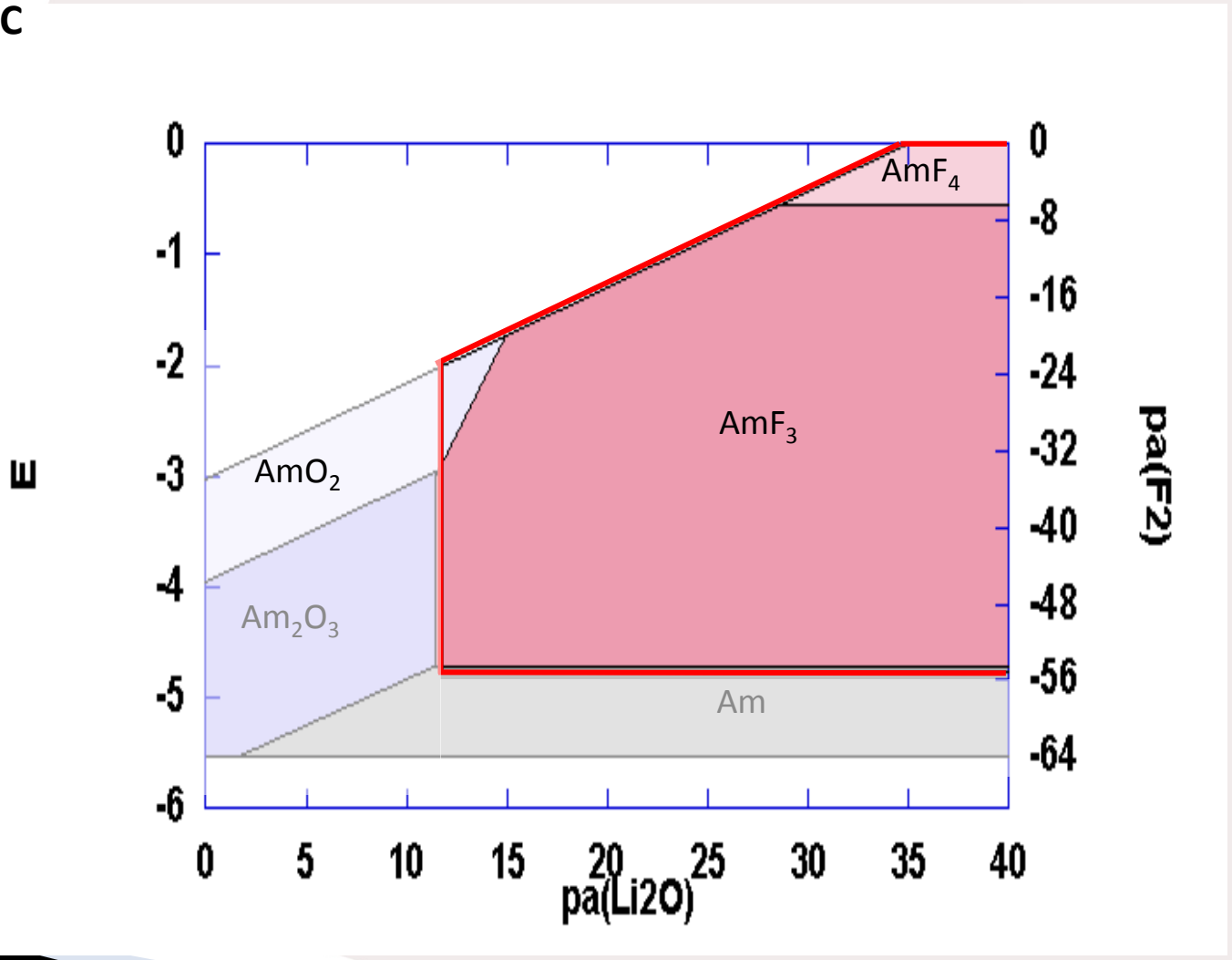
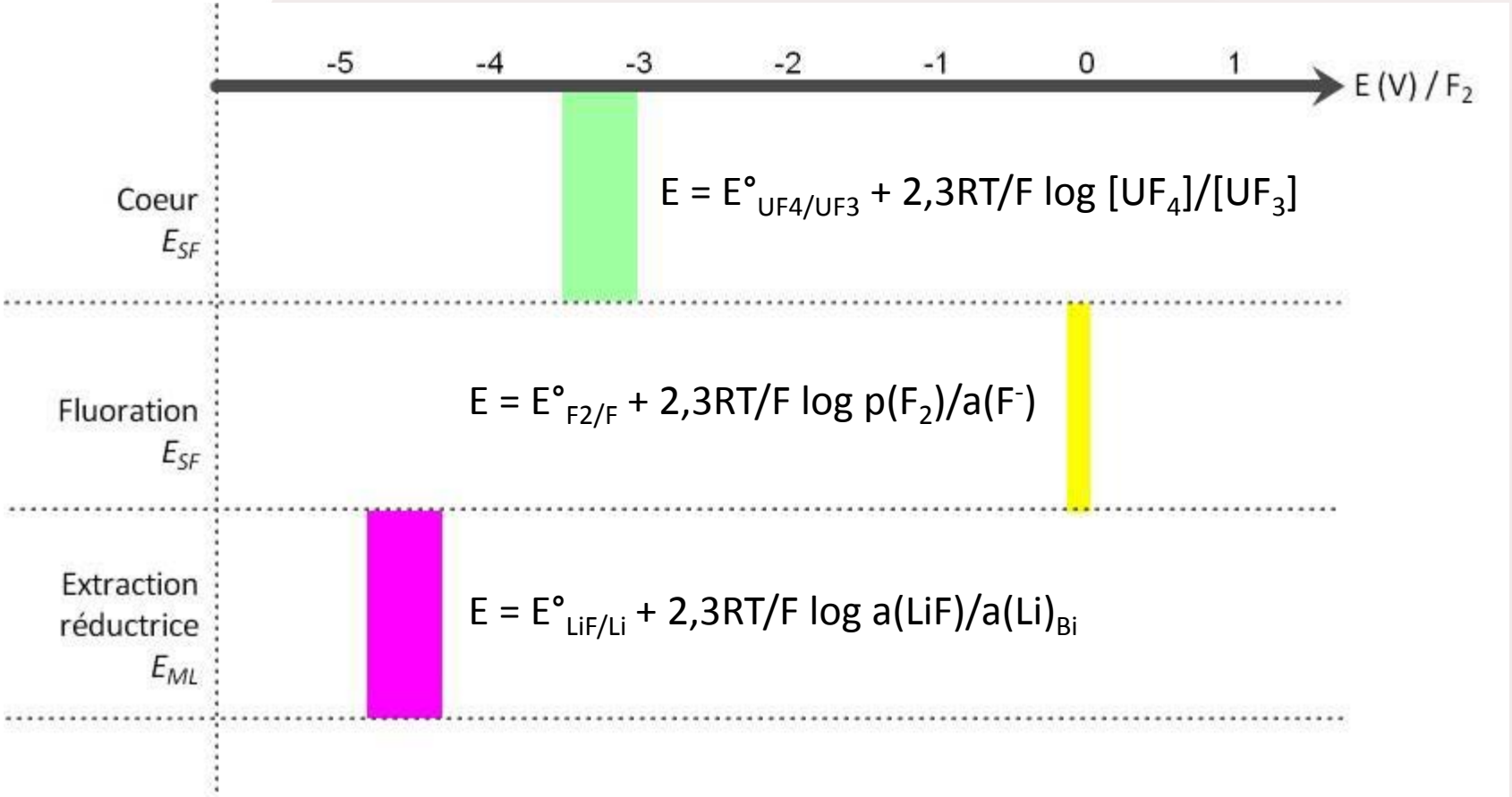


Reprocessing of MSFR fuel



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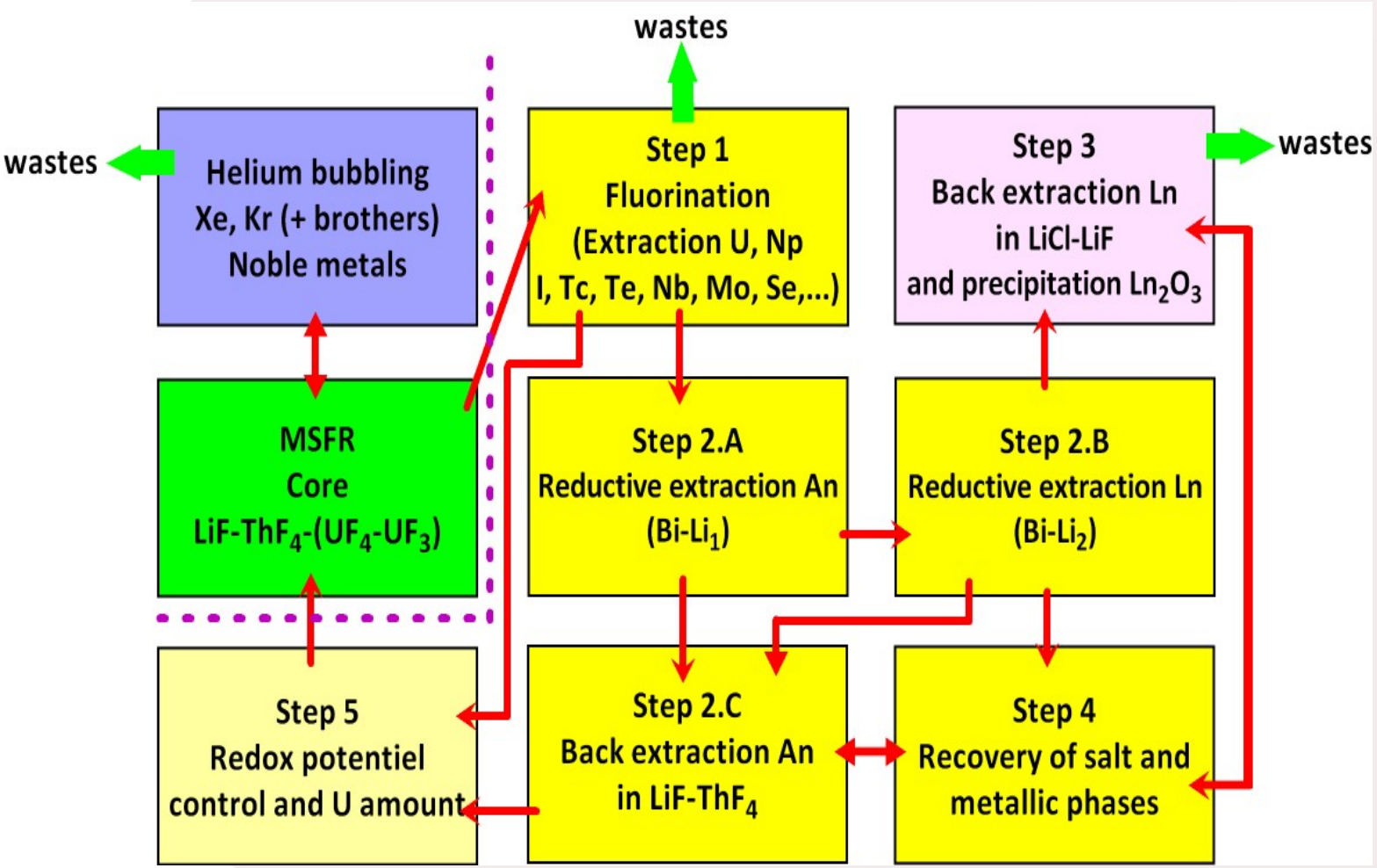
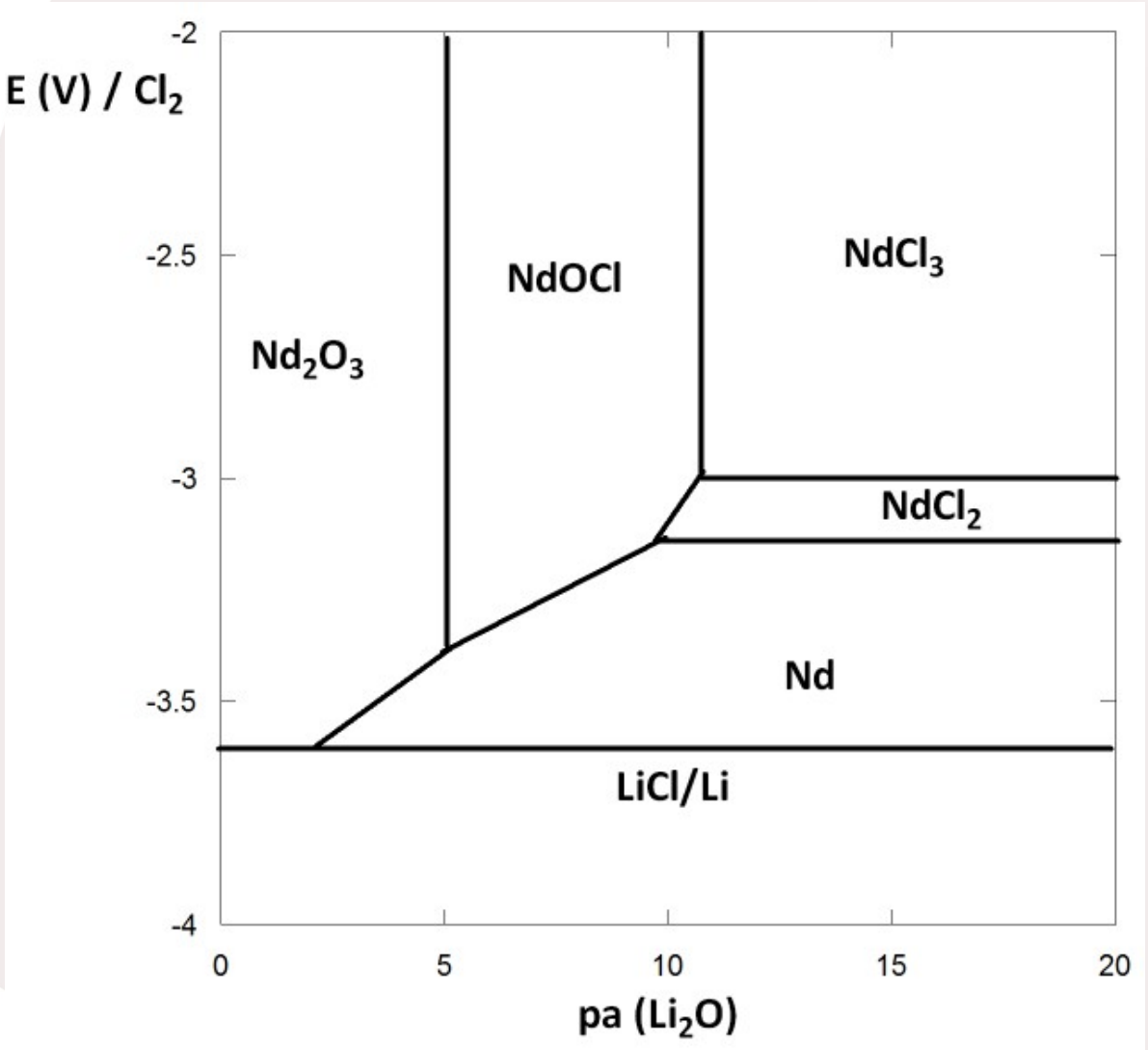
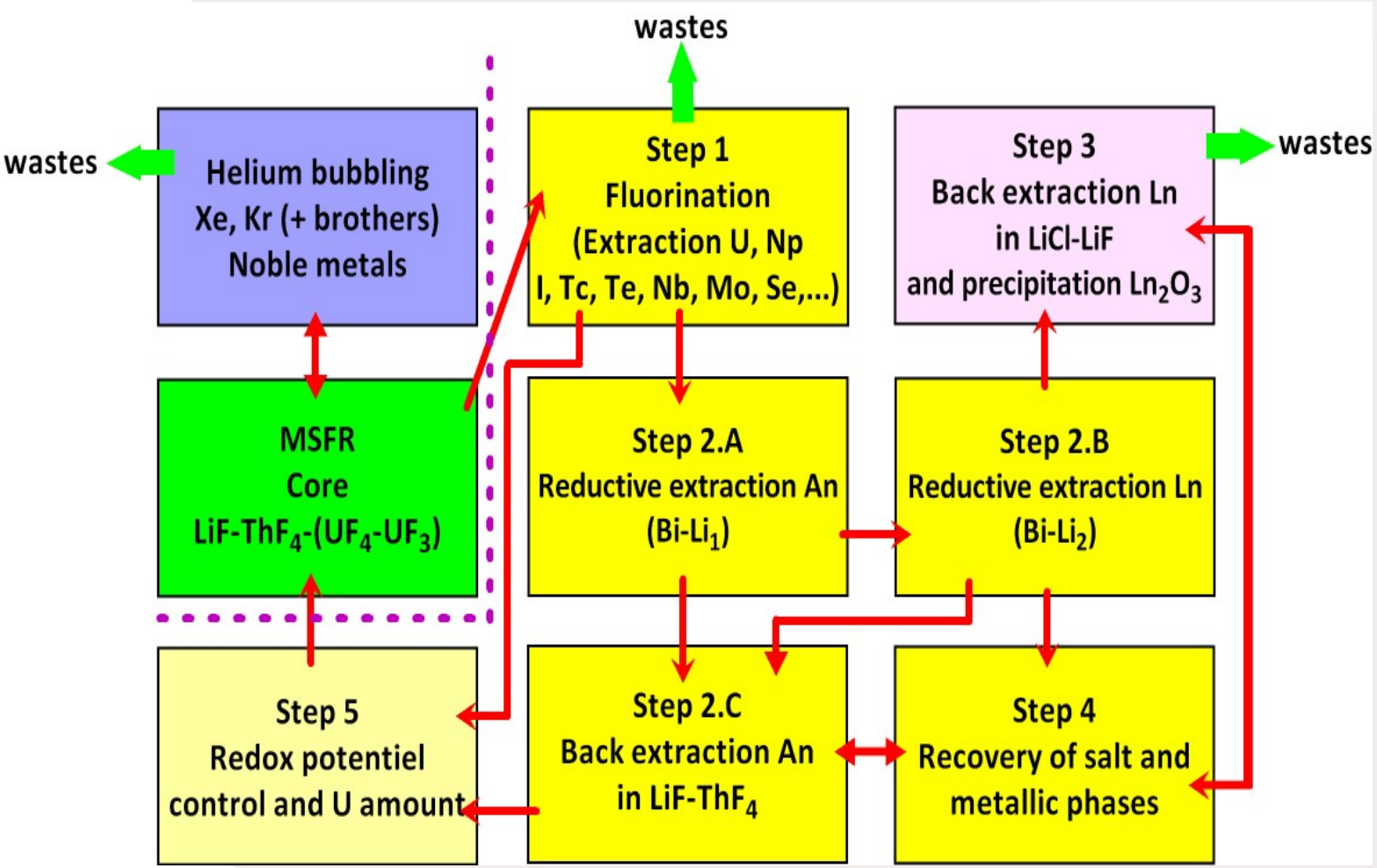


Thermodynamic diagrams

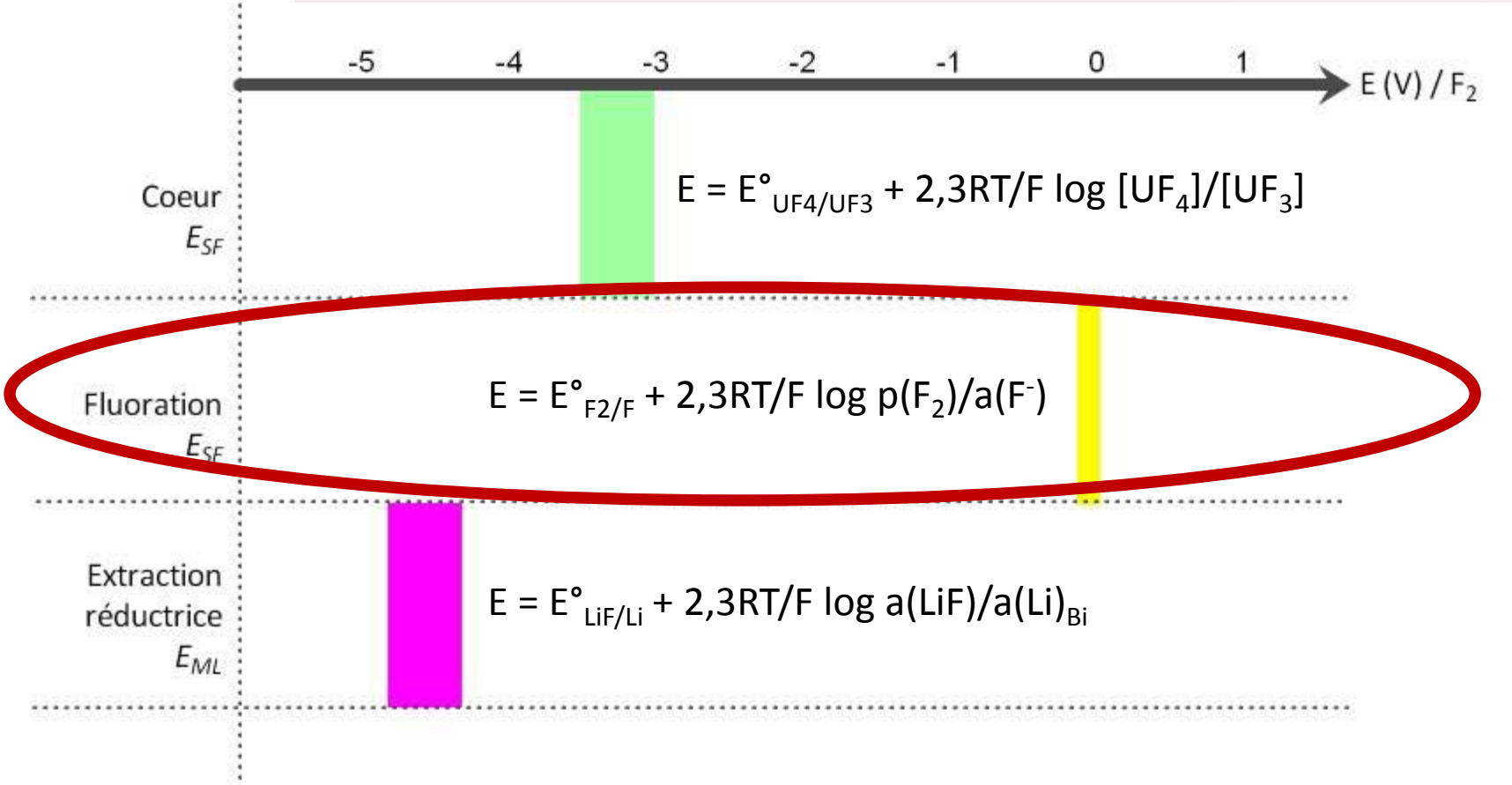
LiCl-KCl 500°C



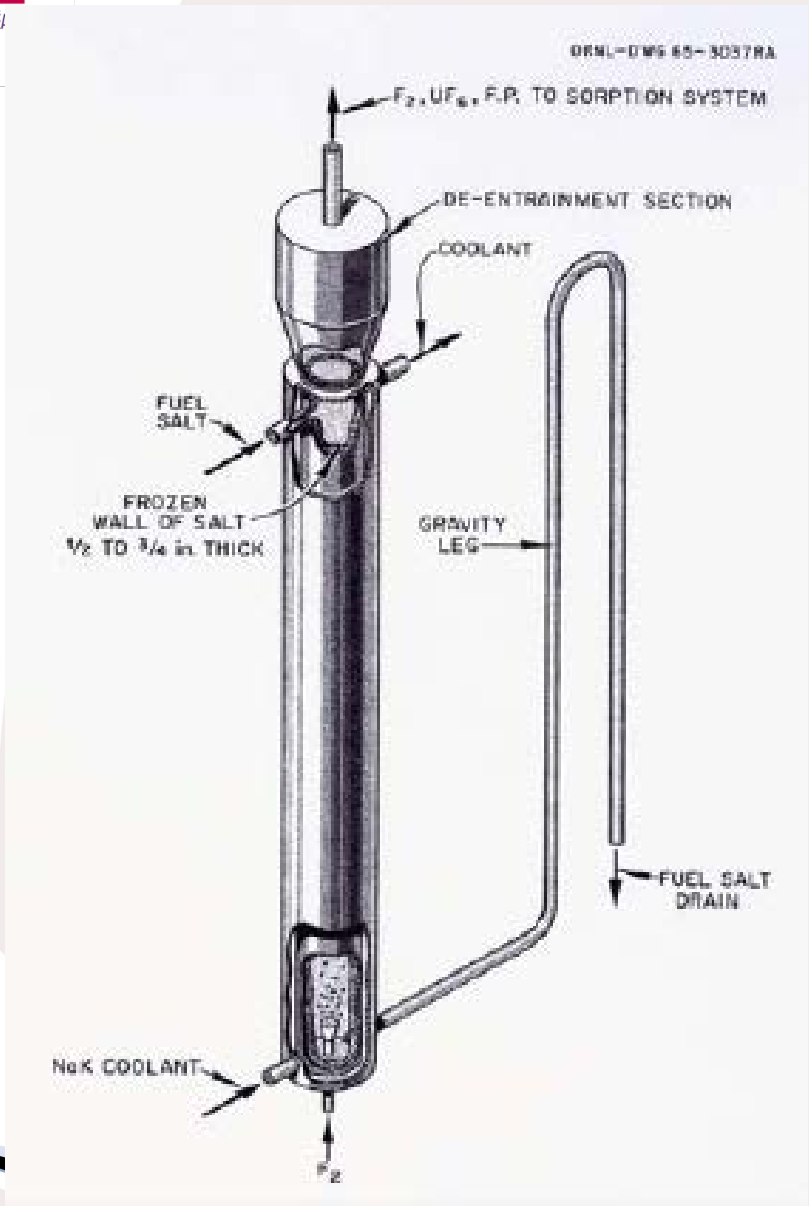
Reprocessing of MSFR fuel



Reprocessing of MSFR fuel fluorination



Fluorination device

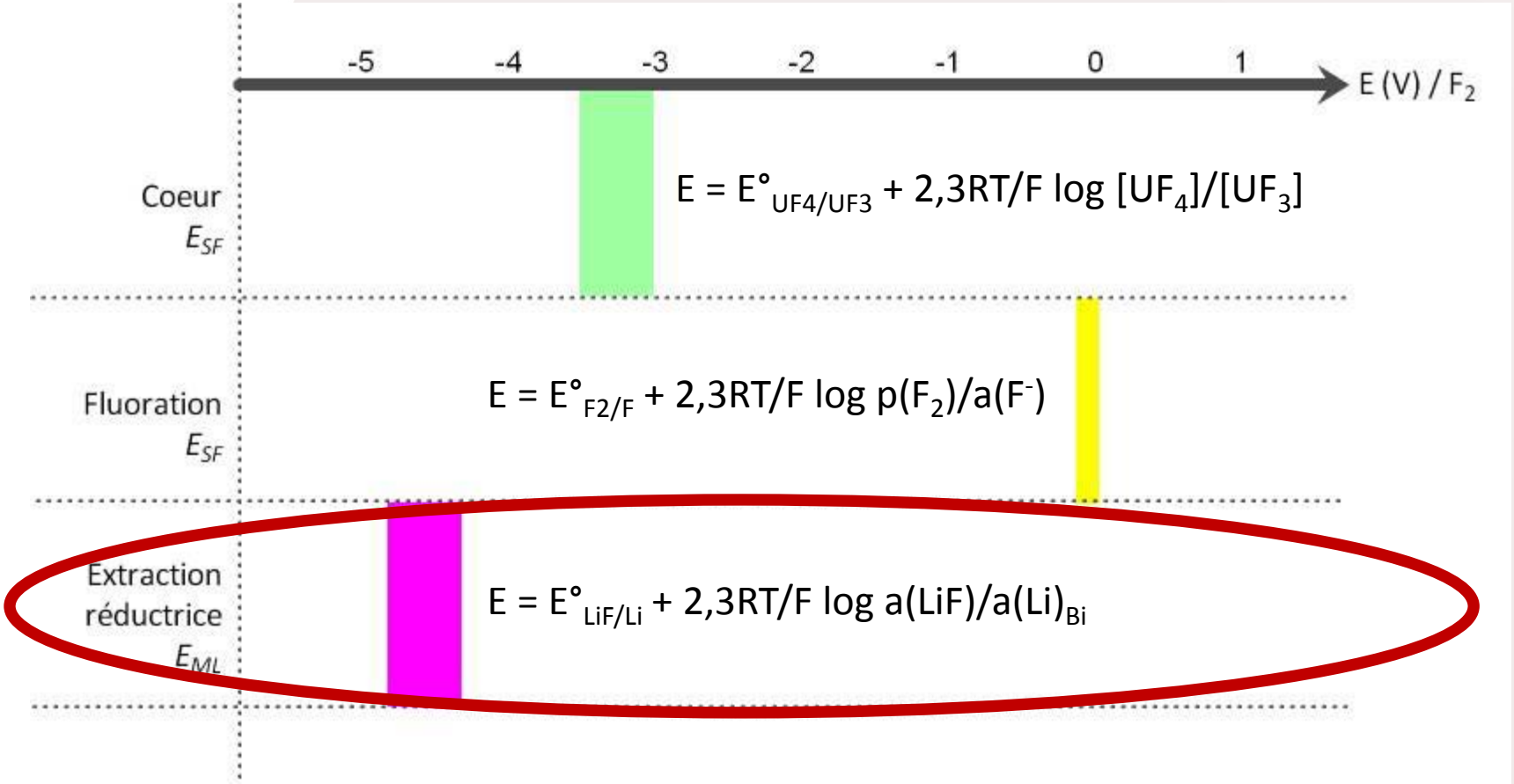


Gas are separated on NaF traps at different temperatures:

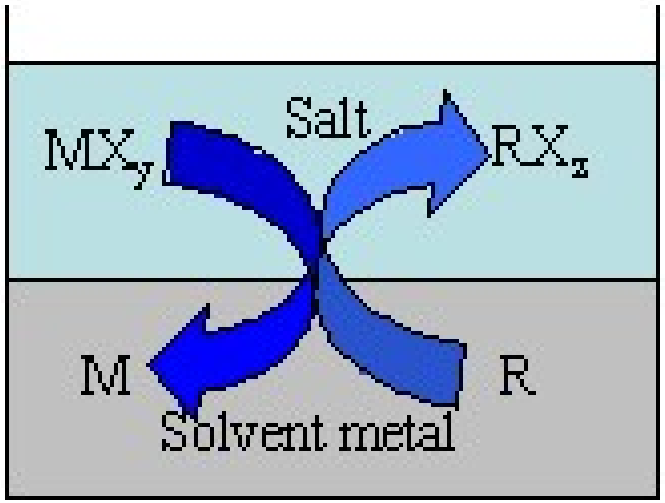
- 400°C adsorption of FP
- 25°C adsorption of U and Np

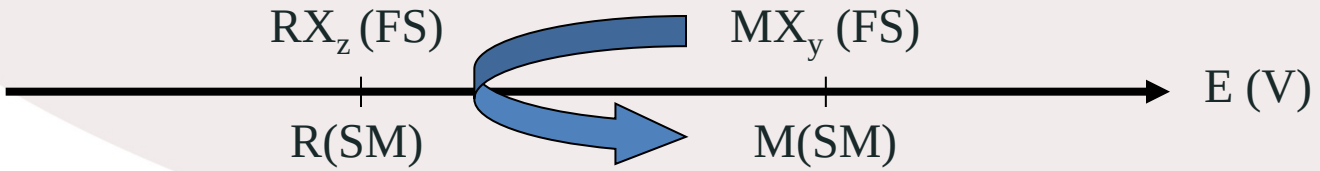
$$UF_4 + F_2(g) \rightarrow UF_6(g)$$

Reprocessing of MSFR fuel fluorination

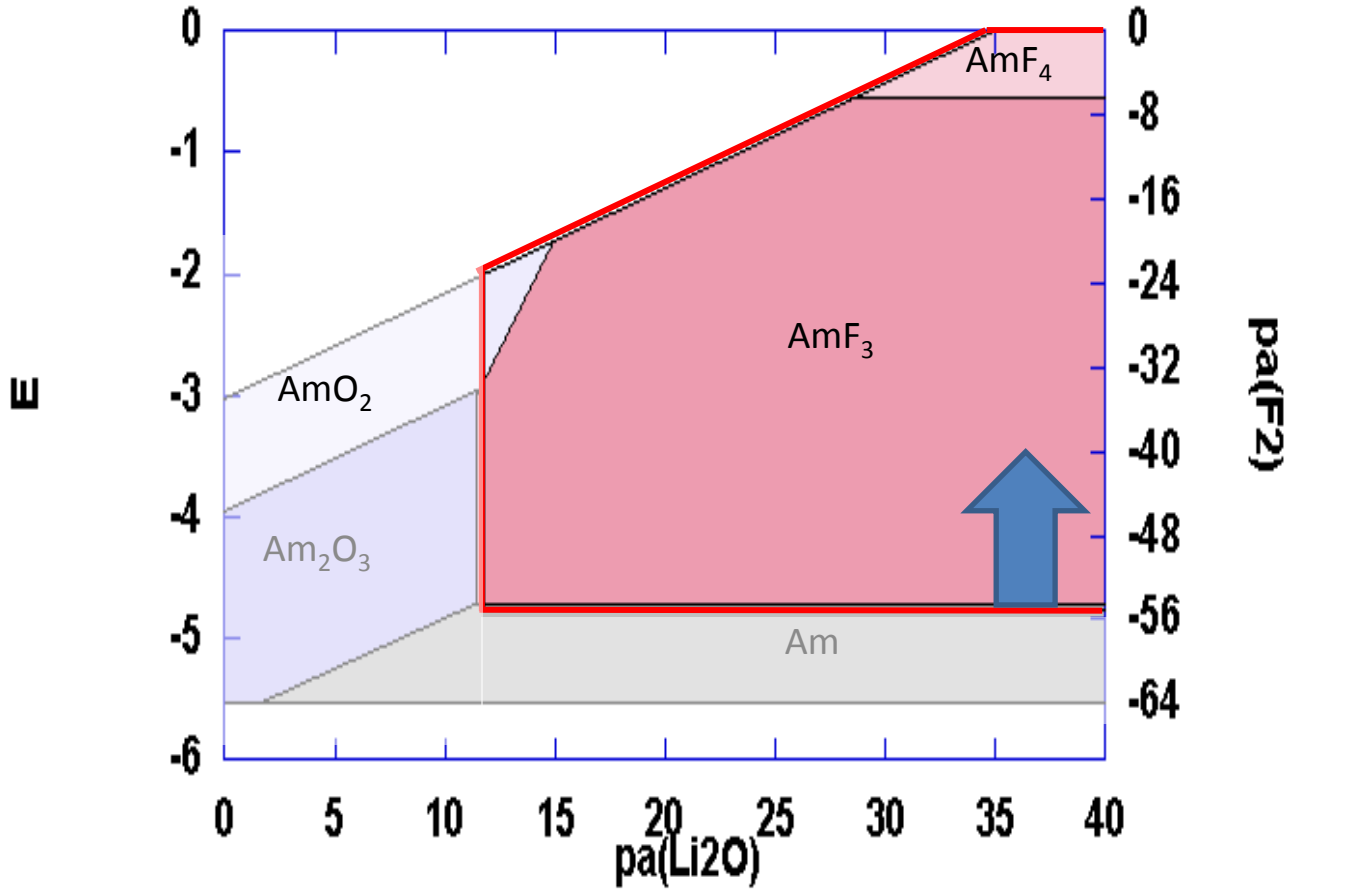


The use of a liquid solvent metal decreases the activity coefficient of the metallic element and increases its stability range





LiF – ThF_4 650°C



Thermodynamic diagrams

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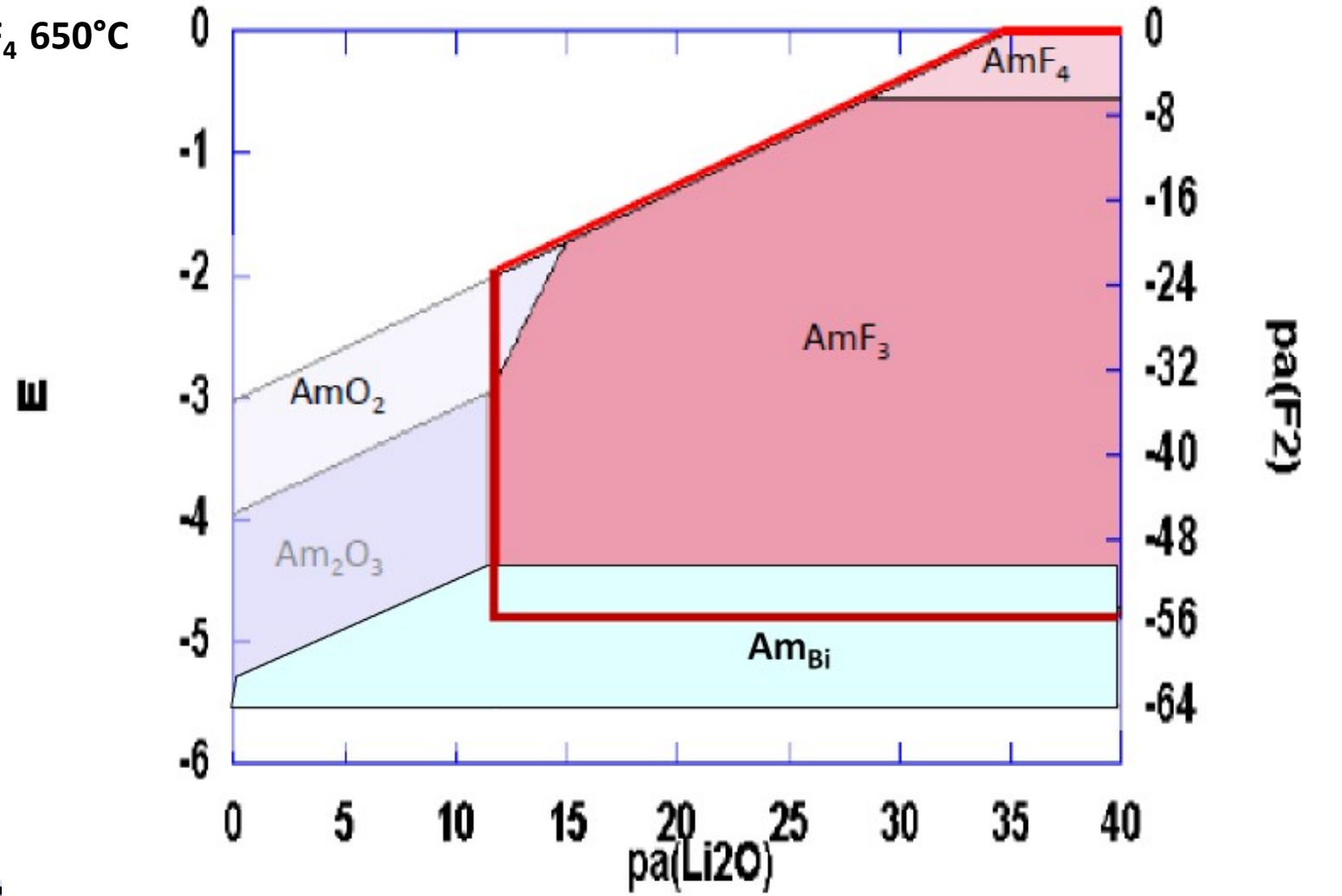


Liquid metal selection

- Liquid-liquid extraction or reductive extraction.

  This process is a molten salt process. The metal has to be liquid in the working temperature range

Metal	Ga	In	Sn	Bi	Tl	Cd	Pb	Zn	Sb	Al
p.f./°C	30	157	232	271	304	321	327	420	631	660
p.é./°C	2204	2072	2602	1564	1473	765	1749	907	1587	2519
σ (barn)	2.9	193.5	0.63	0.033	3.4	2450	0.17	1.1	5.4	0.230

Reductive extraction or liquid-liquid extraction
Definition and analytical relations (1)

- **Liquid(MS)/liquid(LM) extraction**

• Using a reducing agent	Using electrical current
$MX_z(MS) + zLi(LM) \rightarrow M(LM) + zLiX(MS)$	$MX_z(MS) + ze^- \rightarrow M(LM) + zX^-$
• **Equilibrium constant K_M**	
$K_M = \frac{a(LiX)^z_{MS}\, a(M)_{LM}}{a(Li)^z_{LM}\, a(MX_z)_{MS}}$	$E = E°_{MX_z/M} + \frac{2.3RT}{zF} \log \frac{a(MX_z)_{MS}}{a(M)_{LM}}$
• **Gibbs enthalpy of the reaction**	
$\Delta G°_M = zG°(LiX) + G°(M) - zG°(Li) - G°(MX_z)$ $\Delta G°_M = -2.3RT \log K_M$	$\Delta G°_{MX_z/M} = G°(M) + z/2G°(X_2) - G°(MX_z)$ $E°_{MX_z/M} = \frac{-\Delta G°_{MX_z/M}}{zF}$ (with ref : $X_2(g)/X^-$)

Reductive extraction or liquid-liquid extraction
Definition and analytical relations (2)

- **Distribution coefficient D_M**

$$\log D_M = \log \frac{x(M),LM}{x(MX_z),MS}$$

*(Knowing that a(i) = x(i) * γ(i)*
a(i)=activity, x(i)=mole fraction
γ(i) is activity coefficient)

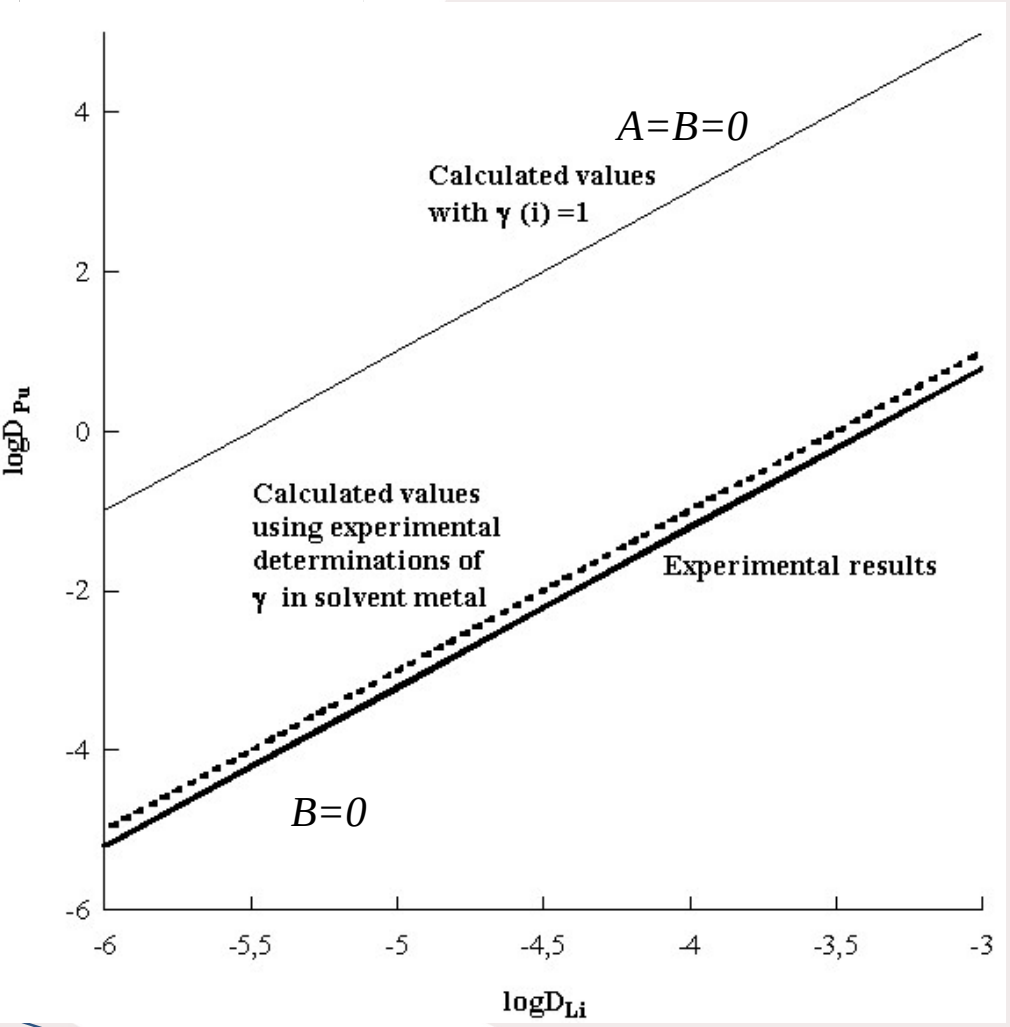
Using a reducing agent

$$\log D_M = \begin{cases} \log K_M + z \log D_{Li} + \log \dfrac{\gamma^z_{Li,LM}}{\gamma_{M,LM}} + \log \dfrac{\gamma_{MX_z,MS}}{\gamma^z_{LiX,MS}} \\ \dfrac{zF}{2.3RT}\left[E^\circ_{MX_z/M} - E\right] + \log \dfrac{\gamma_{MX_z,MS}}{\gamma_{M,LM}} \end{cases}$$

$$E = E^\circ_{LiX/Li} - \frac{2.3RT}{F}\left[\log D_{Li} + \log \gamma_{Li,LM}\right]$$

Using electrical current

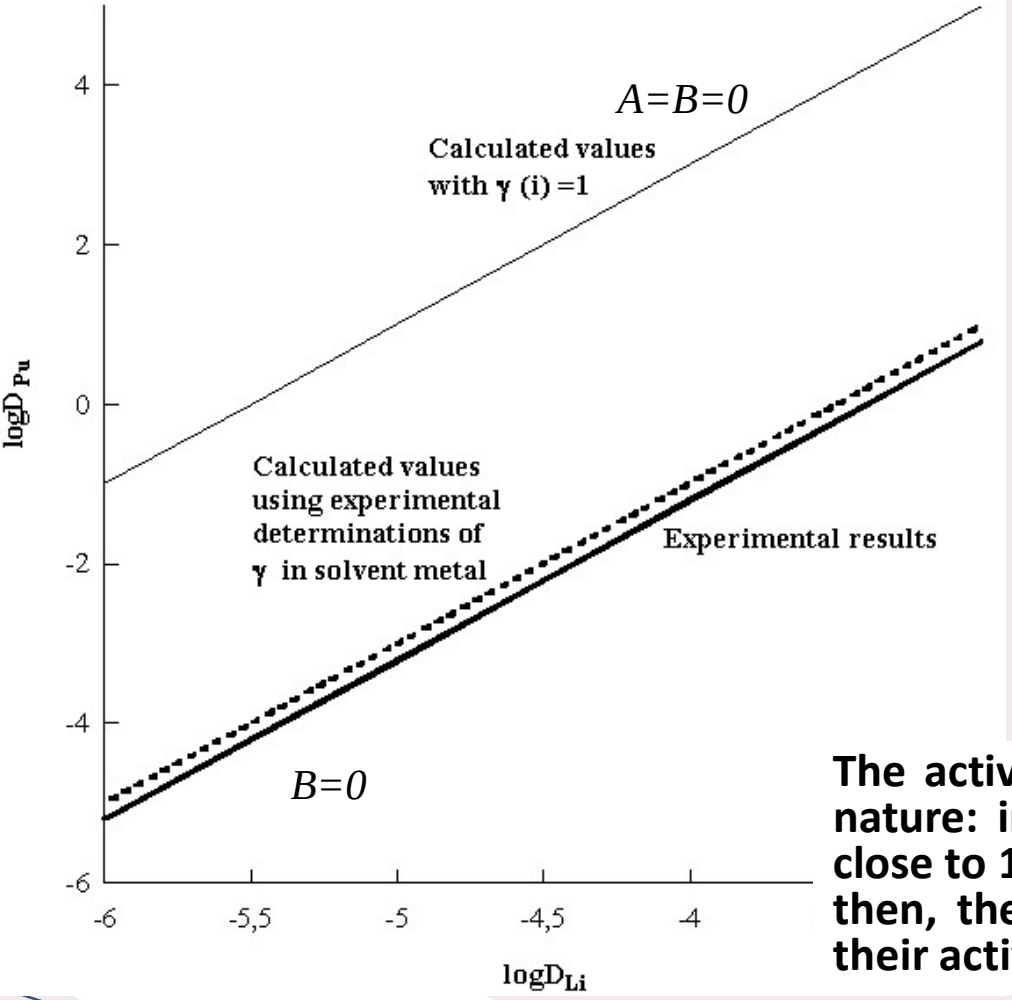
Influence of activity coefficients on the extraction process



$$\log D_M = \log K_M + z \log D_{Li} + \log \frac{\gamma^z_{Li,LM}}{\gamma_{M,LM}} + \log \frac{\gamma_{MX_z,MS}}{\gamma^z_{LiX,MS}}$$

A B

Influence of activity coefficients on the extraction process



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A B

The activity coefficients depend on the molten salt nature: in some case, such as LiF-BeF_2, its value is close to 1 because BeF_2 is one of the most acidic salt: then, the solutes are less solvated by fluoride and their activity coefficient is close to 1

Definition of parameters and analytical relations (3)

- **Selectivity $S(M_1/M_2)$**

$$S(M_1/M_2) = \frac{x(M_1),LM \,/\, x(M_1X_z),MS}{x(M_2),LM \,/\, x(M_2X_{z'}),MS} = \frac{D_{M1}}{D_{M2}}$$

$$\log S(M_1/M_2) = \log D_{M1} - \log D_{M2}$$

- **If z = z' (identical oxidation states for M_1 and M_2), selectivity is no dependent on E or D_{Li}, then:**

$$\log S(M_1/M_2) = \log \frac{K_{M1}}{K_{M2}} * \frac{\gamma_{M2}}{\gamma_{M1}}$$

- **Efficiency $\mu_E(M)$**

$$\mu_E(M) = \frac{n(M),SM}{n(M)_i}$$

$$n(M)_i = n(M),MS + n(M),LM$$

$$\mu_E(M) = \frac{1}{1 + \left[\frac{1}{D_M} * \frac{n_{MS}}{n_{LM}}\right]}$$

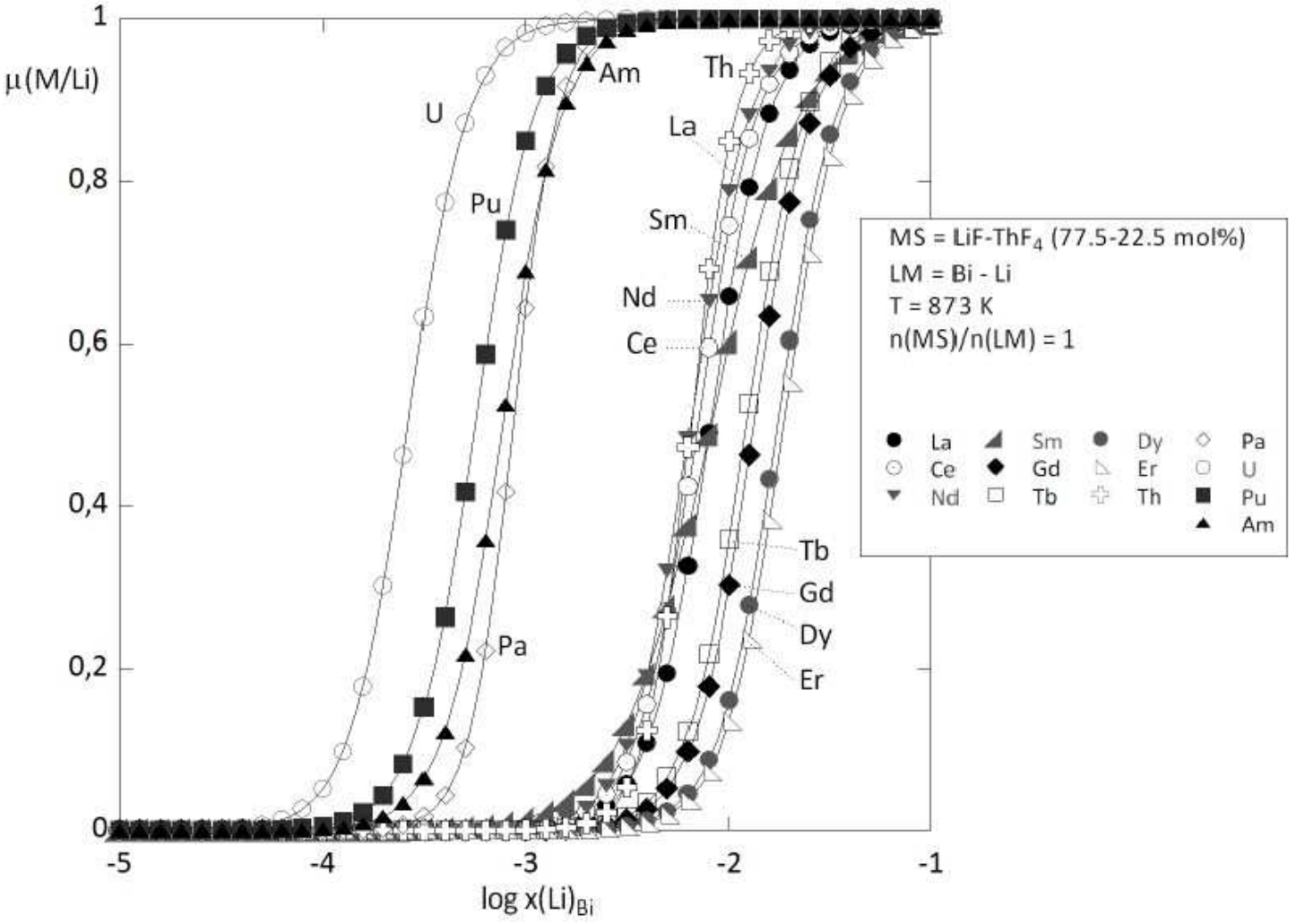
- **Influence of n_{MS} and n_{LM}**

$$\text{If } D_M = 1 \quad (\log D_M = 0) \quad \frac{x(M), LM}{x(MX_z), MS} = 1$$

$$\mu_E(M) = \frac{1}{1 + \left[\frac{1}{D_M} * \frac{n_{MS}}{n_{LM}} \right]}$$

n_{MS}/n_{LM}	1/10	1	10
$\mu_E(M)$ (%)	90.9	50	9

Influence of Li % in liquid metal on extraction efficiency

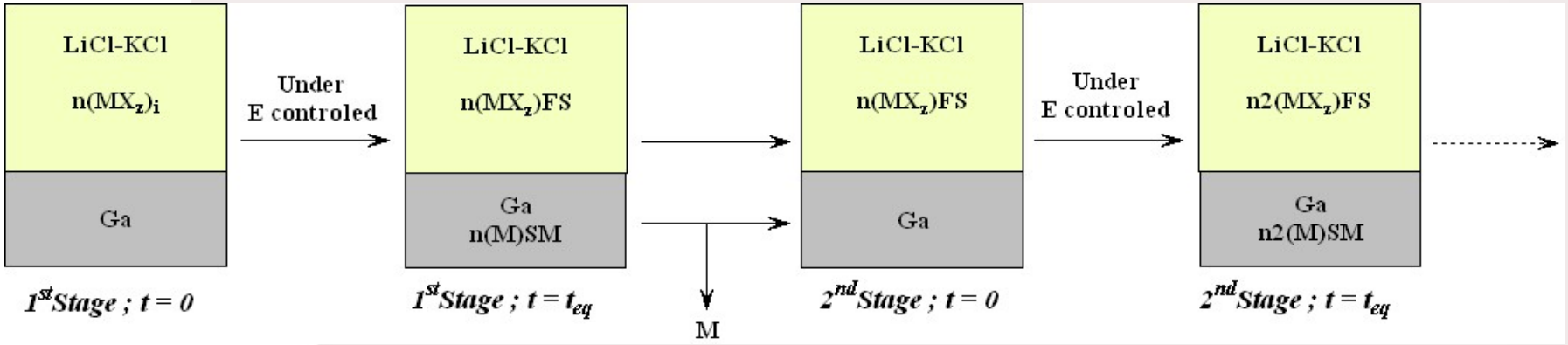


Influence of stages on extraction efficiency (1)

Example

- Molten Salt = Chloride media LiCl-KCl at 450°C
- Liquid metal = Gallium
- $n_{MS} = n_{LM}$
- E = -2.45V

	$\log D_M$	μ_E	$n(M)_i$
Ce	0.99108	0.90738	0.140
Nd	1.8699	0.98669	0.150
Gd	2.8709	0.99866	0.0025



Influence of stages on extraction efficiency (2)

	1st stage			2nd stage			3rd stage		
	n(LM)	n(MS)	$\mu_E t$ (%)	n(LM)	n(MS)	$\mu_E t$ (%)	n(LM)	n(MS)	$\mu_E t$ (%)
Ce	0.127	0.0129	90.7	0.01176	$1.134.10^{-3}$	91.52	$1.03.10^{-3}$	$1.048.10^{-4}$	99.85
Nd	0.148	$1.9965.10^{-3}$	98.67	$1.969.10^{-3}$	$2.657.10^{-5}$	99.98	$2.62.10^{-5}$	$3.503.10^{-7}$	99.99
Gd	0.00249	$3.35.10^{-6}$	99.86	$3.3455.10^{-6}$	$4.489.10^{-9}$	99.997	$4.483.10^{-9}$	$6.015.10^{-12}$	99.998

- Moles extracted as a function of the stages number (nbs)

$$n_{ext} = n_{init} * \{1 - [1 - \mu(M)]^{nbs}\}$$

- Moles not extracted as a function of the stages number (nbs)

$$n_{Next} = n_{init} * [1 - \mu(M)]^{nbs}$$

Comments

- **Extraction processes can be studied using both thermodynamic data (redox potentials) and activity coefficients.**

- **The activity coefficient knowledge (in liquid metal and also in molten salt) is essential for this approach.**

- **Lack of data: Am, Cm, Zr, Te, Se, I…**

Experimental determination of activity coefficients in liquid metals

- **Principle of determination by potentiostatic method (in chloride or fluoride media)**

M (solid) | MCl_3 in molten salt | M (in liquid metal, x_M known)

$$E_1 = E^\circ_{M^{n+}/M} + \frac{2.3RT}{nF}\log\frac{a(MCl_3)_{salt}}{a(M)_{(M)}}$$

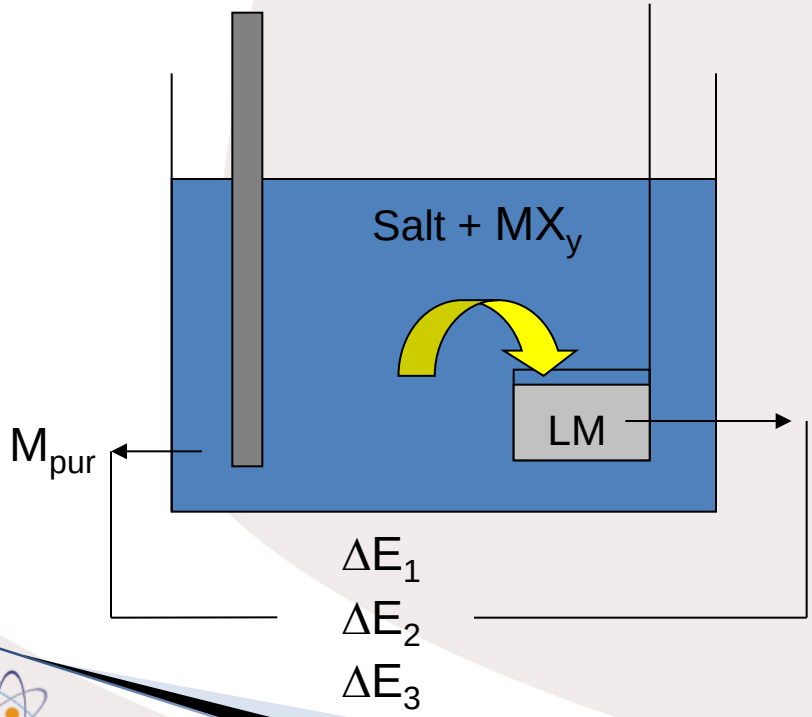
$$E_2 = E^\circ_{M^{n+}/M} + \frac{2.3RT}{nF}\log\frac{a(MCl_3)_{salt}}{a(M)_{(metal)}}$$

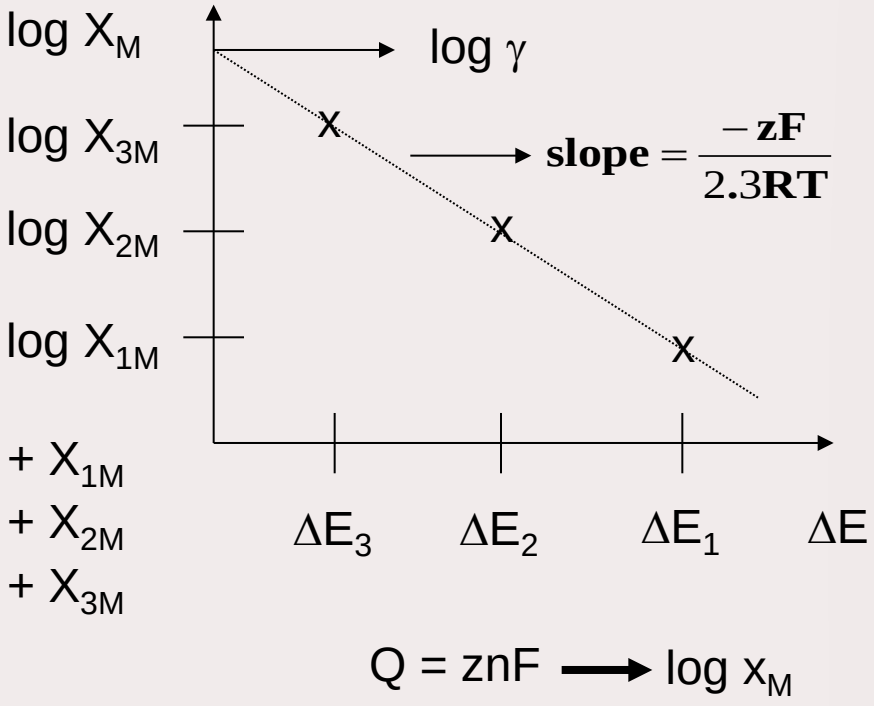
$$\Delta E = E_1 - E_2 = \frac{2.3RT}{nF}\log\frac{a(M)_{(metal)}}{a(M)_{(M)}} = \frac{2.3RT}{nF}\log a(M)_{(metal)}$$

$$\Delta E = \frac{2.3RT}{nF}\log x(M)_{(metal)} + \frac{2.3RT}{nF}\log\gamma(M)_{(metal)} \quad \text{with } a(M) = x(M)*\gamma(M) \text{ and } a(M)_{(M)} = 1$$

Principle of experimental determination of activity coefficient in liquid metal

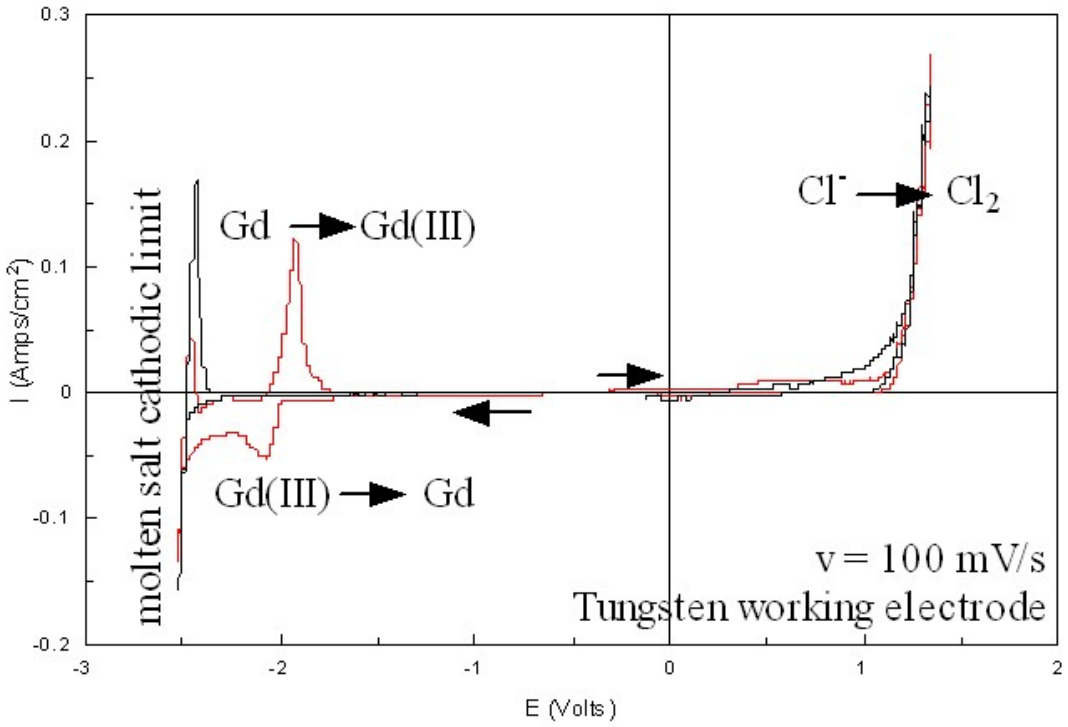
- Determination of potential of pure M
- Liquid metal potential measurement after introduction of various amounts of M in the liquid metal by coulometry at applied potential





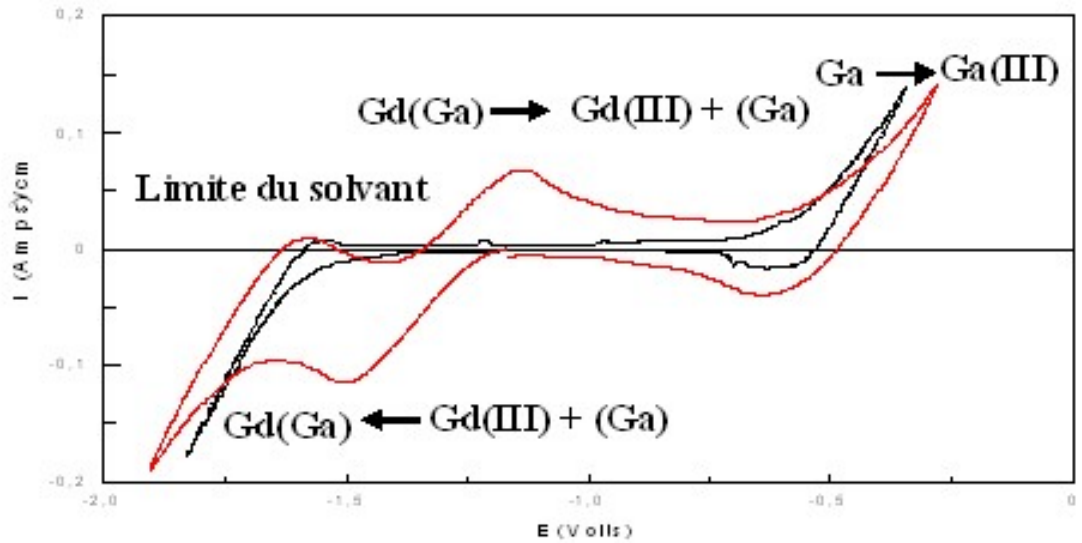
Experimental determination of activity coefficient: example Gd in Ga

- **Voltammogram obtained at 100mV/s on a tungsten working electrode in a molten salt containing 2wt% of $GdCl_3$ in NaCl-$CaCl_2$ at 560°C**



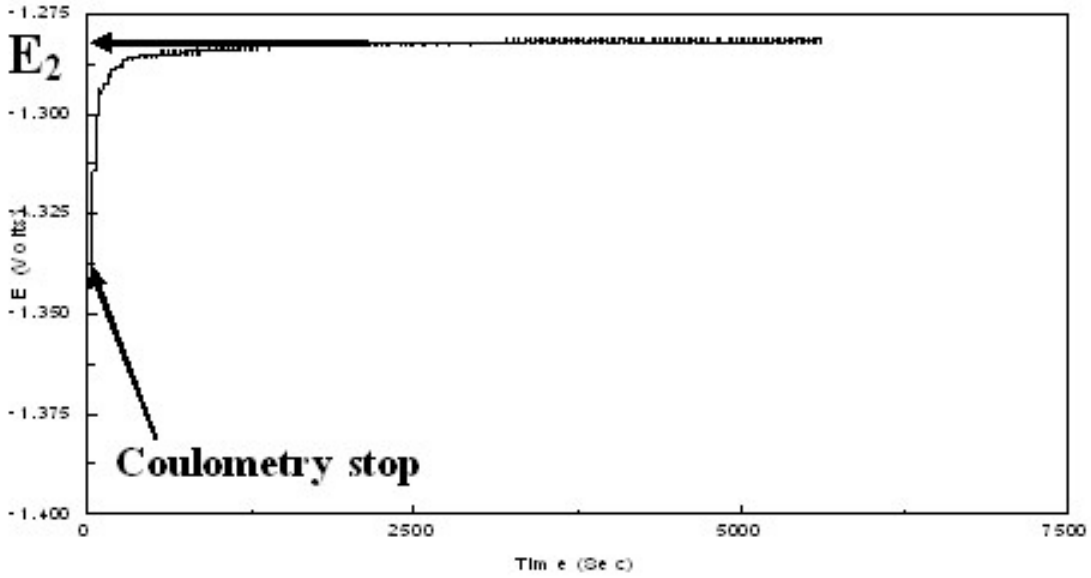
Experimental determination of activity coefficient: example Gd in Ga

- **Cyclic voltammogram realized at 10mV/s on liquid gallium electrode (S = 1.3 cm^2) in NaCl-$CaCl_2$ molten salt at 530 ° C containing 2wt% of $GdCl_3$.**



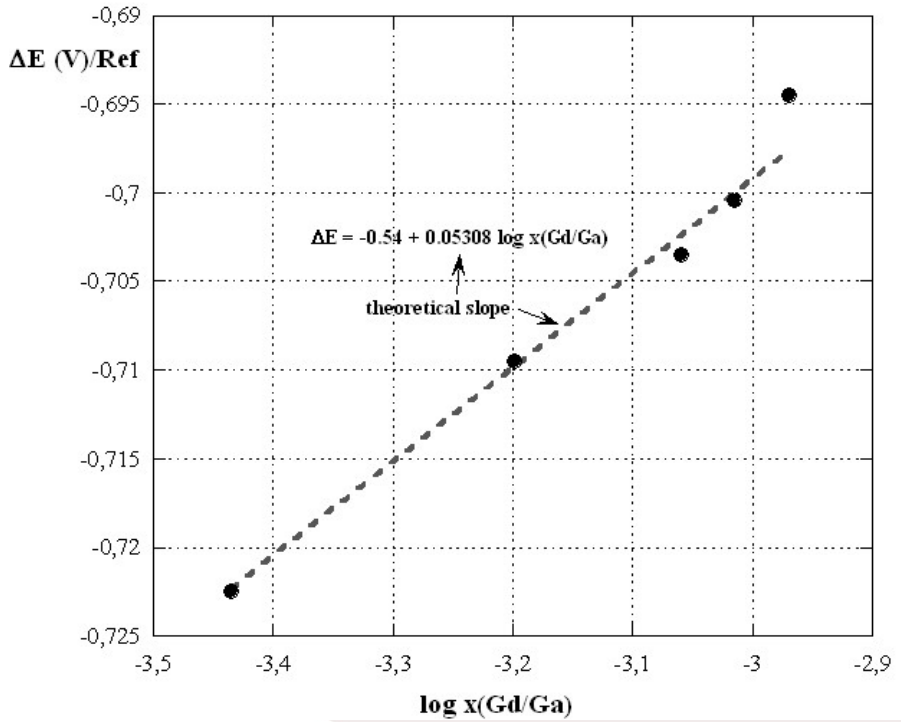
Experimental determination of activity coefficient: example Gd in Ga

- **Open circuit potential measured as a function of time on a liquid gallium electrode after introducing of gadolinium by electrolysis at applied potential (E=-1.65V/Ref)**



Experimental determination of activity coefficient: example Gd in Ga

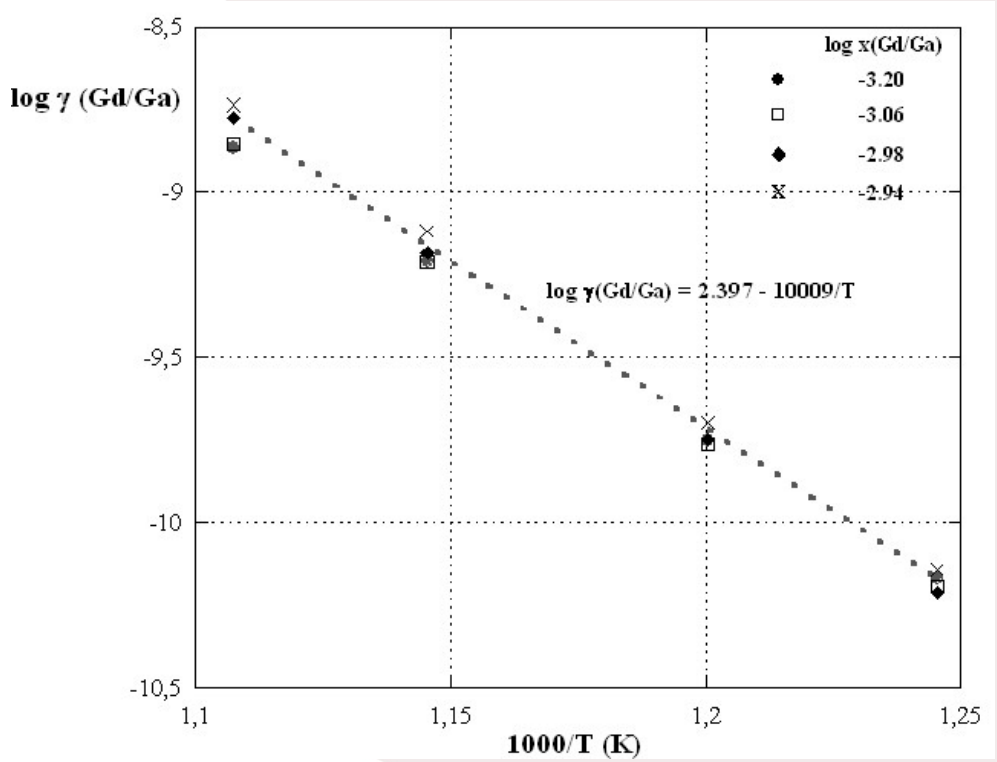
- **Variation of ΔE calculated as a function of the logarithm of the mole fraction of gadolinium contained in liquid gallium at 530° C**



⟶ $\log \gamma(Gd/Ga) = -10.17$

Experimental determination of activity coefficient: example Gd in Ga

- Variation of log γ(Gd/Ga) *vs* 1/T for various Gd mole fraction in liquid gallium



$$\log \gamma(\mathrm{Gd/Ga}) = 2.397 - \frac{10009}{T}$$

Experimental determination of activity coefficients in molten salts

- **Potential measurements of redox systems MCl_x/M**

$$E(MCl_n/M) = E°(MCl_n/M) + \frac{2.3RT}{nF}\log a(MCl_n)$$

$$E(MCl_n/M) = E°(MCl_n/M) + \frac{2.3RT}{nF}(\log x(MCl_n) + \log \gamma(MCl_n))$$

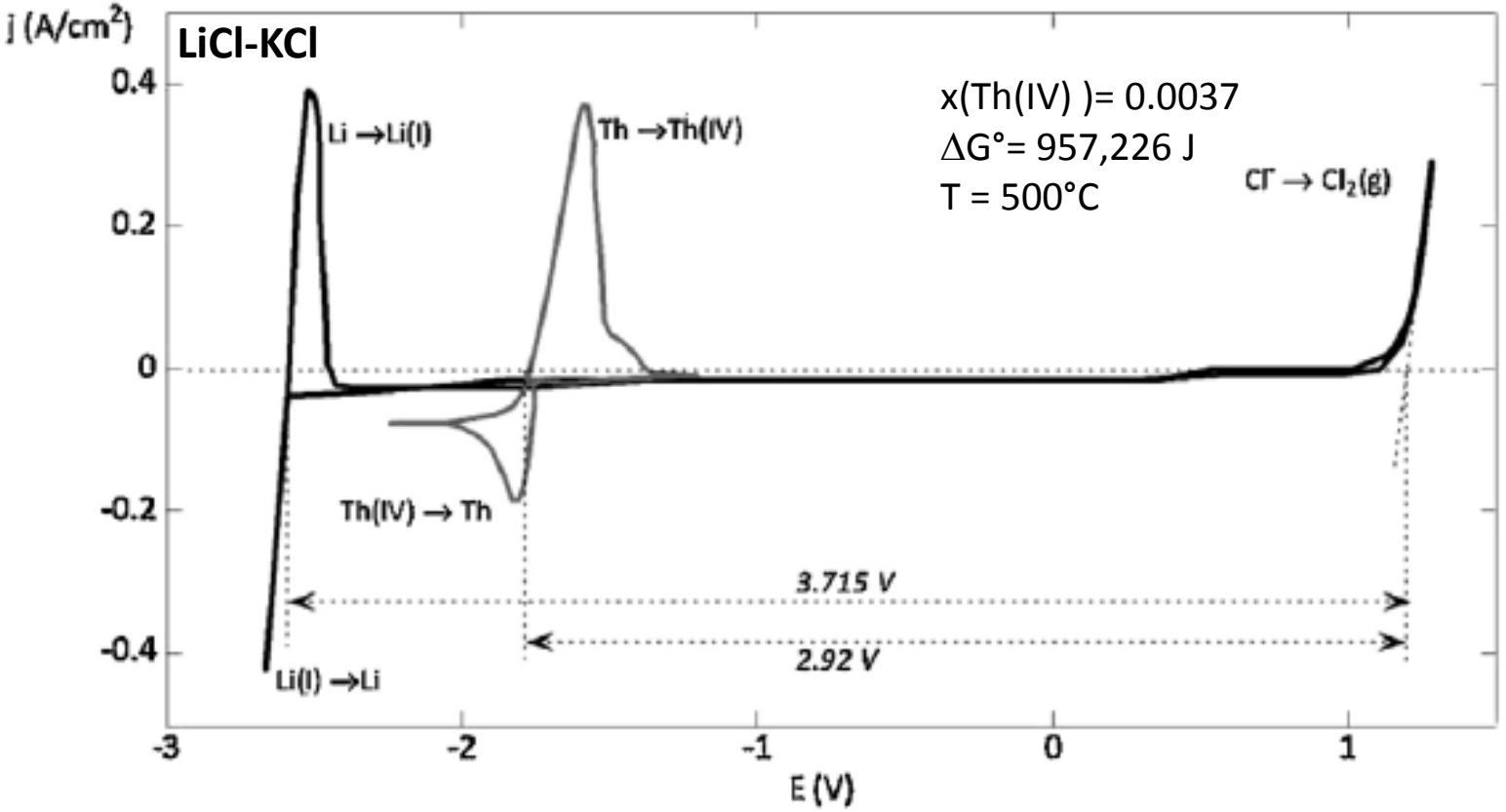
Experimental measurement

Potential calculated from thermochemical data

Experimental conditions

Activity coefficient
Function of T
Function of electrolyte nature

Experimental determination of activity coefficients in molten salts



E_{exp}(Th(IV)/Th) = -2,92 V/Cl_2 = -2,855 -0,065 (overpotential observed on W electrode)

$E°_{thermo}$(Th(IV)/Th) = -2,48 V/Cl_2

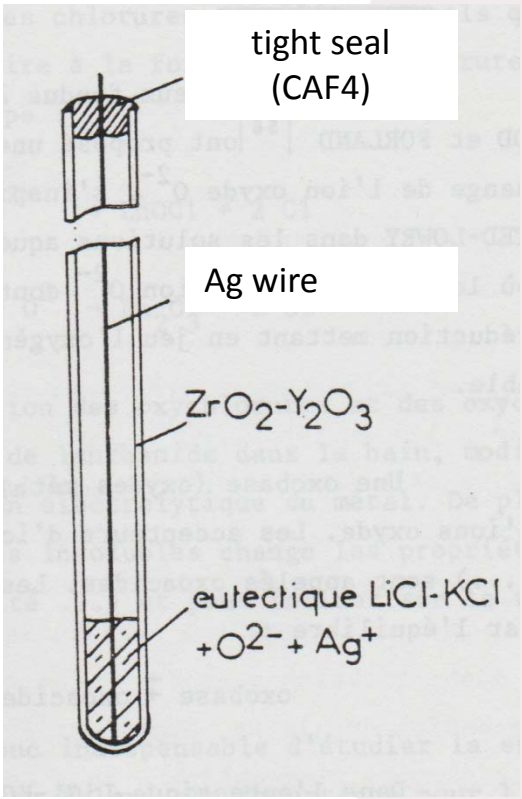
$$E(MCl_n/M) = E°(MCl_n/M) + \frac{2.3RT}{nF}(\log x(MCl_n) + \log \gamma(MCl_n))$$

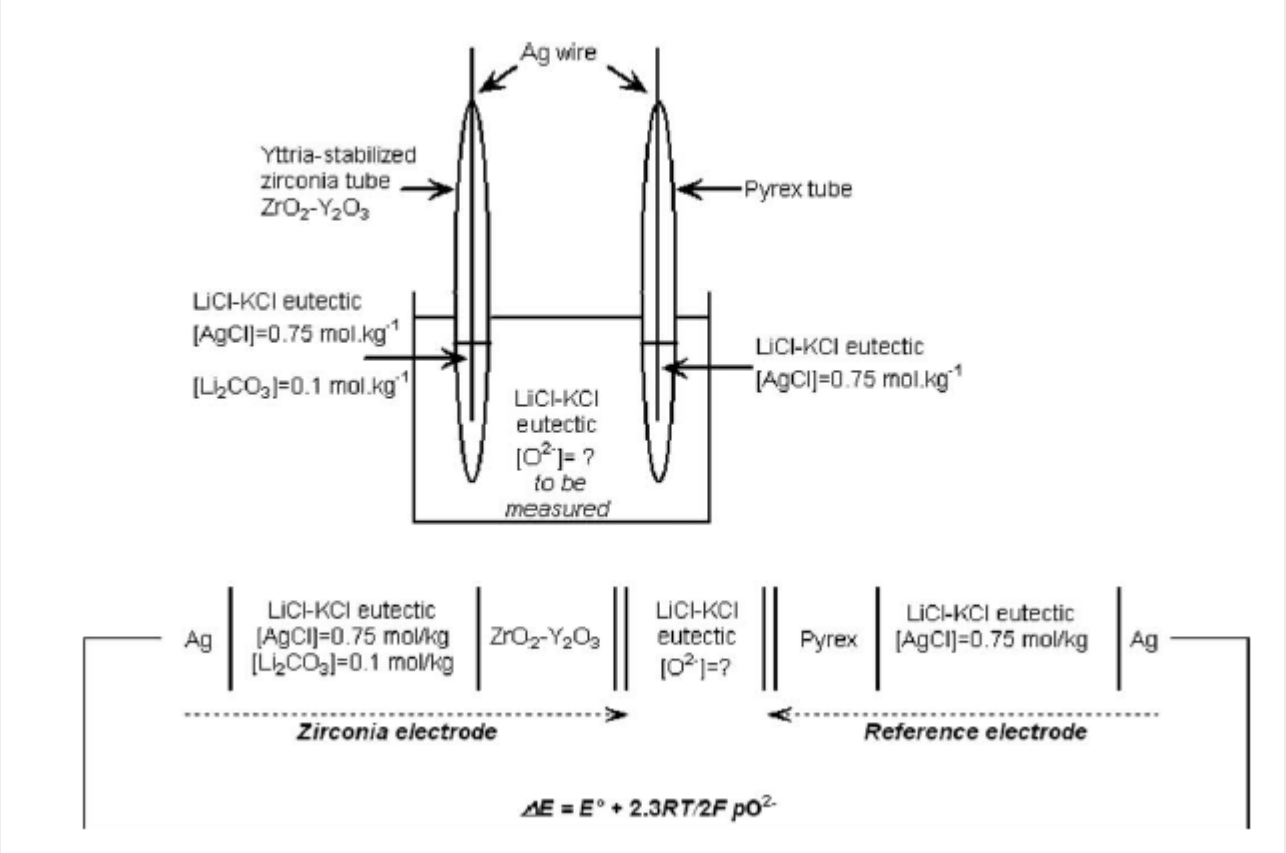
log γ(Th(IV)) = -7,35

Measurement of oxide amount

yttria-stabilized zirconia membrane electrode (YSZME)

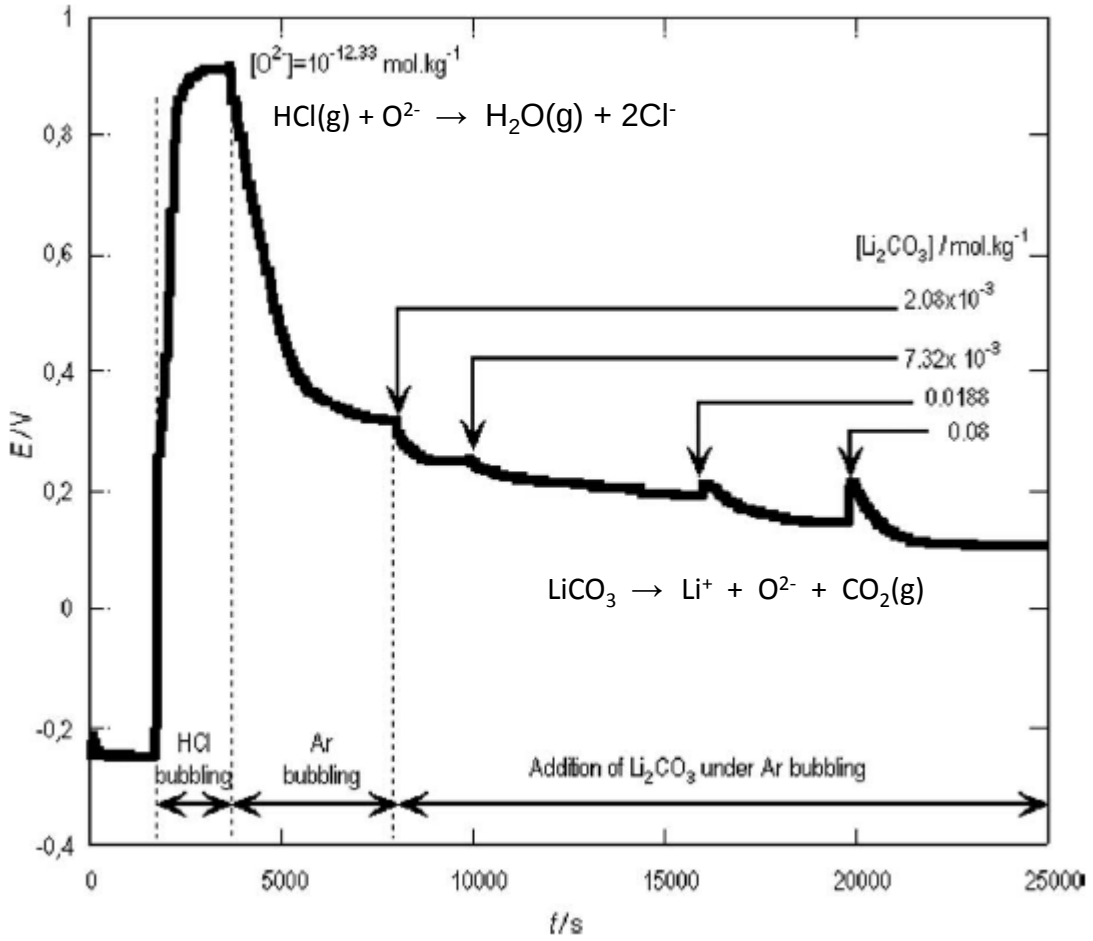
«Zirconia electrode»





Measurement of oxide amount

Calibration of «Zirconia electrode»

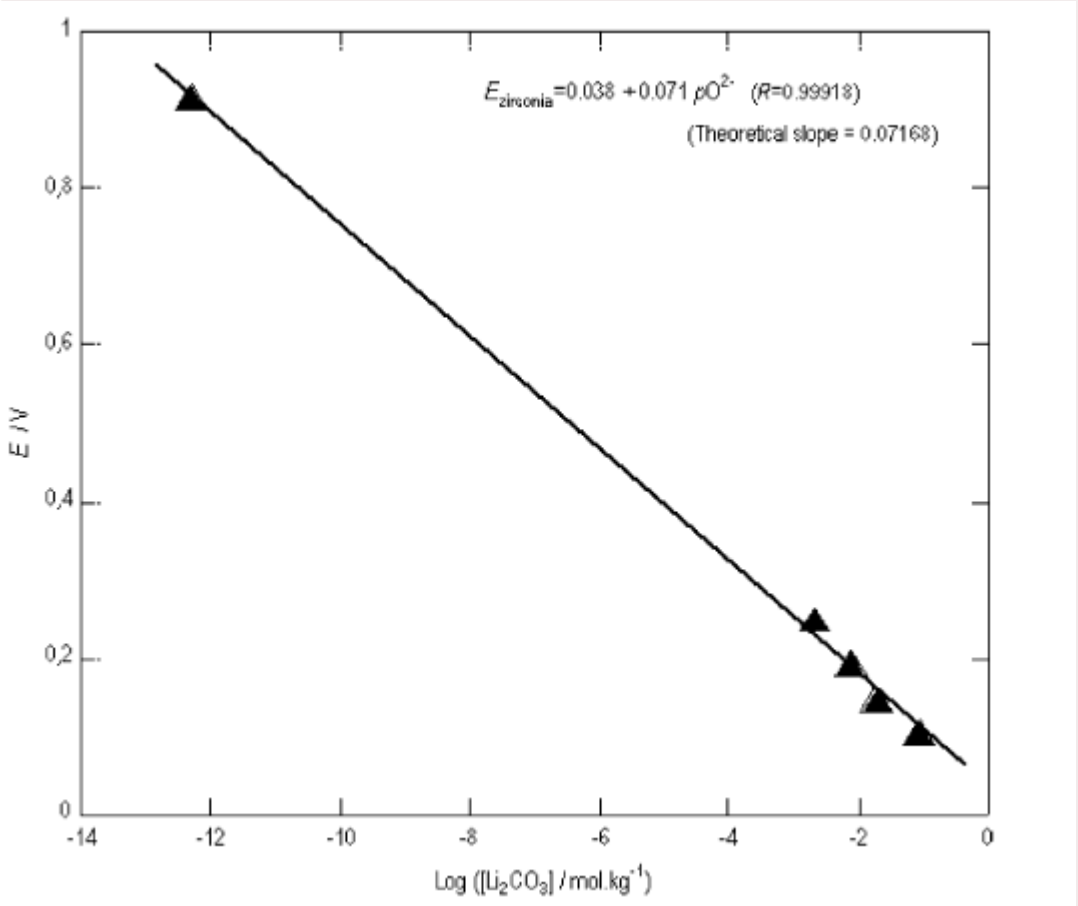


$$K = \frac{a(O^{2-})p(HCl)^2}{p(H_2O)}$$

- K = $10^{-10,33}$ in LiCl-KCl at 450°C
- gas composition
  - p(HCl) = 1 atm
  - $p(H_2O)=10^{-2}$ atm
- during HCl bubbling:
  - $[O^{2-}] = 10^{-12,33}$ mol/kg

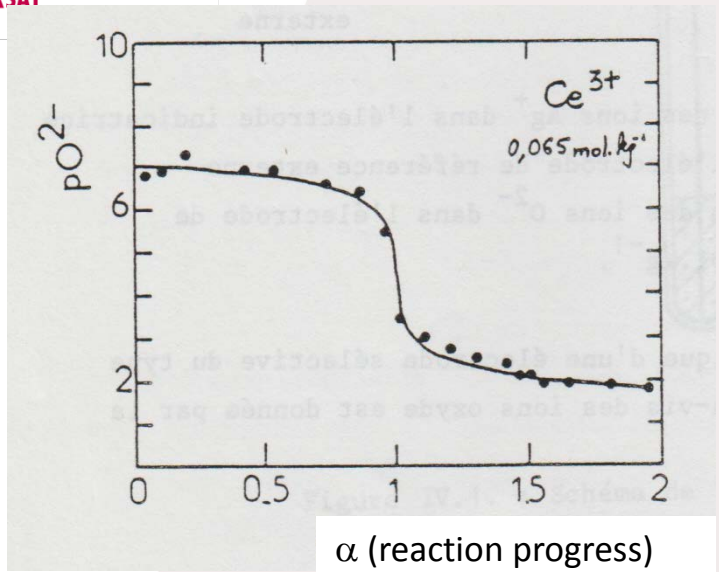
Measurement of oxide amount

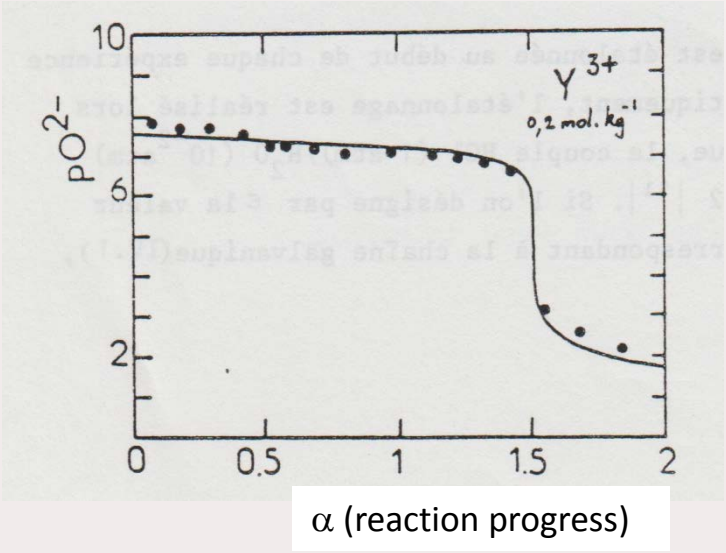
Calibration of «Zirconia electrode»



Measurement of oxide amount

Titration – determination of solubility constant





$Ce^{3+} + O^{2-} + Cl^- \rightarrow CeOCl$

C_0

$C_0(1-\alpha)$ αC_0

$2Y^{3+} + 3O^{2-} \rightarrow Y_2O_3$

C_0

$C_0(1-\alpha)$ αC_0

Mass balances

$C_0 = [Ce^{3+}] + n(CeOCl)/m$

$\alpha C_0 = [O^{2-}] + n(CeOCl)/m$

$K_{S(Ce)} = [Ce^{3+}][O^{2-}]$

$C_0 = [Y^{3+}] + 2n(Y_2O_3)/m$

$\alpha C_0 = [O^{2-}] + 3n(Y_2O_3)/m$

$K_{S(Y)} = [Y^{3+}]^2[O^{2-}]^3$

Fits relation

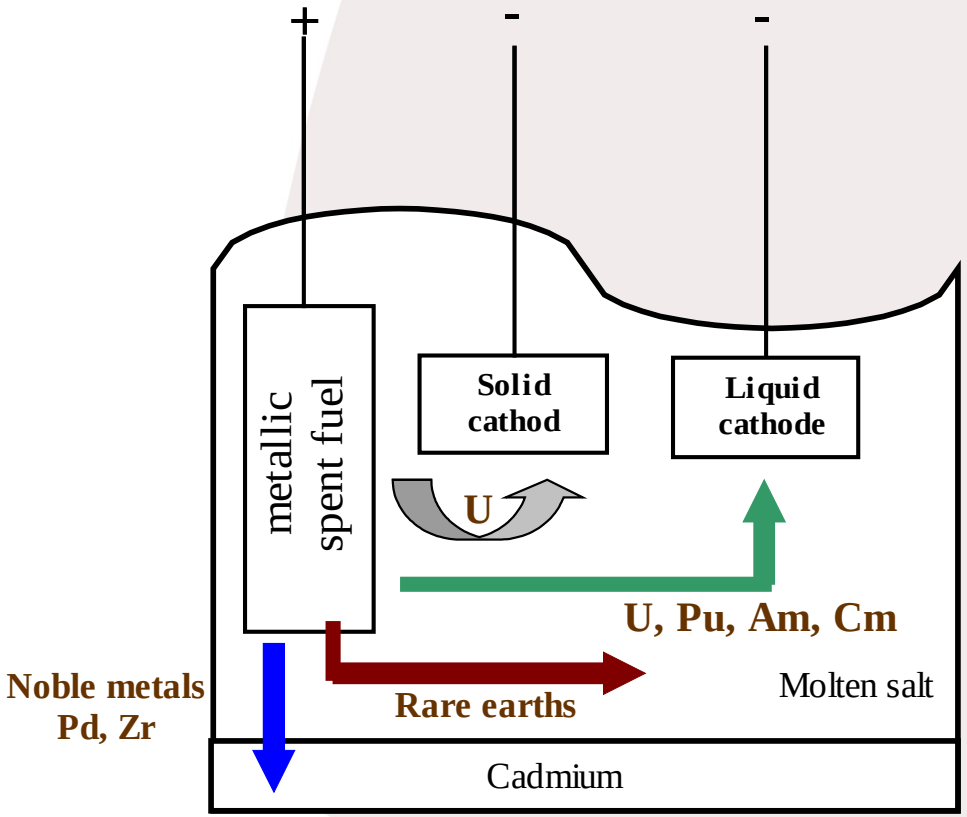
$\alpha = 1 + [O^{2-}]/C_0 - K_{s(Ce)}/[O^{2-}]/C_0$

$pK_{s(Ce)} = 8.7$

$\alpha = 3/2 + [O^{2-}]/C_0 - 3/2/C_0\,(K_{s(Y)}/[O^{2-}])^{1/2}$

$pK_{s(Y)} = 22,8$

Example: electrorefining of IFR (Integrated Fast Reactor) fuel in USA (Argonne)



1- Reduction on solid cathode :
92% d'U, 0.5% Pu and traces of FP

2- Reduction on liquid cathode :
50% U, 50% Pu , Am and traces of FP

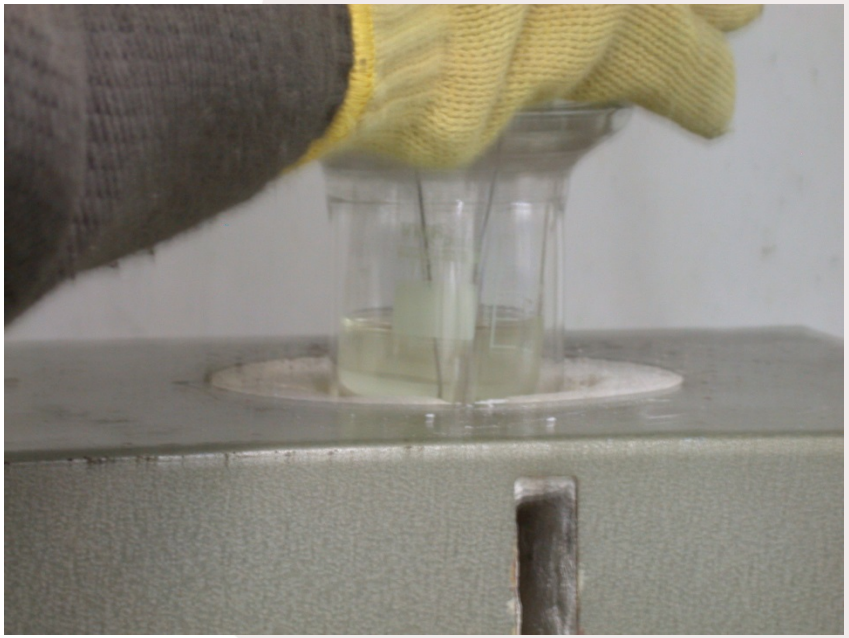
Conclusion

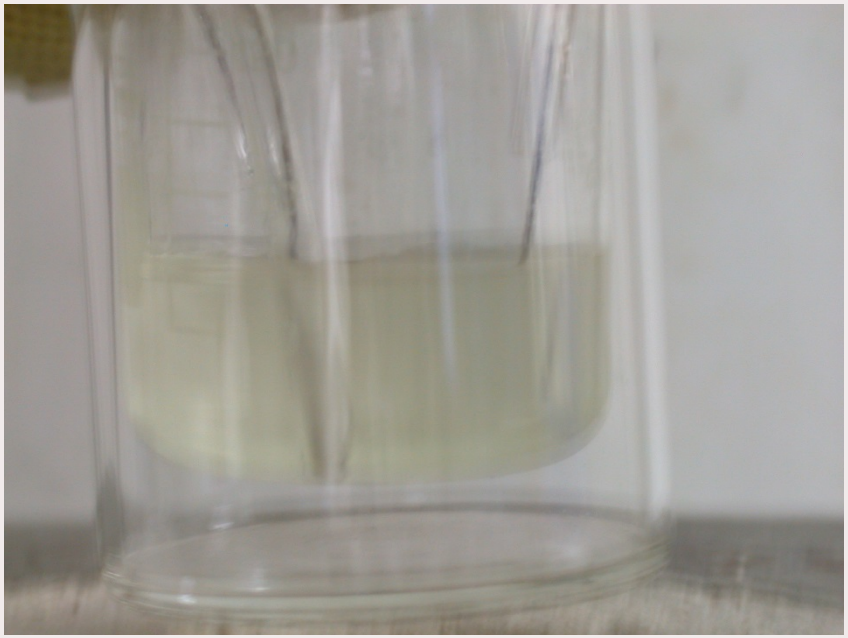
- Thermodynamic approach necessary to propose a reprocessing scheme
- This approach is used both in chloride and fluoride media

Experimental studies:

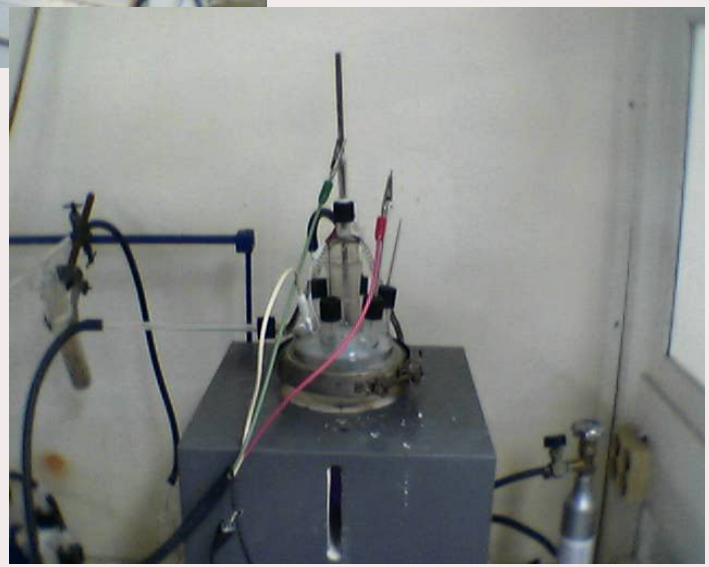
- Determination of parameters in given molten salts
- Experimental tests to estimate the extraction kinetic and validate the reprocessing

Experimental set-up

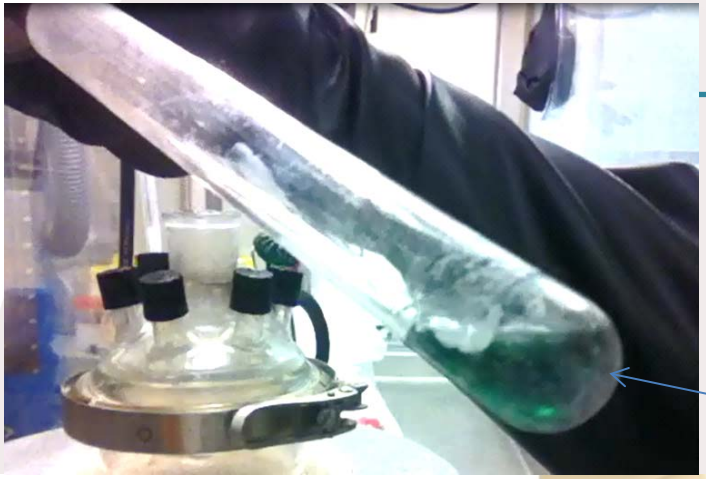
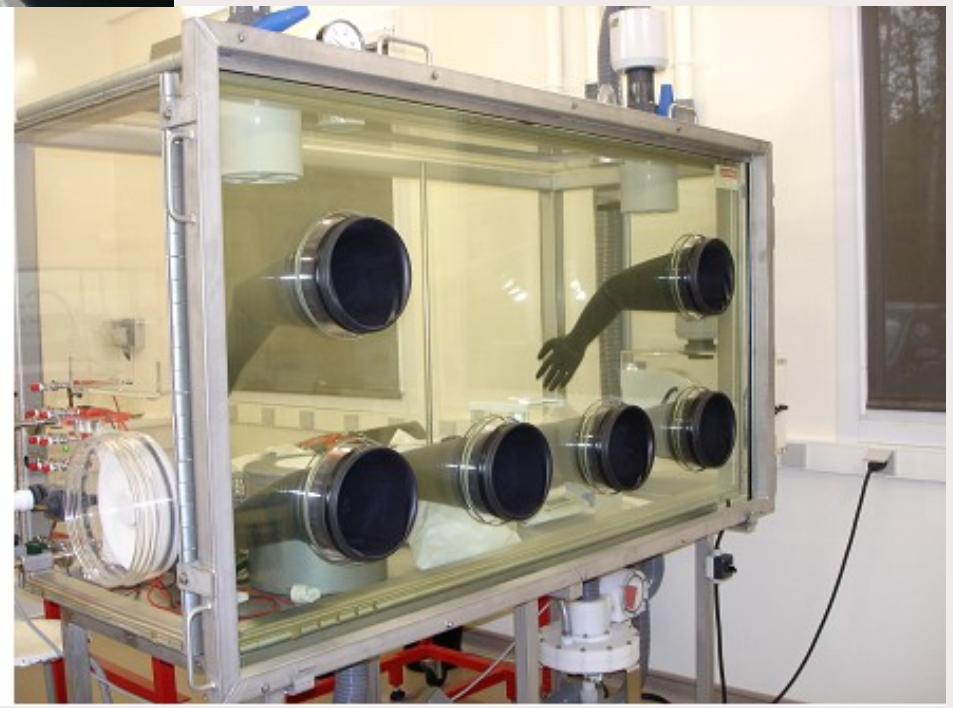




Experimental set-up



Experimental set-up



LiF-ThF_4-UF_4