L10, 2/20: Chemical Thermodynamics

Liquid-liquid miscibility gap example
From
”Thermodynamics of Molten Salt Mixtures”
By J. Lumsden (1966), p. 294.

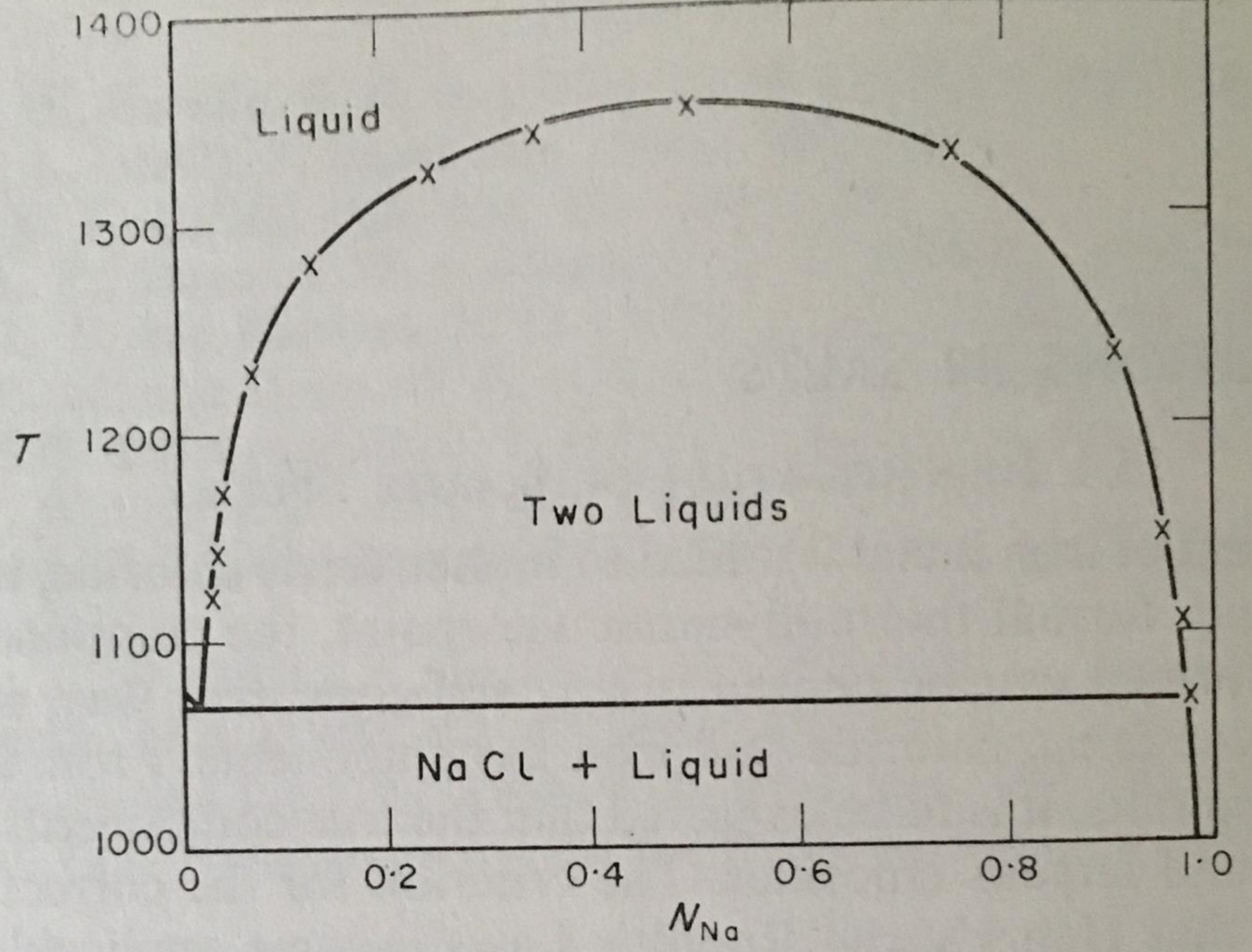

FIG. 1. Sodium and sodium chloride.

Molten Salt Chemistry, vol. 3, p. 243

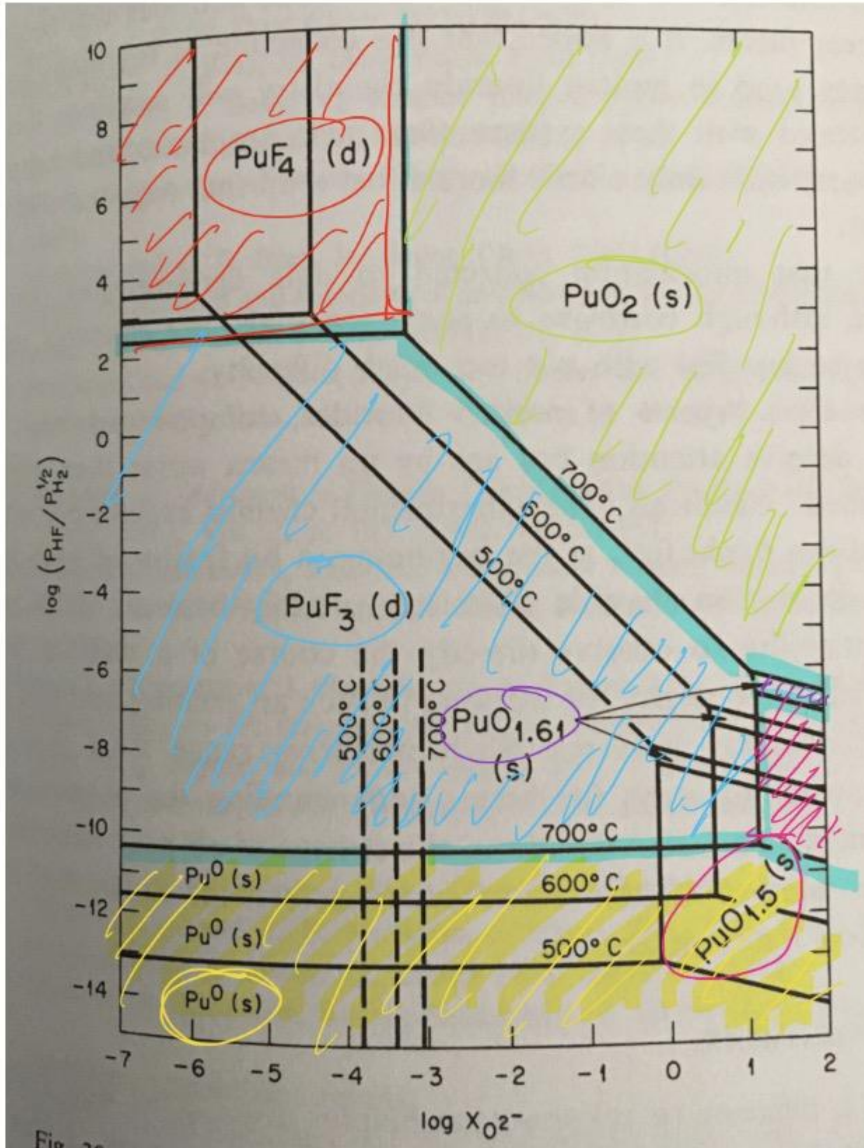

Fig. 30. Pourbaix diagram for plutonium (0.2 mole % PuF_3) in Li_2BeF_4 at various temperatures.

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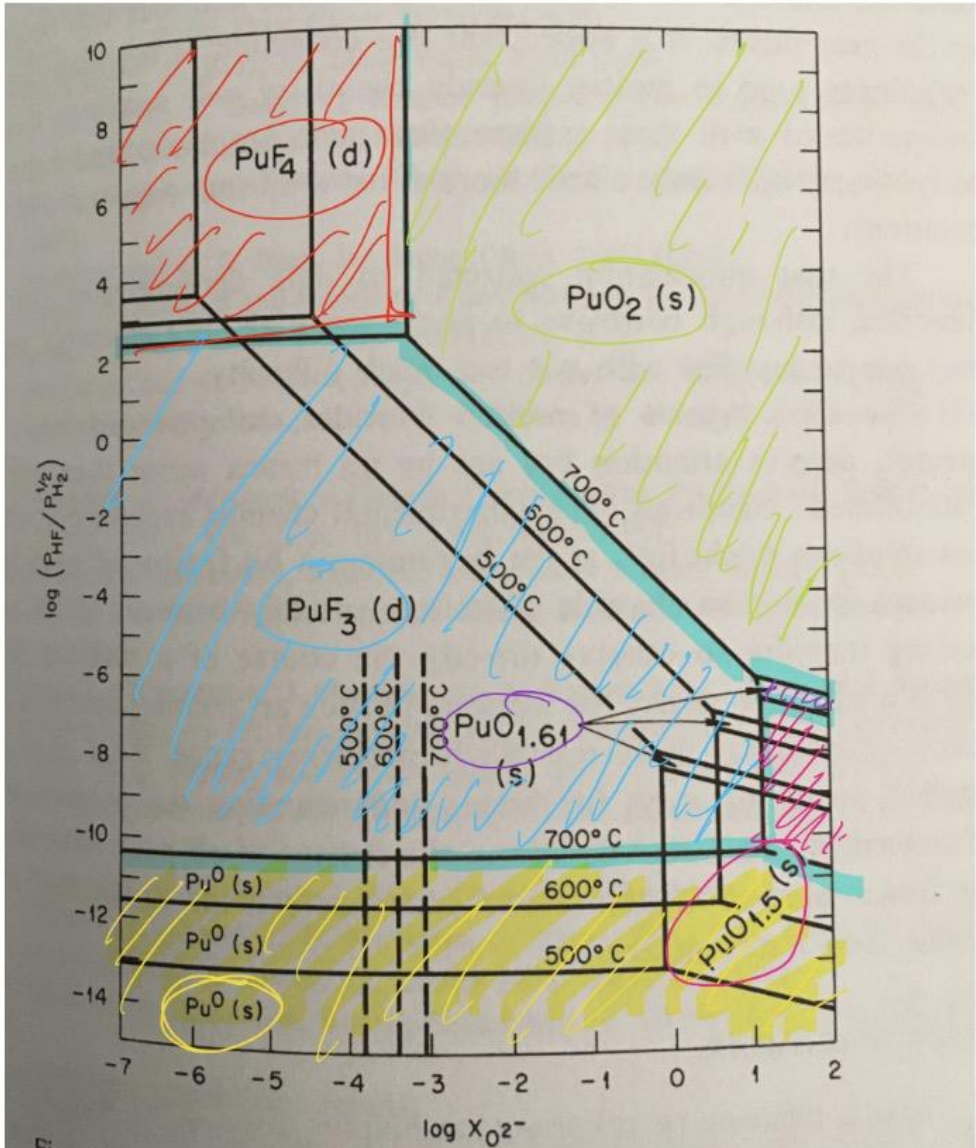


Fig. 30. Pourbaix diagram for plutonium (0.2 mole % PuF_3) in Li_2BeF_4 at various temperatures.

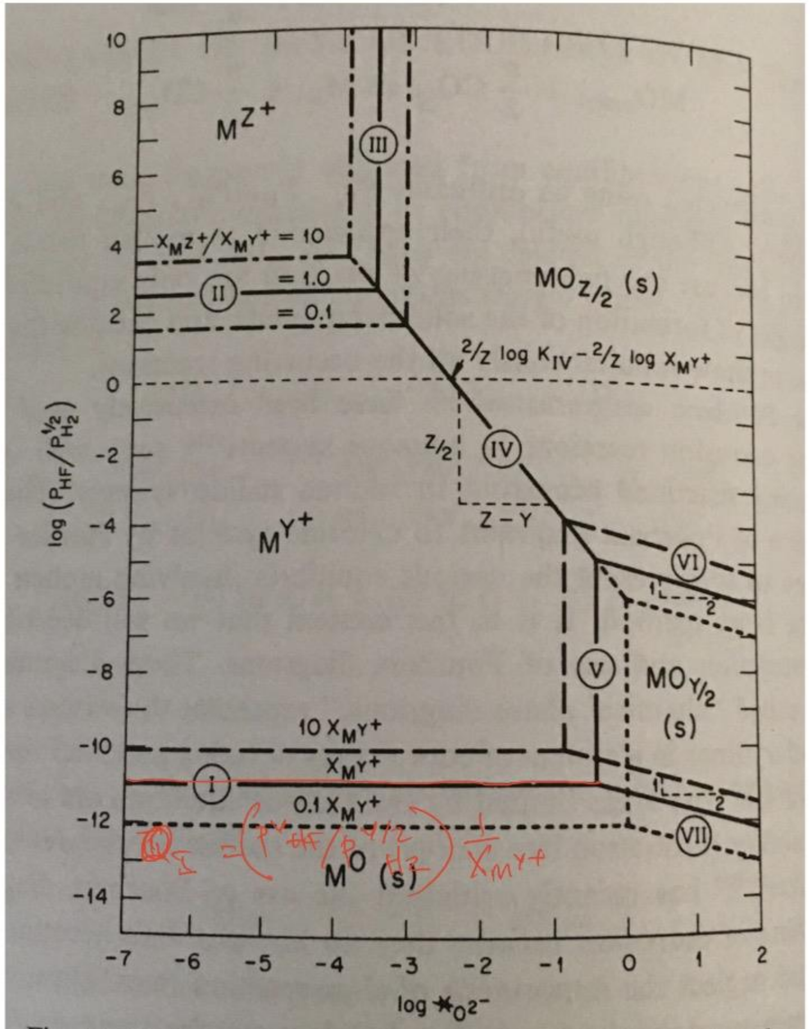


Fig. 29. Hypothetical Pourbaix diagram for several species of a solute M at various concentrations in equilibrium with a molten fluoride at a constant temperature.

$M^{Y+} + \frac{y}{2} H_2(g) + yF^- \rightleftarrows M^0(c) + yHF(g)$

half cell: $M^{Y+} \rightleftarrows M^0(c)$

General Thermodynamics, Olander, Ch. 9

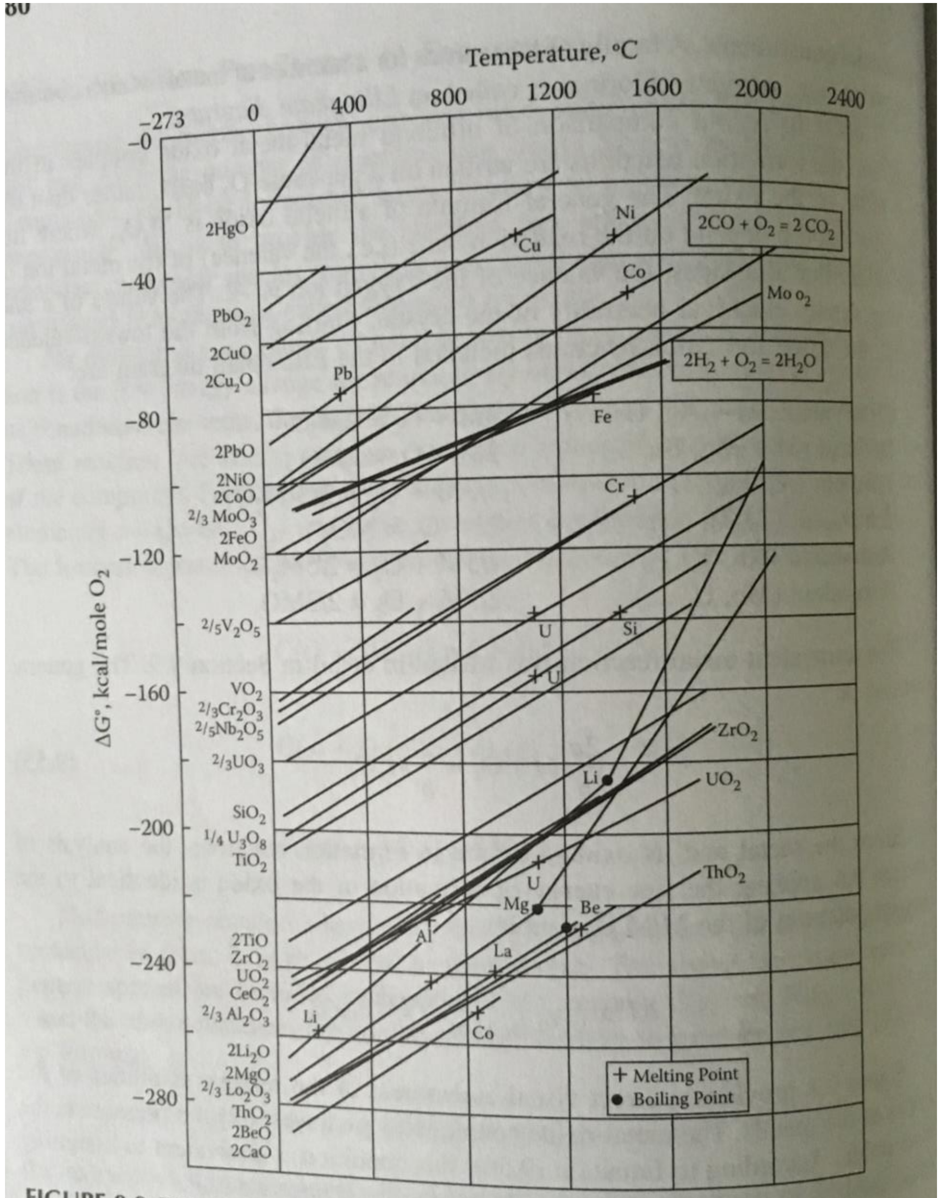
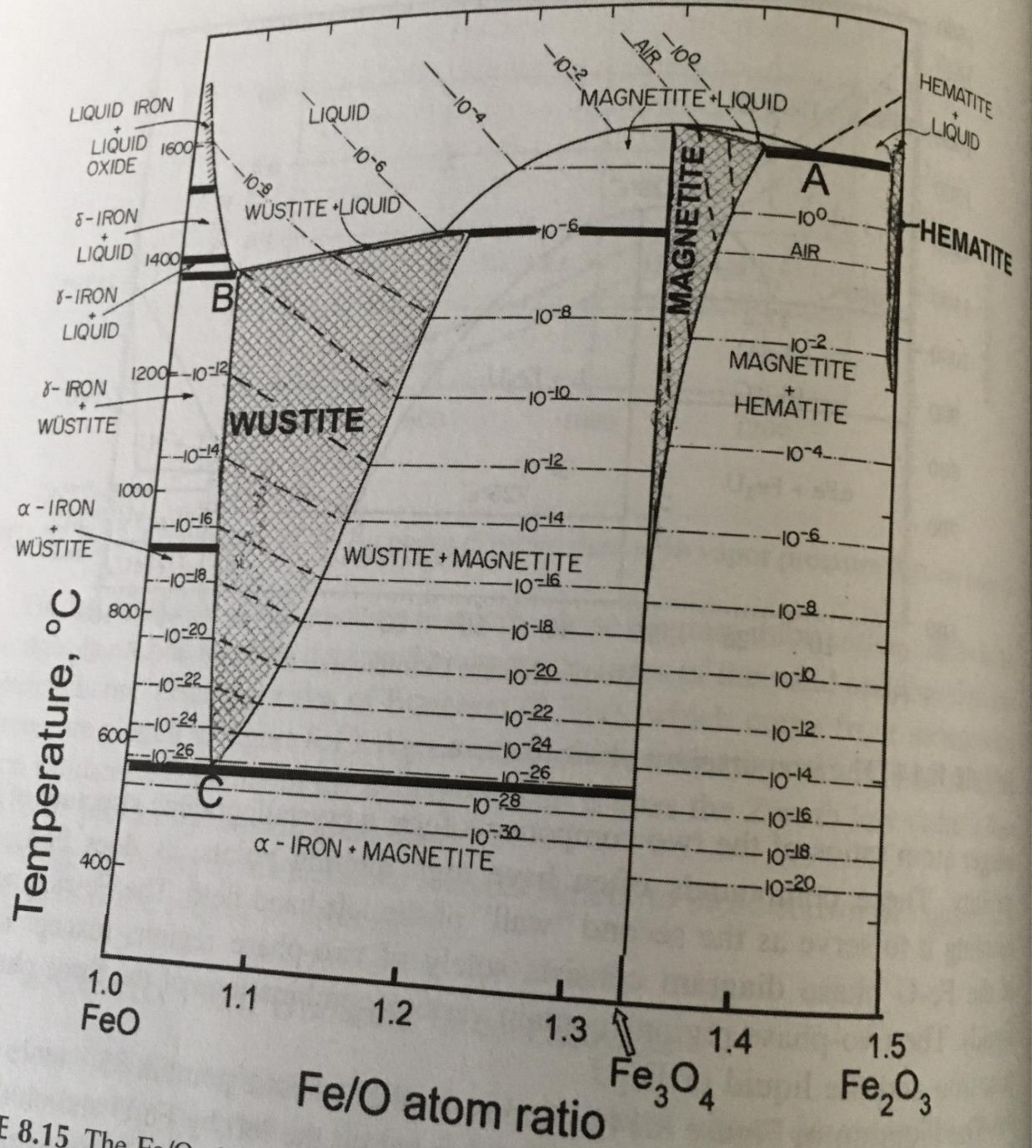


FIGURE 9.8 Ellingham diagram for the free energy of formation of oxides.

General Thermodynamics, Olander, Ch. 8



URE 8.15 The Fe/O phase diagram with oxygen pressure isobars.

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Sylvie. Delpecha, , Céline Cabetb, Cyrine Slima, Gérard S. Picardb. Molten fluorides for nuclear applications. Materials Today. Volume 13, Issue 12, December 2010, Pages 34–41.

Table 1 Pure compounds hydrolysis temperature corresponding to an equilibrium constant (R1) of 1

Reaction	T (°C)
$BeF_2 + H_2O(g) = BeO + 2HF(g)$	700
$ThF_4 + 2H_2O(g) = ThO_2 + 4HF(g)$	850
$ThF_4 + H_2O(g) = ThOF_2 + 2HF(g)$	840
$ZrF_4 + 2H_2O(g) = ZrO_2 + 4HF(g)$	495
$UF_4 + 2H_2O(g) = UO_2 + 4HF(g)$	660
$UF_4 + H_2O(g) = UOF_2 + 2HF(g)$	680
$2LiF + H_2O(g) = Li_2O + 2HF(g)$	3320
$2NaF + H_2O(g) = Na_2O + 2HF(g)$	3300
$2KF + H_2O(g) = K_2O + 2HF(g)$	4200

Sylvie. Delpecha, , Céline Cabetb, Cyrine Slima, Gérard S. Picardb. Molten fluorides for nuclear applications. Materials Today. Volume 13, Issue 12, December 2010, Pages 34–41.

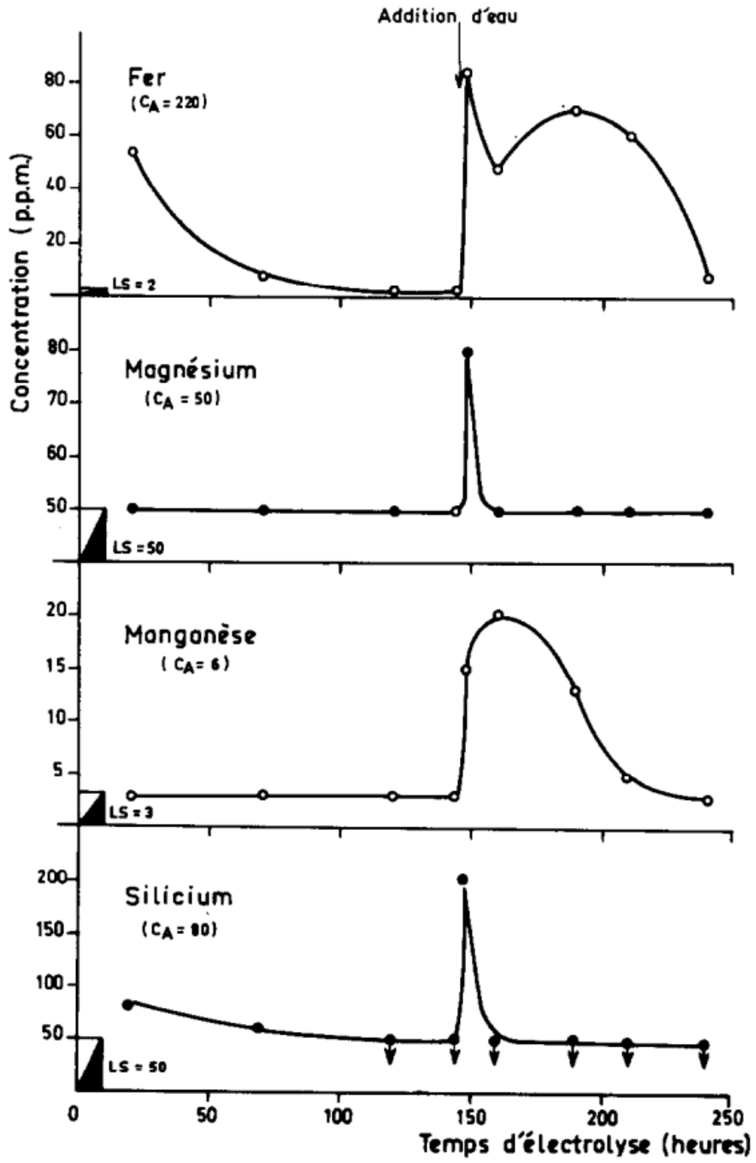

Fig. 4. Influence d'une addition d'eau à l'électrolyte sur la teneur en impuretés de l'uranium déposé. C_A: concentration de l'impureté dans l'anode, L_S: limite de sensibilité de la technique analytique (d'après [12]).

[102] M. A. Bredig. Mixtures of Metals with Molten Halides. Technical Report ORNL-3391, Oak Ridge National Laboratory, 1963.[103]

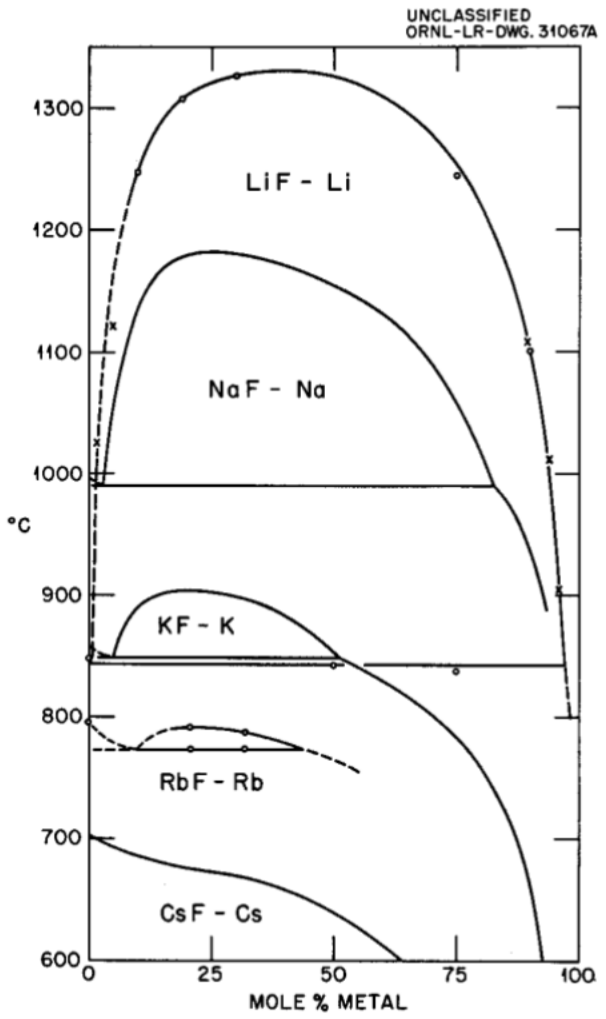

Figure 5.21: Phase diagrams of metal-metal halide systems of the alkali halides [102].

Baes, The Chemistry and Thermodynamics of Molten-Salt-Reactor Fluoride Solutions, 1966

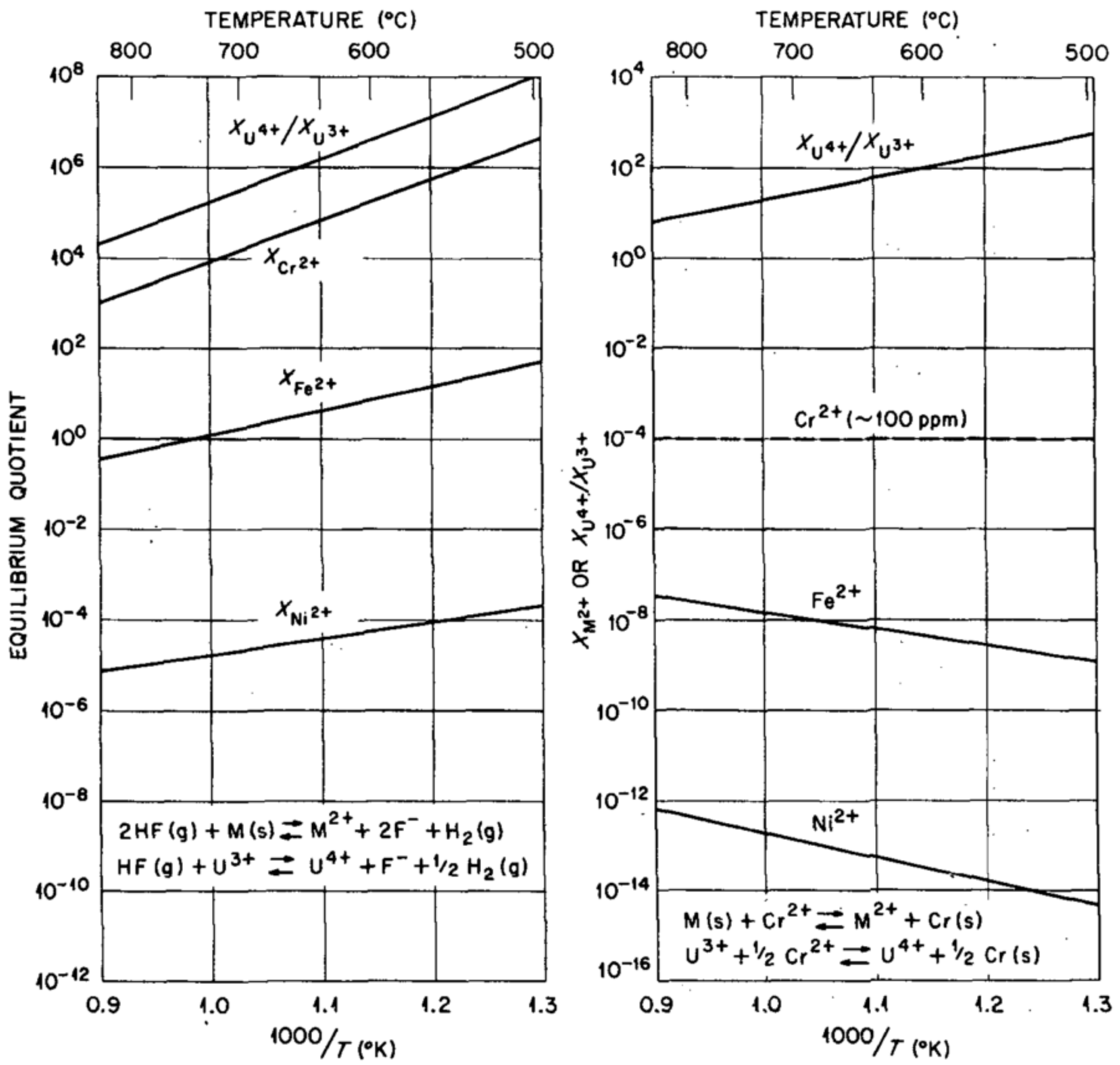

FIG. 2. Oxidation-reduction reactions in LiF-0.33BeF_2. Left; reaction of Cr, Fe, Ni, and U^{3+} with HF (1 atm) and H_2(1 atm); right; mole fractions of FeF_2, NiF_2 and the x(UF_3)/x(UF_3) ratio in equilibrium with 10^{-4} mole fraction CrF_2 and chromium metal.

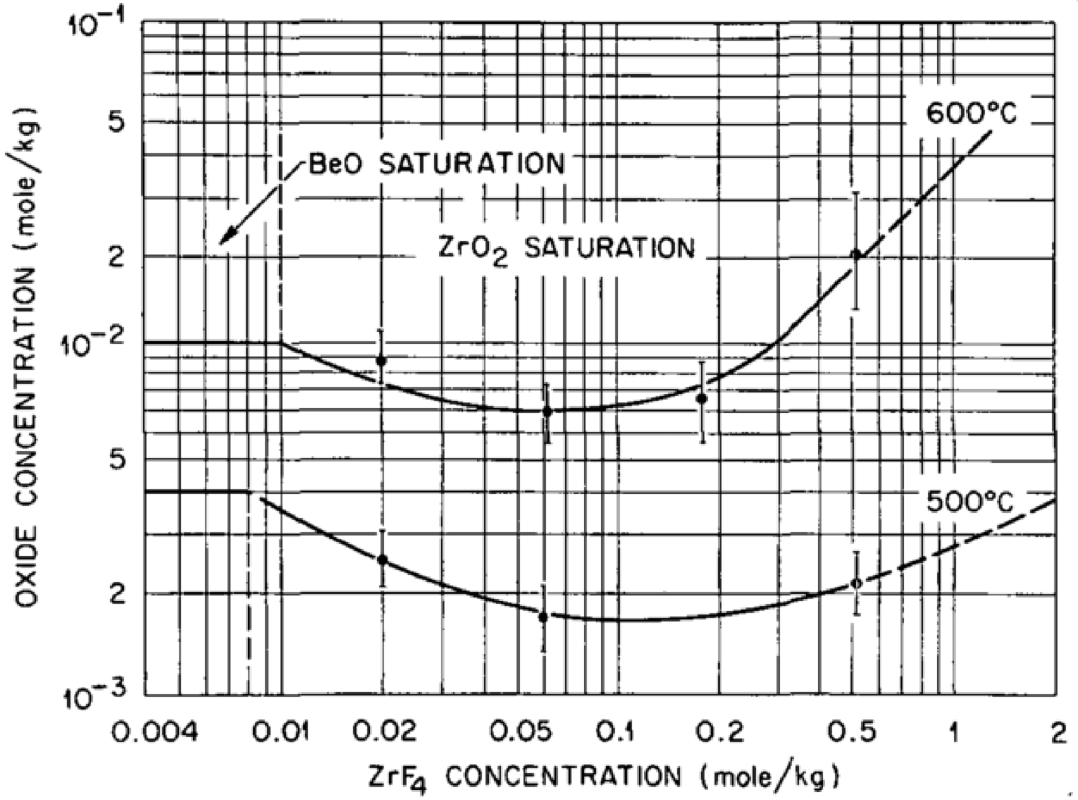

FIG. 4. Oxide concentration at saturation in LiF-0.33BeF_2 as a function of the concentration of ZrF_2 added.

Table I

Reactions in $LiF\text{-}0.33BeF_2$

[$\log K = a + b\,(10^3/T)$]

Reduction Reactions Involving Hydrogen[a]		K[b]	a	b	Est. ± Error in log K	Source[c]
1	$H_2(g) + NiF_2(d) \rightleftharpoons Ni(s) + 2HF(g)$	$(P_{HF})^2/(P_{H_2})(x_{NiF_2})$	8.37	-3.60	0.04	Ref. 4
2	$H_2(g) + FeF_2(d) \rightleftharpoons Fe(s) + 2HF(g)$	$(P_{HF})^2/(P_{H_2})(x_{FeF_2})$	5.20	-5.31	0.02	Ref. 4
3	$H_2(g) + CrF_2(d) \rightleftharpoons Cr(s) + 2HF(g)$	$(P_{HF})^2/(P_{H_2})(x_{CrF_2})$	5.12	-9.06	0.06	Ref. 4
4	$\frac{1}{2}H_2(g) + UF_4(d) \rightleftharpoons UF_3(d) + HF(g)$	$(P_{HF})(x_{UF_3})/(P_{H_2})^{\frac{1}{2}}(x_{UF_4})$	4.07	-9.33	0.02	Ref. 5
5	$H_2(g) + BeF_2(d) \rightleftharpoons Be(s) + 2HF(g)$	$(P_{HF})^2/(P_{H_2})$	7.21	-21.56	0.1	Refs. 6,7
Metathesis Reactions Involving Gases						
6	$H_2O(g) + BeF_2(d) \rightleftharpoons BeO(s) + 2HF(g)$	$(P_{HF})^2/(P_{H_2O})$	4.23	-5.67	0.02	Ref. 9
7	$2H_2O(g) + ZrF_4(d) \rightleftharpoons ZrO_2(s) + 4HF(g)$	$(P_{HF})^4/(P_{H_2O})^2(x_{ZrF_4})$	11.21	-10.66	0.04	Ref. 10
8	$H_2O(g) + 2F^-(d) \rightleftharpoons O^{2-}(d) + 2HF(g)$	$(P_{HF})^2(x_{O^{2-}})/(P_{H_2O})$	4.20	-8.64	0.08	Ref. 9
9	$H_2O(g) + F^-(d) \rightleftharpoons OH^-(d) + HF(g)$	$(P_{HF})(x_{OH^-})/(P_{H_2O})$	-1.03	-2.08	0.04	Ref. 9
10	$H_2S(g) + 2F^-(d) \rightleftharpoons S^{2-}(d) + 2HF(g)$	$(P_{HF})^2(x_{S^{2-}})/(P_{H_2S})$	$\log K(873^\circ K) < -4$		----	Ref. 12
11	$HI(g) + F^-(d) \rightleftharpoons I^-(d) + HF(g)$	$(P_{HF})(x_{I^-})/(P_{HI})$	$\log K(763^\circ K) \leq -3$		----	Ref. 13
Metathesis Reactions Involving Solid Oxides						
12	$ZrO_2(s) + 2BeF_2(d) \rightleftharpoons ZrF_4(d) + 2BeO(s)$	x_{ZrF_4}	-2.75	-0.69	0.05	6,7; Ref. 15
13	$UO_2(s) + 2BeF_2(d) \rightleftharpoons UF_4(d) + 2BeO(s)$	x_{UF_4}	-2.07	-1.74	0.07	12,14; Ref. 15
14	$ZrO_2(s) + UF_4(d) \rightleftharpoons ZrF_4(d) + UO_2(s)$	$(x_{ZrF_4})/(x_{UF_4})$	-0.67	1.05	0.05	Ref. 15
15	$ThO_2(s) + UF_4(d) \rightleftharpoons ThF_4(d) + UO_2(s)$	$(x_{ThF_4})/(x_{UF_4})$	$\log K(1023^\circ K) \approx 1.2$		----	Ref. 18

Table I (continued)

Solubility Reactions	K^b	a	b	Est. ± Error in log K	Source[c]
16 $BeO(s) \rightleftharpoons Be^{2+}(d) + O^{2-}(d)$	$x_{O^{2-}}$	-0.04	-2.96	0.08	6,8
17 $ZrO_2(s) \rightleftharpoons Zr^{4+}(d) + 2O^{2-}(d)$	$(x_{Zr^{4+}})(x_{O^{2-}})^2$	-2.82	-6.62	0.09	7,8
18 $UO_2(s) \rightleftharpoons U^{4+}(d) + 2O^{2-}(d)$	$(x_{U^{4+}})(x_{O^{2-}})^2$	-2.15	-7.66	0.1	14,17
19 $ThO_2(s) \rightleftharpoons Th^{4+}(d) + 2O^{2-}(d)$	$(x_{Th^{4+}})(x_{O^{2-}})^2$	log K(1023°K) ≈ -8.6		---	15,18
20 $NiO(s) \rightleftharpoons Ni^{2+}(d) + O^{2-}(d)$	$(x_{Ni^{2+}})(x_{O^{2-}})$	-2.58	-4.39	---	Eqs. 25, 26, Ref. 32
21 $FeO(s) \rightleftharpoons Fe^{2+}(d) + O^{2-}(d)$	$(x_{Fe^{2+}})(x_{O^{2-}})$	-0.52	-4.12	---	Eqs. 25, 26, Ref. 32
22 $NiF_2(s) \rightleftharpoons NiF_2(d)$	x_{NiF_2}	0.30	-2.07	0.01	Ref. 4
23 $FeF_2(s) \rightleftharpoons FeF_2(d)$	x_{FeF_2}	2.45	-3.05	0.01	Ref. 4
24 $LaF_3(s) \rightleftharpoons LaF_3(d)$	x_{LaF_3}	1.58	-3.38	0.02	Ref. 20
25 $CeF_3(s) \rightleftharpoons CeF_3(d)$	x_{CeF_3}	1.64	-3.38	0.02	Ref. 20
26 $SmF_3(s) \rightleftharpoons SmF_3(d)$	x_{SmF_3}	1.97	-3.38	0.02	Ref. 20
27 $PuF_3(s) \rightleftharpoons PuF_3(d)$	x_{PuF_3}	1.30	-3.15		Ref. 19

[a] The notations (s), (d), and (g) indicate respectively the solid, dissolved, and gaseous states.

[b] P_i is expressed in atmospheres; x_i is the mole fraction and, for LiF-0.33BeF_2, is equal to moles of i/kg of salt/30.03.

[c] Numbers other than reference numbers and numbers of equations in text refer to reactions in this table.