I-1 Gaz idéal

$$PV = nRT = \frac{m}{M} \cdot RT$$

$$PM = \frac{m}{V} RT$$

$$PM = \rho RT$$

$$M = \frac{\rho RT}{P} = \frac{(0.3829)(0.082)(273)}{0.5} = \underline{17.1\ g/mol}$$

I-2

$$PV = nRT$$

$$PV = \frac{m}{M} RT$$

$$\left(\frac{300}{760}\right)(5) = \frac{m}{18.00}(0.082)(423)$$

$$\underline{m = 1.024\ g}$$

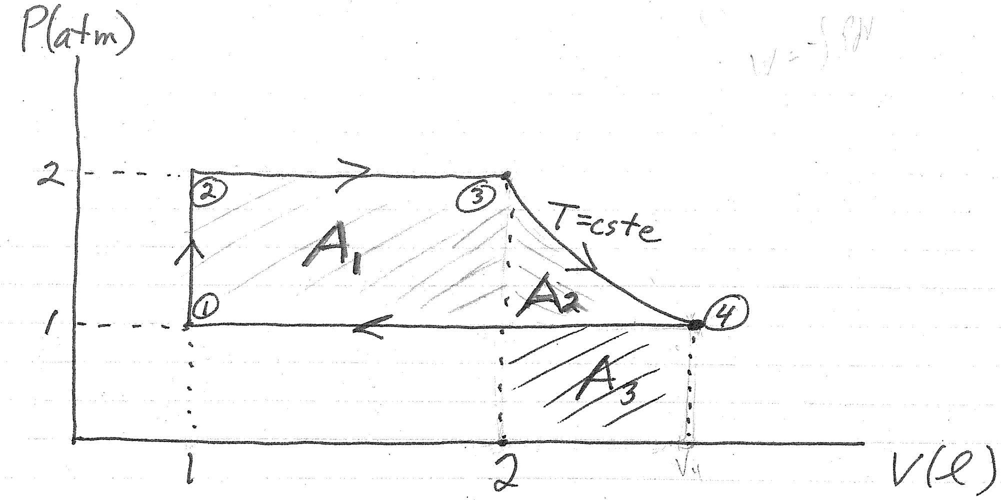
I-3 À 25°C P_{H_2O} est égale à la tension de vapeur de H_2O

$$P_{H_2O}V = nRT = \frac{m}{M} RT$$

$$P = \frac{mRT}{MV} = \frac{(0.230)(0.082)(298)}{(18.00)(10)} = 0.03122\ atm$$

$$= \underline{23.7\ torr}$$

I-4



$$P_3V_3 = P_4V_4 \quad (T = cste)$$

$$V_4 = \frac{P_3V_3}{P_4} = \frac{(2)(2)}{1} = 4\,\ell$$

$$W_{3-4(rev)} = -nRT\ln\left(\frac{V_4}{V_3}\right) = -(P_3V_3)\ln\left(\frac{V_4}{V_3}\right) = -4\ln\frac{4}{2} = -2.77\,\ell\text{-atm}$$

$$(A_2 + A_3) = 2.77$$

$$A_1 = (2-1)(2-1) = 1.00$$

$$A_3 = (4-2)(1-0) = 2.00$$

$$W_{\substack{rev\\ totale}} = -(A_1 + A_2) = -(1.00 + 2.77 - 2.00) = \underline{-1.77\ \ell\text{-atm}}$$

$$\underline{\Delta U = 0} \quad (\text{cyclique})$$

$$\therefore \quad \underline{Q = +1.77\ \ell\text{-atm}}$$

I-5 $H = U + PV$

$\Delta H = \Delta U + \Delta(PV)$

$(Fe_3C(s) + 3O_2) \rightarrow (Fe_3O_4(s) + CO_2)$

$\Delta V_{solides} \approx 0$

$\Delta(PV)_{gaz} = \Delta(nRT) = RT(\Delta n)$

où $\Delta n = (1-3) = -2\ mol$

$$\Delta H = \Delta U + (\Delta n)RT$$
$$= \Delta U - 2RT$$
$$= \Delta U - 2(1.987)(298) = \Delta U - 2(8.315)(298)$$
$$\Delta H = \Delta U - 1180\ cal = -4940\ J \approx -5\ kJ$$
$$\Delta H = -1140 - 5 = -1145\ kJ$$

I-6 (a) $$W_{rev} = -\int P\,dV = -\int_{V_i}^{V_f} \frac{RT}{(V-b)}\,d(V-b) = RT\ln\left(\frac{V_f - b}{V_i - b}\right)$$

$$V_i = \frac{RT + bP_i}{P_i} = \frac{(0.082)(298) + (0.0156)(1.0)}{1.0} = 24.452\ l$$

$V_f = 0.24452$

$$W_{rev} = -RT\ln\left(\frac{0.24452 - 0.0156}{24.452 - 0.0156}\right) = 114.13\ l\text{-atm}$$

(b) $$W_{rev} = -RT\ln\frac{V_f}{V_i} = -RT\ln(10^{-2}) = 112.53\ l\text{-atm}$$

I-7 $W = -P_{ext}\Delta V = -2.0(10-1) = -18\ l\text{-atm}$

$Q = 0$ (adiabatique)

$$\Delta U = Q + W$$
$$= -18$$
$$= n\left(\tfrac{3}{2}\right)R\,\Delta T$$
$$= (3.0)\left(\tfrac{3}{2}\right)(0.082)\,\Delta T$$

$\Delta T = -49°$

$T_f = 25 - 49$

$T_f = -24°C$

II-1

$$\Delta H = \int_{298}^{600.5} C_p(sol)\,dT + \Delta h_f^\circ + \int_{600.5}^{1300} C_p(liq)\,dT$$

$$= \int_{298}^{600.5} (5.82 + 1.90\times10^{-3}T)\,dT + 1225 + \int_{600.5}^{1300} 6.80\,dT$$

$$= 5.82(600.5-298) + \frac{1.90\times10^{-3}}{2}(600.5^2 - 298^2) + 1225 + 6.80(1300-600.5)$$

$\Delta H = 8000$ cal

II-2

$$\begin{tikzcd}[column sep=huge] (PbO)_{1250} \arrow[r, "\Delta H^\circ_{1250}"] \arrow[d, "\Delta H^\circ_1"] & (Pb + \tfrac{1}{2}O_2)_{1250} \\ (PbO)_{298} \arrow[r, "\Delta H^\circ_{298}"', "= +52{,}400 \text{ cal}"'{yshift=-12pt}] & (Pb + \tfrac{1}{2}O_2)_{298} \arrow[u, "\Delta H^\circ_2", shift left=6] \arrow[u, "\Delta H^\circ_3"', shift right=6] \end{tikzcd}$$

Supposons : $\dfrac{(h^\circ_{1300} - h^\circ_{298}) + (h^\circ_{1200} - h^\circ_{298})}{2} \approx (h^\circ_{1250} - h^\circ_{298})$

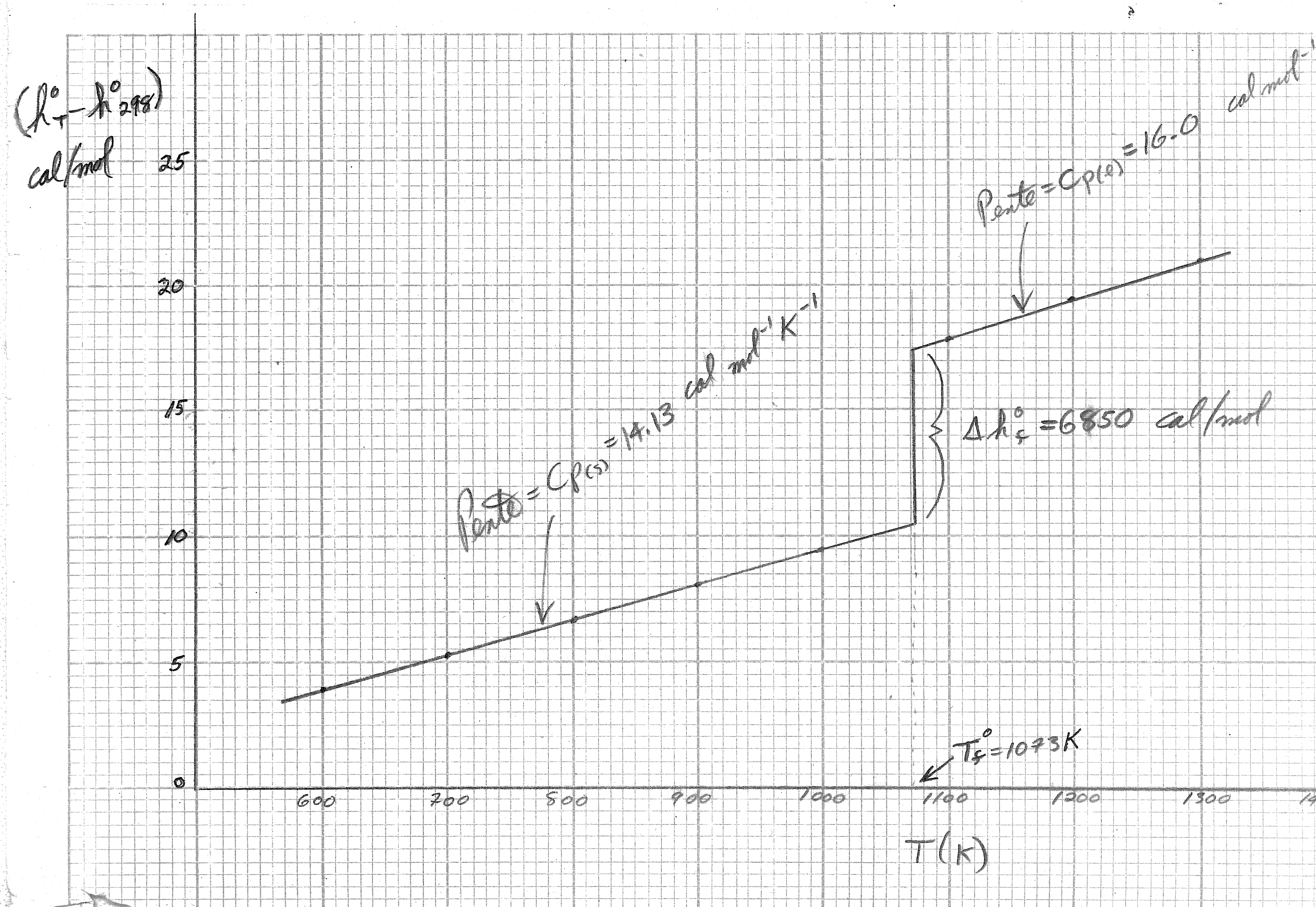
Donc : $\Delta H^\circ_2 = (h^\circ_{1250} - h^\circ_{298})_{Pb} \approx 7660$

$\Delta H^\circ_3 = \frac{1}{2}(h^\circ_{1250} - h^\circ_{298})_{O_2} = \frac{1}{2}(7457)$

$\Delta H^\circ_1 = -(h^\circ_{1250} - h^\circ_{298})_{PbO} = -15975$

$$\Delta H^\circ_{1250} = \Delta H^\circ_{298} + (\Delta H^\circ_1 + \Delta H^\circ_2 + \Delta H^\circ_3)$$

$\Delta H^\circ_{1250} = +47810$ cal


$(h^o_T - h^o_{298})$
cal/mol
0
5
10
15
20
25
600
700
800
900
1000
1100
1200
1300
1400
T (K)
Pente = $C_{p(s)}$ = 14.13 cal mol^{-1} K^{-1}
Pente = $C_{p(\ell)}$ = 16.0 cal mol^{-1} K^{-1}
Δh^o_f = 6850 cal/mol
T^o_f = 1073 K

II - 4

20 tonnes courtes = 2000 livres × 20

$$= \frac{20(2000)(453.6)}{63.54} = 2.85550 \times 10^5 \text{ mol}$$

Pour refroidi 20 tonnes de Cu de 1473 K jusqu'à 1423 K :

$$\Delta H = 2.85550 \times 10^5 \int_{1473}^{1423} C_p(l)\,dT = -1.071 \times 10^8 \text{ cal.}$$

Pour chauffer n mol de Cu de 25°C jusqu'à 1423 K :

$$\Delta H = n\left[\int_{298}^{1356} C_p(s)\,dT + 3120 + \int_{1356}^{1423} C_p(l)\,dT\right]$$

$$= 10660\,n \text{ cal.}$$

Pertes $= -10^6$ cal.

$$\therefore \quad -1.071 \times 10^8 + 10660\,n + 1.0 \times 10^6 = 0$$

$n = 9953$ mol

$$n = \frac{9953(63.54)}{453.6} = \underline{1394 \text{ livres}}$$

II-5

$$\begin{tikzcd}
& (CaO + CO_2)_{1073} \\
(CaCO_3)_{298} \arrow[ur, "\Delta H^\circ_{totale}"] \arrow[r, "\Delta H^\circ_{298}"'] & (CaO + CO_2)_{298} \arrow[u, "\Delta H^\circ_1 \quad \Delta H^\circ_2"']
\end{tikzcd}$$

$$\Delta H^\circ_{totale} = \Delta H^\circ_{298} + \Delta H^\circ_1 + \Delta H^\circ_2$$

$$= \pm 177800 + \int_{298}^{1073} \left(C_{p(CaO)} + C_{p(CO_2)}\right) dT$$

$$= 177800 + 75605$$

$$= 253405 \text{ J/(mol } CaCO_3)$$

Pour 1000 kg de CaO

$$\Delta H^\circ = \frac{10^6}{56.0}(253405) = 4.527 \times 10^9 \text{ J}$$

$$= 4.527 \times 10^9 \text{ watt-sec.}$$

$$= \underline{1257 \text{ kwatt-h}}$$

II-6

$$\begin{tikzcd}
& (Al_2O_3 + 2Cr(l))_{2173} \\
(2Al + Cr_2O_3)_{298} \arrow[ur, "\Delta H^\circ_{totale}"] \arrow[r, "\Delta H^\circ_{298}"'] & (Al_2O_3 + 2Cr(s))_{298} \arrow[u, "\Delta H^\circ_1 \quad \Delta H^\circ_2"']
\end{tikzcd}$$

$$\Delta H^\circ_{totale} = \Delta H^\circ_{298} + \Delta H^\circ_1 + \Delta H^\circ_2$$

$$\Delta H^\circ_{298} = -400{,}000 + 270{,}000 = -130{,}000$$

$$\Delta H^\circ_1 = \int_{298}^{2173} C_p(Al_2O_3)\, dT$$

$$\Delta H^\circ_2 = 2\int_{298}^{2123} C_{p(Cr(s))} dT + 2\Delta h^\circ_{fus(Cr)} + 2\int_{2123}^{2173} C_{p(Cr(l))}\, dT$$

$$\underline{\Delta H^\circ_{totale} = -32526 \text{ cal.}} = \underline{\text{Pertes}}$$

II-7

$$CH_4 + 2O_2 + 2\left(\frac{0.79}{0.21}\right)N_2 = \left(CO_2 + 2H_2O + 2\left(\frac{0.79}{0.21}\right)N_2\right)$$

$$\Delta H^o_{298} = -94.05 - 2(57.80) + 17.89 = -191.76 \text{ kcal.}$$

$$\Sigma C_p(\text{produits}) = C_p(CO_2) + 2C_p(H_2O) + 7.5238\ C_p(N_2)$$
$$= 75.00 + 14.95(10^{-3})T - 1.88(10^5)\ T^{-2}$$

$$\Delta H_{totale} = -191760 + \int_{298}^{T} (\Sigma C_p)\, dT = 0$$

$$191760 = 75.00(T-298) + \frac{14.95(10^{-3})}{2}(T^2 - 298^2)$$
$$+ 1.88(10^5)\left(\frac{1}{T} - \frac{1}{298}\right)$$

$$f(T) = 7.48(10^{-3})T^2 + 1.88(10^5)\left(\frac{1}{T}\right) + 75.00\,T - 215405 = 0$$

Solution par approximations successives

$T = 2330\,K$

II-8

$$CH_4 + 10O_2 + 37.619\,N_2 = CO_2 + 2H_2O + 8O_2 + 37.619\,N_2$$

$$\Delta H^o_{298} = -801993 \text{ J}$$

$T(K)$	$(h^o_T - h^o_{298})(CO_2 + 2H_2O + 8O_2 + 37.619N_2)$
1000	$33094 + 2(26018) + 8(22542) + 37.619(21506)$ $= 1{,}074{,}500$
900	$914{,}200$
800	$756{,}220$

Supposez $(h^o_T - h^o_{298})$ soit linéaire entre 800K et 900K

$$\frac{801993 - 756220}{914200 - 756220} = 0.29$$

$T = 800 + 29$

$T = 829\,K$

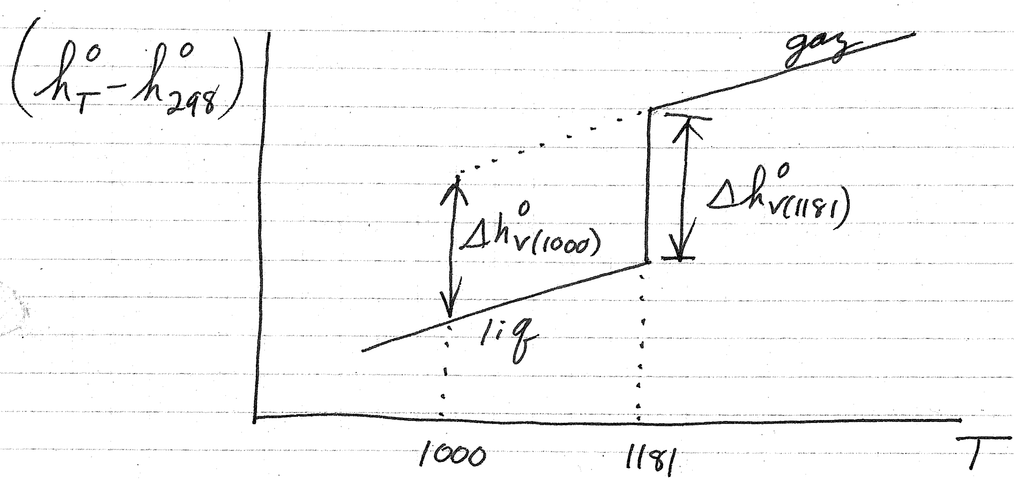
II - 9

$$\begin{tikzcd} Zn(l)_{1181} \arrow[r, "\Delta h^o_{v(1181)}"] & Zn(g)_{1181} \arrow[d] \\ Zn(l)_{1000} \arrow[u] \arrow[r, "\Delta h^o_{v(1000)}"'] & Zn(g)_{1000} \end{tikzcd}$$

$$\Delta H^o_{v(1000)} = \Delta H^o_{v(1181)} + \int_{1000}^{1181} (C_p(l) - C_p(g))\,dT$$

$$= 115310 + (1181-1000)(10.36)$$

$$= \underline{117190 \text{ J/mol}}$$



II-10

$$
\begin{tikzcd}[column sep=huge, row sep=huge]
{[Al(l)]_{T_f^\circ = 932\,K}} \arrow[r, "\Delta H = -x\Delta h_f^\circ = -10750x"] & {[xAl(s) + (1-x)Al(l)]_{932}} \\
{[Al(l)]_{900K}} \arrow[u, "{\Delta H = \int_{900}^{932} C_{p(l)}\,dT = 29.29(32) = 937}"] \arrow[ur, "\Delta H_{TOT} = 0 \text{ (adiabatique)}"'] &
\end{tikzcd}
$$

$$937 - 10750x = 0$$

$$\underline{x = 0.087}$$

II-11 Supposez 1 mol de solution finale

$5\,g\ Si = 0.178\ mol$
$95\,g\ Fe = 1.70\ mol$

$$\left.\begin{array}{l} X_{Si} = \frac{0.178}{1.878} = 0.0948 \\ X_{Fe} = 1 - 0.0948 = 0.9052 \end{array}\right] \text{composition finale}$$

$$\left[\underbrace{\begin{bmatrix} 0.0948\ Si \\ 0.0948\ Fe \end{bmatrix}}_{(FeSi)}{}_{25°C} + \begin{array}{c}(0.9052 - 0.0948) \\ = 0.8104\end{array}\ Fe(l)_{1600°C} \right] \text{état initial}$$

$$\downarrow \Delta H_1$$

$$\left[\underbrace{\begin{bmatrix} 0.0948\ Si \\ 0.0948\ Fe \end{bmatrix}}_{(FeSi)}{}_{1600°C} + 0.8104\ Fe_{1600°C} \right]$$

$$\downarrow \Delta H_2$$

$$\left[0.0948\ Si + 0.9052\ Fe \right]_{1600°C}$$

$$\downarrow \Delta H_3$$

$$\left[1\ mol\ solution \right]_{1600°C}$$

$$\downarrow \Delta H_4$$

$$\left[1\ mol\ solution \right]_{T}$$

$\Delta H_1 = 0.1896(19000) = 3600$ (où $0.1896 = 2(0.0948)$)

$\Delta H_2 = 0.1896(-\Delta h^{mix}_{X=0.5}) = 0.1896(8930) = 1696$

$\Delta H_3 = \Delta h^{mix}_{X_{Si}=0.0948} \approx -2650$

$$\Delta H_4 = \int_{1873}^{T} \left(0.0948(7.4) + 0.9052(10.0)\right) dT = 9.754\,T - 18250$$

$\Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 = 0$ (adiabatique)

$\underline{T \approx 1600\,K \approx 1330°C}$

III-1 $dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$dV = V\alpha dT - VK dP$

$dV = 0$

$V\alpha dT = VK dP$

$dP = \frac{\alpha}{K} dT$

$\Delta P = \frac{\alpha}{K}\Delta T = \frac{2.07(10^{-4})}{4.50(10^{-5})}(10)$

$\Delta P = 46 \text{ atm}$

III-2 $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = a + b(T-273)$

$dV_P = V\alpha dT$

$\ln\frac{V_f}{V_i} = \int_{T_i=273}^{T_f=373}(a+b(T-273))\,dT$

$V_i = 1.0 \text{ ml} \qquad a = 0.18182 \times 10^{-3}$

$b = 0.0156 \times 10^{-6}$

$V_f = 1.0183 \text{ ml.}$

IV-1

$P_i V_i = nRT \qquad V_i = \frac{3(.082)(300)}{20} = 3.69\,l$

$P_f V_f = nRT \qquad V_f = \frac{3(.082)(300)}{2} = 36.9\,l.$

(a) $W_{rev} = -nRT \ln \frac{V_f}{V_i} = -3(\cancel{1.987}\;8.315)(300) \ln(10)$

$= -17230\ J$

$\Delta U = Q + W = 0$

$Q = +17230$ Joules

$\Delta S = \frac{Q_{rev}}{T} = \frac{17230}{300}$

$\Delta S = 57.446\ J/K$

$\Delta S_{ent} = -\frac{Q}{T} = \frac{-17230}{T} = -57.446\ J/K$

$\Delta S_{TOT} = 0$

(b) $\Delta S = 57.446\ J/K$ (mêmes états initiaux et finaux que dans (a))

$\Delta S_{ent} = \frac{-Q}{T}$

$W = -\int P_{ext}\, dV = -P_{ext} \Delta V = -2.0(36.9 - 3.69)$

$= -66.42\ l\text{-atm}$

$= -6728\ J$

$\Delta U = 0$

$Q = +6728\ J.$

$\Delta S_{ent} = \frac{-6728}{300} = -22.43\ /K$

$\Delta S_{TOT} = 57.446 - 22.43$

$\Delta S_{TOT} = +35.02\ J/K > 0$ (spontané)

IV-2 $\Delta E = -mg\Delta x$

$= -(1.0)(9.8)(1.0)$

$\Delta E = -9.8\ J$

$\Delta U = 0$

$W = 0$

$Q = -9.8\ J$

$\Delta S = 0$

$\Delta S_{ent} = \frac{-(-9.8)}{298} = +0.033\ J/K$

$\Delta S_{TOT} = +0.033\ J/K$

IV-3 $\Delta S_A = \frac{1000}{373.15}$

$\Delta S_B = -\frac{1000}{473.15}$

$\Delta S_{TOT} = 0.57\ J/K$

IV-4 $\Delta S_{benzine} = -\frac{9887}{(273.15+5.5)}$

$\Delta S_{eau} = \frac{9887}{273.15}$

$\Delta S_{TOTAL} = 0.714\ J/K$

IV-5 Règle de Trouton : $\Delta S^\circ_v \approx 88\ J/mol\,K$

$\Delta H^\circ_v = T\Delta S^\circ_v$

$= 1184(88)\ J/mol$

$\Delta H^\circ_v \approx 104\ kJ/mol$

IV-6

$$\begin{tikzcd}
Zn(l) \arrow[r, "{\Delta h^\circ_{420} = -1740,\ \Delta S^\circ_{420}}", "{T^\circ_f = 420°C}"'] & Zn(s) \arrow[d, "{\Delta H_2,\ \Delta S_2}"] \\
Zn(l) \arrow[u, "{\Delta H_1,\ \Delta S_1}"] \arrow[r, "{\Delta h^\circ_{400},\ \Delta S^\circ_{400}}", "{400°C}"'] & Zn(s)
\end{tikzcd}$$

(a) $\Delta S^\circ_{420} = \dfrac{Q_{rev}}{T} = \dfrac{-1740}{693.15} = -2.510$ cal/mol K

$\Delta S_{\substack{ent \\ (420)}} = \dfrac{-Q}{T} = \dfrac{1740}{693.15} = +2.510$ cal/mol K

$\Delta S_{TOT} = 0$

(b) $\Delta h^\circ_{400} = \Delta h^\circ_{420} + \Delta H_1 + \Delta H_2$

$= \Delta h^\circ_{420} + \int_{673}^{693} (Cp(l) - Cp(s))\,dT$

$= -1740 + 0.51(20) = -1730$

$\Delta S^\circ_{400} = \Delta S^\circ_{420} + \Delta S_1 + \Delta S_2$

$= -2.510 + \int_{673}^{693} \dfrac{Cp(l) - Cp(s)}{T}\,dT$

$= -2.510 + 0.51 \ln \dfrac{693}{673}$

$\Delta S^\circ_{400} = -2.495$ cal/mol K

$\Delta S_{\substack{ent \\ (400)}} = \dfrac{-\Delta h_{400}}{T} = \dfrac{1730}{673.15} = 2.570$ cal/K

$\Delta S_{TOT} = +0.075$ cal/K

V-1 $Ni + \frac{1}{2}O_2 = NiO \quad \Delta G^{o}_{1000} = -148350\ J.$

$CO + \frac{1}{2}O_2 = CO_2 \quad \Delta G^{o}_{1000} = -195700\ J.$

méthode (i) $Ni + CO_2 = NiO + CO \quad \Delta G^{o} = -148350 - (-195700)$

$= 47350$

$= -RT \ln K$

$K = 3.36 \times 10^{-3} = \left(\frac{P_{CO}}{P_{CO_2}}\right)_{équil}$

$Q = \frac{P_{CO}}{P_{CO_2}} = \frac{5}{15} = 0.333 > K$

$\therefore$ NiO réduit

méthode (ii) $Ni + CO_2 = NiO + CO$

$\Delta G = \Delta G^{o} + RT \ln \frac{P_{CO}}{P_{CO_2}}$

$= 47350 + 8.315(1000) \ln \frac{5}{15}$

$= 38215 > 0$

$\therefore$ NiO réduit

méthode (iii) $Ni + \frac{1}{2}O_2 = NiO \quad \Delta G^{o} = -RT \ln \frac{1}{P_{O_2}^{1/2}}$

$P_{O_2} = 3.19 \times 10^{-16}$ atm

$CO + \frac{1}{2}O_2 = CO_2 \quad \Delta G^{o} = -RT \ln \frac{P_{CO_2}}{P_{CO} \cdot P_{O_2}^{1/2}}$

$= -RT \ln \frac{15}{5(P_{O_2}^{1/2})}$

$P_{O_2} = 3.25 \times 10^{-20} < 3.19 \times 10^{-16}$

$\therefore$ NiO réduit

V-2 $Cu_2S = 2Cu + \frac{1}{2}S_2 \quad \Delta G^\circ_{1000K} =$ 100.74 kJ

$Mo_2S_3 = 2Mo + \frac{3}{2}S_2 \quad \Delta G^\circ_{1000K} =$ 345.2 kJ

$Mo_2S_3 + 6Cu = 3Cu_2S + 2Mo$

$\Delta G^\circ = 345.2 - 3(100.74) = 43.1\,kJ > 0$

$\Delta G = \Delta G^\circ > 0$

$\therefore$ Mo_2S_3 n'est pas réduit

V-3 $H_2 + \frac{1}{2}O_2 = H_2O \quad \Delta G^\circ_{1000} = -45800 = -RT\ln K$

$K = 1.024 \times 10^{10} = \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{1/2}} = \frac{1}{(6.0 \times 10^{-3})} \frac{1}{P_{O_2}^{1/2}}$

$P_{O_2} = 2.65 \times 10^{-16}\,atm$

$Ni + \frac{1}{2}O_2 = NiO \quad K = 5.6 \times 10^7 = \frac{1}{P_{O_2}^{1/2}}$

$P_{O_2} = 3.19 \times 10^{-16} > 2.65 \times 10^{-16}$

$\therefore$ NiO est réduit

V-4 $Ni + H_2S = NiS + H_2$

$\Delta G = \Delta G^\circ + RT\ln \frac{P_{H_2}}{P_{H_2S}}$

$= -33450 + RT\ln(50.0)$

$= -4174$

$\Delta G < 0$

$\frac{3}{2}Ni + H_2S = \frac{1}{2}Ni_3S_2 + H_2$

$\Delta G = \Delta G^\circ + RT\ln \frac{P_{H_2}}{P_{H_2S}} = -18530 + RT\ln(50)$

$= 10746$

> 0

$\therefore$ NiS est produit

V-5 $N_2 + O_2 = 2NO$

	N_2	O_2	NO
Entrée	79	21	0
Equilibre	$(79-x)$	$(21-x)$	$2x$

$n_{TOT} = 100$

$$P_{NO} = \frac{n_{NO}}{n_{TOT}} \cdot P_{TOT} = \frac{2x}{100}(1) = \frac{2x}{100}$$

$$P_{O_2} = \frac{21-x}{100}(1)$$

$$P_{N_2} = \frac{79-x}{100}(1)$$

$$K = \frac{P_{NO}^2}{P_{N_2} \cdot P_{O_2}} = \frac{(2x/100)^2}{\left(\frac{79-x}{100}\right)\left(\frac{21-x}{100}\right)} = 1.10 \times 10^{-3}$$

$x = 0.66$

$$\% NO = \frac{n_{NO}}{n_{TOT}} \times 100$$

$$= 1.32\%$$

V-6

Si le $SrCO_3$ est tout seul au début

$$SrCO_3 = SrO + CO_2 \quad ①$$

$$P_{TOT} = P_{CO_2} = \frac{2.47}{760} = 3.25 \times 10^{-3} atm$$

$$K_{①} = P_{CO_2} = 3.25 \times 10^{-3}$$

Si les 3 solides sont dans le contenant

$$SrCO_3 = SrO + CO_2 \qquad K_{①} = 3.25 \times 10^{-3}$$

$$P_{CO_2} = 3.25 \times 10^{-3}$$

$$C + CO_2 = 2CO \quad ② \qquad K_{②} = \frac{P_{CO}^2}{P_{CO_2}}$$

$$P_{CO} = P_{TOT} - P_{CO_2} = \frac{171 - 2.47}{760} = 0.2218 \text{ atm.}$$

$$K_2 = \frac{(0.2218)^2}{3.25 \times 10^{-3}} = 15.14$$

$$\Delta G_2^\circ = -RT \ln K$$

$$\underline{\Delta G_2^\circ = -25480 \text{ J}}$$

V - 7 $\quad n_{PCl_5} = \frac{3.6}{M_{PCl_5}} = \frac{3.6}{208} = 0.0173$ mol.

$PCl_5 = PCl_3 + Cl_2$

	$PCl_5(g)$	$PCl_3(g)$	$Cl_2(g)$
Entrée	0.0173	0	0
Equilibre	$(0.0173-x)$	x	x

$$n_{TOT} = (0.0173+x)$$

$$P_{TOT} V = n_{TOT} RT$$

$$(1)(1) = (0.0173+x)(0.082)(473)$$

$$x = 0.008482$$

$$P_{PCl_5} = \frac{(0.0173-x)}{(0.0173+x)} \cdot (1) = 0.343 \text{ atm}$$

$$P_{PCl_3} = P_{Cl_2} = \frac{x}{(0.0173+x)}(1) = 0.329 \text{ atm}.$$

$$K = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}}$$

$$K = 0.316$$

$\underline{V-8}$ $2CO + O_2 = 2CO_2$ $\Delta G° = -304.8$ kJ.

$2H_2 + O_2 = 2H_2O$ $\Delta G° = -330.7$ kJ.

$CO + H_2O = CO_2 + H_2$ $\Delta G° = \frac{-304.8 + 330.7}{2} = 12.95$ kJ $= -RT\ln K$

$K = 0.354$

	CO	H_2O	CO_2	H_2
Entrée	1	1	0	0
Equilibre	1-x	1-x	x	x

$n_{TOT} = 2$

$K = \frac{x^2/4}{(1-x)^2/4} = 0.354$

$x = 0.373$

Composition: $\underline{\% CO_2 = \% H_2} = \frac{0.373}{2} \times 100 = \underline{18.7\%}$

$\underline{\% CO = \% H_2O} = \frac{(1-0.373)}{2} \times 100 = \underline{31.4\%}$

$2CO + O_2 = 2CO_2$ $\Delta G° = -304.8$ kJ $= -RT\ln K$

$K = 4.123 \times 10^{10} = \left(\frac{P_{CO_2}}{P_{CO}}\right)^2 \left(\frac{1}{P_{O_2}}\right) = \left(\frac{18.7}{31.4}\right)^2 \left(\frac{1}{P_{O_2}}\right)$

$\underline{P_{O_2} = 8.6 \times 10^{-12} \text{ atm}}$

V-9 $H_2S = H_2 + \frac{1}{2}S_2$

	H_2	S_2	H_2S
Entrée	0.1	0	0.1
Equilibre	$0.1+x$	$\frac{1}{2}x$	$0.1-x$

$$n_{TOT} = 0.2+0.5x$$

$$P_{H_2S} = \frac{(0.1-x)}{(0.2+0.5x)} P_{TOT}$$

$$P_{H_2} = \frac{(0.1+x)}{(0.2+0.5x)} P_{TOT}$$

$$P_{S_2} = \frac{0.5x}{(0.2+0.5x)} P_{TOT}$$

$$P_{TOT} V = n_{TOT} RT$$

$$P_{TOT} = (0.2+0.5x)\frac{RT}{V} = (0.2+0.5x)\left(\frac{0.082(1273)}{100.0}\right)$$

$$= (0.2+0.5x)(1.044)$$

$$P_{H_2S} = 1.044(0.1-x)$$
$$P_{H_2} = 1.044(0.1+x)$$
$$P_{S_2} = 1.044(0.5x)$$

$$\Delta G^\circ = 27380 J = -RT\ln K$$

$$K = 7.521 \times 10^{-2} = \frac{P_{S_2}^{1/2} \cdot P_{H_2}}{P_{H_2S}}$$

$$x = 0.0082$$

$$P_{TOT} = (0.2+0.5x)(1.044) = 0.2131 atm.$$

$$P_{H_2S} = 1.044(0.1-x) = 0.0958 atm$$

$$P_{H_2} = 0.1129 atm$$

$$P_{S_2} = 0.0043 atm$$

V-10 $\quad SO_3 = SO_2 + \frac{1}{2}O_2$

$\Delta G^\circ = -12830\ J = -RT\ln K$

$K_{1200K} = 3.619$

	SO_3	SO_2	O_2
Entrée	1	0	0
Equilibre	$1-x$	x	$x/2$

$n_{TOT} = (1 + x/2) \qquad P_{TOT} = \left[\frac{1200}{298}\ \frac{(1+x/2)}{1}\right]$

$P_{SO_3} = \frac{n_{SO_3}}{n_{TOT}} \cdot P_{TOT} = \frac{1-x}{1+\frac{x}{2}}\left(\frac{1200}{298}\right)\left(1+\frac{x}{2}\right) = 4.027(1-x)$

$P_{SO_2} = \frac{x}{1+x/2} \cdot P_{TOT} = 4.027\,x$

$P_{O_2} = \frac{x/2}{1+x/2} \cdot P_{TOT} = 4.027(x/2)$

$K = \frac{P_{O_2}^{1/2} \cdot P_{SO_2}}{P_{SO_3}} = 3.619 = \frac{2.014^{(1/2)}\, x^{1/2}\, x}{(1-x)}$ erreur

$x = \cancel{0.685}$ 0.7469 (solution numérique)

$P_{SO_3} = \cancel{1.27\ atm}$ 1.019 atm

$P_{SO_2} = \cancel{2.76\ atm}$ 3.0077 atm

$P_{O_2} = \cancel{1.38\ atm}$ 1.504 atm

à 298° $\quad P_{TOT}^{=1.0}\, V = n_{TOT} R(298) \qquad V = (1)R(298)$

à 1200° $\quad P_{TOT}\, V = n_{TOT} R(1200)$

$P_{TOT} = \frac{(1+x/2)\cancel{R}\,1200}{\cancel{R}(298)}$

V-11 $C + CO_2 = 2CO$

$$\Delta G^o = 2(-26700 - 20.95T) - (-94200 - 0.2T)$$
$$= -RT\ln K$$

$$K_{1873K} = 22551 = P_{CO}^2 / P_{CO_2}$$

$$P_{O_2} + P_{CO} + P_{CO_2} = 1 \qquad P_{O_2} \ll 1$$

$$P_{CO} \gg P_{CO_2}$$

$$\therefore \underline{P_{CO} \approx 1 \text{ atm}}$$

$$\underline{P_{CO_2} = 4.43 \times 10^{-5}}$$

$C + \frac{1}{2}O_2 = CO \qquad \Delta G^o_{1873K} = -65939 \text{ cal} = -RT\ln K$

$$K = 4.9514 \times 10^7 = \frac{P_{CO}}{P_{O_2}^{1/2}} = \frac{1.0}{P_{O_2}^{1/2}}$$

$$\underline{P_{O_2} = 4.08 \times 10^{-16} \text{ atm}}$$

V-12 $Mo + 2H_2O = MoO_2 + 2H_2$

$$\Delta G^o = -393 - 2(-192) = -9.0 \text{ kJ}$$

$$P_{H_2O} = \frac{24}{760} = 0.0316 \text{ atm}$$

$$P_{H_2} = 1 - P_{H_2O} = 0.9684 \text{ atm}.$$

$$\Delta G = \Delta G^o + RT\ln\left(\frac{P_{H_2}}{P_{H_2O}}\right)^2$$
$$= +46.9 \text{ kJ}$$

$\Delta G > 0$ Donc, le Mo n'est pas oxydé

Autre méthode : $Mo + O_2 = MoO_2 \qquad P_{O_2} = 2.8 \times 10^{-21}$

$H_2 + \frac{1}{2}O_2 = H_2O$ avec $\frac{P_{H_2}}{P_{H_2O}} = \frac{0.9684}{0.0316} \Rightarrow P_{O_2} = 1.01 \times 10^{-23} < 2.8 \times 10^{-21}$

Donc, pas oxydé

V-13 $\Delta h^o_{373} = 41086$ J/mol.

Parceque 373 = température d'ébullition

$\Delta g^o_{373} = 0$

$\Delta S^o_{373} = \frac{41086}{373} = 110.15$ J/mol·K

$$\Delta h^o_{473} = \Delta h^o_{373} + \int_{373}^{473} (Cp(g) - Cp(\ell))\,dT$$

$\underline{\Delta h^o_{473} = 37044 \text{ J/mol}}$

$$\Delta S^o_{473} = \Delta S^o_{373} + \int_{373}^{473} \frac{(Cp(g) - Cp(\ell))}{T}\,dT$$

$\underline{\Delta S^o_{473} = 100.55 \text{ J/mol K}}$

$\Delta g^o_{473} = \Delta h^o_{473} - 473\,\Delta S^o_{473}$

$\underline{\Delta g^o_{473} = -10516 \text{ J/mol}} = -RT\ln P_{H_2O}$

$\underline{P_{H_2O} = 14.50 \text{ atm}}$

V-14 $2Al + \frac{3}{2}O_2 \xRightarrow{600K} Al_2O_3$

$\downarrow \quad\quad \downarrow \quad\quad\quad \uparrow$

$2Al + \frac{3}{2}O_2 \xRightarrow[298K]{} Al_2O_3$

$$\Delta H^o_{600} = \Delta H^o_{298} + \int_{298}^{600} \left(Cp_{Al_2O_3} - 2Cp_{Al} - \frac{3}{2}Cp_{O_2}\right)dT = -1675.27 + (0.27)(10^{-3})(302) = \underline{-1675.19 \text{ kJ}}$$

$\Delta S^o_{298} = 50.936 - \frac{3}{2}(205.037) - 2\,(28.322) = -313.264$ J/K

$$\Delta S^o_{600} = \Delta S^o_{298} + \int_{298}^{600} \frac{\Delta Cp}{T}\,dT = \Delta S^o_{298} + 0.27\ln\frac{600}{298} = \underline{-313.075 \text{ J/}}$$

$\Delta G^o_{600} = \Delta H^o_{600} - 600\,\Delta S^o_{600}$

$= \underline{-1487.35} \text{ kJ} = -R(600)\ln K_{600}$

$\underline{K_{600} = 2.97 \times 10^{129}}$

V-15 $CO_2 + C = 2CO$

$\Delta H^o_{298} = 2(-110.541) - (-393.505) = 172.423 \text{ kJ}$

$\Delta S^o_{298} = 2(197.552) - 5.740 - 213.660 = 175.704 \text{ J/mol·K}$

$\Delta C_p = 2C_p(CO) - C_p(CO_2) - C_p(C)$

$= 12.568 - 39.777 \times 10^{-3} T + 9.096 \times 10^5 T^{-2} + 17.385 \times 10^{-6} T^2$

$$\Delta H^o_{1000} = \Delta H^o_{298} + \int_{298}^{1000} \Delta C_p dT = 170908$$

$$\Delta S^o_{1000} = \Delta S^o_{298} + \int_{298}^{1000} \left(\frac{\Delta C_p}{T}\right) dT = 175.583$$

$$\Delta G^o_{1000} = \Delta H^o_{1000} - 1000 \Delta S^o_{1000} = \underline{-4675 \text{ J}}$$

V-16 $\quad \frac{1}{2}S_2 + O_2 = SO_2 \qquad \Delta G^\circ = -289990 = -RT\ln K$

$$K_{1000} = 1.409 \times 10^{15} = \frac{p_{SO_2}}{p_{O_2} \cdot p_{S_2}^{1/2}} = \frac{1.0}{(10^{-2})\, p_{S_2}^{1/2}}$$

$$p_{S_2} = \cancel{5.04 \times 10^{-27}}$$

OK

① $Ni + \frac{1}{2}O_2 = NiO \qquad \Delta G_{①} = \Delta G^\circ + RT\ln p_{O_2}^{-1/2} = -146020 + RT\ln\left(\frac{1}{10^{-2}}\right)^{1/2}$
$= -126874$ J

② $Ni + SO_2 + O_2 = NiSO_4 \qquad \Delta G_{②} = \Delta G^\circ + RT\ln \frac{1}{p_{O_2} \cdot p_{SO_2}}$

$$= -200460 + RT\ln\frac{1}{10^{-2}(1.0)} = -162168$$

③ $Ni + \frac{1}{2}S_2 = NiS \qquad \Delta G_{③} = \Delta G^\circ + RT\ln\frac{1}{p_{S_2}^{1/2}}$

$$= -74370 + RT\ln\frac{1}{(5.04 \times 10^{-27})^{1/2}}$$

$$= \cancel{190825}$$

OK

$\Delta G_2^\circ < \Delta G_1^\circ < \Delta G_3^\circ$

$\therefore$ $NiSO_4$ produit

Considérez: $NiO + SO_2 + \frac{1}{2}O_2 = NiSO_4$

$$\Delta G = (\Delta G_2 - \Delta G_1) < 0$$

Donc, si du NiO se produit, il réagira pour donner du $NiSO_4$ qui sera le seul et unique produit

V-16 Méthode 2

$P_{O_2} = 10^{-2}$ $\quad P_{SO_2} = 1$ $\quad P_{S_2} = 5.04 \times 10^{-27}$

$Ni + \frac{1}{2} O_2 = NiO$ $\quad \Delta G^\circ = -RT \ln K = -146020$

$K = \dfrac{1}{\left(P_{O_2}^{1/2}\right)_{equil}}$ $\quad P_{O_2\,(equil)} = 5.6 \times 10^{-16} < 10^{-2}$

Donc, NiO est plus stable que Ni

$Ni + \frac{1}{2} S_2 = NiS$ $\quad \Delta G^\circ = -RT \ln\left(\dfrac{1}{P_{S_2}^{1/2}}\right)_{equil} = -74370$

$P_{S_2\,(equil)} = 2 \times 10^{-8} > 5.04 \times 10^{-27}$

Donc, NiS est moins stable que Ni

$Ni + SO_2 + O_2 = NiSO_4$ $\quad \Delta G^\circ = -RT \ln\left(\dfrac{1}{P_{O_2} \cdot P_{SO_2}}\right)_{equil} = -200460$

$\left(P_{O_2} \cdot P_{SO_2}\right)_{equil} = 3.4 \times 10^{-11} < (1) \cdot (10^{-2})$

Donc, $NiSO_4$ est plus stable que Ni

Il reste de décider si $NiSO_4$ est plus ou moins stable que NiO.

$NiO + \frac{1}{2} O_2 + SO_2 = NiSO_4$

$\Delta G^\circ = -200460 - (-146020) = -54440 = -RT \ln \dfrac{1}{\left(P_{O_2}^{1/2} \cdot P_{SO_2}\right)_{equil}}$

$\left(P_{O_2}^{1/2} \cdot P_{SO_2}\right)_{equil} = 1.43 (10^{-3}) < (10^{-2})^{1/2} (1.0)$

Donc, $NiSO_4$ est plus stable que NiO

Donc: $NiSO_4$ sera le produit le plus stable

V-16 Methode 3 $P_{O_2} = 10^{-2}$ $P_{SO_2} = 1.0$

$Ni + SO_2 + O_2 = NiSO_4$ $\Delta G = \Delta G^\circ + RT \ln \frac{1}{10^{-2}(1.0)} = -162168 < 0$

$Ni + \frac{1}{2}O_2 = NiO$ $\Delta G = \Delta G^\circ + RT \ln \frac{1}{P_{O_2}^{1/2}} = \Delta G^\circ + RT \ln \frac{1}{(10^{-2})^{1/2}}$

$= -126874 < 0$

$Ni + SO_2 = NiS + O_2$ $\Delta G^\circ = -74370 - (-289990) = 215620$

$\Delta G = \Delta G^\circ + RT \ln \frac{P_{O_2}}{P_{SO_2}} = 215620 + R(1000) \ln\left(\frac{10^{-2}}{1.0}\right)$

$= 177330 > 0$

$NiO + \frac{1}{2}O_2 + SO_2 = NiSO_4$

$\Delta G = \Delta G^\circ + RT \ln \frac{1}{P_{O_2}^{1/2} \cdot P_{SO_2}}$

$= (-200460) - (-146020) + RT \ln \frac{1}{(10^{-2})^{1/2}(1.0)}$

$= -35294 < 0$

Donc: $NiSO_4$ est le plus stable

V-17

$$H_2 + \frac{1}{2}O_2 = H_2O$$

$$\Delta G^\circ = -178128 = -RT\ln K$$

$$K_{1273} = 2.040 \times 10^7 = \frac{p_{H_2O}}{p_{H_2}}\left(\frac{1}{p_{O_2}^{1/2}}\right) = \left(\frac{1}{1}\right)\left(\frac{1}{p_{O_2}}\right)^{1/2}$$

$$p_{O_2} = 2.402 \times 10^{-15}$$

$$Fe + \frac{1}{2}O_2 = FeO \quad \Delta G = \Delta G^\circ + RT\ln \frac{1}{p_{O_2}^{1/2}} = -189776 + R(1273)\ln\frac{1}{(2.402\times10^{-15})^{1/2}}$$

$$= -11620 \text{ J}$$

Donc, FeO est plus stable que Fe

$$3FeO + \frac{1}{2}O_2 = Fe_3O_4 \quad \Delta G = \Delta G^\circ + RT\ln\frac{1}{p_{O_2}^{1/2}}$$

$$= -138130 + RT\ln\left(1/(2.402\times10^{-15})\right)^{1/2}$$

$$= 40030 \text{ J}.$$

Donc FeO plus stable que Fe_3O_4

(Pas nécessaire de faire le calcul pour le Fe_2O_3)

Donc: FeO sera le seul et unique produit.

V-18

$$\begin{array}{ccc} \text{Graphite} & \xrightarrow[\Delta G]{P} & \text{Diamant} \\ \downarrow & & \uparrow \\ \text{Graphite} & \xrightarrow[\Delta G^\circ]{P^\circ = 1} & \text{Diamant} \end{array}$$

$$\Delta G = \Delta G^\circ + \int_1^P (v_{di} - v_{gr})\,dP = 0 \qquad \text{où: } v = \text{volume molaire}$$

$$\Delta G^\circ = -\int_1^P (v_{di} - v_{gr})\,dP \approx (v_{gr} - v_{di})(P-1)$$

$$\begin{cases} v_{gr} = \frac{12.0}{1000}\left(\frac{1}{2.25}\right) = 5.333 \times 10^{-3}\ l/mol \\ v_{di} = \frac{12.00}{1000}\left(\frac{1}{3.52}\right) = 3.4091 \times 10^{-3}\ l/mol \end{cases}$$

$$\Delta G^\circ = 2866 \text{ J/mol} = 28.29\ l\,atm/mol$$

$$P - 1 = \frac{\Delta G^\circ}{v_{gr} - v_{di}}$$

$$\underline{P = 14700 \text{ atm}}$$

$\underline{V-19}$ $Si + I_2 = SiI_2$ ①

(a) $K_1 = \dfrac{P_{SiI_2}}{a_{Si} \cdot P_{I_2}} = \dfrac{0.0564}{0.0126} = 4.4762$

$I_2 = 2I$ ②

$K_2 = \dfrac{P_I^2}{P_{I_2}} = \dfrac{(0.0876)^2}{0.0126} = 0.6090$

$Si + 2I_2 = SiI_4$ ③

$K_3 = \dfrac{P_{SiI_4}}{P_{I_2}^2} = \dfrac{0.0583}{(0.0126)^2} = 367.22$

(b)

$Si + 2I_2 = SiI_4$

2 mol de gaz à gauche
1 mol à droite

Donc, augmenter P ⇒ réaction déplacée vers la droite

$Si + 4I = SiI_4$

4 mol à gauche, 2 mol à droite ⇒ même chose

$Si + 2I = SiI_2$

2 mol à gauche, 1 mol à droite ⇒ même chose

$Si + I_2 = SiI_2$

1 mol de gaz à gauche, 1 mol à droite ⇒ P a peu d'effet.

Dans tous les cas, une augmentation de P donne lieu à une diminution de la quantité de Si (solide)

VI-1 $\quad C + CO_2 = 2CO$

$$K = \frac{P_{CO}^2}{P_{CO_2} \cdot a_C}$$

Graphite pur: $a_C = 1$ $\quad K = \frac{0.9705^2}{(0.0295)(1.0)}$

Acier: $\quad K = \frac{(0.934)^2}{(0.066)\, a_C}$

$a_C = 0.414$

VI-2 $\quad 2Cu + \frac{1}{2}O_2 = Cu_2O$

$\Delta G^0_{1273} = -77780 = -RT \ln K$

$$K = 1510 = \frac{a_{Cu_2O}}{a_{Cu}^2 \cdot p_{O_2}^{1/2}} = \frac{1.0}{(3.54 X_{Cu})^2 (0.21)^{1/2}}$$

$X_{Cu} = 0.0107$

VI-3 (a) $Cu_2O + \frac{1}{2}O_2 = 2CuO$

$\Delta G^0_{1400K} = 2(-35560) - (-73220) = +2100 > 0$

Donc Cu_2O est stable

(b) $2Cu + \frac{1}{2}O_2 = Cu_2O$

$\Delta G^0_{1400} = -73220 = -RT \ln K$

$$K = 539.63 = \frac{a_{Cu_2O}}{p_{O_2}^{1/2}\, a_{Cu}^2} = \frac{1.0}{(1.0)^{1/2}(0.20 X_{Cu})^2}$$

$X_{Cu} = 0.22$

Pas une bonne méthode

VI-4

$$2Ag(l) + 3Zn(l) = Ag_2Zn_3(s)$$

$$\Delta G^\circ_{773} = -127{,}600 = -RT\ln K$$

$$K = 4.19\times10^{8} = \frac{a_{Ag_2Zn_3}}{a_{Ag}^2\cdot a_{Zn}^3}$$

$$= \frac{1.0}{(2.027X_{Ag})^2(11\times0.0146)^3}$$

$$\underline{X_{Ag} = 3.75\times10^{-4}}$$

VI-5

$$Pb + ZnCl_2 = PbCl_2 + Zn$$

$$\Delta G^\circ_{673} = -264180-(-316440) = -RT\ln K$$

$$K = 8.781\times10^{-5} = \frac{a_{Zn}\cdot a_{PbCl_2}}{a_{Pb}\cdot a_{ZnCl_2}}$$

Solution des chlorures idéale: $\begin{cases} a_{PbCl_2} = X_{PbCl_2} = 0.01 \\ a_{ZnCl_2} = 0.99 \end{cases}$

alliage: $a_{Zn} = \gamma^\circ_{Zn}\cdot X_{Zn} = 27X_{Zn}$

$a_{Pb} \approx 1.00$

$$8.781\times10^{-5} = \frac{(27X_{Zn})(0.01)}{(1.0)(0.99)}$$

$$\underline{X_{Zn} = 3.22\times10^{-4}}$$

VI - 6

$$Co + NiO \Rightarrow Ni + CoO$$

$$\Delta G^{o}_{1650K} = -118683 - (-95655) = -RT\ln K$$

$$K = 5.359 = \left(\frac{a_{CoO}}{a_{NiO}}\right)\left(\frac{a_{Ni}}{a_{Co}}\right) = \frac{X_{CoO}\ (1-X_{Co})}{(1-X_{CoO})\ X_{Co}} = \frac{X_{CoO}\ (0.49)}{(1-X_{CoO})\ (0.51)}$$

$$\underline{X_{CoO} = 0.848}$$

VI - 7 $\quad 3Na + AlF_3 = 3NaF + Al$

$$\Delta G^{o} = -(-1117.13) - 3(440.37) = -R(1293)\ln K$$

$$K_{1293} = 1.742 \times 10^{8} = \frac{a_{Al} \cdot a^{3}_{NaF}}{(\gamma_{Na} X_{Na})^{3} \cdot a_{AlF_3}} = \frac{(1.0)(0.414)^{3}}{(165 X_{Na})^{3}(4.562 \times 10^{-4})}$$

$$X_{Na} = 58 \times 10^{-6}$$
$$\underline{= 58\ ppm}$$

VI - 8

$$4Cu + Ni_3S_2 = 2Cu_2S + 3Ni$$

$$\Delta G^{o}_{700} = -219420 - (-216730) = -2690\,J. = -RT\ln K$$

$$K = 1.54 = \frac{a_{Ni}^{3} \cdot a^{2}_{Cu_2S}}{a^{4}_{Cu} \cdot a_{Ni_3S_2}}$$

$$Q = \frac{(0.172)^{3}(1.0)^{2}}{(0.88)^{4}(1.0)} = 0.01$$

$$Q < K$$

Done: Cu₂S ~~ext~~ stable

VI-9 $a_{Zn} = \gamma^{\circ}_{Zn} \cdot X_{Zn} = (11)(0.01 \times 10^{-2}) = 11 \times 10^{-4}$

$a_{Zn} = (P_{Zn}/P^{\circ}_{Zn})$

$\log P = \log P^{\circ} + \log a_{Zn}$

$= \left(-\frac{6670}{T} + 12.00 - 1.126 \log_{10} T\right) + \log(11 \times 10^{-4})$

où $T = 773\,K$

$\underline{P = 1.45 \times 10^{-3} \text{ torr}}$

VI-10 $Zn(l) = Zn(g)$

$\Delta G^{\circ} = 115330 - 97.737\,T = -RT \ln \frac{P_{Zn}}{a_{Zn}}$

$\frac{P_{Zn}}{a_{Zn}} = 1.932$

$Mg(l) = Mg(g)$

$\Delta G^{\circ} = 127400 - 93.470\,T = -RT \ln \frac{P_{Mg}}{a_{Mg}}$

$\frac{P_{Mg}}{a_{Mg}} = 0.3619$

$(P_{Mg} + P_{Zn}) = 1.0 = (1.932\,a_{Zn} + 0.3619\,a_{Mg})$

$1.0 = 1.932\,X_{Zn} + 0.3619(1 - X_{Zn})$

$\underline{X_{Zn}(liq) = 0.4064}$

$P_{Zn} = 1.932\,X_{Zn} = 1.932(0.4064) = 0.785 \text{ atm}$

$P_{TOTAL} = 1.0$

Donc: $\underline{X_{Zn}(gaz) = 0.785}$

VI - 11

$$n_{cd}\ (\text{condensé}) = \frac{11.24}{M_{cd}} = \frac{11.24}{112.4} = 0.100\ \text{mol}$$

$$V_{Ar} = 6.4 \times 10^3 \times 1.00\ l = 6400\ l$$

$$n_{Ar} = \frac{PV}{RT} = \frac{(1.0)(6400)}{(0.082)(700)} = 111.5\ \text{mol}$$

$$P_{cd} = \frac{n_{cd}}{n_{TOT}}(P_{TOT}) = \frac{0.100}{111.5}(1.0) = 8.961 \times 10^{-4}\ \text{atm}$$

$$P^o_{cd} = 0.0033$$

$$a_{cd} = \frac{P_{cd}}{P^o_{cd}} = 0.272$$

VI - 12 (a) $H_2 + CO_2 = H_2O + CO$ $\quad \Delta G^o = -197380 + 202355 = -RT\ln K$

$$K_{923} = 0.523 = \frac{P_{CO} \cdot P_{H_2O}}{P_{H_2} \cdot P_{CO_2}} = \frac{(0.289)(4.33)}{(3.52)\ P_{CO_2}}$$

$$P_{CO_2} = 0.680\ \text{atm}$$

$K_2CO_3 + H_2O = 2KOH + CO_2$ $\quad \Delta G^o = 216112 = -RT\ln K$

$$K = 5.871 \times 10^{-13} = \frac{(0.680)\ P_{KOH}^2}{(0.075)(4.33)}$$

$$P_{KOH} = 5.295 \times 10^{-7}\ \text{atm}$$

$KOH + H_2O = KOH \cdot H_2O$ $\quad \Delta G^o = -4728 = -RT\ln K$

$$K = 1.852 = \frac{P_{KOH \cdot H_2O}}{(5.295 \times 10^{-7})(4.33)}$$

$$P_{KOH \cdot H_2O} = 4.246 \times 10^{-6}\ \text{atm}$$

(b) $\dot{n}_{gaz} = \frac{P\dot{V}}{RT} = \frac{10(100)}{(0.082)(4.33)} = 13.21\ \text{mol/h}$

1 mol du gaz contient $\left[\frac{(5.295 \times 10^{-7} + 4.246 \times 10^{-6})}{10.0}\right] \times 39.098 = 1.867 \times 10^{-5}$ g potassium

Donc: $\text{Pertes} = (1.867 \times 10^{-5}) \times (13.21)$

$$= 2.47 \times 10^{-4}\ \text{g/h}$$

$\underline{VII-1}$ $\quad d\left(\frac{\Delta G^\circ}{T}\right)/d\left(\frac{1}{T}\right) = \Delta H^\circ$

$$\Delta H^\circ = -T^2 \frac{d(\Delta G^\circ/T)}{dT} = -T^2 \frac{d}{dT}\left(-\frac{388000}{T} - 7.65 \ln T + \cdots\right)$$

$$= -388000 + 7.65\,T - 4.06 \times 10^{-3}\, T^2 + 1.254 \times 10^5\, T^{-1}$$

$\underline{\text{à } 800\,K}$ $\quad \underline{\Delta H^\circ = -384320 \text{ J}}$

$\underline{VII-2}$ $\quad 2\,HgO(s) = 2\,Hg(g) + O_2(g)$

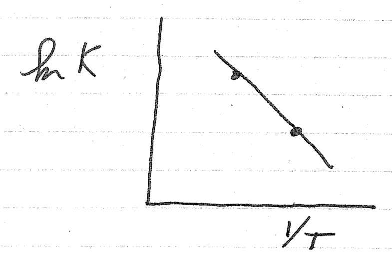
On commence avec <u>seulement</u> du HgO

Donc $P_{O_2} = \frac{1}{2} P_{Hg} = \frac{1}{3} P_{TOT}$

$$K = P_{Hg}^2 \cdot P_{O_2} = \frac{4}{27} P_{TOT}^3$$

à $T_1 = 380°C = 653\,K$ $\quad K_{T_1} = 9.45 \times 10^{-4}$

à $T_2 = 420°C = 693\,K$ $\quad K_{T_2} = 1.96 \times 10^{-2}$



<u>Supposition</u>: $\Delta H^\circ \neq f(T)$

Donc $\ln K$ vs. $1/T$ est une ligne droite

Extrapoler graphiquement

<u>ou</u>: $\ln K = a + b\left(\frac{1}{T}\right)$

$\ln(9.45 \times 10^{-4}) = a + b/653 \qquad -6.964 = a + b\left(\frac{1}{653}\right)$

$\ln(1.96 \times 10^{-2}) = a + b/693 \qquad -3.932 = a + b\left(\frac{1}{693}\right)$

$-3.0321 = b(8.839 \times 10^{-5}) \qquad b = -3.43 \times 10^4$

$a =$

$$\ln K = 45.57 - 3.43 \times 10^4/T$$

Quand $P_{TOT} = 1$ $\quad K = \frac{4}{27}$ et $\ln K = -1.910 = 45.57 - 3.43 \times 10^4/T$

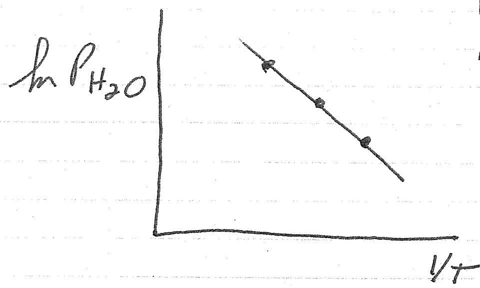
$T = 722\,K$

$\underline{T = 449°C}$

VII - 3 $\quad H_2O(l) = H_2O(g)$

$$\Delta G^\circ_v = -RT \ln P_{H_2O} = \Delta H^\circ_v - T\Delta S^\circ_v$$

$$\boxed{\ln P_{H_2O} = \frac{\Delta S^\circ_v}{R} - \frac{\Delta H^\circ_v}{R}\left(\frac{1}{T}\right)}$$



Supposer: $\Delta H^\circ_v \neq f(T)$

Pente $= (-\Delta H^\circ_v/R)$

Solution graphique ou analytique

P_{H_2O} à 75°C = 0.380 atm.

VII - 4 $\quad TiCl_4(l) = TiCl_4(g)$

$$\Delta G^\circ = -RT \ln P_{TiCl_4}$$

à 373 K, $P = 0.356$ atm

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-R(373)\ln(0.356) = 36600 - 373\,\Delta S^\circ \Rightarrow \Delta S^\circ = 89.536$$

$$\Delta G^\circ = 36600 - 89.536\,T$$

Quand $P = 1.0$ atm, $\Delta G^\circ = 0$

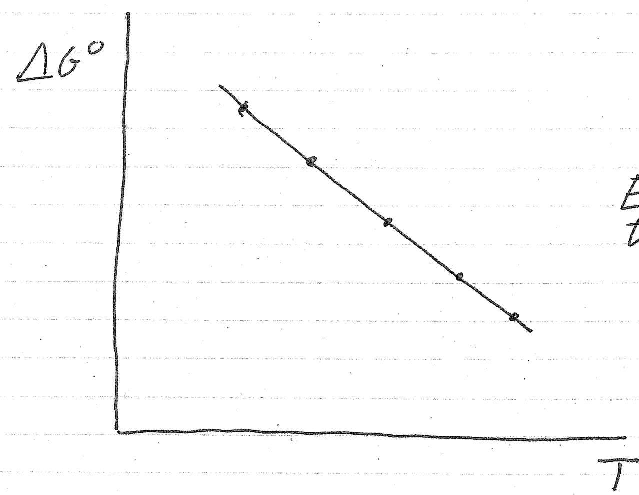
$$36600 - 89.536\,T = 0$$

$$\underline{T = 409\,K = 136°C}$$

VII - 5 $3Ni + 2H_2S = Ni_3S_2 + 2H_2$

$K = (P_{H_2}/P_{H_2S})^2 \quad \Delta G^\circ = -RT\ln K = +2RT\ln(P_{H_2S}/P_{H_2})$

T(°C)	T(K)	ΔG° (kJ)
700	973	−101.372
800	1073	−105.586
900	1173	−111.148
1000	1273	−116.923
1100	1373	−123.823



$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

En supposant un ligne droite, tracez la ligne à la main

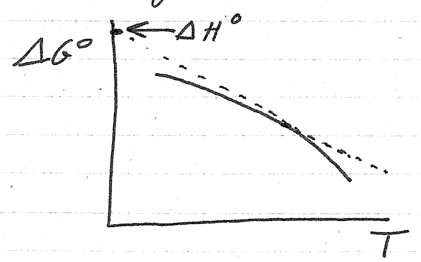
$\Delta G^\circ \approx -46\cancel{00} - 56.5T$ J.

$\Delta H^\circ = -46000$ J

$\Delta S^\circ = 56.5$ J/K

Bien sur, avec une ligne droite, $\Delta C_p = 0$

En réalité, il y a une légère courbure



$\frac{d(\Delta H^\circ)}{dT} > 0$

c.à.d. $\Delta C_p > 0$

VIII-1 Mg, Ca, Mn

VIII-2 Cu, Pb

VIII-3 Ti, Ca

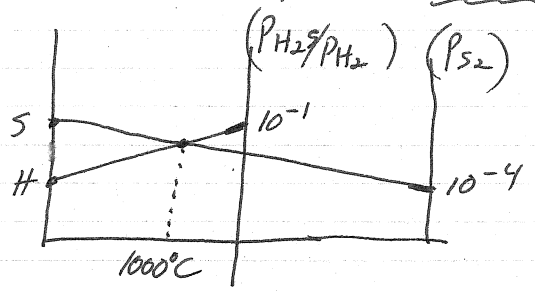
VIII-4 Pour Pt/PtS $P_{S_2} \approx 10^{-3}$ atm à 900°C

Donc, la réponse est <u>NON</u> (PtS sera produit)

VIII-5 1000K = 723°C

Ni/NiO $P_{H_2}/P_{H_2O} \approx \underline{10^{-2}}$ à l'équilibre

VIII-6



$P_{H_2S}/P_{H_2} = 10^{-1}$

VIII-7 Pour Co/CoO à 1000°C $(P_{CO}/P_{CO_2})_{\text{équilibre}} \approx 10^{-1.4}$

$$\left(\frac{P_{CO}}{P_{CO_2}}\right)_{\text{réel}} = \frac{1}{10} = 10^{-1} > 10^{-1.4}$$

<u>Donc</u>: CoO sera <u>réduit</u>

VIII-8 $C + CO_2 = 2CO$

$$\Delta G^\circ_{1400°C} = -29 \text{ kcal (diagramme des carbures)}$$

$$= -RT\ln \frac{P_{CO}^2}{P_{CO_2}}$$

$$P_{CO}^2/P_{CO_2} = 6147$$

et $P_{CO} + P_{CO_2} = 0.2$

$P_{CO} \gg P_{CO_2}$ Donc $P_{CO} \approx 0.2$ atm

$$\frac{P_{CO}}{P_{CO_2}} = \frac{6147}{0.2} = \underline{3.1 \times 10^4}$$

VIII-9 Ti/TiO_2 à 1000°C $P_{O_2} = 10^{-28}$ atm ← meilleur

Cu/Cu_2O à 500°C $P_{O_2} = 10^{-16}$ atm

VIII - 9 Ti/TiO_2 à 1000°C $P_{O_2} = 10^{-28}$ atm

Cu/Cu_2O à 500°C $P_{O_2} = 10^{-16}$ atm

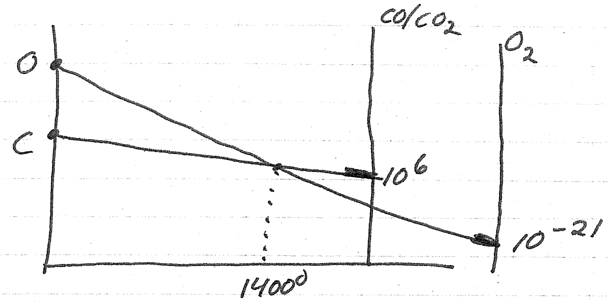
Donc: Cu est meilleur

VIII - 10 Ti/TiO_2 à 1400°C $(P_{CO}/P_{CO_2})_{\text{équilibre}} = 10^5$

(i) $P_{CO}/P_{CO_2} = 1/10^{-6} = 10^6 > 10^5$

Donc: Ti n'est pas oxydé

(ii)



$P_{O_2} = 10^{-21}$ atm

VIII - 11 $C + CO_2 = 2CO$

$\Delta G^0_{1600°C} = -37$ kcal (Diagramme des carbures)

$= -RT\ln K$

$K = 20782 = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(1.2)^2}{P_{CO_2}}$

$P_{CO_2} = 6.9 \times 10^{-5}$ atm

$2C + O_2 = 2CO$

$\Delta G^0_{1600°C} = -132$ kcal (diagramme d'oxydes)

$= -RT\ln K$

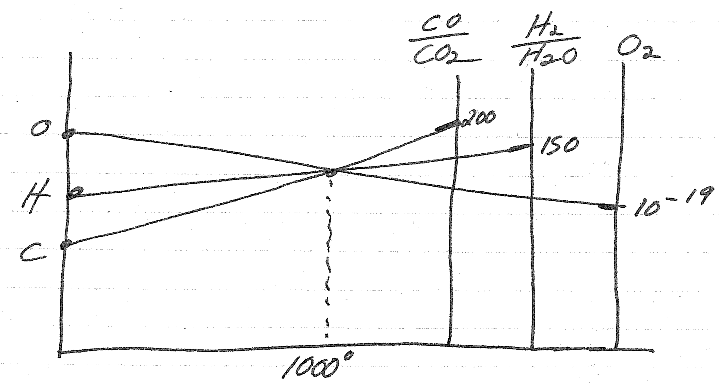
$K = 2.533 \times 10^{15} = \frac{P_{CO}^2}{P_{O_2}} = \frac{(1.2)^2}{P_{O_2}}$

$P_{O_2} = 5.7 \times 10^{-16}$ atm

VIII-12 $\frac{P_{CO}}{P_{CO_2}} = \frac{0.5}{2.5\times10^{-3}} = 200$

Donc : $P_{O_2} = 10^{-19}$ (Diagramme d'oxydes)

Donc: $\frac{P_{H_2}}{P_{H_2O}} \simeq 150$ (Diagramme d'oxydes)



Donc $P_{H_2O} = (0.5)/150 = 3.3\times10^{-3}$

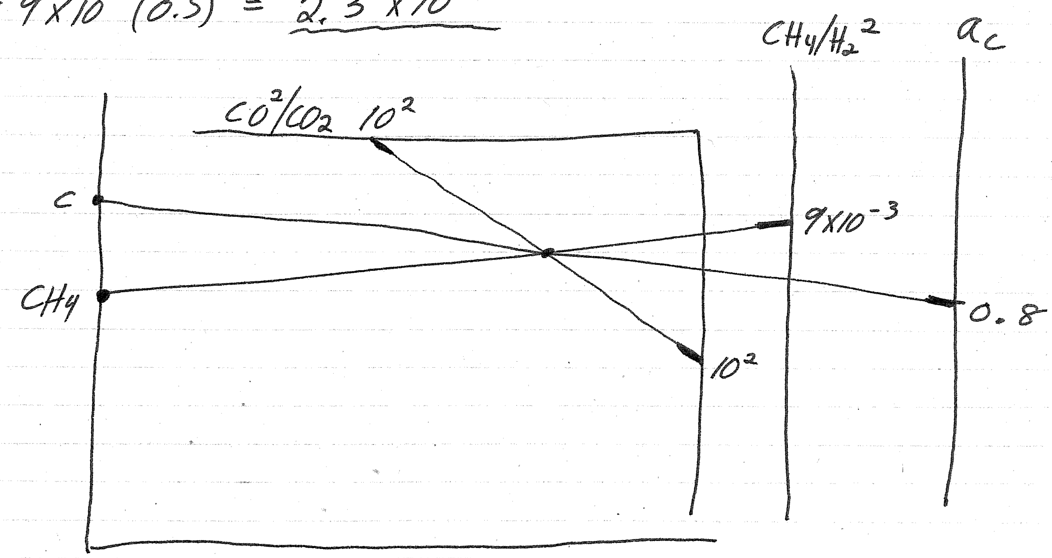
Maintenant, avec le diagramme des carbures :

$P_{CO}^2/P_{CO_2} = \frac{(0.5)^2}{2.5\times10^{-3}} = 10^2$

Donc : $a_c = 0.8$

et $P_{CH_4}/P_{H_2}^2 = 9\times10^{-3}$

Donc: $P_{CH_4} = 9\times10^{-3}(0.5)^2 = 2.3\times10^{-3}$



VIII - 13 $\quad C(s) + CO_2(g) = 2CO(g)$

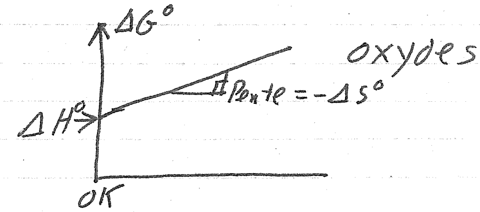
$\Delta S^\circ = 2S^\circ_{CO} - S^\circ_{CO_2} - S^\circ_C$

S°_{CO} et $S^\circ_{CO_2} > S^\circ_C$ parce que CO et CO_2 sont gazeux

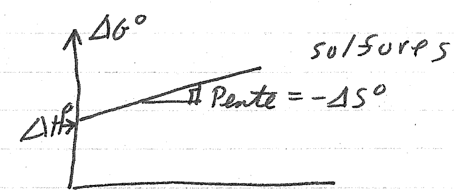
Donc $\Delta S^\circ > 0$

$d(\Delta G^\circ)/dT = $ Pente $= -\Delta S^\circ < 0$

VIII - 14 $\quad 4\,Cu + O_2 = 2\,Cu_2O$ ①



$4\,Cu + S_2 = 2\,Cu_2S$ ②



$Cu_2O + \frac{1}{2}S_2 = Cu_2S + \frac{1}{2}O_2$

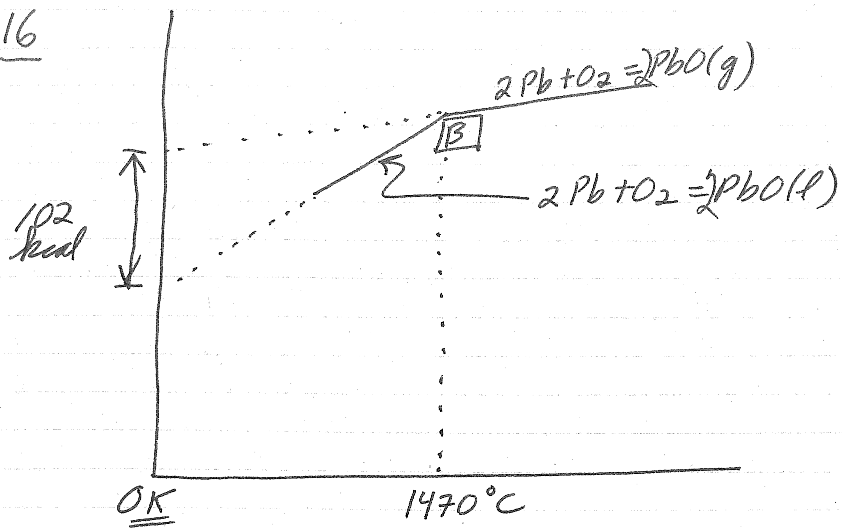
$\Delta G^\circ = (\Delta G^\circ_2 - \Delta G^\circ_1)/2 \quad \approx 0$ à $800°C$

$\Delta H^\circ = (\Delta H^\circ_2 - \Delta H^\circ_1)/2 \quad \approx 8$ kcal

$\Delta S^\circ = (\Delta S^\circ_2 - \Delta S^\circ_1)/2 \quad \approx 7.4$ cal/K

VIII - 15 $\quad FeO$ (même principe que VIII - 19)

VIII - 16



$$\Delta h^\circ_{v\,(PbO)} = \frac{102}{2} = \underline{51\ kcal/mol}$$

VIII - 17

$$2H_2 + O_2 = 2H_2O$$

$$\Delta G^\circ = -84\ kcal\ à\ 1000°C$$

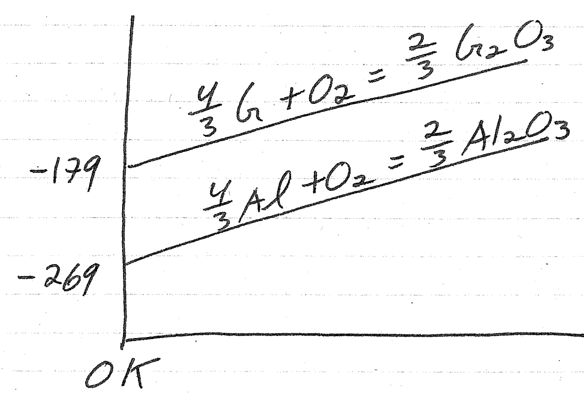
$$-84000 = -R(1273)\ln K$$

$$K = 2.645 \times 10^{14}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

$$K = (2.645 \times 10^{14})^{1/2} = \underline{1.6 \times 10^7}$$

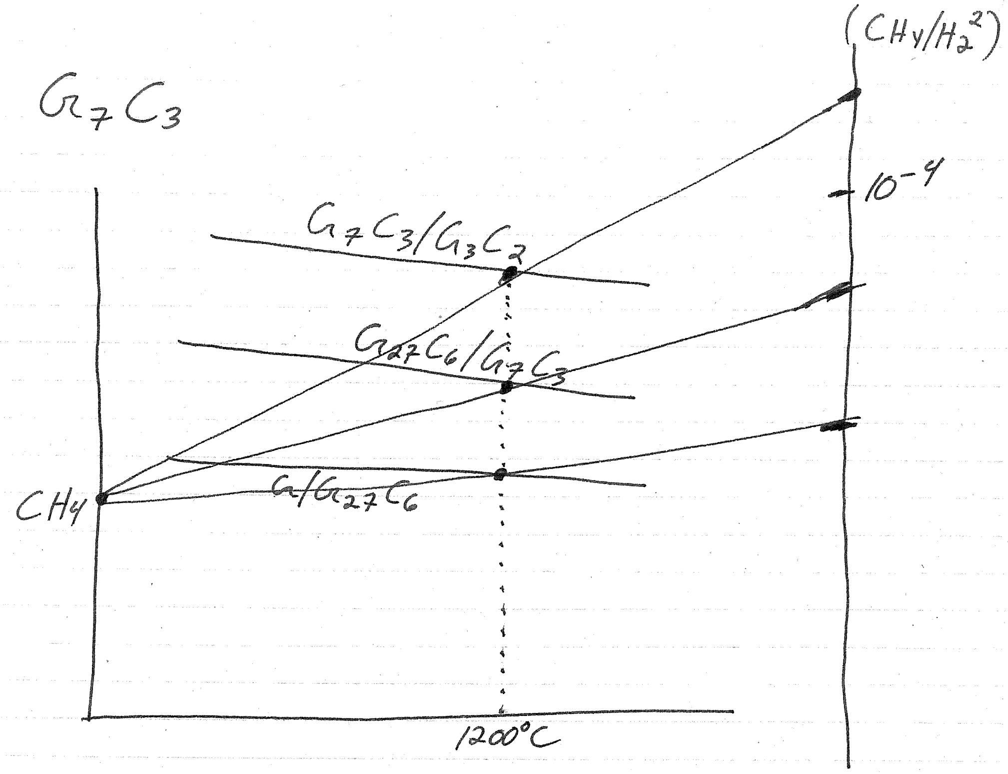
VIII - 18



$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr$$

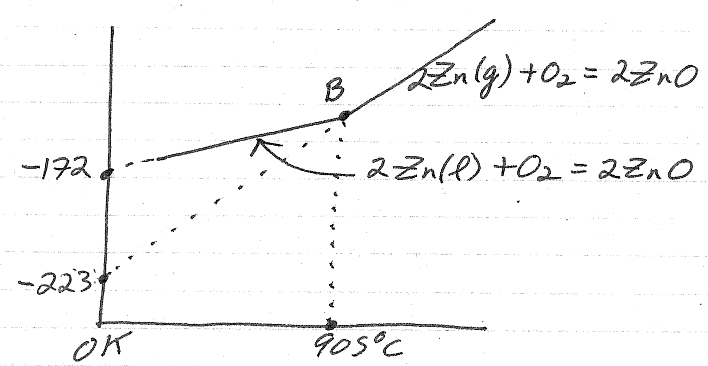
$$\Delta H_0 = 1.5(-269 + 179) = \underline{-135\ kcal}$$

VIII - 19 Cr_7C_3



VIII -20 FeO (même principe que VIII-19)

VIII -21



$$\Delta h^\circ_{v(Zn)} = \frac{-172 - (-223)}{2} = 25.5 \text{ kcal/mol}$$

$\Delta G^\circ_v = 0$ à $905°C = 1178 K$

$$\Delta G^\circ_v = \Delta H^\circ_v - T\Delta S^\circ_v$$
$$0 = 25500 - 1178\,\Delta S^\circ_v$$
$$\Delta S^\circ_v = 21.647 \text{ cal/mol K}$$

$$\Delta G^\circ_v = 25500 - 21.647\,T$$
$$= -RT \ln P_{Zn}$$

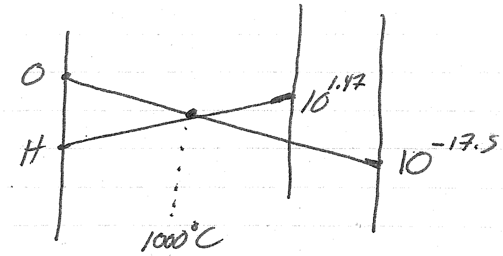
$P_{Zn} = 0.1$: $-RT \ln(0.1) = 25500 - 21.647\,T$

$\underline{T = 972 K = 699°C}$

VIII-22 $\frac{P_{H_2}}{P_{H_2O}} = \frac{1-0.0325}{0.0325} = 29.77$

$\log_{10} \frac{P_{H_2}}{P_{H_2O}} = 1.47$

$P_{O_2} = 10^{-17.5}$



VIII-23

Avec $p_{O_2} = 10^{-11}$, avec le diagramme d'oxydes, à 1600°C

$p_{CO}/p_{CO_2} \simeq 2\times10^2$

$p_{CO} = 1$

Donc $p_{CO_2} = 10^{-2}\times 0.5$

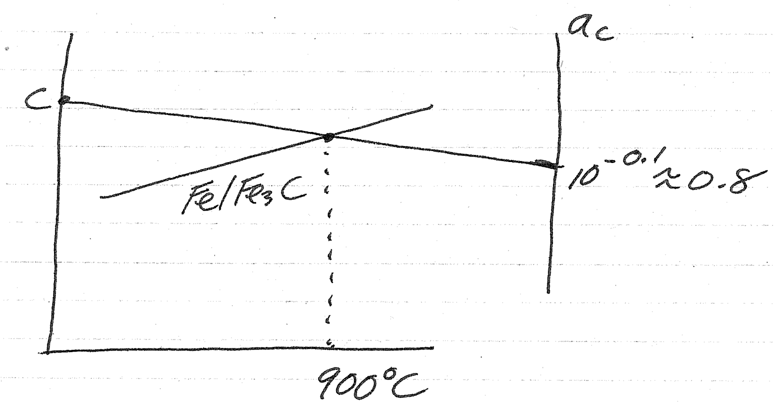
Donc $p_{CO}^2/p_{CO_2} \approx 2\times10^2$

Avec le diagramme de carbures

$a_C = 10^{-2} = \gamma_C^\circ X_C = (0.55)X_C$

$X_C \approx 0.02$

VIII-24

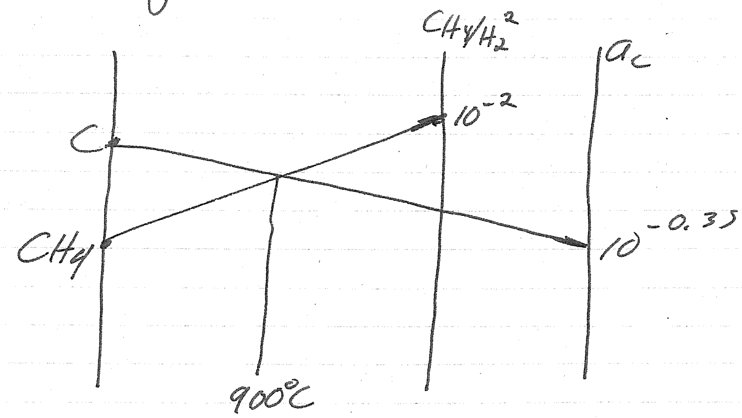


$a_C = 0.8 = \gamma_C^\circ \cdot X_C = 16 X_C$

$X_C = 0.05$

VIII-25 $\quad X_c = 0.006\left(\frac{55.85}{12.00}\right) = 0.028$

$$a_c = \gamma_c^{\circ} \cdot X_c = 16(0.028) = 0.45 = 10^{-0.35}$$

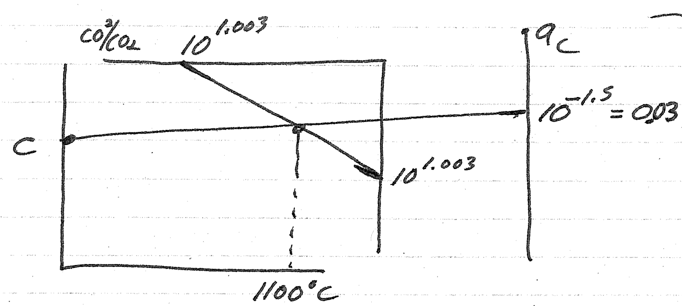


$$\underline{P_{CH_4}/P_{H_2}^2 \approx 10^{-2}}$$

VIII-26 (a) $\quad P_{CO} + P_{CO_2} = 1 \qquad P_{CO}/P_{CO_2} = 11$

$P_{CO} = 11/12 \qquad P_{CO_2} = 1/12 \qquad \underline{\frac{P_{CO}^2}{P_{CO_2}} = 10.08 = 10^{1.003}}$

(b)



$\underline{a_c = 0.03}$

(c) $\quad X_c = a_c/\gamma_c^{\circ} = 0.03/8.5$

$\underline{X_c = 4 \times 10^{-3}}$

(d) $\quad P_{CO} + P_{CO_2} = 0.1 \qquad P_{CO}/P_{CO_2} = 11 \qquad P_{CO} = 0.092 \qquad P_{CO_2} = 0.0083$

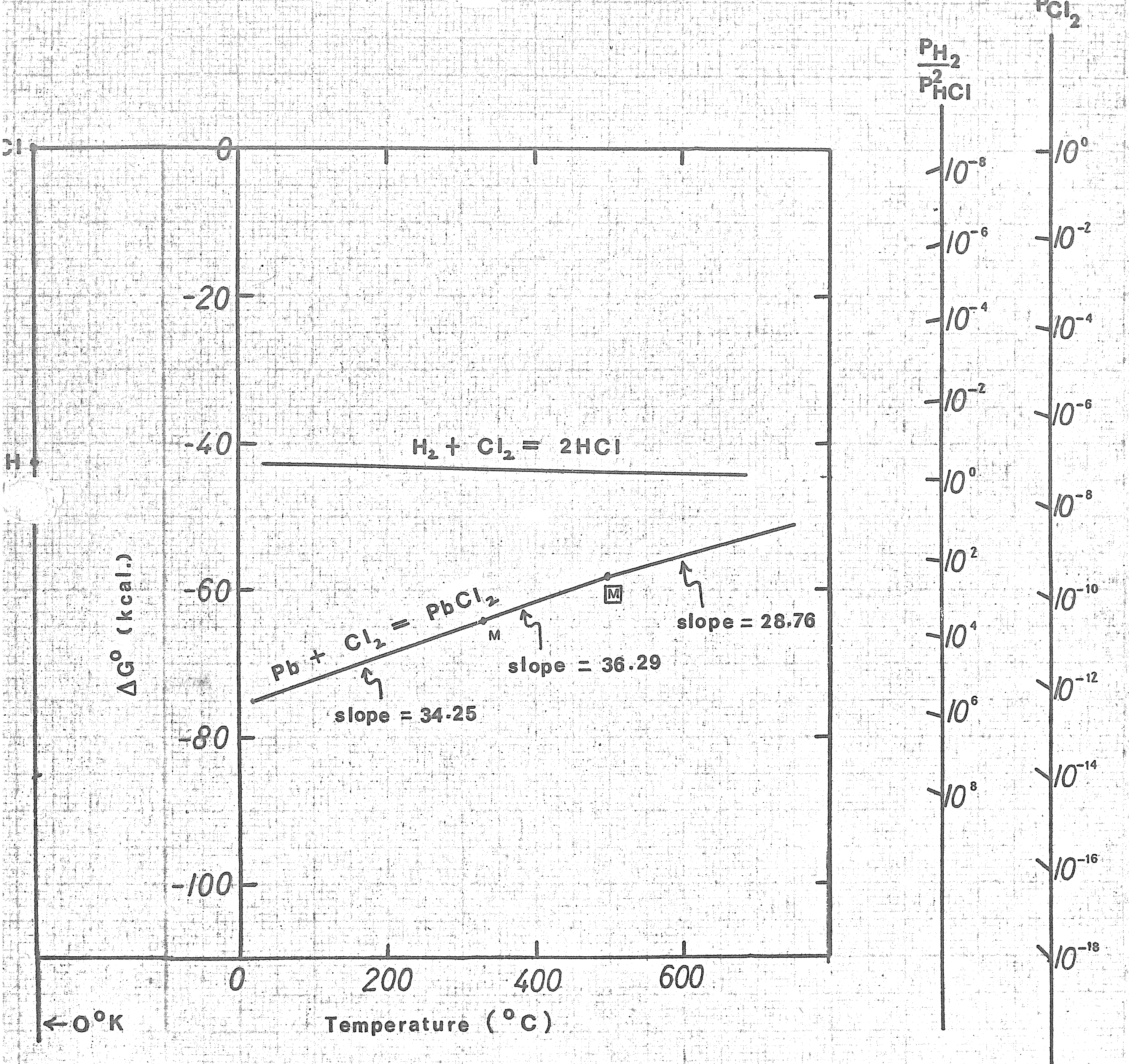
$P_{CO}^2/P_{CO_2} = 1.009 = 10^{0}$

La même construction donne, maintenant, $a_c = 10^{-2.6} = 0.0025$

$X_c = a_c/\gamma_c^{\circ} = 0.0025/8.5$

$\underline{X_c \approx 3 \times 10^{-4}}$

VIII-27



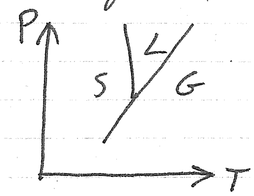
P_{Cl_2}
$\frac{P_{H_2}}{P^2_{HCl}}$
Cl
H
0
-20
-40
-60
-80
-100
$H_2 + Cl_2 = 2HCl$
$Pb + Cl_2 = PbCl_2$
M
M
slope = 34.25
slope = 36.29
slope = 28.76
ΔG^o (kcal.)
0
200
400
600
Temperature (^oC)
← 0^oK
10^{-8}
10^{-6}
10^{-4}
10^{-2}
10^0
10^2
10^4
10^6
10^8
10^0
10^{-2}
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
10^{-18}

IX-1 (a) T°_v est la température où $P = 760$ torr

$$\log(760) = \frac{-6620}{T} - 1.255 \log T + 12.34$$

$$T^\circ_v = 1181\ K$$

(b) Le point triple est le point d'intersection des courbes $S \rightleftharpoons G$ et $L \rightleftharpoons G$



$$\left(\frac{-6850}{T} - 0.755 \log T + 11.24\right) = \left(\frac{-6620}{T} - 1.255 \log T + 12.34\right)$$

$$T = 708\ K$$

(c) Equation de Clausius-Clapeyron $d(\ln P)/d(\frac{1}{T}) = -\frac{\Delta h_v}{R}$

$$\frac{d(\ln P)}{dT} = \frac{\Delta h_v}{RT^2} = 2.303 \frac{d(\log P)}{dT}$$

$$= 2.303\left(\frac{6620}{T^2} - \frac{1.255}{2.303}\left(\frac{1}{T}\right)\right)$$

$$\Delta h_v = 126750 - 10.434\,T \text{ J/mol}$$

à $T^\circ_v = 1181\ K$: $\Delta h^\circ_v = 114.43$ kJ/mol

(d) On calcule Δh_s (s = "sublimation") de la même façon :

$$\frac{\Delta h_s}{RT^2} = 2.303 \frac{d(\log P)}{dT} = 2.303\left(\frac{6850}{T^2}\right) - (0.755/T)$$

$$\Delta h_s = 131150 - 6.277\,T \text{ J/mol}$$

Mais: $\Delta h_v = (h_g - h_\ell)$

$\Delta h_s = (h_g - h_s)$

Donc: $\Delta h_{fusion} = (h_\ell - h_s) = (\Delta h_s - \Delta h_v)$

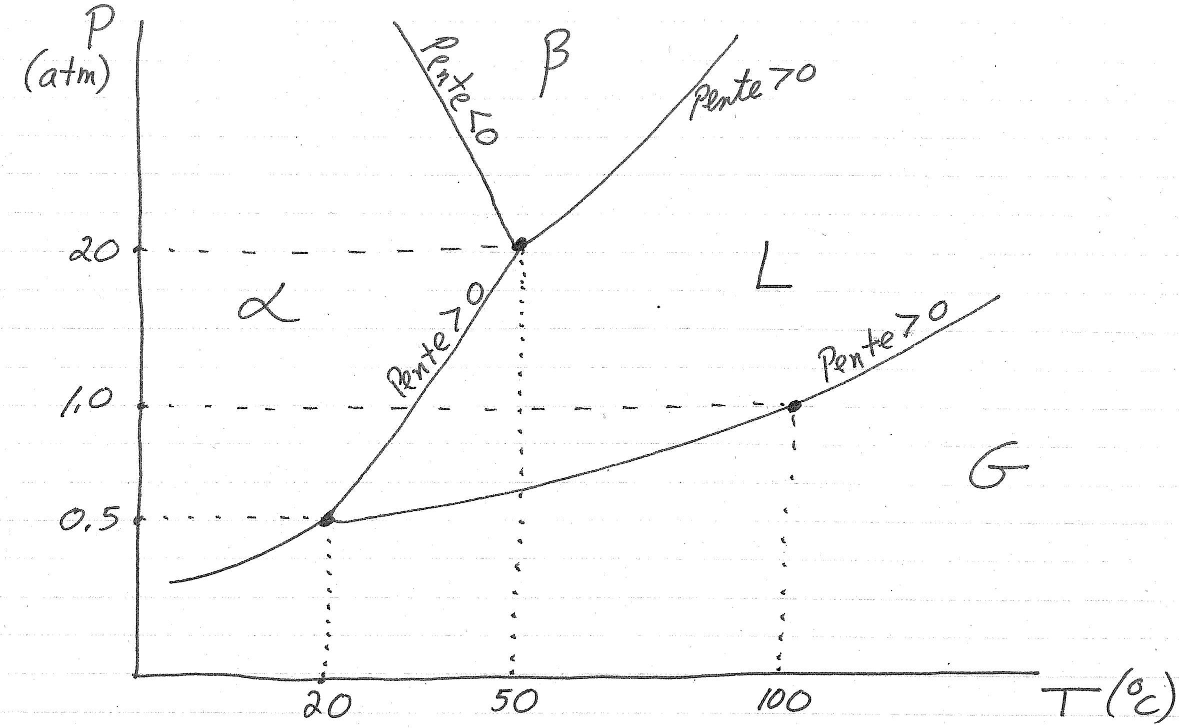
$$\Delta h_{fusion} = 4400 + 4.157\,T$$

à 708 K : $\Delta h_{fusion} = 7343$ J/mol

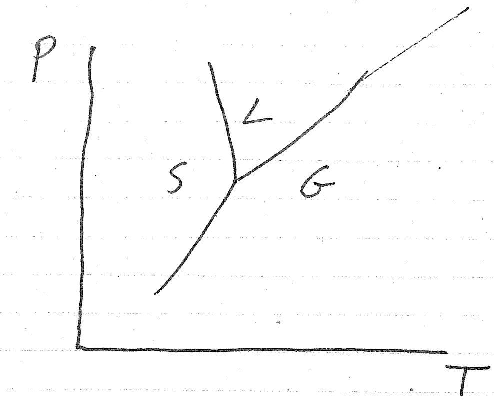
(e) $\Delta C_p = (C_p(\ell) - C_p(s)) = d(\Delta h_{fusion})/dT$

$\Delta C_p = 4.157$ J/mol K

IX-2



IX-3



Ligne L/G $\quad d(\ln P)/d(\frac{1}{T}) = -\Delta h_v/R$

$$\ln P = a + b(\tfrac{1}{T})$$

$P = 1$ atm quand $T = 183.0°C = 456.15 K \quad \ln(1) = 0 = a + b(\frac{1}{456.15})$

$P = \frac{100}{760}$ atm quand $T = 116.5°C = 389.65 K \quad \ln(\frac{100}{760}) = -2.0282 = a + b(\frac{1}{389.65})$

$$\ln P = 11.884 - (5421/T) \quad ①$$

$$\Delta h_v = 5421\, R = 45068 \text{ J/mol } I_2$$

Ligne S/G $\quad \Delta h_s = h_g - h_s \quad$ (s="sublimation")

$\Delta h_v = h_g - h_\ell$

$\Delta h_f = h_\ell - h_s$

$$\Delta h_s = \Delta h_v + \Delta h_f = 45068 + 15650 = 60718 \text{ J/mol } I_2$$

$$\ln P = a + b(\tfrac{1}{T}) \quad \text{où } b = -\frac{60718}{R} = -7303$$

Quand $T = 38.7°C = 311.85 K$, $P = 1/760$ atm

$$\ln(\tfrac{1}{760}) = a - 7303/311.85$$
$$a = 16.785$$

$$\ln P = 16.785 - (7303/T) \quad ②$$

Le point triple est à l'intersection de ① et ②

$$\left(11.884 - \frac{5421}{T}\right) = \left(16.785 - \frac{7303}{T}\right)$$

$$T = 384 K = \underline{111\ °C}$$

$\ln P = -2.233 \qquad P = 0.1072$ atm

$\qquad\qquad\qquad\qquad P = \underline{81.5 \text{ torr}}$

IX-4 Supposé: La ligne entre S_{II} et S_{III} est un ligne droite

$$\left(\frac{dP}{dT}\right)_{II \to III} \approx \frac{3397-2100}{24.3-(-34.7)} = 21.98 \text{ atm/K} = \frac{\Delta H}{T\Delta V}$$

$$\Delta V_{II \to III} = 0.0215 \text{ ml/g} = 2.15 \times 10^{-5} \text{ l/g}$$

En prenant $T = T_{moyenne} = 268K$

$$\Delta H = 21.98(268)(2.15 \times 10^{-5}) = 0.127 \text{ l-atm/g}$$

Alternativement: $dP = \frac{\Delta H}{\Delta V}\frac{dT}{T}$

$$\Delta P \approx \frac{\Delta H}{\Delta V} \ln \frac{T_2}{T_1}$$

$$(3397-2100) = \frac{\Delta H}{\Delta V} \ln \frac{(24.3+273)}{(-34.7+273)}$$

$$\Delta H = 0.126 \text{ l-atm/g}$$

$$\Delta H = 0.126 \text{ l-atm/g}$$

$$\Delta H = 12.8 \text{ J/g}$$

X-1 (a) $(T_E + \delta)$ $\quad m_\alpha = \dfrac{(0.6-0.4)}{(0.6-0.1)} = 0.4$

$$m_L = \frac{(0.4-0.1)}{(0.6-0.1)} = 0.6$$

(b) $(T_E - \delta)$

$$m_{\alpha(total)} = \frac{(0.9-0.4)}{(0.9-0.1)} = 0.625$$

$$m_{\beta(total)} = (1-0.625) = 0.375$$

(c) $(T_E - \delta)$ $\quad m_{\alpha\text{-proeut.}} = 0.4$

$$m_{\alpha\text{-eutect.}} = (0.625-0.4) = 0.225$$

ou: $m_{\alpha\text{-eut.}} = \left(\dfrac{m_{\alpha\text{-eut}}}{m_{eut}}\right) \cdot m_{eut} = \left(\dfrac{0.9-0.6}{0.9-0.1}\right)(0.6) = 0.225$

ou: $m_{\alpha\text{-eut}} = (m_{eut} - m_{\beta\text{-eut}}) = 0.6 - 0.375 = 0.225$

en plus: $m_{\beta\text{-eut}} = (m_\beta) = 0.375$

(d) (T_R) $\quad m_{\alpha\text{-tot}} = \dfrac{(0.96-0.4)}{(0.96-0.04)} = 0.609$

$$m_{\beta\text{-tot}} = (1-0.609) = 0.391$$

(e) (T_R)

(i) $m_{\beta \text{ dans pro-eut}} = \left(\dfrac{m_{\beta\text{-dans pro-eut}}}{m_{pro\text{-}eut}}\right) m_{pro\text{-}eut} = \dfrac{(0.1-0.04)}{(0.96-0.04)}(0.4) = 0.026$

$$m_{\alpha\text{-pro eut.}} = (0.4-0.026) = 0.374$$

(ii) $m_{\beta \text{ ppté dans } \alpha\text{-eut}} = \left(\dfrac{m_{\beta\text{-ppté dans } \alpha\text{-eut}}}{m_{\alpha\text{-eut}}}\right) m_{\alpha\text{-eut}} = \dfrac{(0.1-0.04)}{(0.96-0.04)}(0.225) = 0.015$

$$m_{\alpha\text{-eut}} = (0.225 - 0.015) = 0.210$$

(iii) $m_{\alpha \text{ ppté dans } \beta\text{-eut}} = \dfrac{(m_{\alpha\text{-ppté dans } \beta\text{-eut}})}{m_{\beta\text{-eut.}}} m_{\beta\text{-eut}} = \dfrac{(0.96-0.9)}{(0.96-0.04)}(0.375) = 0.024$

$$m_{\beta\text{-eut}} = (0.375 - 0.024) = 0.351$$

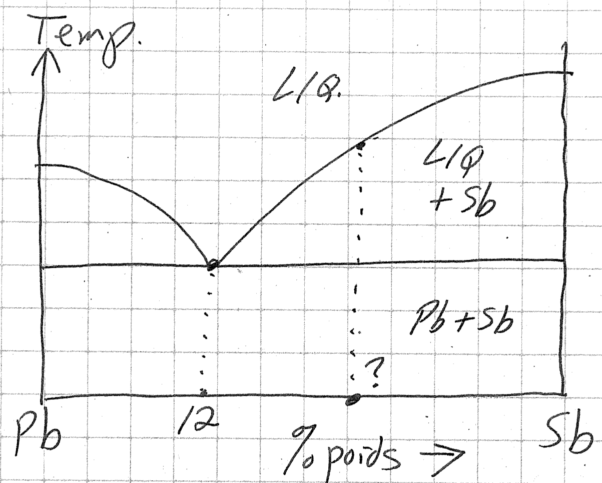
Vérifier: $\sum m_\alpha = m_{\alpha\text{-tot}}$

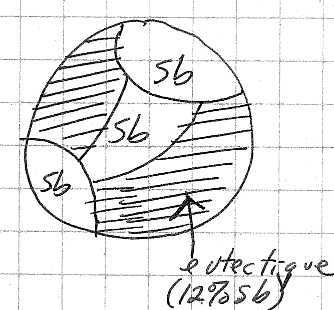
$$0.024 + 0.210 + 0.374 = 0.609 \checkmark$$

$$\sum m_\beta = m_{\beta\text{-tot}}$$

$$0.351 + 0.015 + 0.026 = 0.391 \checkmark$$

X-2





$\rho_{Sb} = (\text{Densité}) = 6.32\ \text{g/ml}$ $\qquad \rho_{Pb} = 11.35\ \text{g/ml}$

[Volume de 1.00g d'eutectique] = [Vol. du Sb là-dedans] + [Vol du Pb là-dedans]

$$= \underbrace{0.12}_{\frac{g.\,Sb}{g.\,total}}\Big(\underbrace{\tfrac{1}{6.32}}_{\frac{ml.\,Sb}{g.\,Sb}}\Big) + \underbrace{0.88}_{\frac{g.\,Pb}{g.\,total}}\Big(\underbrace{\tfrac{1}{11.35}}_{\frac{ml.\,Pb}{g.\,Pb}}\Big) = 0.09653\ (ml/g)$$

$$= 1/\rho_{eutectique}$$

[Densité de l'échantillon] = [masse de 1.0 ml de l'échantillon]

= [masse du Sb là-dedans] + [masse de l'eutectique là-dedans]

$$= \underbrace{(0.5)}_{\frac{ml.\,Sb}{ml.\,total}}\underbrace{(6.32)}_{\frac{g.\,Sb}{ml\,Sb}} + \underbrace{(0.5)}_{\frac{ml.\,eutectique}{ml.\,total}}\Big(\underbrace{\tfrac{1.0}{0.09653}}_{\frac{g.\,d'eutectique}{ml\,eutectique}}\Big) = 8.34\ \text{g/ml}$$

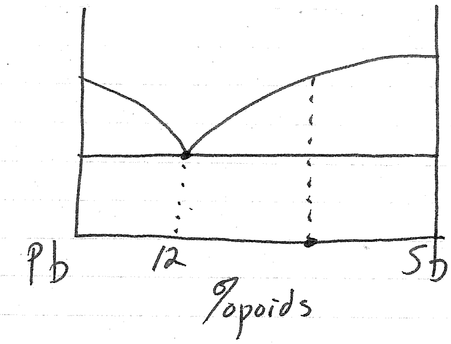
[Volume de 100g de l'échantillon] = 100/8.34

= [Vol. du Sb là-dedans] + [Vol. du Pb là-dedans]

$$= \underbrace{(\%Sb)}_{g\,Sb}\Big(\underbrace{\tfrac{1}{6.32}}_{\frac{ml\,Sb}{g\,Sb}}\Big) + \underbrace{(100 - \%Sb)}_{g.\,Pb}\Big(\underbrace{\tfrac{1}{11.35}}_{\frac{ml\,Pb}{g\,Pb}}\Big)$$

$\%Sb = 45.35$

X-2



$\rho_{Sb} = 6.32$ g/ml.

$\rho_{Pb} = 11.35$ g/ml.

$$\frac{1}{\rho_{eutectique}}\left(\frac{ml}{g}\right) = \underset{\frac{g.Sb}{g.total}}{0.12}\,\Big(\underset{\frac{ml}{g}}{\frac{1}{6.32}}\Big) + \underset{\frac{g.Pb}{g.total}}{0.88}\,\Big(\underset{ml/g}{\frac{1}{11.35}}\Big) = [\text{Volume de } 1.00g \text{ d'eutectique}]$$

$\rho_{eutectique} = 10.36$ g/ml.

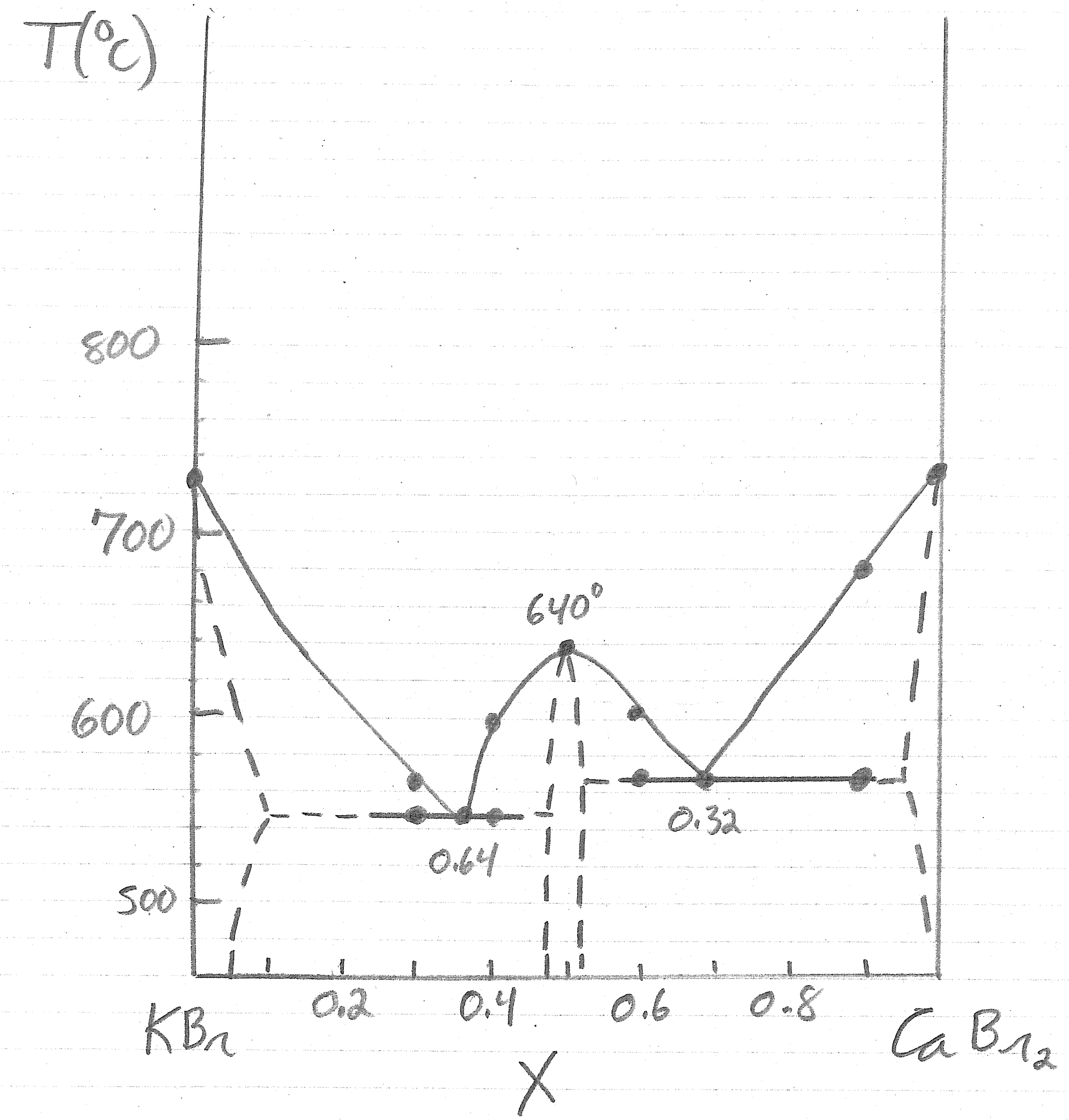
$$\rho_{alliage} = \underset{\frac{ml\,Sb}{ml\,total}}{0.5}\,(\underset{g/ml.}{6.32}) + \underset{\frac{ml.eut.}{ml.tot.}}{0.5}\,(\underset{\frac{g}{ml.}}{10.36}) = 8.34 \text{ g/ml.}$$

$= [\text{masse de } 1.0 \text{ ml. de l'échantillon}]$

$$\frac{100}{\rho_{alliage}} = \frac{(w/o)_{Sb}}{6.32} + \frac{(100-(w/o)_{Sb})}{11.35} = \frac{100}{8.34} = \{\text{Volume de } 100g \text{ de l'échantillon}]$$

$\underline{(w/o)_{Sb} = 45.35\%(\text{poids})}$

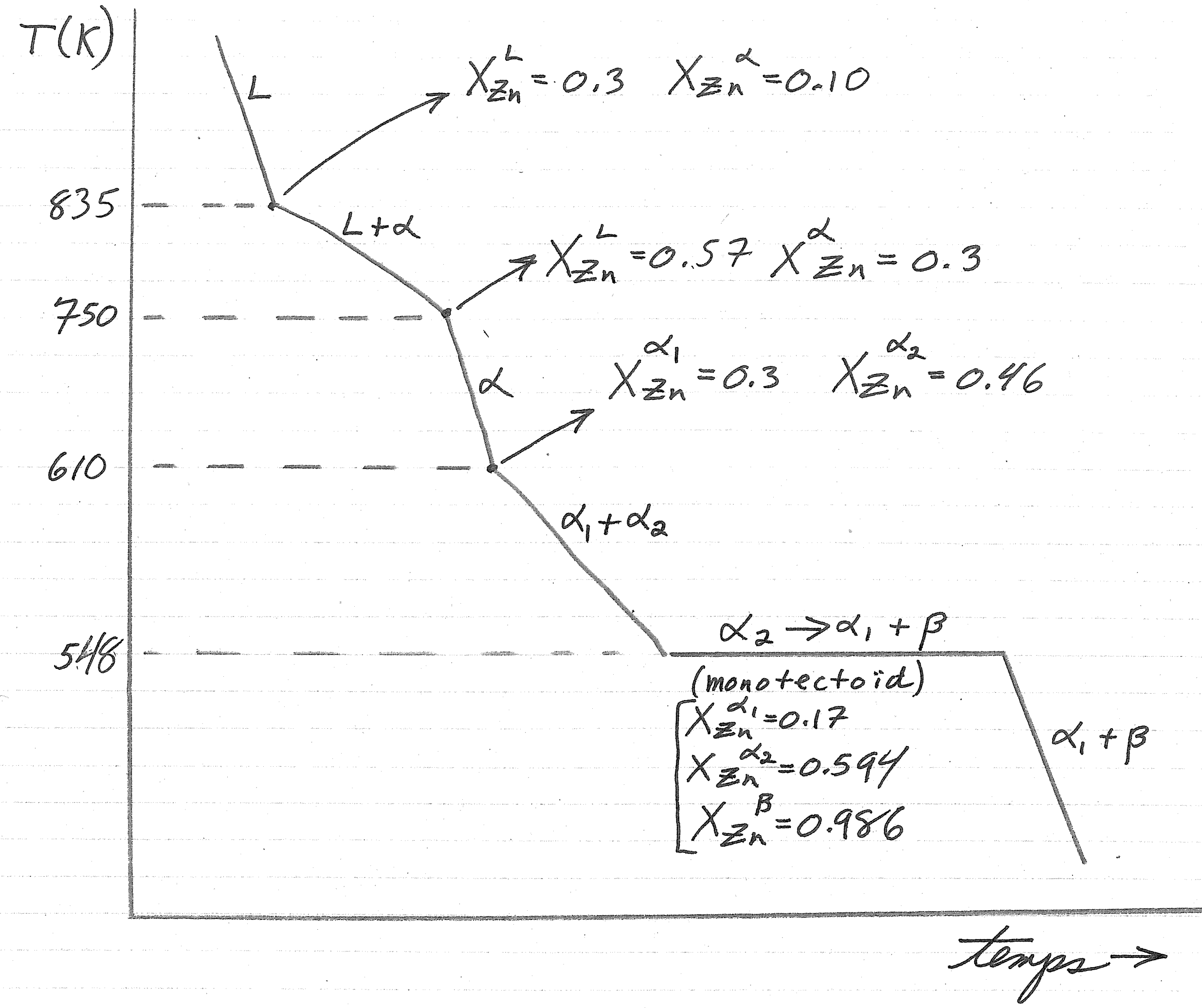
X-3



Dans le vrai diagramme les solubilités dans les solides sont < 1%

X-4

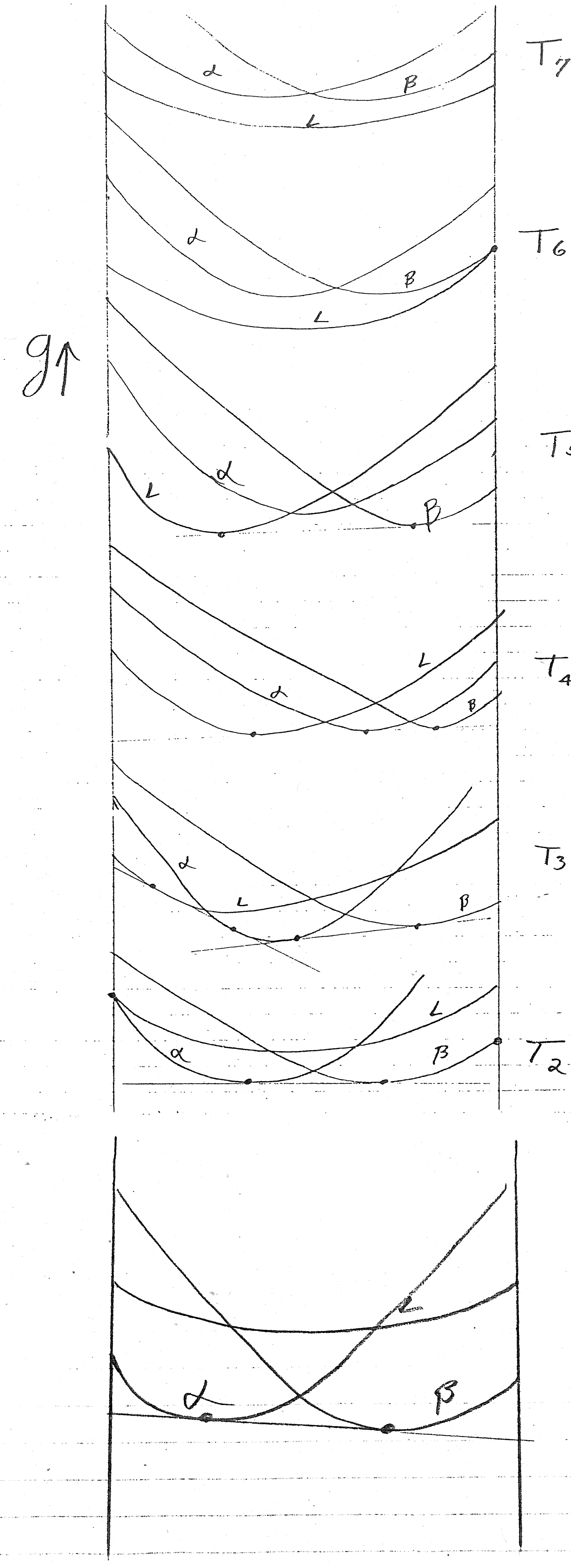
(a)



(b)

T(K)	LIQ	α_1	(α)	α_2	β
900	0.30				
800	0.44		0.17		
700			0.30		
600		0.27		0.50	
500			0.08		0.98
400			0.03		0.99
300			0.01		1.00

X-7



X-8

$$(w/o)_{Sn} = \frac{356.1}{356.1+755.3} \times 100 = 32.0\%$$

$$X_{Sn} = \frac{356.1/118.7}{\frac{356.1}{118.7} + \frac{755.3}{107.9}} = 0.300$$

(a) à 800K

(ε) 0.22 — 0.3 — 0.41 (LIQ)

$X_{Sn} \rightarrow$

$X_{Sn}^{LIQ} = 0.41$

$X_{Sn}^{\epsilon} = 0.22$

$$(w/o)_{Sn}^{LIQ} = \frac{(0.41)(118.7)}{(0.41)(118.7)+(0.59)(107.9)} \times 100 = 43.3\%$$

$$(w/o)_{Sn}^{\epsilon} = \frac{(0.22)(118.7)}{(0.22)(118.7)+(0.78)(107.9)} \times 100 = 23.7\%$$

(ε) 23.7 — 32.0 — 43.3 (LIQ)

$(w/o)_{Sn} \rightarrow$

$$\frac{m^{LIQ}}{m^{TOT}} = \frac{32-23.7}{43.3-23.7} = 0.423$$

$$m_{TOT} = 356.1 + 755.3 = 1111.4g$$

$m_{LIQ} = 470.1g$

$m_{\epsilon} = 641.3g$

(b) à 753°K $L + \epsilon = \epsilon'$ (péritectique)

à 494°K $L \rightarrow \epsilon' + (Sn)$ (eutectique)

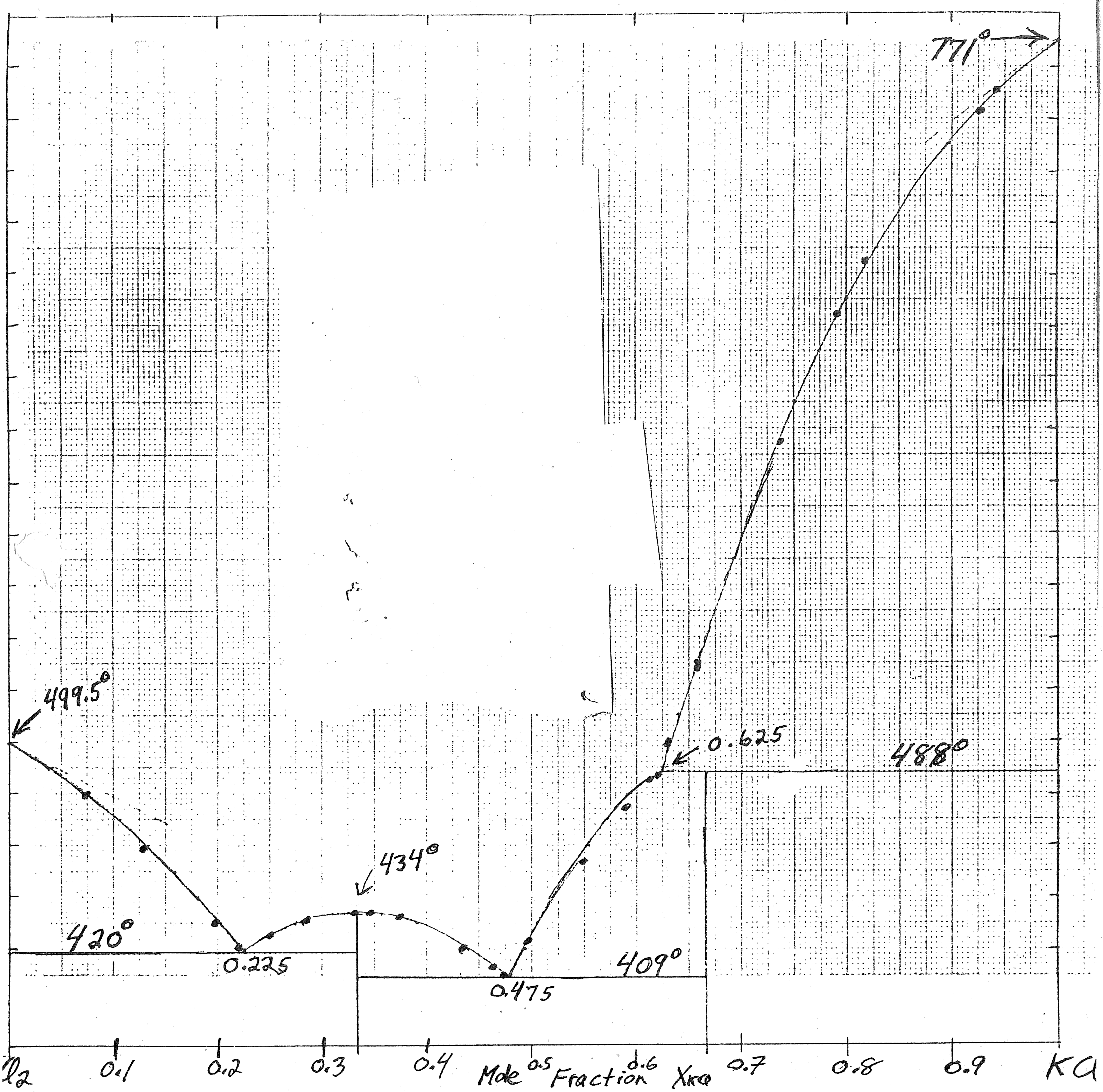
X - 9

1850°	$L \rightarrow L_I + L_{II}$	
1490°	$L_{II} \rightarrow L_I + (\beta Zr)$	monotectique
900°	$L + \beta \rightarrow \alpha$	pēritectique
750°	$L \rightarrow \alpha + \delta$	eutectique
680°	$\delta \rightarrow \gamma + \alpha$	eutectoïde

X-10

2703°	pēritectique
2653°	eutectique
2483°	pēritectoïde

X-II



771°
499.5°
0.625
488°
434°
420°
0.225
409°
0.475
l_2
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
KCl
Mole Fraction X_{KCl}

X-12 (a) A $945 \pm 5°C$
B $936°C$
C $920°C$
D $920°C$

(b) I B
II A
III D
IV C

X-13 (a) A $1760°C$
B $1965°C$
C $\sim 2530°C$
D $2020°C$

(b) A III
B IV
C II
D I

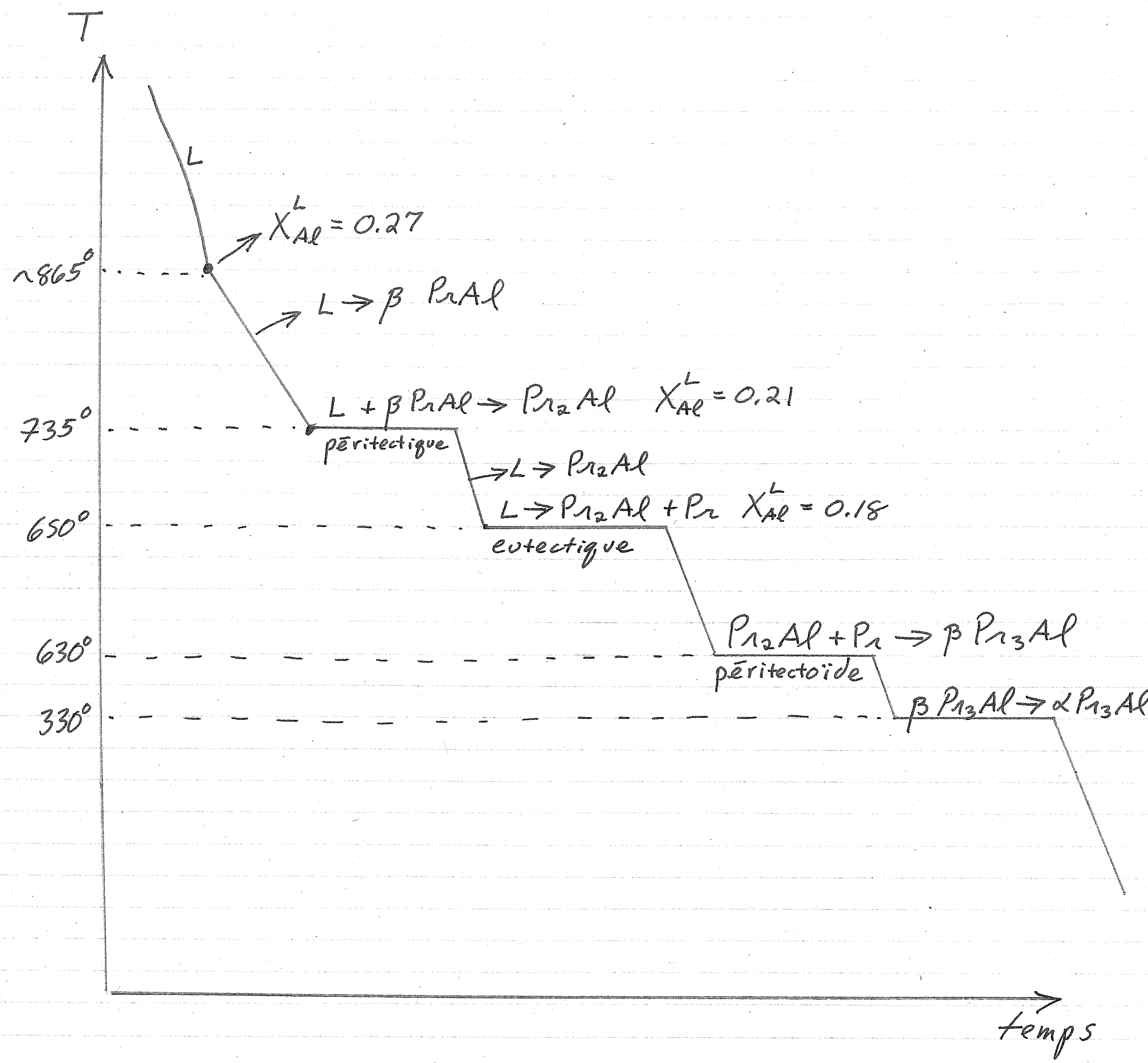
(c) $1760°$ eutectique
$1660°$ eutectoïde
$1965°$ eutectique
$1695°$ péritectoïde

X-14 (a) A $1250 \pm 20°$
B $1165°$
C $1165°$
D $1310 \pm 20°$

(b) A I
B IV
C III
D II

(c) $1375°$ péritectique
$1215°$ eutectique
$1205°$ eutectoïde
$1020°$ eutectoïde

X-15



T
L
$X_{Al}^{L} = 0.27$
~865°
L → β PrAl
735°
L + β PrAl → Pr_2Al $X_{Al}^{L} = 0.21$
péritectique
L → Pr_2Al
L → Pr_2Al + Pr $X_{Al}^{L} = 0.18$
650°
eutectique
Pr_2Al + Pr → β Pr_3Al
630°
péritectoïde
330°
β Pr_3Al → α Pr_3Al
temps

X-16 (a)
A ~1380°
B 1427°
C 1085°
D 1085°
E ~1300°

(b)
A II
B I
C IV
D III

(c) Ti pro-eutectoïde
plus
(Ti + FeTi) eutectoïde

X-17 (a)
A 1440°C
B 1775° ± 5
C 1550°
D 1680°
E 1820° ± 20

(b)
1440° eutectique
1215° eutectoïde
965° péritectoïde
1550° eutectique
1680° eutectique

(c) (i) 1660 ± 10°C Fe_2Ta

à 1440°: $L \rightarrow \delta Fe + Fe_2Ta$
à 1215°: $\delta Fe \rightarrow \gamma Fe + Fe_2Ta$

à 965°C: $\gamma Fe + Fe_2Ta \rightarrow \alpha Fe$

(d) B: 1 seule phase homogène ($33\frac{1}{3}$ % Ta)

C: Pro-eutectique FeTa
+ Eutectique (Fe_2Ta + FeTa) avec 41.5% Ta

D: Pro-eutectique Ta
+ Eutectique (FeTa + (Ta)) avec 64% Ta

E: Précipitées de FeTa dans une matrice de (Ta).

XI - 1

$$g^E_{773} = \Delta g^m_{773} - R(773)(X_{sb} \ln X_{sb} + X_{cd} \ln X_{cd})$$

$$s^E = \frac{\Delta h^m - g^E_{773}}{773}$$

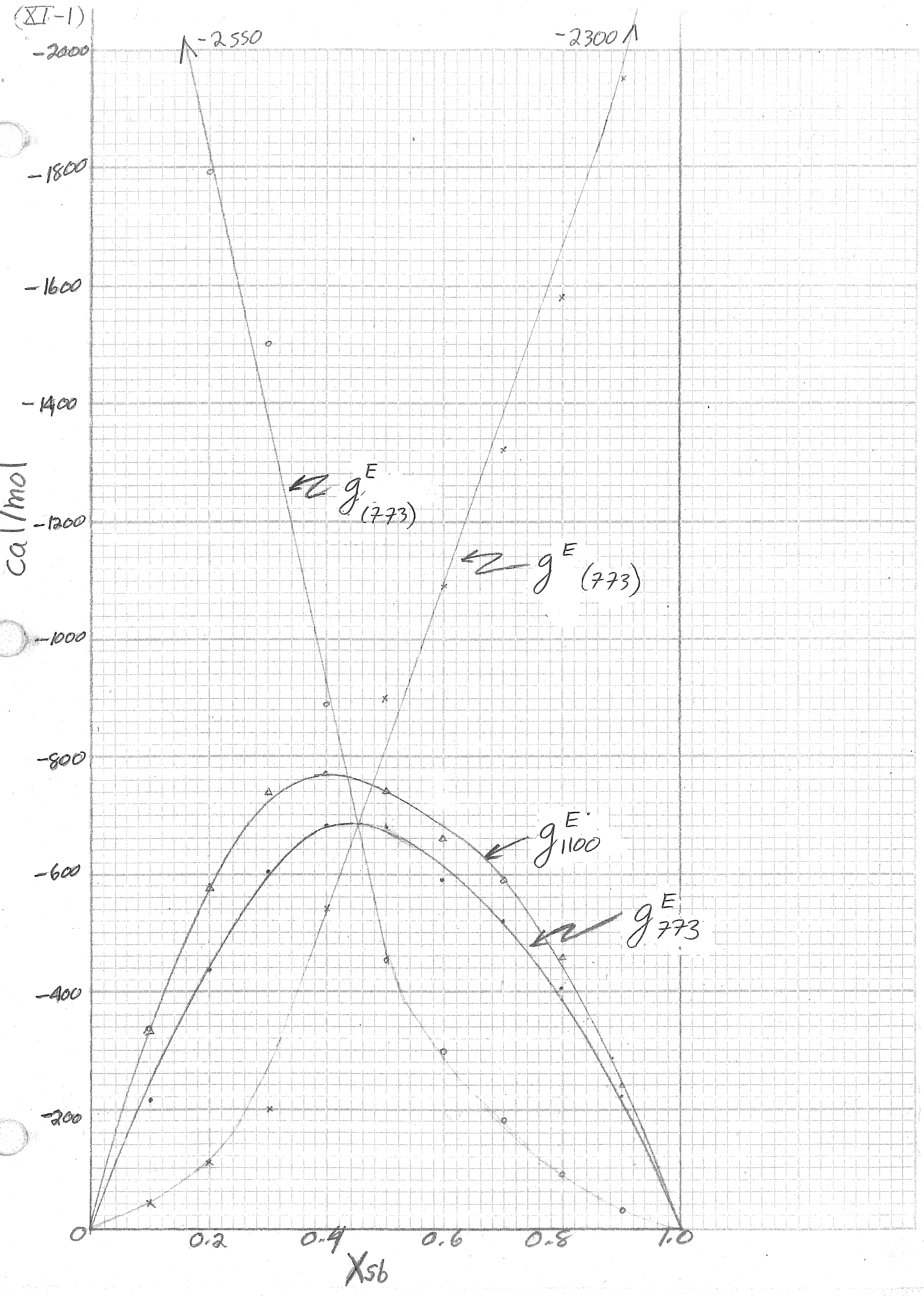
$$g^E_{1100} = \Delta h^m - 1100\, s^E$$

Trouvez $g^E_{cd(773)}$ et $g^E_{sb(773)}$ graphiquement

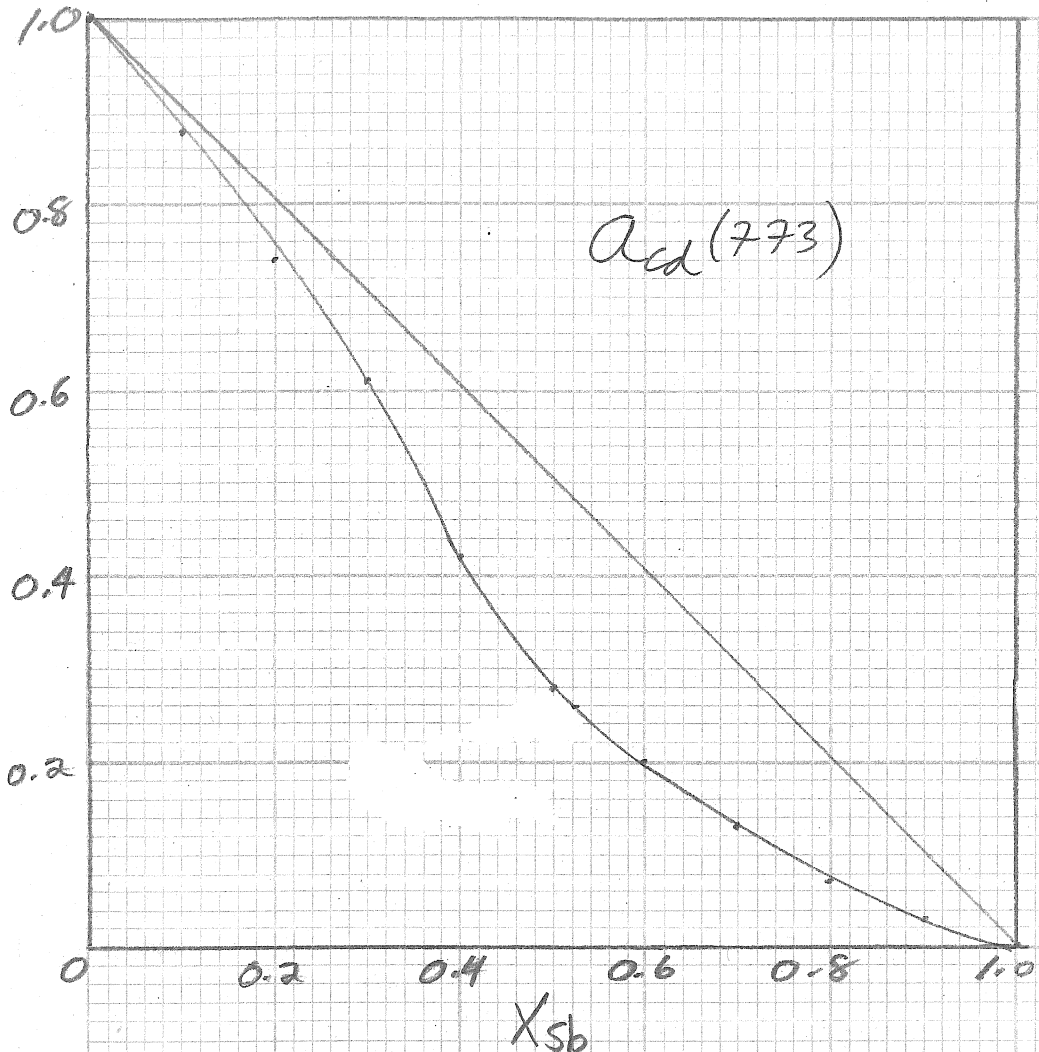
$$g^E_{cd(773)} = RT \ln \gamma_{cd(773)}$$

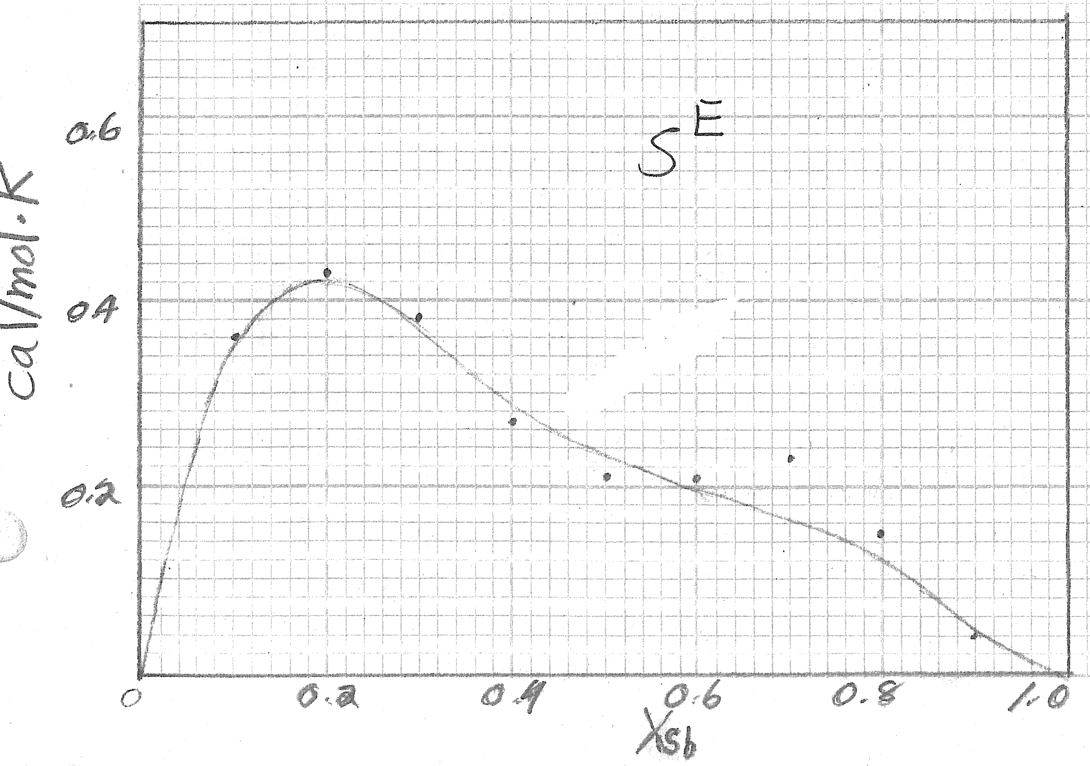
$$a_{cd(773)} = X_{cd} \cdot \gamma_{cd(773)}$$

X_{sb}	g^E_{773}	s^E	$g^E_{cd(773)}$	$g^E_{sb(773)}$	$a_{cd(773)}$	g^E_{1100}
0	0	0	0	-2550	1	0
0.1	-216	0.36	-40	-2150	0.88	-336
0.2	-436	0.43	-110	-1790	0.74	-573
0.3	-602	0.38	-200	-1500	0.61	-728
0.4	-681	0.27	-540	-890	0.42	-767
0.5	-675	0.21	-900	-450	0.28	-741
0.6	-591	0.21	-1090	-300	0.20	-661
0.7	-517	0.23	-1320	-180	0.13	-593
0.8	-406	0.15	-1580	-90	0.07	-455
0.9	-221	0.04	-1950	-30	0.03	-234
1.0	0	0	-2300	0	0	0



(XI-1)
-2550
-2300
-2000
-1800
-1600
-1400
-1200
-1000
-800
-600
-400
-200
0
cal/mol
$g'^E_{(773)}$
$g^E_{(773)}$
g^E_{1100}
g^E_{773}
0.2
0.4
0.6
0.8
1.0
X_{Sb}


1.0
0.8
0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
a_{Cd} (773)
X_{Sb}


0.6
0.4
0.2
0
0.2
0.4
0.6
0.8
1.0
S^E
cal/mol·K
X_{Sb}

XI-2 $\Delta h_{cu} = -31380\, X_{Zn}^2 \qquad s_{cu}^E = 0$

$$\Delta g_{cu} = RT\ln a_{cu} = RT\ln X_{cu} + \Delta h_{cu} - Ts_{cu}^E$$

$$\ln a_{cu} = \ln X_{cu} - \frac{31380(1-X_{cu})^2}{RT}$$

$T = 1400$

$$\ln a_{cu} = \ln X_{cu} - 2.696\,(1-X_{cu})^2$$

X_{cu}	a_{cu} (1400K)
0	0
0.1	0.011
0.2	0.036
0.3	0.080
0.4	0.152
0.5	0.255
0.6	0.390
0.7	0.549
0.8	0.718
0.9	0.876
1.0	1.0

XI-3 $\Delta h_{KCl} = -17860\, X_{LiCl}^2$ J/mol

$s_{KCl}^E = -1.46\, X_{LiCl}^2$ J/mol·K.

$$\Delta g_{KCl} = RT\ln X_{KCl} + \Delta h_{KCl} - Ts_{KCl}^E = RT\ln a_{KCl}$$

$X_{KCl} = 0.25 \qquad T = 1000\text{ K}$

$$R(1000)\ln a_{KCl} = R(1000)\ln(0.25) - 17860(0.75)^2 + 1.46(1000)(0.75)^2$$

$$\underline{a_{KCl} = 0.0824}$$

XI-4 $2Cu(l) + \frac{1}{2}O_2 = Cu_2O(s)$

$$\Delta G^o = -77780\,J = -RT\ln K \qquad T = 1273$$

$$K = 1510 = \frac{a_{Cu_2O}}{a_{Cu}^2 \cdot P_{O_2}^{1/2}} = \frac{1.00}{a_{Cu}^2 (1)^{1/2}}$$

$$a_{Cu} = 0.0257$$

$$\Delta g_{Cu} = RT\ln a_{Cu} = RT\ln X_{Cu} + \Delta h_{Cu}$$
$$= RT\ln X_{Cu} + 13390(1-X_{Cu})^2$$

$$R(1273)\ln(0.0257) = R(1000)\ln X_{Cu} + 13390(1-X_{Cu})^2$$

$$\underline{X_{Cu} = 0.0073}$$

XI-5 $\Delta G^o_{1823} = -73220\,J = -RT\ln K$

$$K = 125 = \frac{a_{Cu_2S} \cdot a_{Pb}}{a_{PbS} \cdot a_{Cu}^2} = \frac{a_{Pb}}{a_{Cu}^2} \quad \text{(sulfures purs)}$$

$$a_{Pb} \approx 1.0$$

$$\Delta h_{Cu} = 42170\,(X_{Pb})^2 \approx 42170$$

$$s^E_{Cu} = 9.6\,(X_{Pb})^2 \approx 9.6$$

$$g^E_{Cu} = RT\ln \gamma_{Cu} = \Delta h_{Cu} - T s^E_{Cu}$$

$$\gamma_{Cu} = 5.08$$

Donc: $K = 125 = \frac{1}{a_{Cu}^2} = \frac{1}{X_{Cu}^2 (5.08)^2}$

$$\underline{X_{Cu} = 0.018}$$

XI-6

$$g_{Cd}^{E} = \Delta h_{Cd} = 8370 X_{Zn}^{2} = RT \ln \gamma_{Cd}$$

Donc: $\begin{cases} \ln a_{Cd} = \ln X_{Cd} + \frac{8370}{RT} X_{Zn}^{2} \\ \ln a_{Zn} = \ln X_{Zn} + \frac{8370}{RT} X_{Cd}^{2} \end{cases}$ et:

$$a_i = P_i / P_i^{\circ}$$

$$\log P_i = \log a_i + \log P_i^{\circ}$$

$$\begin{cases} \log P_{Cd} = \log X_{Cd} + \frac{8370}{2.303RT} X_{Zn}^{2} - \frac{5200}{T} + 5.01 \\ \log P_{Zn} = \log X_{Zn} + \frac{8370}{2.303RT} X_{Cd}^{2} - \frac{5950}{T} + 5.05 \end{cases}$$

mettez $X_{Cd} = 0.1$
$X_{Zn} = 0.9$

$$\begin{cases} \log P_{Cd} = 4.01 - 4846/T \\ \log P_{Zn} = 5.00 - 5946/T \end{cases}$$

(a) Cherchez T où $(P_{Cd} + P_{Zn}) = 1.0$ atm

Approximations successives:

$T(K)$	$(P_{Cd} + P_{Zn})$
1150	1.31
1100	0.79
1125	1.02
1120	0.97
1123	1.01
1122	0.99

Donc $\underline{T = 1122\,K}$

(b) $\log P_{Cd} = 4.01 - 4846/1122 \qquad P_{Cd} = 0.50$
$\log P_{Zn} = 5.00 - 5946/1122 \qquad P_{Zn} = 0.50$

Loi de Dalton: $\begin{cases} X_{Cd}(gaz) = 0.5 (P_{TOT}) = 0.5 \\ X_{Zn}(gaz) = 0.5 \end{cases}$

XI - 7

$$Pb + 2HCl = PbCl_2 + H_2 \quad \Delta G^\circ = -242040 - 2(-99370)$$
$$= -RT\ln K$$
$$K = 672.1$$

$$Sn + 2HCl = SnCl_2 + H_2 \quad \Delta G^\circ = -236810 - 2(-99370)$$
$$= -RT\ln K$$
$$K = 306.3$$

$$\begin{cases} 672.1 = \left(\frac{P_{H_2}}{P_{HCl}^2}\right)\left(\frac{a_{PbCl_2}}{a_{Pb}}\right) = (470)\frac{X_{PbCl_2}}{a_{Pb}} \\ 306.3 = \left(\frac{P_{H_2}}{P_{HCl}^2}\right)\left(\frac{a_{SnCl_2}}{a_{Sn}}\right) = (470)\frac{X_{SnCl_2}}{a_{Sn}} \end{cases}$$

$$X_{PbCl_2} + X_{SnCl_2} = 1.0$$

$$\left(\frac{672.6}{470}\right)a_{Pb} + \left(\frac{306.3}{470}\right)a_{Sn} = 1.0$$

$$\begin{cases} RT\ln a_{Pb} = RT\ln X_{Pb} + 20(1-X_{Pb})^2 \\ RT\ln a_{Sn} = RT\ln (1-X_{Pb})^2 + 20X_{Pb}^2 \end{cases}$$

$$\begin{cases} \ln a_{Pb} = \ln X_{Pb} + 0.830(1-X_{Pb})^2 \\ \ln a_{Sn} = \ln (1-X_{Pb}) + 0.830 X_{Pb}^2 \end{cases}$$

$$1.431 X_{Pb} e^{0.830(1-X_{Pb})^2} + 0.652(1-X_{Pb})e^{0.830 X_{Pb}^2} = 1.0$$

Solution par approximations successives

$\underline{X_{Pb}\text{(alliage)} = 0.175}$ $\quad a_{Pb} = 0.308$

$$672.1 = 470\left(\frac{X_{PbCl_2}}{0.308}\right) \quad \underline{X_{PbCl_2} = 0.44}$$

XI – 8

$$RT\ln a_{Zn} = RT\ln X_{Zn} + \Delta h_{Zn} - Ts^E_{Zn}$$

$$= RT\ln X_{Zn} - 19250\, X_{Cu}^2 + 0$$

$$\log a_{Zn} = \log X_{Zn} - \frac{19250}{2.303RT} X_{Cu}^2$$

$X_{Zn} = 0.4 \qquad X_{Cu} = 0.6$

$$\log a_{Zn} = \log(0.4) - \frac{19250}{2.303\,RT}(0.6)^2$$

$$\log a_{Zn} = -0.398 - 362/T$$

$$a_{Zn} = P_{Zn}/P^o_{Zn}$$

$$\log P_{Zn} = \log a_{Zn} + \log P^o_{Zn}$$

$$\log P_{Zn} = -0.398 - 362/T - 6620/T - 1.255\log T + 12.34$$

$P_{Zn} = 760$ torr

$$\log(760) = -0.398 - 362/T - 6620/T - 1.255\log T + 12.34$$

par approximations successives

$T \approx 1350\,K$

XI-9 La teneur minimale en Sn est réalisée au moment où le PbO commence à se produire

$$Sn + 2PbO = SnO_2 + 2Pb$$

$$\Delta G^\circ = -583900 - 2(-219700) = -RT\ln K$$

$$K = 2.727 \times 10^9 = \frac{a_{Pb}^2 \cdot a_{SnO_2}}{(\gamma_{Sn} \cdot X_{Sn})\, a_{PbO}^2}$$

$$a_{PbO} = a_{SnO_2} = 1$$

$$a_{Pb} \approx 1$$

$$g_{Sn}^E = RT\ln\gamma_{Sn} = 5520 X_{Pb}^2 = 5520$$

$$\gamma_{Sn} = 2.29$$

$$2.727 \times 10^9 = \frac{1}{2.29 X_{Sn}}$$

$$\underline{X_{Sn} = 1.6 \times 10^{-10}}$$

XI-10 Supposons Δh_i et $s_i^E \neq f(T)$

$X_{Ag} = 0.8,\ T = 1600\,K$

$$\Delta g_{Ag} = RT\ln a_{Ag} = \Delta h_{Ag} - T\Delta s_{Ag}$$

$$R(1600)\ln a_{Ag} = 290 - 1600(0.52)$$

$$R(1600)\ln a_{Cu} = 2600 - 1600(3.96)$$

$$\begin{cases} a_{Ag}\,(1600K) = 0.8433 \\ a_{Cu}\,(1600K) = 0.3088 \end{cases}$$

$$Ag + CuS_{1/2} = Cu + AgS_{1/2}$$

$$\Delta G^\circ = (940 - 0.852T) - (1300 - 0.930T)$$

$$\Delta G^\circ_{1600} = -235.20 = -RT\ln K$$

$$K = 0.929^{-1} = \frac{a_{AgS_{1/2}} \cdot a_{Cu}}{a_{CuS_{1/2}} \cdot a_{Ag}} = \frac{X_{AgS_{1/2}}\,(0.3088)}{X_{CuS_{1/2}}\,(0.8433)}$$

$= 1,076$

$$\underline{X_{AgS_{1/2}} = 0.72}$$

0,746

XI-11

$X_{Ni} = 0.95$ $\quad T = 1200K.$

$X_{Fe} = 0.05$

$$g^E_{Fe} = RT\ln\gamma_{Fe} = (0.95)^2(3656 - 7668(0.95))$$

$$\gamma_{Fe} = 0.2740$$

$$a_{Fe} = X_{Fe}\cdot\gamma_{Fe} = 0.0137$$

$$g^E_{Ni} = RT\ln\gamma_{Ni} = (0.05)^2(-178 - 7668(0.95))$$

$$\gamma_{Ni} = 0.9927$$

$$a_{Ni} = 0.9430$$

$$NiFe_2O_4 + Fe = Fe_3O_4 + Ni$$

$$\Delta G^o = -167125 - (-152605) = -RT\ln K$$

$$K = 311.2 = \frac{a_{Ni}\, a_{Fe_3O_4}}{a_{Fe}\cdot a_{NiFe_2O_4}} = \frac{(0.9430)\,X_{Fe_3O_4}}{(0.0137)(1 - X_{Fe_3O_4})}$$

$$\underline{X_{Fe_3O_4} = 0.819}$$

XI-12

$$Fe + \tfrac{1}{2}O_2 = FeO \qquad -146000 = -RT\ln\frac{X_{FeO}}{X_{Fe}(7.0\times10^{-11})^{1/2}}$$

$$X_{FeO} = 0.102\,X_{Fe}$$

$$Mn + \tfrac{1}{2}O_2 = MnO \qquad -247000 = -RT\ln\frac{X_{MnO}}{X_{Mn}(7.0\times10^{-11})^{1/2}}$$

$$X_{MnO} = 64.2\,X_{Mn}$$

$$(1 - X_{FeO}) = 64.2(1 - X_{Fe})$$

$$\underline{X_{Fe} = 0.986}$$

$$\underline{X_{FeO} = 0.101}$$

XI-13

$Ag + CuCl = Cu + AgCl$

$\Delta G^{o}_{1000K} = -79910 + 91840 = -RT\ln K = 11930\,J.$

$$K = \frac{a_{AgCl} \cdot a_{Cu}}{a_{CuCl} \cdot a_{Ag}} = \frac{(\gamma_{AgCl} \cdot X_{AgCl})\, a_{Cu}}{(\gamma_{CuCl} \cdot X_{CuCl})\, a_{Ag}}$$

La composition critique, X'_{AgCl}, est la composition qui satisfait cette équation avec $a_{Cu} = a_{Ag} = 1.0$

$$-11930 = RT\ln X_{AgCl} - RT\ln(1 - X_{AgCl}) + g^{E}_{AgCl} - g^{E}_{CuCl}$$

$$-11930 = RT\ln \frac{X_{AgCl}}{(1 - X_{AgCl})} - 837(1 - X_{AgCl})^2 + 837\,X^2_{AgCl}$$

$$f(X_{AgCl}) = \ln \frac{X_{AgCl}}{(1 - X_{AgCl})} + 0.1007\left(X^2_{AgCl} - (1 - X_{AgCl})^2\right) + 1.4350 = 0$$

X_{AgCl}	$f(X_{AgCl})$
0.17	-0.217
0.19	-0.077
0.20	-0.012
0.205	0.0203
0.202	0.001

$\underline{X_{AgCl} = 0.202}$

XI-14 (a) (i) $10(-560) = \underline{-5600\,cal}$

(ii) $0.01(-1779) = \underline{-17.79\,cal}$

(b) $g^{E}_{Li} = \Delta h_{Li} + 0 = -1847 = RT\ln \gamma_{Li}$

$\gamma_{Li} = 0.3947$

$a_{Li} = 0.4\,\gamma_{Li}$

$\underline{a_{Li} = 0.158}$

XII-1

$$X_1\, d(\Delta h_1) + X_2\, d(\Delta h_2) = 0$$

$$(1-X_2)\frac{d\Delta h_1}{dX_2} + X_2\frac{d(\Delta h_2)}{dX_2} = 0$$

$$(1-X_2)\left(2(-2345)X_2 + 3(776)X_2^2\right) + X_2\left(4690 - 2(3509)X_2 + 3(776X_2^2\right)$$

$$0 = 0$$

Q.E.D. (Oui)

XII-2

$$X_{cd}\, d\ln\gamma_{cd} + X_{Zn}\, d\ln\gamma_{Zn} = 0$$

$$\int_{X_{cd}=1} d\ln\gamma_{cd} = -\int_{X_{cd}=1} \frac{X_{Zn}}{X_{cd}}\, d\ln\gamma_{Zn}$$

$$\ln\gamma_{cd} = -\int_{X_{cd}=1}^{X_{cd}} \frac{X_{Zn}}{\cancel{X_{cd}}}\left(2(0.87)\cancel{X_{cd}} - 3(0.30)X_{cd}^2\right)dX_{cd}$$

$$(X_{Zn} = 1 - X_{cd})$$

$$= -\int_{X_{cd}=1}^{X_{cd}} \left(1.74 - 2.64\,X_{cd} + 0.90\,X_{cd}^2\right)dX_{cd}$$

$$= -\left[1.74X_{cd} - 1.32\,X_{cd}^2 + 0.30\,X_{cd}^3\right]_1^{X_{cd}}$$

$$= -1.74X_{cd} + 1.32\,X_{cd}^2 - 0.30\,X_{cd}^3 + (1.74 - 1.32 + 0.30)$$

$$\ln\gamma_{cd} = 0.72 - 1.74\,X_{cd} + 1.32\,X_{cd}^2 - 0.30\,X_{cd}^3$$

or: $= 0.42X_{Zn}^2 + 0.30X_{Zn}^3$

Autre methode: Suppose $\ln\gamma_{cd} = aX_{Zn}^2 + bX_{Zn}^3$

$$X_{cd}\, d\ln\gamma_{cd} + X_{Zn}\, d\ln\gamma_{Zn} = 0 \qquad (dX_{cd} = -dX_{Zn})$$

$$X_{cd}(2aX_{Zn} + 3bX_{Zn}^2) = X_{Zn}\left(2(0.87)X_{cd} - 3(0.30)X_{cd}^2\right)$$

$$(1-X_{Zn})(2aX_{Zn} + 3bX_{Zn}^2) = X_{Zn}\left(1.74(1-X_{Zn}) - 0.90(1 - 2X_{Zn} + X_{Zn}^2)\right)$$

$$2aX_{Zn} + 3bX_{Zn}^2 - 2aX_{Zn}^2 - 3bX_{Zn}^3 = 1.74X_{Zn} - 1.74X_{Zn}^2 - 0.90X_{Zn} + 1.80X_{Zn}^2 - 0.90X_{Zn}^3$$

$$X_{Zn}(2a - 1.74 + 0.90) + X_{Zn}^2(3b - 2a + 1.74 - 1.80) + X_{Zn}^3(-3b + 0.90) = 0$$

$$2a - 0.84 = 0 \Rightarrow a = 0.42$$

$$3b - 2a - 0.06 = 0$$

$$-3b + 0.90 = 0 \Rightarrow b = 0.30$$

Verify: $3(0.3) - 2(0.42) - 0.06 = 0$ ✓

Done: $\ln\gamma_{cd} = 0.42\,X_{Zn}^2 + 0.30X_{Zn}^3$

XII - 3

$$\Delta h = X_1 X_2 (3.535 - 1.895(2X_2 - 1))$$

$$= X_1 X_2 (5.43 - 3.79 X_2) = (X_2 - X_2^2)(5.43 - 3.79X_2)$$

$$= 5.43X_2 - 9.22X_2^2 + 3.79X_2^3$$

$$\Delta h_1 = \Delta h + X_2 \frac{d\Delta h}{dX_1} = \Delta h - X_2 \frac{d\Delta h}{dX_2}$$

$$\Delta h_1 = X_1 X_2 (5.43 - 3.79X_2) - X_2(5.43 - 18.44X_2 + 11.37X_2^2)$$

$$= 5.43X_2 - 9.22X_2^2 + 3.79X_2^3 - 5.43X_2 + 18.44X_2^2 - 11.37X_2^3$$

$$= 9.22X_2^2 - 7.58X_2^3$$

$$\Delta h_1 = X_2^2(9.22 - 7.58X_2)$$

$$\underline{\Delta h_1 = X_2^2(5.43 - 3.79(2X_2 - 1))}$$

XII - 4

$$X_A \, dg_A^E + X_B \, dg_B^E = 0 \qquad g_A^E = \omega X_B^n$$

$$dg_B^E = -\frac{X_A}{X_B}\frac{dg_A^E}{dX_B} \cdot dX_B$$

$$= -\frac{X_A}{X_B}\omega n X_B^{n-1} dX_B \qquad X_A = 1 - X_B$$

$$= \omega n (X_B^{n-1} - X_B^{n-2}) dX_B$$

$$\int_{X_B=1}^{X_B} dg_B^E = g_B^E - 0 = \omega n \int_{X_B=1}^{X_B} (X_B^{n-1} - X_B^{n-2}) \, dX_B$$

$$= \omega n \left[\frac{X_B^n}{n} - \frac{X_B^{n-1}}{n-1} - \frac{1}{n} + \frac{1}{n-1}\right]$$

$$g_B^E = \omega\left(X_B^n - 1 - \frac{n}{n-1}(X_B^{n-1} - 1)\right)$$

$$g_{Sn}^E = 1268\left(X_{Sn}^{1.9} - 1 - \frac{1.9}{0.9}(X_{Sn}^{0.9} - 1)\right)$$

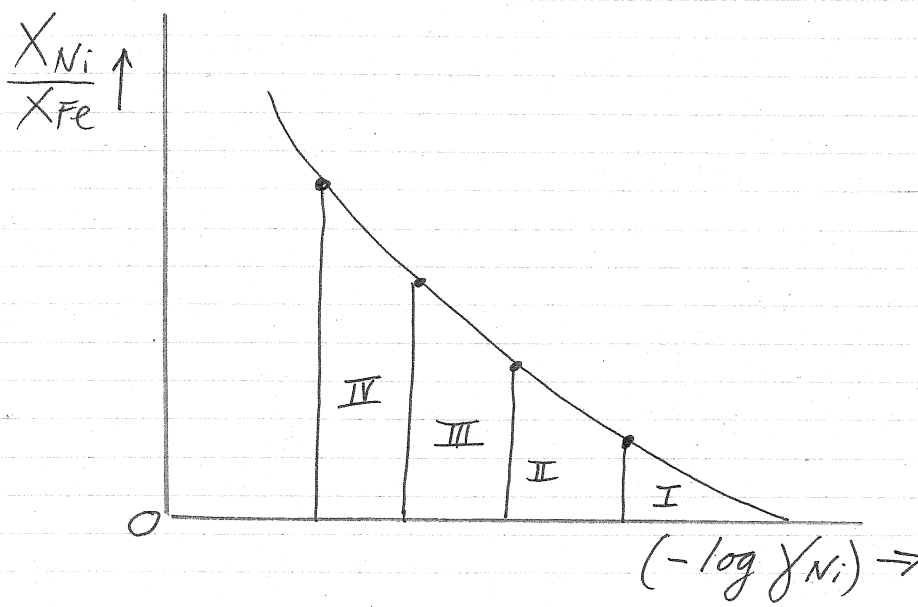
$$= 1268\left(X_{Sn}^{1.9} - 2.111\,X_{Sn}^{0.9} + 1.111\right)$$

XII - 5

(a)

X_{Ni}	X_{Ni}/X_{Fe}	$\log a_{Ni} = \log \frac{P_{Ni}}{P^o_{Ni}} = (\log P_{Ni} + 1.755)$	$\log \gamma_{Ni} = \log \frac{a_{Ni}}{X_{Ni}}$
0	0	$-\infty$	−0.21 (extrapolé)
0.100	0.111	−1.19	−0.1950
0.198	0.287	−0.87	−0.1717
0.408	0.689	−0.51	−0.1257
0.638	1.761	−0.26	−0.0698
1.000	∞	0	0

$$\log \gamma_{Fe} = -\int_{\frac{X_{Ni}}{X_{Fe}}=0}^{X_{Ni}/X_{Fe}} \left(\frac{X_{Ni}}{X_{Fe}}\right) d\log \gamma_{Ni}$$



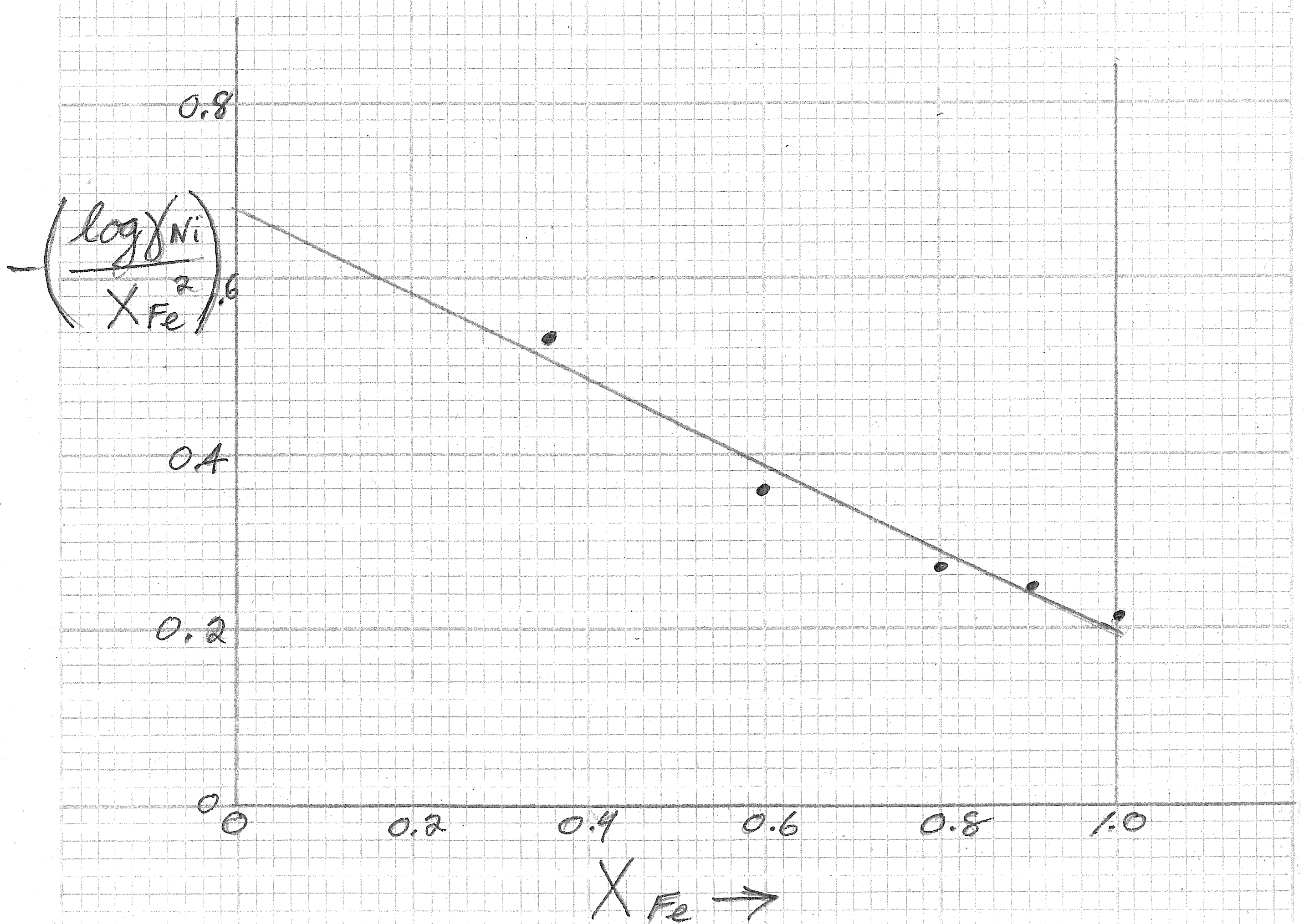
X_{Ni}	aire	Σ(aire)	$\log \gamma_{Fe}$
0	0	0	0
0.100	I = 0.0011	0.0011	−0.0011
0.198	II = 0.0036	0.0047	−0.0047
0.408	III = 0.0233	0.0280	−0.0280
0.638	IV = 0.0761	0.1041	−0.1041

(b)

X_{Ni}	$\log \gamma_{Ni}/X_{Fe}^2$
0	−0.21
0.100	−0.2407
0.198	−0.2669
0.408	−0.3587
0.638	−0.5326

Voir graphique
Lissez "à la main"

(XII - 5)



0.8
$-\left(\frac{\log \gamma_{Ni}}{X_{Fe}^2}\right)$
.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1.0
$X_{Fe} \rightarrow$

(XII – 5 suite)

$$\log \gamma_{Ni} / X_{Fe}^2 = -0.68 + 0.49 X_{Fe}$$

$$\underline{\log \gamma_{Ni} = X_{Fe}^2 (-0.68 + 0.49 X_{Fe})}$$

Suppose: $\log \gamma_{Fe} = X_{Ni}^2 (a + b X_{Ni})$

$$X_{Fe}\, d\log\gamma_{Fe} + X_{Ni}\, d\log\gamma_{Ni} = 0 \qquad (dX_{Fe} = -dX_{Ni})$$

$$X_{Fe}(2a X_{Ni} + 3b X_{Ni}^2) = X_{Ni}(-1.36 X_{Fe} + 1.47 X_{Fe}^2)$$

$$(1 - X_{Ni})(2a X_{Ni} + 3b X_{Ni}^2) = X_{Ni}\left(-1.36(1 - X_{Ni}) + 1.47(1 - 2X_{Ni} + X_{Ni}^2)\right)$$

$$2a X_{Ni} + 3b X_{Ni}^2 - 2a X_{Ni}^2 - 3b X_{Ni}^3 = -1.36 X_{Ni} + 1.36 X_{Ni}^2 + 1.47 X_{Ni} - 2.94 X_{Ni}^2 + 1.47 X_{Ni}^3$$

$$X_{Ni}(2a + 1.36 - 1.47) + X_{Ni}^2(3b - 2a - 1.36 + 2.94) + X_{Ni}^3(-3b - 1.47) = 0$$

$$2a - 0.11 = 0 \quad \Rightarrow a = 0.055$$

$$3b - 2a + 1.58 = 0$$

$$-3b - 1.47 = 0 \quad \Rightarrow b = -0.49$$

Verify: $3(-0.49) - 2(0.055) + 1.58 = 0$ ✓

$$\underline{\log \gamma_{Fe} \quad X_{Ni}^2 (0.05 - 0.49 X_{Ni})}$$

$= (1 - 2X_{Fe} + X_{Fe}^2)(-.44 + .49 X_{Fe})$ ✓

$= -.44 + .49X + .88X - .98X^2$

$\quad -.44X^2 + .49X^3$

$= -.44 + 1.37X - 1.42X^2 + .49X^3$

X_{Ni}	$\log \gamma_{Fe}$
0	0
0.100	−0.00001
0.198	−0.0018
0.408	−0.025
0.638	−0.107
1.000	−0.44

(cf. avec le tableau de la partie (a))

OR: $\log \gamma_{Fe} = -\int_{X_{Fe}=1}^{X_{Fe}} \frac{X_{Ni}}{X_{Fe}}\, d\log\gamma_{Ni}$ ~~$= \int X_{Fe} X_{Ni} (-0.68 + 0.49 X_{Fe})$~~

$$= -\int \frac{(1 - X_{Fe})}{\cancel{X_{Fe}}} \left(2\cancel{X_{Fe}}(-0.68) + 3 X_{Fe}^{\cancel{2}}(0.49)\right) dX_{Fe}$$

$$= -\int (1 - X_{Fe})\left[(-1.36) + 1.47 X_{Fe}\right] dX_{Fe} = \int_{X_{Fe}=1} \left(1.36 - 2.83 X_{Fe} + 1.47 X_{Fe}^2\right) dX_{Fe}$$

$$= \left[1.36 X_{Fe} - \frac{2.83}{2} X_{Fe}^2 + \frac{1.47}{3} X_{Fe}^3\right]_1^{X_{Fe}}$$

$$= 1.36 X_{Fe} - 1.415 X_{Fe}^2 + 0.49 X_{Fe}^3 - 0.435$$

$$= X_{Ni}^2 (0.05 - 0.49 X_{Ni})$$

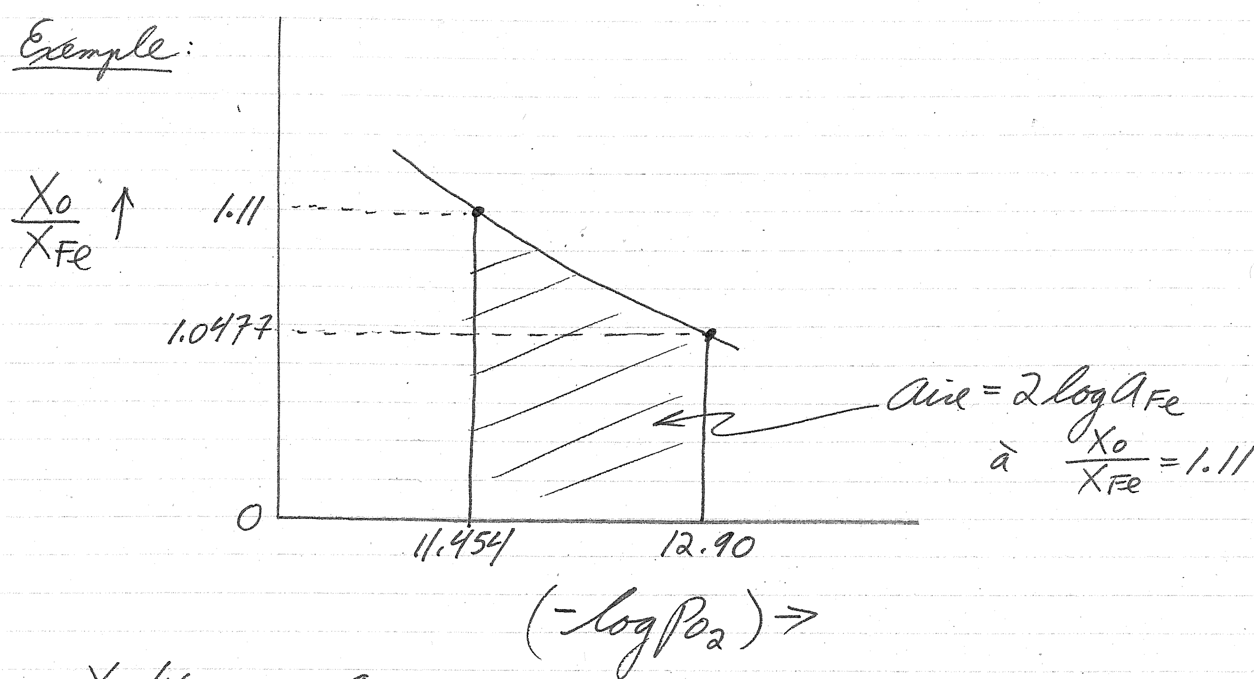
XII - 6 (a) $\frac{1}{2} O_2 (g) \rightleftarrows [O]$ dissous

$$a_O / p_{O_2}^{1/2} = K \qquad d \log a_O = \frac{1}{2} d \log p_{O_2}$$

$$X_O \, d\log a_O + X_{Fe} \, d\log a_{Fe} = 0$$

$$\log a_{Fe} = \int_{a_{Fe}=1}^{a_{Fe}} d\log a_{Fe} = -\int_{a_{Fe}=1}^{a_{Fe}} \frac{X_O}{X_{Fe}} d\log a_O = -\frac{1}{2} \int_{\frac{X_O}{X_{Fe}}=1.0477}^{X_O/X_{Fe}} \left(\frac{X_O}{X_{Fe}}\right) d\log p_{O_2}$$

Exemple:



X_O/X_{Fe}	a_{Fe}
1.0477	1.000
1.055	0.824
1.07	0.560
1.09	0.305
1.11	0.160
1.14	0.060
1.153	0.040

(b) $x Fe + \frac{1}{2} O_2 = Fe_x O \qquad \Delta G^\circ = -RT \ln K$

Supposition: $\Delta G^\circ = cst$
$K \neq f(x)$

$$K = a_{Fe_xO} / (a_{Fe})^x (p_{O_2})^{1/2}$$

$$\log K = \log \underset{\sim}{(1.0)} - x \log a_{Fe} - \frac{1}{2} \log p_{O_2}$$

Lorsque $1/x = 1.0477$, $a_{Fe} = 1$

Donc: $\log K = -\frac{1}{2}(-12.90) = 6.45$

(XII-6 suite)

Donc: $\log a_{Fe} = -\frac{1}{x}\left(6.45 + \frac{1}{2}\log p_{O_2}\right)$

$1/x = X_O/X_{Fe}$	a_{Fe}
1.0477	1.000
1.055	0.821
1.07	0.539
1.09	0.297
1.11	0.157
1.14	0.058
1.153	0.0372

L'accord avec la partie (a) est excellent

(c) Tracez la courbe de a_{Fe} versus $\log p_{O_2}$

Lorsque $a_{Fe} = 0.1$, $\log p_{O_2} = -11.12$

$$p_{O_2} = 7.59 \times 10^{-12}$$

$$H_2 + \tfrac{1}{2}O_2 = H_2O \qquad \Delta G^\circ = -169.1 = -RT\ln K$$

$$K = 2.72 \times 10^{6} = \left(\frac{P_{H_2O}}{P_{H_2}}\right)\left(\frac{1}{P_{O_2}^{1/2}}\right)$$

$$\left(\frac{P_{H_2}}{P_{H_2O}}\right) = 0.13$$

$\underline{\text{XII} - 7}$ $\quad X_A \, d\ln a_A + X_B \, d\ln a_B = 0$

$$X_A \, d\ln a_A + (1 - X_A) \, d\ln a_B = 0$$

$$X_A \, d\ln\left(\frac{a_A}{a_B}\right) + d\ln a_B = 0$$

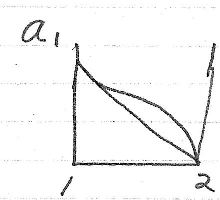
$$\ln a_B - \ln a_{B(X')} = \int_{X'}^{X} d\ln a_B = -\int_{X'}^{X} X_A \, d\ln\left(\frac{a_A}{a_B}\right)$$

etc.

$\underline{\text{XII} - 8}$ $\quad X_1 \, d\ln\gamma_1 + X_2 \, d\ln\gamma_2 = 0$

$X_1 \to 1 \quad d\ln\gamma_1 \to 0$ (Raoult)

(<u>N.B.</u>: pas seulement $\ln\gamma_1 = 0$ mais, <u>en plus</u>, $d\ln\gamma_1 \to 0$)



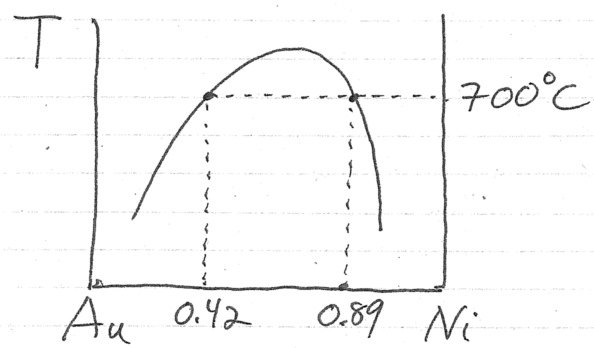
<u>Donc</u>: $d\ln\gamma_2 \neq \infty$

<u>Donc</u>: $\gamma_2 \neq \infty$ (Loi de Henry)

XIII-1 $\Delta g^m_{973} = \Delta h^m - 973\,\Delta s^m$

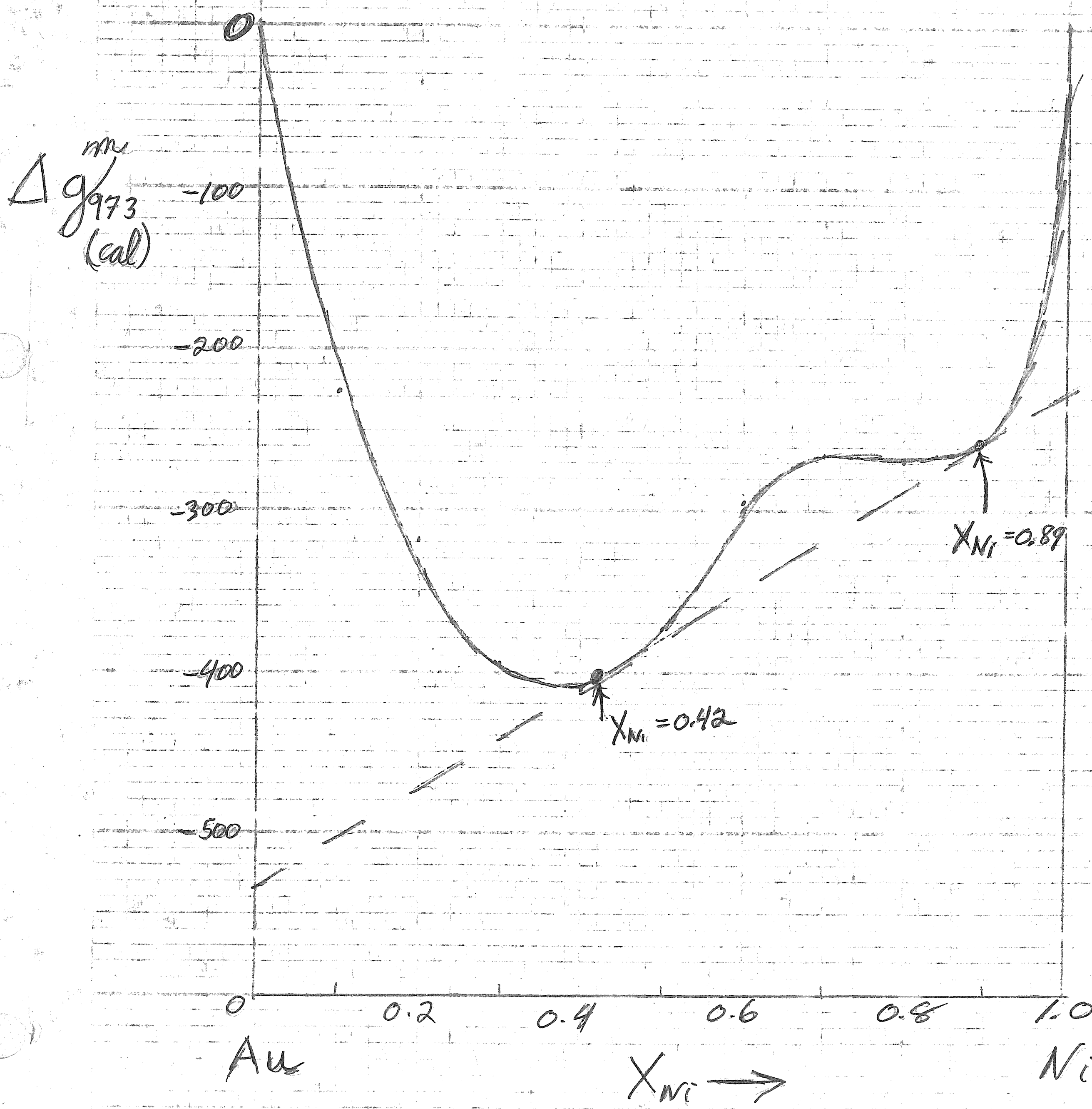
X_{Ni}	Δg^m_{973}
0.1	-226
0.2	-319
0.3	-395
0.4	-412
0.5	-373
0.6	-295
0.7	-264
0.8	-269
0.9	-256

Voir graphique



Solubilité de Ni dans l'or = 42% molaire

(XIII-1)



0
Δg^{m}_{973} (cal)
-100
-200
-300
-400
-500
0
0.2
0.4
0.6
0.8
1.0
Au
Ni
$X_{Ni} \rightarrow$
$X_{Ni} = 0.42$
$X_{Ni} = 0.89$

$\underline{\text{XIII}-2}$ $\quad RT\ln a^{l}_{Sn} = -\Delta g^{o}_{fusion\,(Sn)}$

$$RT\ln X_{Sn} + g^{E}_{Sn} = -\Delta h^{o}_{fusion}\left(1 - T/T^{o}_{f}\right)$$

$$RT\ln(0.75) + 5523(1-0.75)^2 = -7196\left(1 - T/505\right)$$

$$T\left(R\ln 0.75 - \frac{7196}{505}\right) = -7196 - 5523(1-0.75)^2$$

$$\underline{T = 453\,K}$$

$\underline{\text{XIII}-3}$ $\quad RT\ln a^{l}_{cd} - RT\ln a^{s}_{cd} = -\Delta h^{o}_{fusion}\left(1 - T/T^{o}_{f}\right)$

(a) 485K

$$R(485)\ln a^{l}_{cd} - 0 = -6109\left(1 - \frac{485}{594}\right)$$

$$\underline{a^{l}_{cd} = 0.76} \quad (\text{à } T = 485\,K \text{ à } X_{cd} = 0.7)$$

(b) $\Delta g_{cd} = \Delta h_{cd} - T\Delta S_{cd} = RT\ln a_{cd}$

$$R(485)\ln a_{cd(485)} = 982 - 485\Delta S_{cd}$$

$$\Delta S_{cd} = 4.3063$$

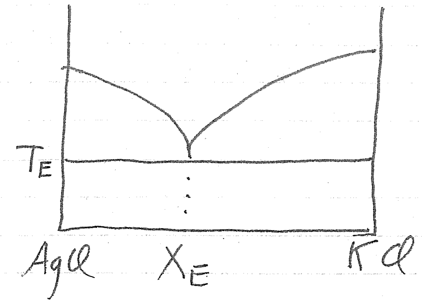
$$\Delta g_{cd} = 982 - 4.3063\,T$$

$\underline{\text{à } T = 900K}$

$$R(900)\ln a_{cd(900)} = 982 - 4.3063(900)$$

$$\underline{a_{cd}(900) = 0.68}$$

XIII-4



$$\begin{cases} RT_E \ln X^E_{AgCl} = -\Delta h^\circ_{f(AgCl)}\left(1 - T_E/T^\circ_{f(AgCl)}\right) \\ RT_E \ln (1-X^E_{AgCl}) = -\Delta h^\circ_{f(KCl)}\left(1 - T_E/T^\circ_{f(KCl)}\right) \end{cases}$$

$$\begin{cases} RT_E \ln(1-X^E_{KCl}) = -13200\,(1 - T_E/728) \\ RT_E \ln X^E_{KCl} = -25520\,(1 - T_E/1043) \end{cases}$$

$$\begin{cases} T_E\left(R\ln(1-X) - 18.1319\right) = -13200 \\ T_E\left(R\ln X - 24.4679\right) = -25520 \end{cases}$$

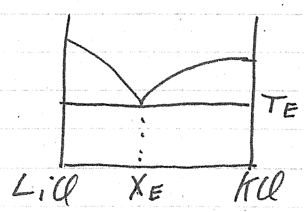
$$\frac{+13200}{R\ln(1-X) - 18.1319} = \frac{+25520}{R\ln X - 24.4679}$$

$$\ln X_{KCl(E)} - 1.933 \ln(1 - X_{KCl(E)}) + 1.269 = 0$$

Par approximations successives: $\underline{X_{KCl(E)} = 0.19}$

$T_E = 665\ K = \underline{392^\circ C}$

XIII-5



$$\begin{cases} RT \ln X_{LiCl(E)} - 17860\, X^2_{KCl(E)} + 1.46\, X^2_{KCl(E)}\, T_E = -19870\left(1 - \frac{T_E}{883}\right) \\ RT \ln X_{KCl(E)} - 17860\, X^2_{LiCl(E)} + 1.46\, X^2_{LiCl(E)}\, T_E = -26570\left(1 - \frac{T_E}{1045}\right) \end{cases}$$

Eliminez T: $(-26570 + 17860 X^2_{LiCl})(R\ln X_{LiCl} + 1.46 X^2_{KCl} - 22.503)$

$= (-19870 + 17860 X^2_{KCl})(R\ln X_{KCl} + 1.46 X^2_{LiCl} - 25.426)$

$X_{KCl} + X_{LiCl} = 1$

approximations successives: $X^E_{KCl} \approx 0.42$

$T^E = 629\,K$

XIII-6 $n_O = 0.16/16 = 0.01\,mol$

$n_{Ag} = 100/107.9 = 0.9268\,mol$

$X_{Ag} = (0.9268/0.9368) = 0.9893$

$RT\ln X_{Ag} = -2700\left(1 - \frac{T}{961+273}\right)$ Loi de Raoult $(X_{Ag} \approx 1)$

$\underline{T = 1222\,K = 949°C}$

XIII-7 $\frac{dX_B}{dT} = \frac{\Delta h_f^o}{RT_f^2 \cdot \nu}$

$\Delta T = \nu \Delta X_B \cdot \frac{RT_f^2}{\Delta h_f}$

$\Delta T = \nu\,(0.01)\,\frac{R(1074)^2}{28160} = 3.4\nu$

(a) $\nu = 1$ $\Delta T = 3.4$ $T = 801 - 3.4 = 797.6$

(b) $\nu = 1$ $\Delta T = 3.4$ $T = 801 - 3.4 = 797.6$

(c) $\nu = 2$ $\Delta T = 6.8$ $T = 801 - 6.8 = 794.2$

(d) $\nu = 3$ $\Delta T = 10.2$ $T = 801 - 10.2 = 790.8$

XIII - 8

Liquidus du Cd:

$$RT\ln a_{cd} = \Delta h_{cd} - T\Delta s_{cd} \qquad \text{Supposez : } \Delta h_{cd} \neq f(T),\ \Delta s_{cd} \neq f(T)$$

$$\Delta s_{cd} = \frac{-773R\ln a_{cd(773)} + \Delta h_{cd}}{773}$$

$$RT\ln a_{cd} = \Delta h_{cd} - T\left(\frac{-773R\ln a_{cd(773)} + \Delta h_{cd}}{773}\right)$$

$$RT\ln a_{cd} = RT\ln a_{cd(773)} + \Delta h_{cd}\left(1 - \frac{T}{773}\right)$$

Mais: $RT\ln a_{cd} = -\Delta h^o_{fus(cd)}\left(1 - \frac{T}{T_{f\,cd}}\right)$ selon le liquidus

$$RT\ln a_{cd(773)} + \Delta h_{cd}\left(1 - \frac{T}{773}\right) = -\Delta h^o_{fus(cd)}\left(1 - \frac{T}{T_{f(cd)}}\right)$$

$$T\left(R\ln a_{cd(773)} - \frac{\Delta h_{cd}}{773} - \frac{\Delta h^o_{f(cd)}}{T^o_{f(cd)}}\right) = -\left(\Delta h^o_{fus(cd)} - \Delta h_{cd}\right)$$

$$T = \left(\Delta h^o_{fus(cd)} + \Delta h_{cd}\right) \Big/ \left(\frac{\Delta h_{cd}}{773} + \frac{\Delta h^o_{f(cd)}}{T^o_{f(cd)}} - R\ln a_{cd(773)}\right)$$

Choisissez une composition et calculez T(liquidus)

Liquidus du Sn:

$$T = \left(\Delta h^o_{fus(Sn)} + \Delta h_{Sn}\right) \Big/ \left(\frac{\Delta h_{Sn}}{773} + \frac{\Delta h^o_{f(Sn)}}{T^o_{f(Sn)}} - R\ln a_{Sn(773)}\right)$$

X_{cd}	T(liquidus)(Cd)	T(liquidus)(Sn)
1.0	594	
0.9	552	
0.8	523	
0.7	504	
0.6	486	
0.5	470	
0.4	449	428
0.3	428	441
0.2		456
0.1		478
0		505

Voir à la figure

Provenances des erreurs:
- Solubilité à l'état solide
- $\alpha \to \beta$ transformation du Sn
- Δh^o_{fusion} (barres d'incertitude)

XIII - 11

$$RT\ln a_{Sn}^{l} - RT\ln a_{Sn}^{s} = -\Delta h_{f(Sn)}^{\circ}\left(1 - \frac{T}{T_{f(Sn)}^{\circ}}\right)$$

$$RT\ln X_{Sn}^{l} + RT\ln \gamma_{Sn}^{l} - RT\ln X_{Sn}^{s} - RT\ln \gamma_{Sn}^{s} = -\Delta h_{f(Sn)}^{\circ}\left(1 - \frac{T}{T_{f}^{\circ}}\right)$$

$$R(453)\ln(0.73) + 5520(0.27)^2 - R(453)\ln X_{Sn}^{s} - 0 = -6990\left(1 - \frac{453}{505}\right)$$

$$X_{Sn}^{s} = 0.983$$

XIII-12

$$RT\ln X_{LiF} = -\Delta h^{\circ}_{fus(LiF)}\left(1-\frac{T}{848+273}\right)$$

$$RT\ln X_{NaF} = -\Delta h^{\circ}_{fus(NaF)}\left(1-\frac{T}{992+273}\right)$$

$$RT\ln X_{KF} = -\Delta h^{\circ}_{fus(KF)}\left(1-\frac{T}{857+273}\right)$$

$$X_{LiF} + X_{NaF} + X_{KF} = 1$$

Solution:
$$\begin{cases} X_{LiF} = 0.40 \\ X_{NaF} = 0.22 \\ X_{KF} = 0.37 \end{cases}$$

$$T = 852\,K$$

XIII-15 $RT\ln X_{Nb} = -\Delta h^\circ_f\left(1 - \frac{T}{T^\circ_f}\right)$

$$X_{Nb} = \frac{(99/92.91)}{\frac{99}{92.91} + \frac{1}{195.1}} = 0.99521$$

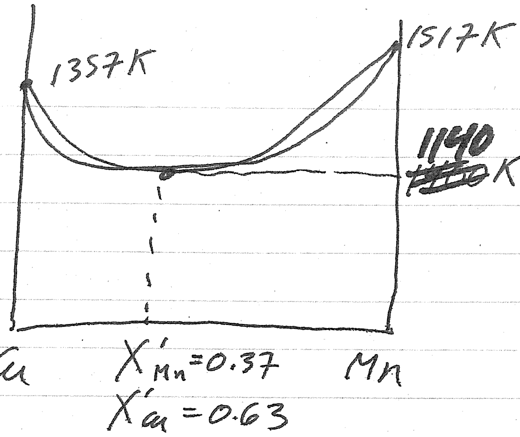
$T = 2729\,K$

$T^\circ_f = 2740\,K$

$$R(2729)\ln(0.99521) = -\Delta h^\circ_f\left(1 - \frac{2729}{2740}\right)$$

$$\Delta h^\circ_f = 27135 \text{ J/mol.}$$

XIII-16



$$RT\ln\frac{a_{Cu}^{l}}{a_{Cu}^{s}} = -\Delta h^{\circ}_{fus(Cu)}\left(1-\frac{T}{1357}\right)$$

$$RT\ln\frac{a_{Mn}^{l}}{a_{Mn}^{s}} = -\Delta h^{\circ}_{fus(Mn)}\left(1-\frac{T}{1517}\right)$$

Liquid Ideal: $\Rightarrow a_{Cu}^{l} = X_{Cu}^{l} = 0.63 \qquad a_{Mn}^{l} = X_{Mn}^{l} = 0.37$

Solid: $\Delta h^{s} = X_{Cu}X_{Mn}(a+bX_{Mn}) \Rightarrow \begin{cases} \Delta h^{s}_{Mn} = (2b+a)X_{Cu}^{2} - 2bX_{Cu}^{3} \\ \Delta h^{s}_{Cu} = (a-b)X_{Mn}^{2} + 2bX_{Mn}^{3} \end{cases}$

Suppose: $s^{E(sol)} = 0$

$$\begin{cases} RT\cancel{\ln X_{Cu}} - RT\cancel{\ln X_{Cu}} \overbrace{-(a-b)X_{Mn}^{2} - 2bX_{Mn}^{3}}^{=-g^{E}_{Cu}=-\Delta h_{Cu}} = -\Delta h^{\circ}_{fus(Cu)}\left(1-\frac{T}{1357}\right) \\ RT\cancel{\ln X_{Mn}} - RT\cancel{\ln X_{Mn}} - \underbrace{(2b+a)X_{Cu}^{2} + 2bX_{Cu}^{3}}_{=-g^{E}_{Mn}=-\Delta h_{Mn}} = -\Delta h^{\circ}_{fus(Mn)}\left(1-\frac{T}{1517}\right) \end{cases}$$

$X_{Cu} = 0.63$
$X_{Mn} = 0.37$

Solution: $a = 13640$ J
$b = -5980$ J.

XIII-18 $\quad g^E = (a + bX_1)X_1X_2$ $\quad \begin{pmatrix} X_1 = X_{Pb} \\ X_2 = X_{Zn} \end{pmatrix}$

$$\Delta g = RT(X_1 \ln X_1 + X_2 \ln X_2) + (a + bX_1)X_1X_2$$

$$(X_2 = 1 - X_1)$$

$$\begin{cases} \dfrac{d\Delta g}{dX_1} = RT\left(\ln X_1 + 1 - \dfrac{1}{1-X_1} - \ln(1-X_1) + \dfrac{X_1}{1-X_1}\right) + a + 2(b-a)X_1 - 3bX_1^2 \\ \dfrac{d^2\Delta g}{dX_1^2} = RT\left(\dfrac{1}{X_1} + \dfrac{1}{1-X_1}\right) + 2(b-a) - 6bX_1 \\ \dfrac{d^3\Delta g}{dX_1^3} = RT\left(-\dfrac{1}{X_1^2} + \dfrac{1}{(1-X_1)^2}\right) - 6b \end{cases}$$

$$\frac{d^2\Delta g}{dX_1^2} = 0 \Rightarrow \frac{RT}{X_1X_2} + 2(b-a) - 6bX = 0$$

$$\frac{d^3\Delta g}{dX_1^3} = 0 \Rightarrow \frac{RT(X_1^2 - X_2^2)}{X_1^2X_2^2} - 6b = 0$$

where: $T = T_c = 1065K$

$X_1 = X_{1(c)} = 0.29$

$X_2 = X_{2(c)} = 0.71$

Solution: $a = 19874\ J$

$b = -14644\ J$

XIII-23

$CO_2 + C = 2CO$

$$\Delta G^\circ = 2(-26700 - 20.95T) - (-94200 - 0.2T)$$
$$= 40800 - 41.70T$$

$$\Delta G^\circ_{1373} = -16454 = -RT\ln K$$

$$K = 416 = \frac{P_{CO}^2}{P_{CO_2} \cdot (\gamma_c X_c)}$$

$X_c = 0.082$ (saturé en Fe_3C à 1100°C)

(a) $$416 = \frac{(1.0)^2}{(3.45\times10^{-3})\,\gamma_c\,(0.082)}$$

$$\gamma_c = 8.5$$

(b) $3Fe + C = Fe_3C$

$$K = \frac{a_{Fe_3C}}{a_{Fe}^3 \cdot a_c}$$

La solution est Henrienne

$a_{Fe} = X_{Fe}$

$a_c = \gamma_c X_c$

à la limite de solubilité:

$$K_{1373} = \frac{1.0}{(0.918)^3 (8.5)(0.082)}$$

$$\Delta G^\circ = -RT\ln K$$

$$\Delta G^\circ_{1373} = \underline{-1686\ cal}$$

XIII - 25

T > T_{Tr}

$$RT \ln a_B = -\Delta g^o_{B(fus)}$$

$$\ln X_B + \ln \gamma_B = -\Delta g^o_{B(fus)}/RT$$

$$d(\ln X_B)/d(\tfrac{1}{T}) = \frac{d}{d(\frac{1}{T})}\left[-\Delta g^o_{B(fus)}/RT - \ln \gamma_B\right]$$

T < T_{Tr}

$$RT \ln a_B = -\Delta g^o_{B(fus)} - \Delta g^o_{B(\alpha\to\beta)}$$

$$d(\ln X_B)/d(\tfrac{1}{T}) = \frac{d}{d(\frac{1}{T})}\left[-\Delta g^o_{B(fus)}/RT - \ln \gamma_B\right] - \frac{d}{d(\frac{1}{T})}\left(\Delta g^o_{B(\alpha\to\beta)}/RT\right)$$

T = T_{Tr}

$$\left(\frac{d\ln X_B}{d(\frac{1}{T})}\right)_{T>T_{Tr}} - \left(\frac{d\ln X_B}{d(\frac{1}{T})}\right)_{T<T_{Tr}} = \frac{d(\Delta g^o_{B(\alpha\to\beta)}/RT)}{d(\frac{1}{T})} = \frac{\Delta h^o_{B(\alpha\to\beta)}}{R}$$

$$\left(\frac{dX_B}{dT}\right)_{T>T_{Tr}} - \left(\frac{dX_B}{dT}\right)_{T<T_{Tr}} = -\frac{X_B\,\Delta h^o_{B(\alpha\to\beta)}}{RT_{Tr}^2}$$

where: X_B = value of X_B at point P

$\Delta h^o_B = \Delta h^o_{B(\alpha\to\beta)}$ at T_{Tr}

XIII - 27

$$RT\ln a_A = -\Delta g^\circ_{fus(A)} = -(\Delta h^\circ_{fus} - T\Delta s^\circ_{fus})$$

$$RT\ln X_A + (\Delta h_A - Ts^E_A) = -(\Delta h^\circ_{fus(A)} - T\Delta s^\circ_{fus(A)})$$

$$\ln X_A = -(\Delta h^\circ_{fus(A)} + \Delta h_A)/RT + (\Delta s^\circ_{fus(A)} + s^E_A)R$$

Quand $X_A \to 0$ (Henry's Law)

$\Delta h_A \approx cst$ Also: $\Delta h^\circ_{fus(A)} \approx cst$

$s^E_A \approx cst$ $\Delta s^\circ_{fus(A)} \approx cst)$

$$\frac{d(\ln X_A)}{d(\frac{1}{T})} \approx -(\Delta h^\circ_{fus(A)} + \Delta h_A)/R \approx \underline{cst}.$$

XIII - 28

$$g_A^E = -8000 X_B^2$$
$$g_B^E = -8000 X_A^2$$

$$g_{A_2B} - g^\circ_{A_2B} = RT\ln a_{A_2B} = -\Delta g^\circ_{f(A_2B)} = -\Delta h^\circ_{f(A_2B)} \left(1 - \frac{T}{1400}\right)$$

$$\begin{cases} g_{A_2B} = 2g_A + g_B \\ g^\circ_{A_2B} = \text{value of } g_{A_2B} \text{ at } X_B = 1/3 \end{cases}$$

$$\left(2RT\ln X_A + RT\ln X_B + 2g_A^E + g_B^E\right) - \left(2RT\ln(2/3) + RT\ln\left(\tfrac{1}{3}\right)\right.$$
$$\left. + 2g_A^E(X_B = 1/3) + g_B^E(X_B = 1/3)\right) = -\Delta h^\circ_f\left(1 - T/1400\right)$$

Eutectic at 940 K at $X_B = 0.06$

Substitute + solve $\Rightarrow \Delta h^\circ_{fus} = 29900\ J$

Eutectic at 930 K at $X_B = 0.72$

Substitute + solve $\Rightarrow \Delta h^\circ_{fus} = 32910\ J$.

(Average = 31.5 kJ/mol A_2B)

XIII - 32

At eutectic composition:

$$RT\ln a_{NaCl} = -27990\left(1 - \frac{548+273}{801+273}\right)$$

$$T = (548+273)$$

$$a_{NaCl} = 0.381$$

$$R(548+273)\ln a_{Na_2ZrCl_6} = -16740\left(1 - \frac{548+273}{646+273}\right)$$

$$a_{Na_2ZrCl_6} = 0.770$$

$$Na_2ZrCl_6 = 2\,NaCl + ZrCl_4$$

$$K = \frac{a_{NaCl}^2 \cdot P_{ZrCl_4}}{a_{Na_2ZrCl_6}}$$

$$K = \frac{(0.381)^2(0.06859)}{(0.770)} = 0.01293$$

$$\Delta G^\circ = -RT\ln K = -R(548+273)\ln(0.01293)$$

$$\Delta G^\circ = +29678 \quad J$$

$X^l = X^s$ Liq. idéale

$\underline{XIII}$ - 33

$$\begin{cases} \cancel{RT\ln X_B^l} - \cancel{RT\ln X_B^s} - RT\ln \gamma_B^s = -28660\left(1-\frac{T}{1073}\right) \\ \cancel{RT\ln X_A^l} - \cancel{RT\ln X_A^s} - RT\ln \gamma_A^s = -13350\left(1-\frac{T}{887}\right) \end{cases}$$

$$\begin{cases} 13390\, X_A^2 = 28660\left(1-\frac{T}{1073}\right) \\ 13390\, X_B^2 = 13350\left(1-\frac{T}{887}\right) \end{cases}$$

$$\begin{cases} X_B = 0.28 \\ T = 815K \end{cases}$$

✓

XVI-1

$$\Delta T = \nu X \left(\frac{R T_f^{\circ 2}}{\Delta H_f^\circ} \right)$$

$\Delta T = -5$
$\nu = 3 \quad (Ca^{2+}, Cl^-, Cl^-)$
$T_f^\circ = 273.15 \text{ K}$
$\Delta h_f^\circ = 6.025 \text{ kJ/mol}$

$$X = X_{CaCl_2} = 0.0161 \text{ (mol } CaCl_2 \text{/mol solution)}$$

$$\text{masse } CaCl_2 = \underbrace{\left(\frac{0.0161}{1-0.0161}\right)}_{\frac{\text{mol } CaCl_2}{\text{mol } H_2O}} \times \underbrace{\left(\frac{10^4}{18.00}\right)}_{\text{mol } H_2O \text{ dans } 10^4 g \ (1 l = 10^3 g)} \times \underbrace{110}_{\text{masse moleculaire du } CaCl_2} = \underline{990 \text{ g}}$$

XVI-2 $\quad K = \dfrac{(m_{Ag} m_{Br}) \gamma_{Ag} \gamma_{Br}}{1.0} = 7.7 \times 10^{-13}$

$$m_{Ag} = m_{Br} = \text{"} m_{AgBr} \text{"} = \left(\frac{7.7 \times 10^{-13}}{\gamma_{Ag}\gamma_{Br}}\right)^{1/2} = \frac{8.78 \times 10^{-7}}{(\gamma_{Ag}\gamma_{Br})^{1/2}}$$
$$= \text{"}m\text{"}$$

(i) $I = \frac{1}{2}\left(m_{Ag}(1)^2 + m_{Br}(1)^2\right) = \frac{1}{2}(m + m) = m$

$$\log \gamma_{Ag} = -0.509(1)\sqrt{I} = -0.509\, m^{1/2}$$
$$\log \gamma_{Br} = -0.509(1)\sqrt{I} = -0.509\, m^{1/2}$$
$$\log(\gamma_{Ag}\gamma_{Br})^{1/2} = -0.509\, m^{1/2}$$

Donc: $\log m = \log(8.78 \times 10^{-7}) + 0.509\, m^{1/2}$

$$m \doteq \underline{8.78 \times 10^{-7}}$$

(ii) $I = \frac{1}{2}\left(m_{Ag}(1)^2 + m_{Br}(1)^2 + m_{Na}(1)^2 + m_{Cl}(1)^2\right)$

Mais m_{Ag} et $m_{Br} \ll m_{Na}$ et m_{Cl}

$$I \approx \tfrac{1}{2}\left((0.01)(1)^2 + (0.01)(1)^2\right) = 0.01$$

$$\log(\gamma_{Ag}\gamma_{Br})^{1/2} = -0.509(1)\sqrt{I} = -0.0509$$

$$(\gamma_{Ag}\gamma_{Br})^{1/2} = 0.89$$

$$m = 8.78 \times 10^{-7}/0.89 = \underline{9.88 \times 10^{-7}}$$

(Solubilité augmentée parce que NaCl et AgBr n'ont pas d'ion encommun)

$\underline{XVII-2}$ $\left\{ \begin{array}{l} N^0 = \text{Nombre d'atomes} = 6.023 \times 10^{23} \\ N_v = \text{Nombre de lacune} = 10^{17} \end{array} \right.$

(i) $$\Omega^{config} = \frac{(N^0+N_v)!}{N^0!\,N_v!} \approx 10^{6.77\times10^{17}}$$

$$\Delta S^{config} \approx -R\left(X_v \ln X_v + (1-X_v)\ln(1-X_v)\right) \approx -R\left(X_v \ln X_v\right)$$

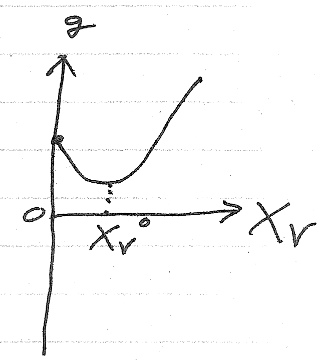
$$= -R\left(\frac{10^{17}}{6.023\times10^{23}}\right)\ln\left(\frac{10^{17}}{6.023\times10^{23}}\right) = 2.16\times10^{-5}\ \text{J/mol-K}$$

(ii) $$\left[\begin{array}{l} h = h^0 + h_v X_v \\ s^{nc} = s^0 + s_v X_v \\ s^{conf.} = -R(X_v \ln X_v) \end{array}\right.$$

$$g = (h^0 + h_v X_v) - T(s^0 + s_v X_v) + RT\left[(X_v \ln X_v) + (1-X_v)\ln(1-X_v)\right]$$

$$\frac{dg}{dX_v} = (h_v - Ts_v) + RT\ln X_v = 0$$

$$X_v^0 = e^{-(h_v - Ts_v)/RT}$$



(iii) $$X_v^0 = e^{-(422500 - T(8.4))/RT}$$

à T=800K: $\underline{X_v^0 = 5.0\times10^{-5}}$

XVII (3) $a_{KCl} = X_{K^+} X_{Cl^-} = (1) \dfrac{n_{Cl^-}}{n_{Cl^-} + n_{MgCl_4^{2-}}}$

$$= \frac{(n_{KCl} - 2n_{MgCl_2})}{(n_{KCl} - 2n_{MgCl_2}) + n_{MgCl_2}} = \frac{X_{KCl} - 2X_{MgCl_2}}{X_{KCl} - X_{MgCl_2}}$$

$$= (1 - 3X_{MgCl_2}) / (1 - 2X_{MgCl_2})$$

XVII (4) (a) $RT \ln a_{NaCl} = -\Delta h^\circ_{fusion} \left(1 - T/T^\circ_{fusion}\right)$

(no solid solubility)

X_{ZrCl_4}	$T(K)$	$a_{NaCl}^{(liq)}$
0	1074	1.00
0.112	1023	0.86
0.202	948	0.66
0.274	821	0.38

(b) $ZrCl_6^{2-}$ anions

$$a_{NaCl} = X_{Na^+} X_{Cl^-} = (1) \frac{(n_{NaCl} - 2n_{ZrCl_4})}{(n_{NaCl} - 2n_{ZrCl_4}) + n_{ZrCl_4}} = \frac{1 - 3X_{ZrCl_4}}{1 - 2X_{ZrCl_4}}$$

XVII (5) (a) $a_{Fe_3O_4} = X_{Fe^{2+}} \cdot X_{Fe^{3+}}^2 \cdot X_{O^=}^4 = (1) X_{Fe^{3+}}^2 (1)^4$

$Fe_1^{2+} (Fe_{2-3\xi}^{3+} Cr_{3\xi}^{3+}) O_4$

$$X_{Fe^{3+}} = \frac{(2 - 3\xi)}{(2 - 3\xi) + 3\xi} = 1 - 3\xi/2$$

$$a_{Fe_3O_4} = (1 - 3\xi/2)^2$$

(b) At this boundary, FeO, spinel and $O_2(g)$ are in equilibrium

$$K = \frac{a_{Fe_3O_4}}{a_{FeO}^3 \, p_{O_2}^{1/2}} = (2 \times 10^{-8})^{-1/2} = \frac{(1 - 3\xi/2)^2}{(1)^3 \, p_{O_2}^{1/2}} \Rightarrow$$

ξ	p_{O_2}
0.5	7.8×10^{-11}
0.3	1.8×10^{-9}
0.1	1.05×10^{-8}
0	2×10^{-8}

XVII -(6) $a_{Na_2CO_3} = X_{Na}^2 = X_{Na_2CO_3}^2$ $\quad a_{Li_2CO_3} = (1 - X_{Na_2CO_3})^2$

$$\begin{cases} \underline{\underline{2}} RT \ln X_{Na_2CO_3} = -7090\left(1 - \frac{T}{1123}\right) \\ \underline{\underline{2}} RT \ln (1 - X_{Na_2CO_3}) = -10700\left(1 - \frac{T}{973}\right) \end{cases}$$

Solve iteratively: $\underline{X = 0.496 \quad T = 780K}$

XVII -(7) $n_{Ca^{2+}} = 0.75$ $\quad n_{Na^+} = 2(0.05) = 0.10$

$n_{Fe^{2+}} = 0.05$ $\quad n_{SiO_4^{4-}} = 0.15$

$n_{O^{2-}} = (0.75 + 0.05 + 0.05) - 2(0.15) = 0.55$

$X_{Ca^{2+}} = (0.75/(0.75 + 0.10 + 0.05)) = 0.8333$

$X_{O^{2-}} = 0.55/(0.15 + 0.55) = 0.7857$

$a_{CaO} = X_{Ca^{2+}} \cdot X_{O^{2-}} = \underline{0.6548}$

$RT \ln a_{CaO} = -\Delta h^\circ_{fus}(1 - T/T^\circ_f)$

$\underline{T = 2561K = 2288^\circ C}$

XVII – 8

$$G = +2RT\left(X_i \ln X_i + (1-X_i)\ln(1-X_i)\right) + (\Delta h^\circ - T\Delta s^\circ)X_i$$

$$\frac{dG}{dX_i} = +2RT\left(\ln X_i + \cancel{1} - \ln(1-X_i) \cancel{-1}\right) + (\Delta h^\circ - T\Delta s^\circ) = 0$$

$$\ln X_i = -\frac{(\Delta h^\circ - T\Delta s^\circ)}{2RT}$$

$$X_i = e^{-\frac{(\Delta h^\circ - T\Delta s^\circ)}{2RT}}$$

$$\sigma = n q \mu$$

$$\ln\sigma = \underbrace{\ln(q\mu) + C}_{\sim const} + \ln X_i = A - \frac{(\Delta h^\circ - T\Delta s^\circ)}{2R}\left(\frac{1}{T}\right)$$

$$\boxed{B = -\frac{\Delta g^\circ}{2R}}$$

(b) Increase $Ag_i^{\bullet}$ Hence $\sigma \uparrow$

(c) $[Ag_i^{\bullet}][V_{Ag}'] = K$

Add $CdBr_2 \Rightarrow [V_{Ag}']\uparrow \Rightarrow [Ag_i^{\bullet}]\downarrow \Rightarrow \sigma\downarrow$

If add a lot, then V_{Ag}' start to conduct and $\sigma \uparrow$ again

~~(d) James Sangster got~~ $\cancel{s^E = X_A X_B(-0.162 - 1.252 X_{RbCl})}$ ~~cal/mol °K~~

XVII -(10)

$$a_{BaCl_2} = X_{Ba} X_{Cl}^2 = (1)\left(\frac{n_{Cl}}{n_{Cl}+n_{ZrCl_6}}\right)^2$$

$$= \left(\frac{2\cancel{X}_{BaCl_2} - 2X_{ZrCl_4}}{2\cancel{X}_{BaCl_2} - 2X_{ZrCl_4} + X_{ZrCl_4}}\right)$$

$$= \left(\frac{2-4X_{ZrCl_4}}{2-3X_{ZrCl_4}}\right)^2$$

$$RT\ln a_{BaCl_2} = -\Delta h^o_{fus}\left(1 - T/T^o_{fus}\right)$$

$$\ln\left(\frac{2-0.4}{2-0.3}\right)^2 = -\frac{4000}{R}\left(\frac{1}{T} - \frac{1}{1235}\right)$$

$$\underline{T = 1149\text{ K}}$$

XVII -(14)

SiO_2	60 kg	=	998.6 moles
CaO	84.1 kg	=	1499.6 moles
FeO	107.8 kg	=	1500.3 moles

$n_{Ca^{2+}} = 1499.6$

$n_{Fe^{2+}} = 1500.3$

$\Sigma_+ = 2999.3$

$n_{SiO_4^{4-}} = 998.6$

$n_{O^{2-}} = 1500.3 + 1499.6 - 2(998.6) = 1002.8$

$\Sigma_- = 2001.4$

$$a_{FeO} = X_{Fe^{2+}} \cdot X_{O^{2-}} = \left(\frac{1500.3}{2999.3}\right)\left(\frac{1002.8}{2001.4}\right) = 0.25$$

$2Fe + O_2 = 2FeO \qquad \Delta G^o = -RT\ln K \qquad K_{1800K} = 239086$

$$= \frac{a_{FeO}^2}{a_{Fe}^2 \cdot p_{O_2}} = \frac{(0.25)^2}{(1)^2 p_{O_2}} \Rightarrow p_{O_2} = \underline{2.61\times10^{-10}}$$

$O_2 = 2O$ $\qquad K_{1800} = X_O^2/p_{O_2} = 1.515\times10^4 = X_O^2/(2.61\times10^{-10})$

$$X_O = \underline{1.99\times10^{-3}}$$

XVII – 12

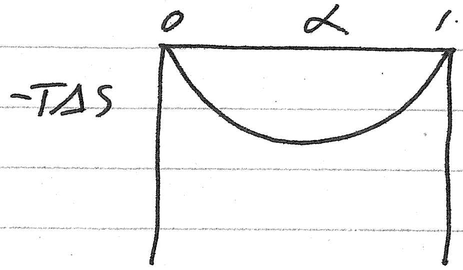
$S = -2\left(\frac{1}{2}\right)R\left(\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha)\right)$

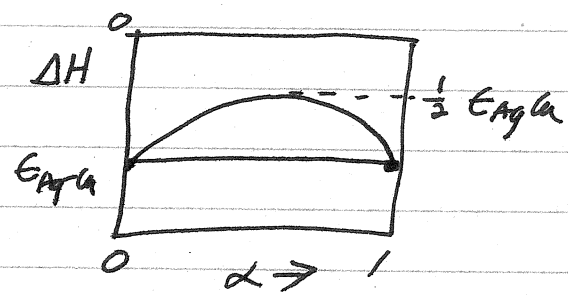
$H = \left(\alpha^2 + (1-\alpha)^2\right)\epsilon_{Ag-Cu}$ (Let $\epsilon_{Ag-Ag} = \epsilon_{CuCu} = 0$)

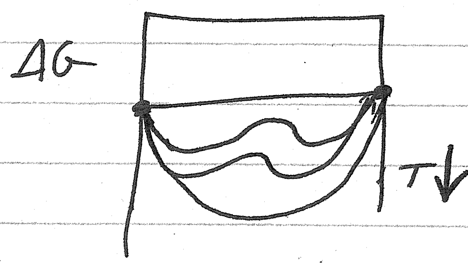
$= (2\alpha^2 - 2\alpha + 1)\epsilon_{Ag-Cu}$

$\frac{dG}{d\alpha} = RT\left(\ln\alpha - \ln(1-\alpha)\right) + (4\alpha - 2)\epsilon_{Ag-Cu} = 0$ where: $\epsilon_{Ag-Cu} < 0$

où ϵ = énergie (d'un mole de liaisons)



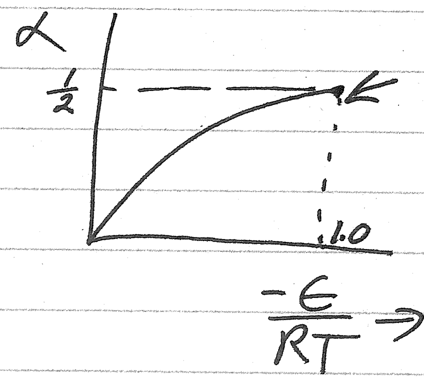




Always a solⁿ at $\alpha = \frac{1}{2}$

Below T_c, also a solⁿ at

$\ln\left(\frac{\alpha}{1-\alpha}\right) = \frac{(2-4\alpha)[\epsilon_{Ag-Cu}]}{RT}$



$\frac{d^2\Delta G}{d\alpha^2} = RT\left(\frac{1}{\alpha} + \frac{1}{1-\alpha}\right) + 4\epsilon = 0$

$\frac{RT}{\alpha(1-\alpha)} = -4\epsilon$

$\frac{-\epsilon}{RT} = 1$

Take 1 mole of components as basis

XVII-16 $\qquad X_{Sb} + X_{In} = 1$ (component fractions)

$$\Delta H^{mix} = n_{InSb} \cdot \Delta h_{ASS}$$

$$\Delta S^{mix} = -R\left(\frac{n_{InSb}}{\cancel{n_{TOT}}}\ln\frac{n_{InSb}}{n_{TOT}} + \frac{n_{In}}{\cancel{n_{TOT}}}\ln\frac{n_{In}}{n_{TOT}} + \frac{n_{Sb}}{\cancel{n_{TOT}}}\ln\frac{n_{Sb}}{n_{TOT}}\right)\cancel{n_{TOT}}$$

where: $n_{TOT} = n_{InSb} + n_{In} + n_{Sb}$

where: $n_{In} = X_{In} - n_{InSb}$ and $n_{Sb} = X_{Sb} - n_{InSb}$

$n_{TOT} = 1 - n_{InSb}$

$$\frac{d\Delta G^{mix}}{dn_{InSb}} = \Delta h_{ASS} + RT\left(\ln\frac{n_{InSb}}{n_{TOT}} - \ln\frac{n_{In}}{n_{TOT}} - \ln\frac{n_{Sb}}{n_{TOT}}\right.$$

$$+ \cancel{n_{InSb}}\left(\frac{\cancel{n_{TOT}}}{\cancel{n_{InSb}}}\right)\left(\cancel{\frac{1}{n_{TOT}}} + \frac{n_{InSb}}{n_{TOT}^2}\right)$$

$$+ \cancel{n_{In}}\left(\frac{\cancel{n_{TOT}}}{\cancel{n_{In}}}\right)\left(\cancel{\frac{-1}{n_{TOT}}} + \frac{n_{In}}{n_{TOT}^2}\right)$$

$$\left. + \cancel{n_{Sb}}\left(\frac{\cancel{n_{TOT}}}{\cancel{n_{Sb}}}\right)\left(\cancel{\frac{-1}{n_{TOT}}} + \frac{n_{Sb}}{n_{TOT}^2}\right)\right)$$

$$= \Delta h_{ASS} + RT\left(\ln\frac{n_{InSb} \cdot n_{TOT}}{n_{In} \cdot n_{Sb}} + \frac{\cancel{n_{TOT} + n_{InSb} - n_{TOT} + n_{In} - n_{TOT} + n_{Sb}}}{n_{TOT}}\right)$$

$$= \Delta h_{ASS} + RT\ln\frac{n_{InSb}(1-n_{InSb})}{(X_{In}-n_{InSb})(X_{Sb}-n_{InSb})} = 0$$

$$\frac{n_{InSb}(1-n_{InSb})}{(X_{In}-n_{InSb})(X_{Sb}-n_{InSb})} = \frac{X_{InSb}}{X'_{\text{"In"}}X'_{\text{"Sb"}}} = K = e^{-\Delta h_{ASS}/RT}$$

(like a gas)

↓

Solve for n_{InSb} at any composition (X_{Sb}, X_{In})

XVII - (17) (a) $n_{Fe^{2+}} = 70$ $n_{SiO_4^{4-}} = 10$

$n_{Ca^{2+}} = 15$ $n_{O^{2-}} = 70 + 15 + 5 - 2(10) = 70$

$n_{Cu^+} = 10$

$\Sigma + = 95$ $\Sigma - = 80$

$$a_{FeO} = X_{Fe^{2+}} X_{O^{2-}} = \left(\frac{70}{95}\right)\left(\frac{70}{80}\right) = \underline{0.64}$$

$$a_{Cu_2O} = X_{Cu^+}^2 \cdot X_{O^{2-}} = \left(\frac{10}{95}\right)^2\left(\frac{70}{80}\right) = \underline{0.0097}$$

(b) $4Cu + O_2 = 2Cu_2O$ $p^{\circ}_{O_2} = 2 \times 10^{-3}$ (Ellingham)

$$\frac{p_{O_2}}{a^2_{Cu_2O}} = p^{\circ}_{O_2}$$

$$p_{O_2} = (2.0 \times 10^{-3})(0.0097)^2 = 1.88 \times 10^{-7}$$

$2Fe + O_2 = 2FeO$ $p^{\circ}_{O_2}(1600°C) = 7.1 \times 10^{-9}$ (Ellingham)

$$p_{O_2} \cdot a^2_{Fe} / a^2_{FeO} = p^{\circ}_{O_2}$$

$$a_{Fe} = \left(\frac{(7.1 \times 10^{-9})(0.64)^2}{(1.88 \times 10^{-7})}\right)^{1/2} = 0.124 = \gamma \cdot X_{Fe} = 10.5\, X_{Fe}$$

$$X_{Fe} = \underline{\underline{0.012}}$$

XVII - 18

$$K = \frac{[Ag_i][V_{Ag}]}{a_{AgBr}} = [Ag_i][V_{Ag}]$$

$$[V_{Ag}] \approx X_{CdBr_2} \quad \therefore \quad [Ag_i] \approx K/X_{CdBr_2}$$

$$\frac{\sigma}{e} = [Ag_i]\mu_{Ag_i} + [V_{Ag}]\mu_{V_{Ag}}$$

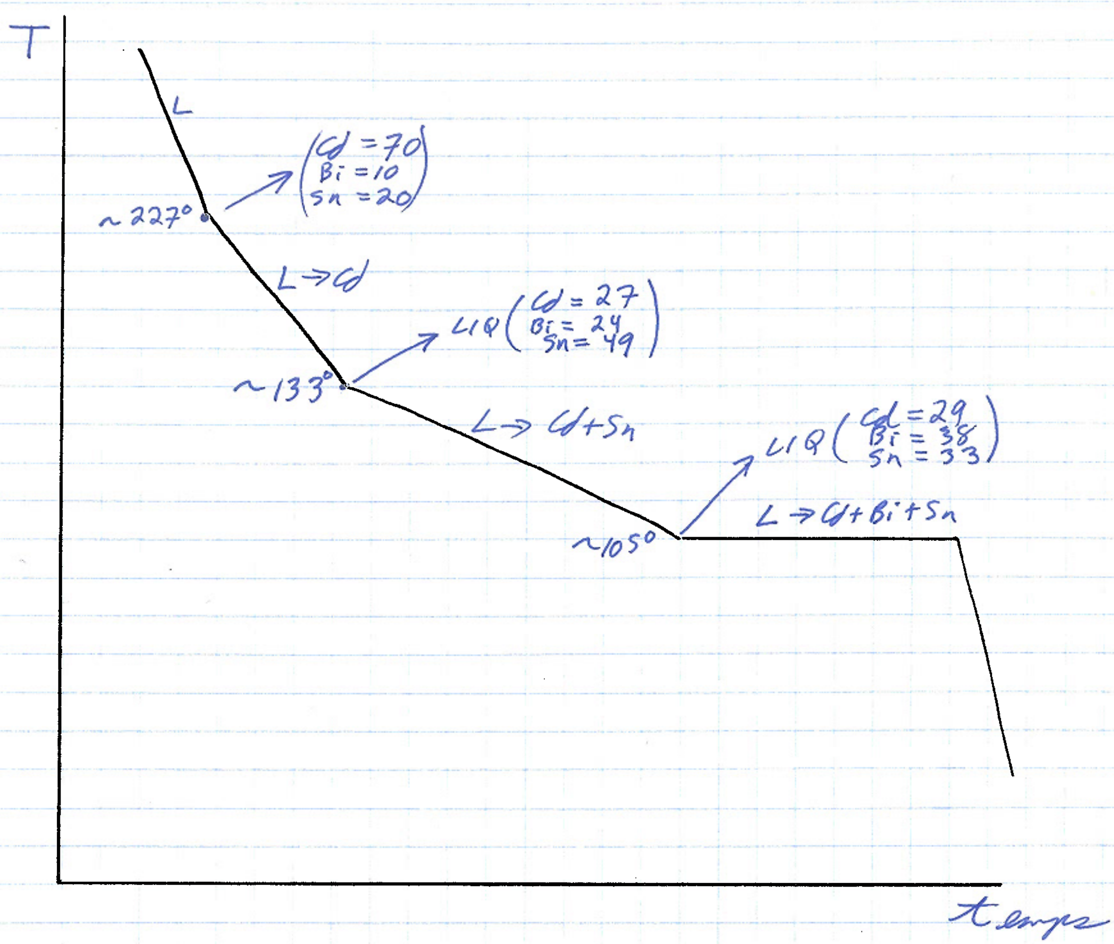
$$\sigma = \frac{eK\mu_i}{X} + e\mu_v X$$

$$\frac{d\sigma}{dX} = \frac{-eK\mu_i}{X^2} + e\mu_v = 0$$

$$X^2_{min} = \frac{K\mu_i}{\mu_v}$$

$$X_{CdBr_2 (min)} = \left(\frac{K\mu_{Ag_i}}{\mu_{V_{Ag}}}\right)^{1/2}$$

XVIII - 1



250°C — 100% LIQ (Cd = 70%, Bi = 10%, Sn = 20%)

200°C — LIQUID au pt. Y (Cd = 58%, Bi = 14%, Sn = 28%)

$$\frac{n^{Cd}}{n^{TOT}} = \frac{GY}{CY} = 0.28 \qquad \frac{n^{L}}{n^{TOT}} = 0.72$$

125°C — LIQUID au pt. W (Cd = 28%, Bi = 27%, Sn = 45%)
Cd pro-eutectique (100% Cd)
Cd-Sn eutectique binaire (Composition = ?)

Calculer d'abord au point B: $\frac{n^{Cd\,pro\text{-}eut}}{n^{TOT}} = \frac{BG}{BC} = 0.58$ (ça ne change plus)

Au point W: $\frac{n^{L}}{n^{TOT}} = \frac{VG}{VW} = 0.35 \qquad \frac{n^{eut.\,binaire}}{n^{TOT}} = (1 - 0.58 - 0.35) = 0.07$

Composition de l'eutectique binaire (X_{Cd} X_{Sn})
Faire des bilans de masse pour Cd, (Bi) Sn:

$$0.28(0.35) + 1.00(0.58) + 0.07X_{Cd} = 0.70 \qquad X_{Cd} = 0.31$$
$$0.45(0.35) + 0.07X_{Sn} = 0.20 \qquad X_{Sn} = 0.61$$
$$0.27(0.35) = 0.10 \text{ (Vérification)}$$

$\Sigma \neq 1.00$ imprécision de calcul

(XVIII - 1 suite)

25°C $\frac{n^{cd\ pro\text{-}eut}}{n^{TOT}} = 0.58$ (pas changé)

LIQUID → EUT. TERNAIRE au point E
(Cd = 29%, Bi = 38%, Sn = 33%)

$$\frac{n^{L}}{n^{TOT}} = \frac{n^{Eut.tern}}{n^{TOT}} = \frac{GZ}{EZ} = 0.26$$

$$\frac{n^{eut.bin}}{n^{TOT}} = (1 - 0.58 - 0.26) = 0.16$$

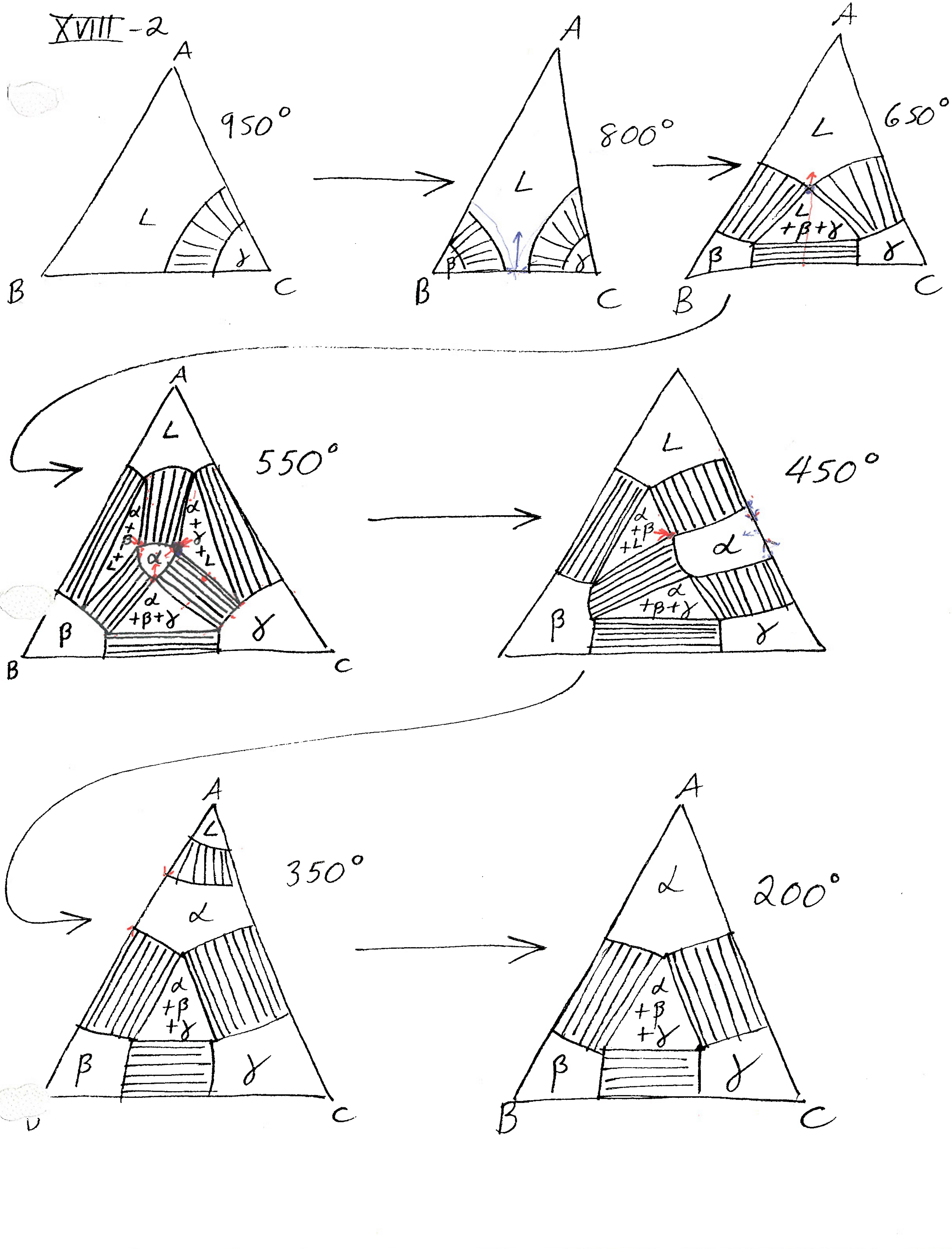
Bilans de masse pour trouver la composition de l'eutectique binaire

$(0.29)(0.26) + 0.58 + 0.16\,X_{cd} = 0.70$ $\quad X_{cd} = 0.28$

$(0.33)(0.26) + 0.16\,X_{Sn} = 0.20$ $\quad X_{Sn} = 0.72$ $\quad (\Sigma = 1.00)$

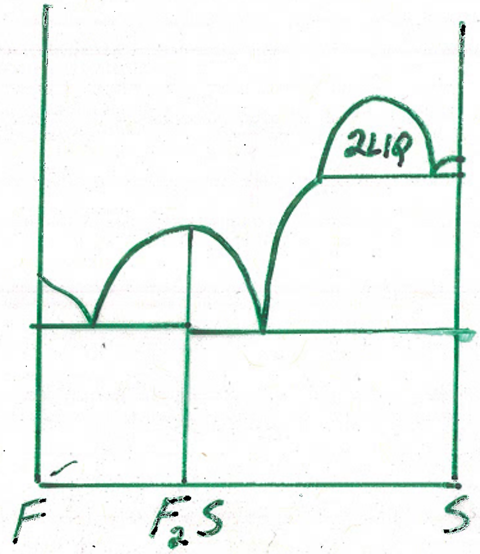
$(0.38)(0.26) = 0.10$ (Vérification)

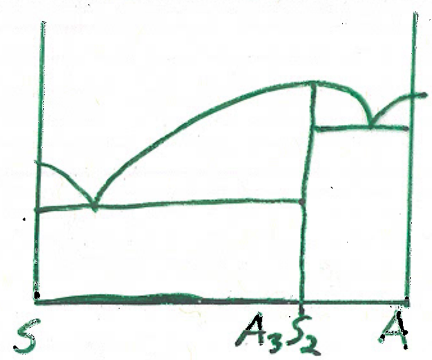
XVIII-2

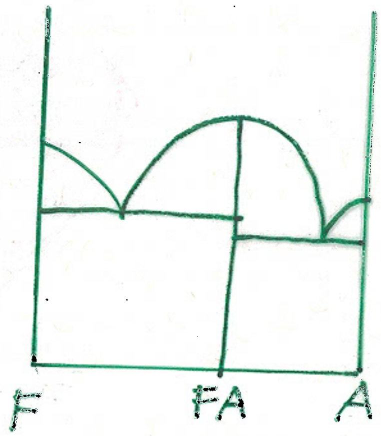


A
B
C
950°
L
γ
800°
L
β
γ
650°
L
L+β+γ
β
γ
550°
L
α+β+L
α+γ+L
α
α+β+γ
β
γ
450°
L
α+β+L
α
α+β+γ
β
γ
350°
L
α
α+β+γ
β
γ
200°
α
α+β+γ
β
γ

XVIII-3





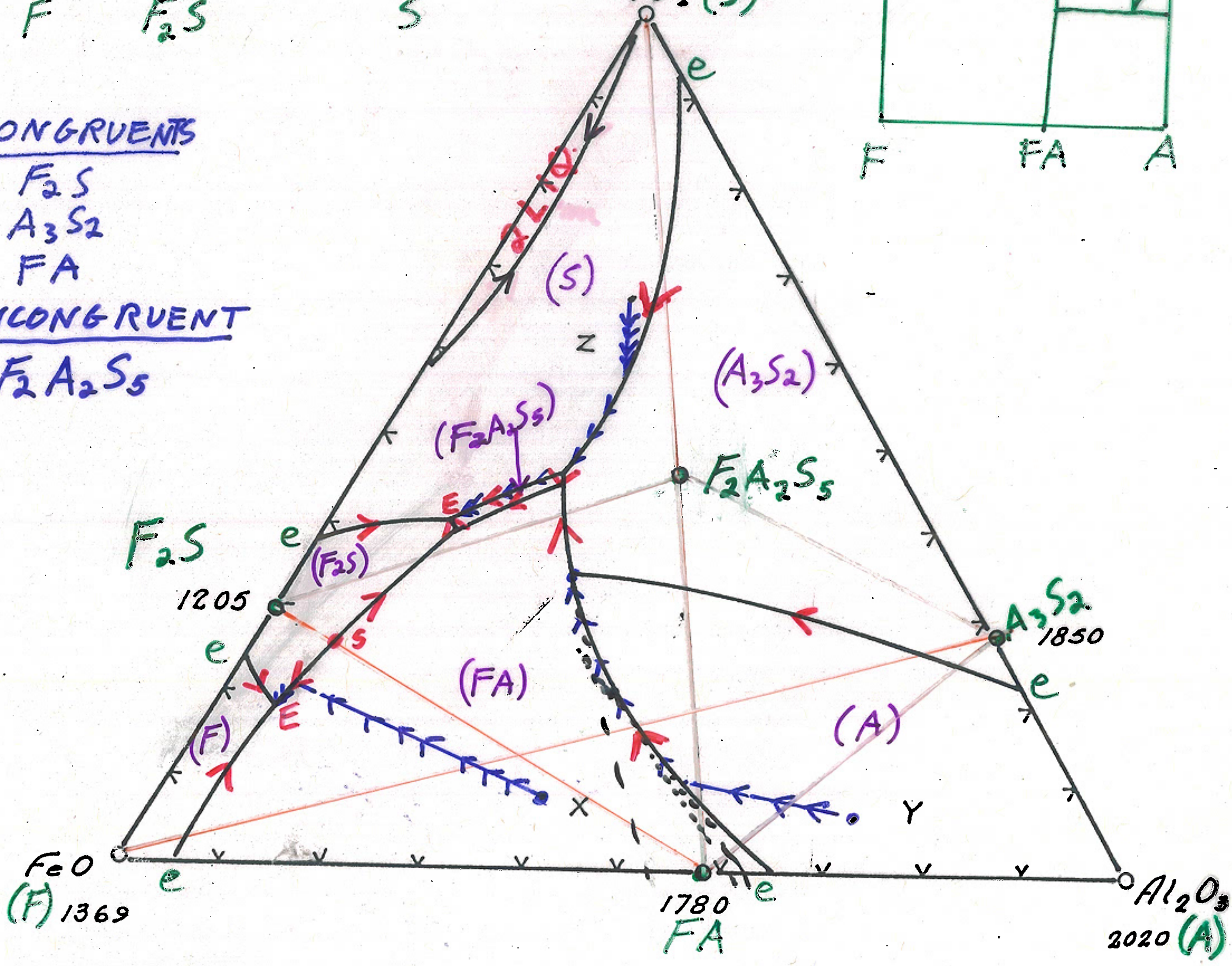


CONGRUENTS

F_2S
A_3S_2
FA

INCONGRUENT

$F_2A_2S_5$



QUASI-BINAIRES

$F-F_2S$
F_2S-S
$S-A_3S_2$
A_3S_2-A
$F-FA$
$FA-A$

$FA-F_2S$

FIGURE XVIII-3

QUASI-TERNAIRE

$FA-F-F_2S$

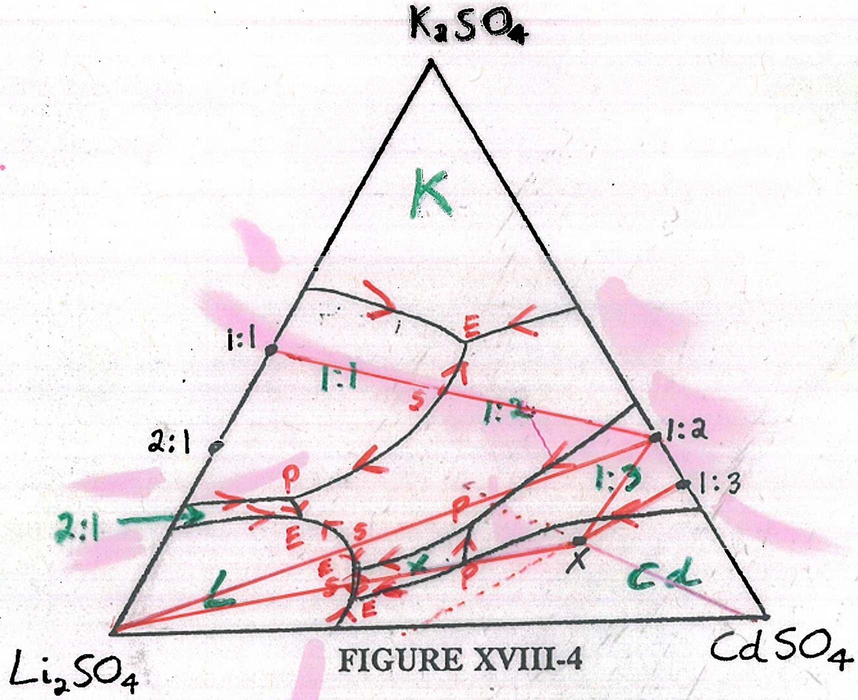


FIGURE XVIII-4

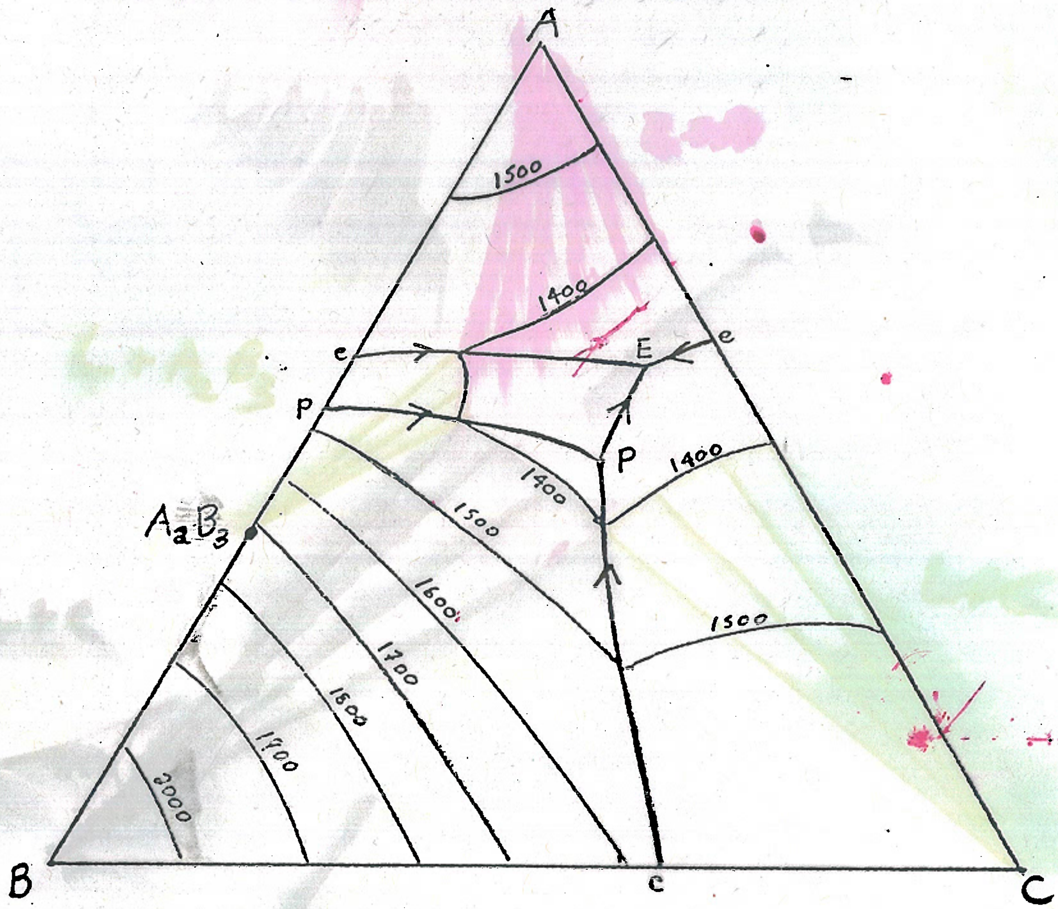


FIGURE XVIII-5

XVIII -6

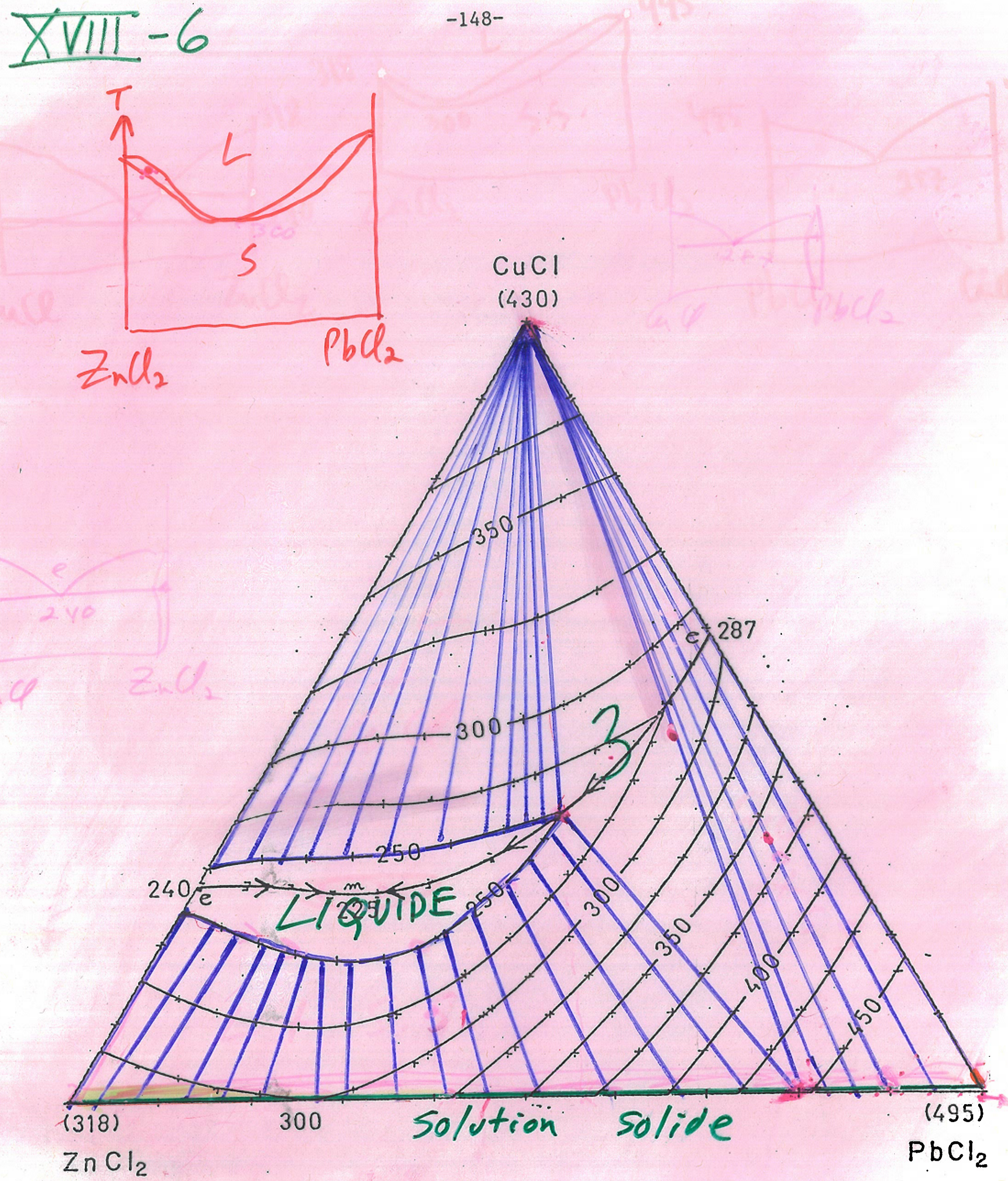


FIGURE XVIII-6

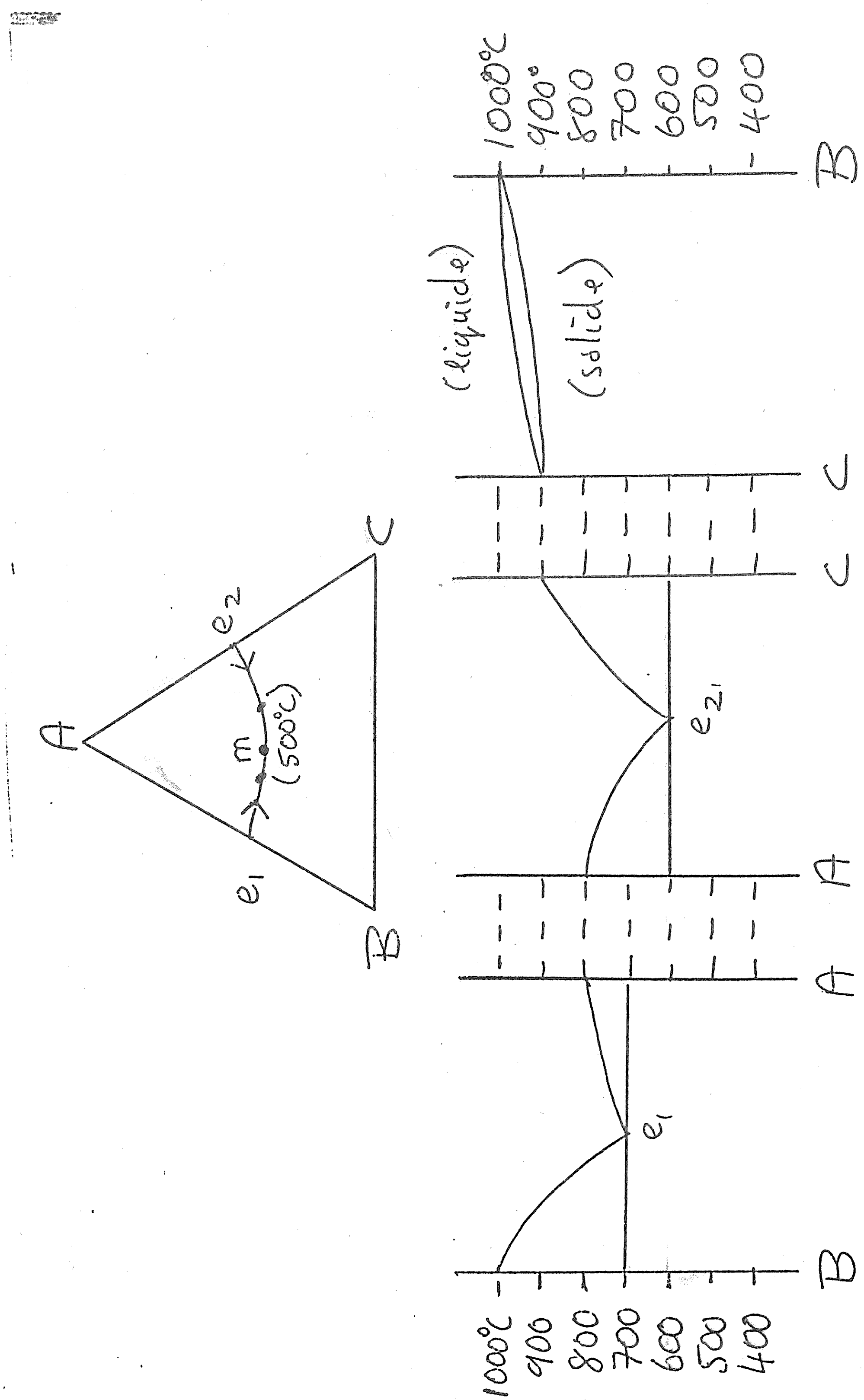


FIGURE XVIII-7

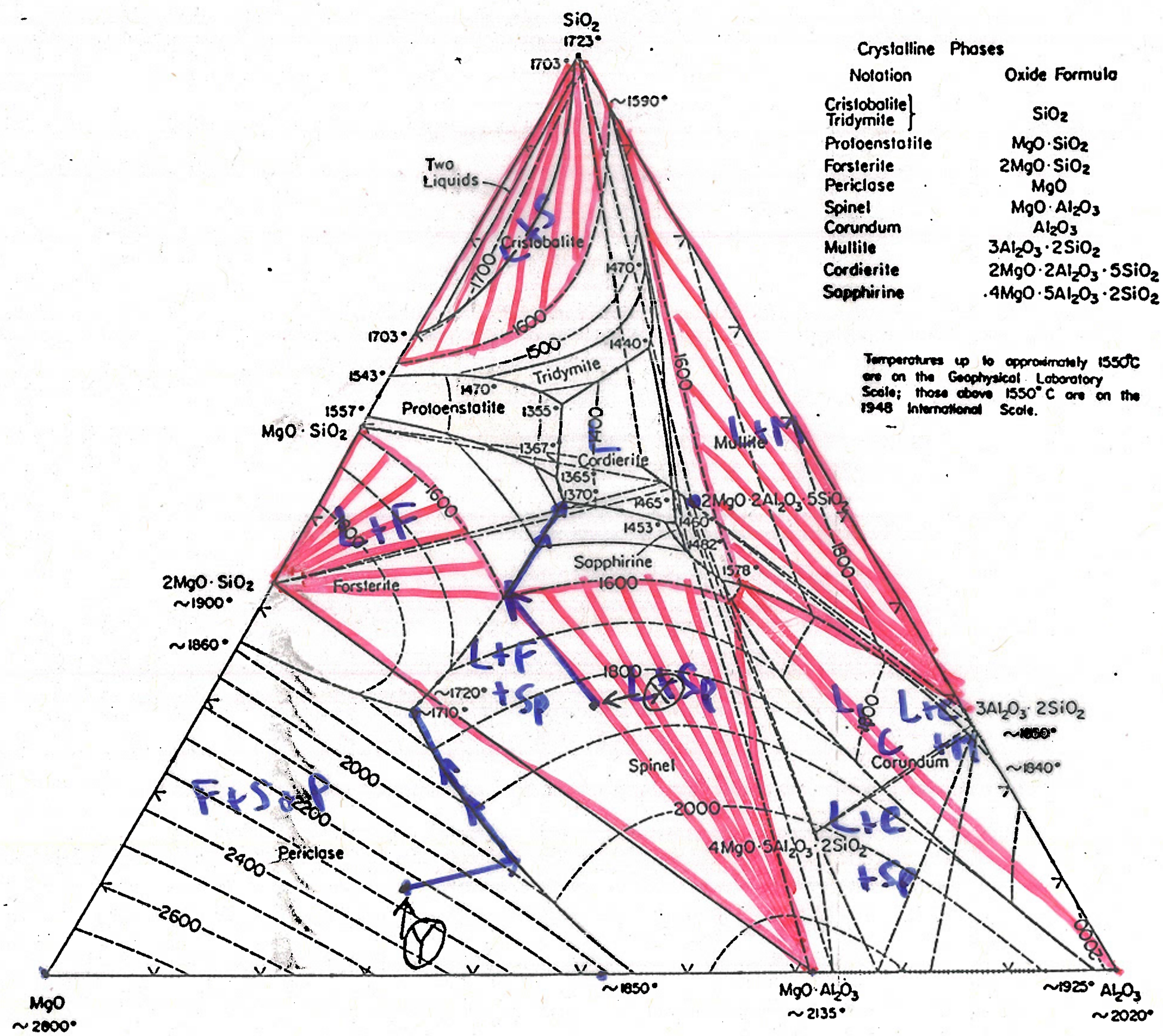
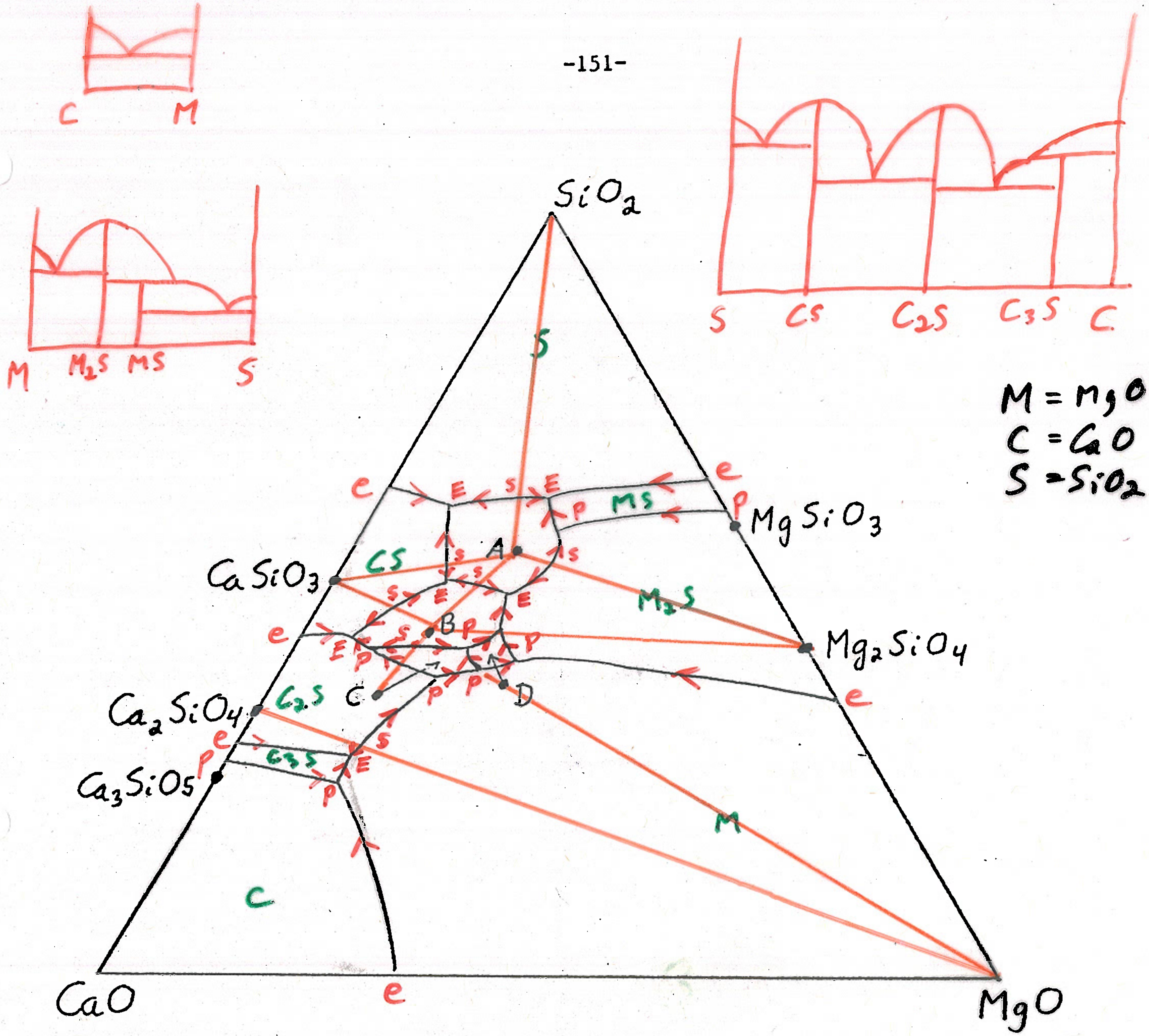


FIGURE XVIII-8



Quasi-binaires

A – S
A – CS
A – B
A – M_2S
B – CS
B – M_2S
M – C_2S

M – M_2S
M_2S – S

S – CS
S – C_2S
CS – C_2S
CS – C
C_2S – C

A = $CaO \cdot MgO \cdot 2SiO_2$ (congruent)

B = $2CaO \cdot MgO \cdot 2SiO_2$ (congruent)

C = $3CaO \cdot MgO \cdot 2SiO_2$ (incongruent)

D = $CaO \cdot MgO \cdot SiO_2$ (incongruent)

(les liquidus de C et D sont indiqués par les flêches)

FIGURE XVIII-9

XVIII-10

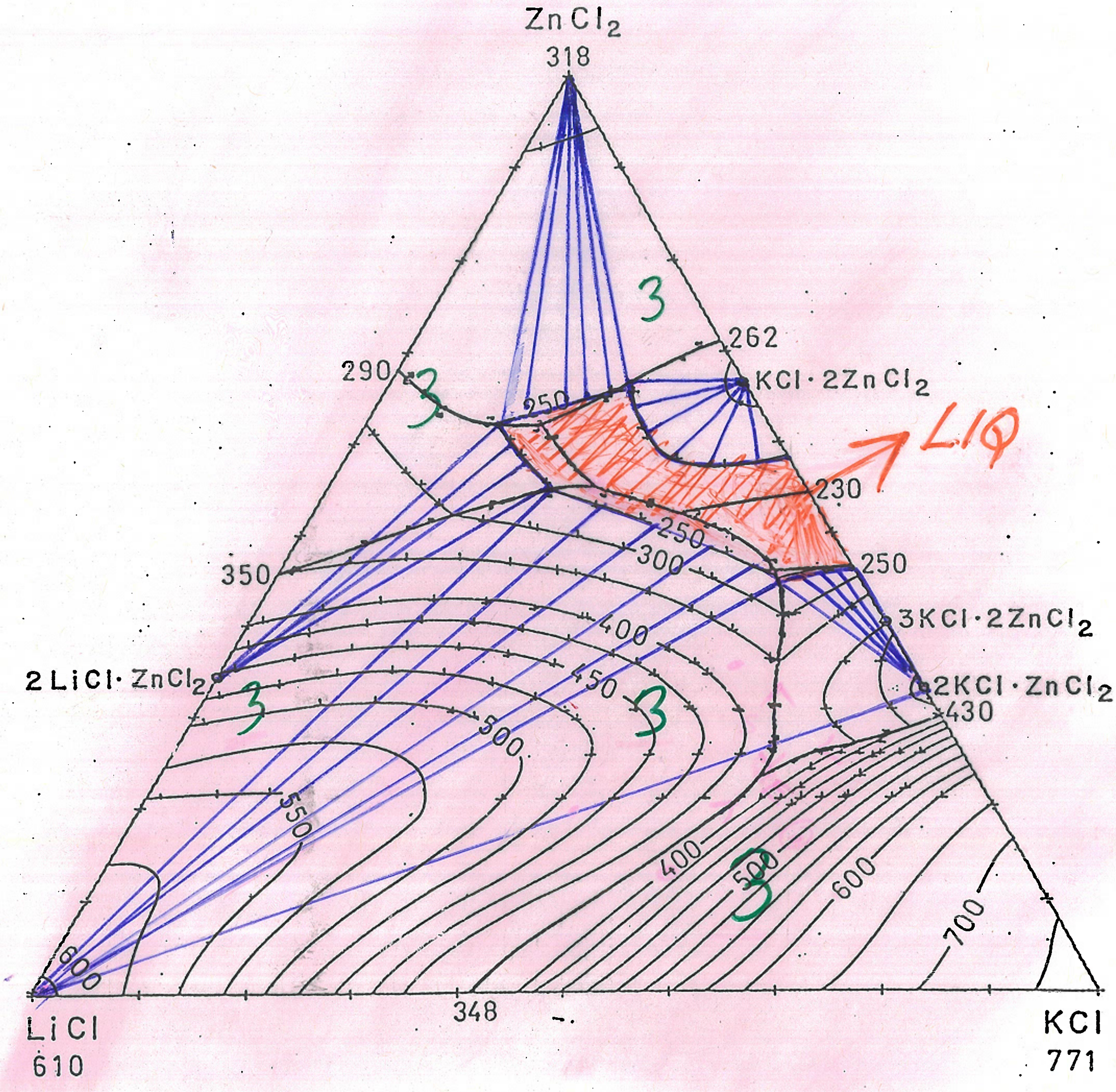


FIGURE XVIII-10

XVIII -11

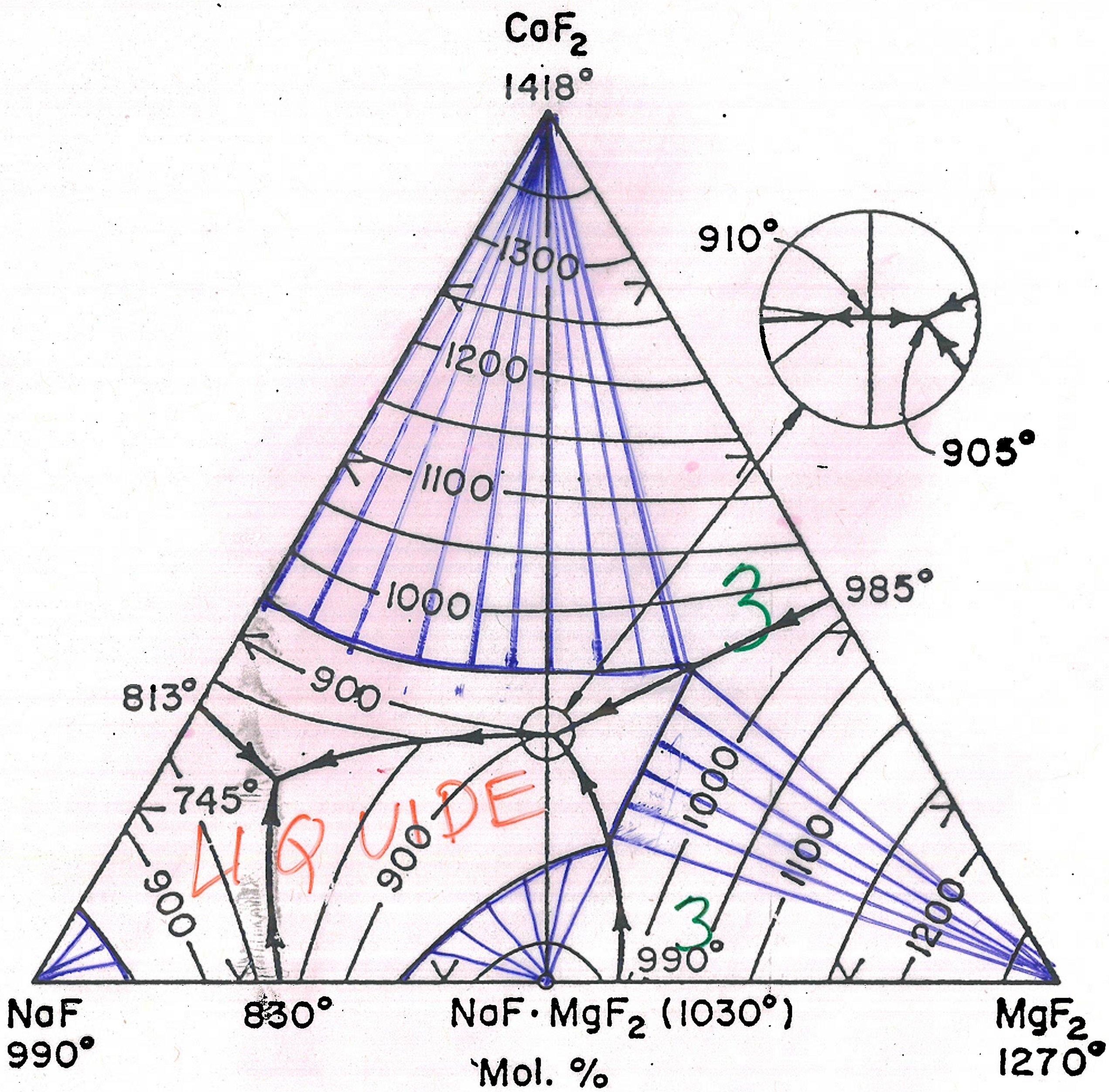


FIGURE XVIII-11

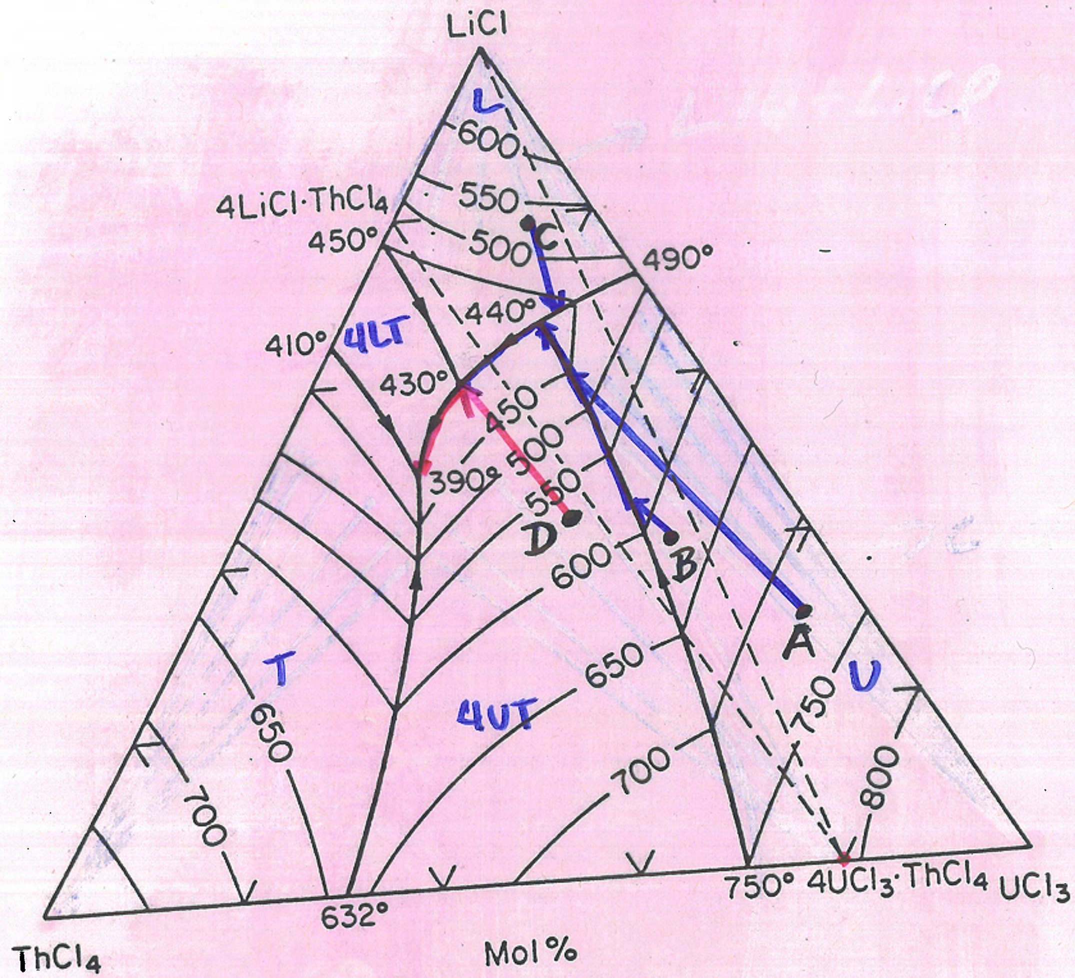


FIGURE XVIII-12

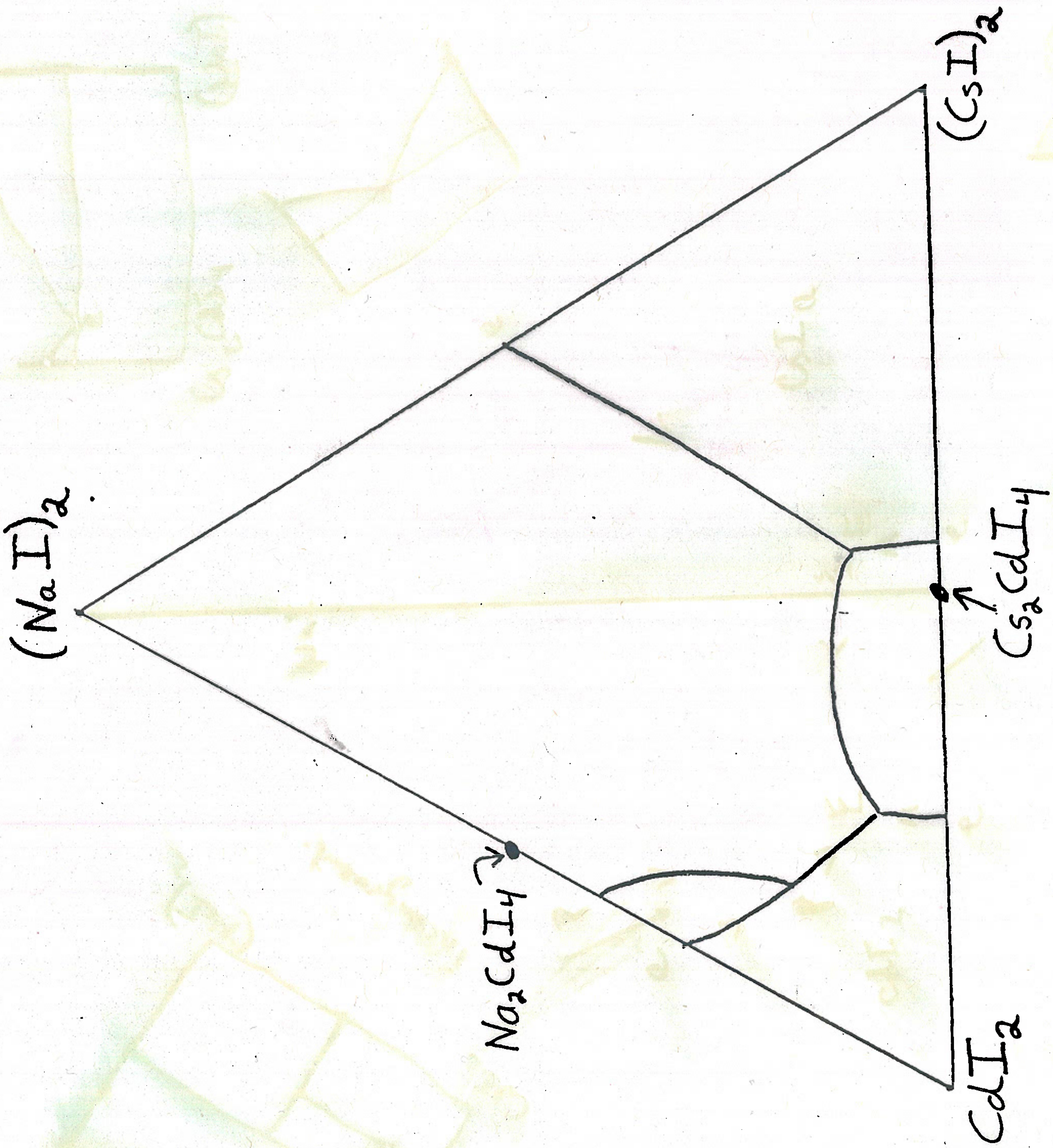
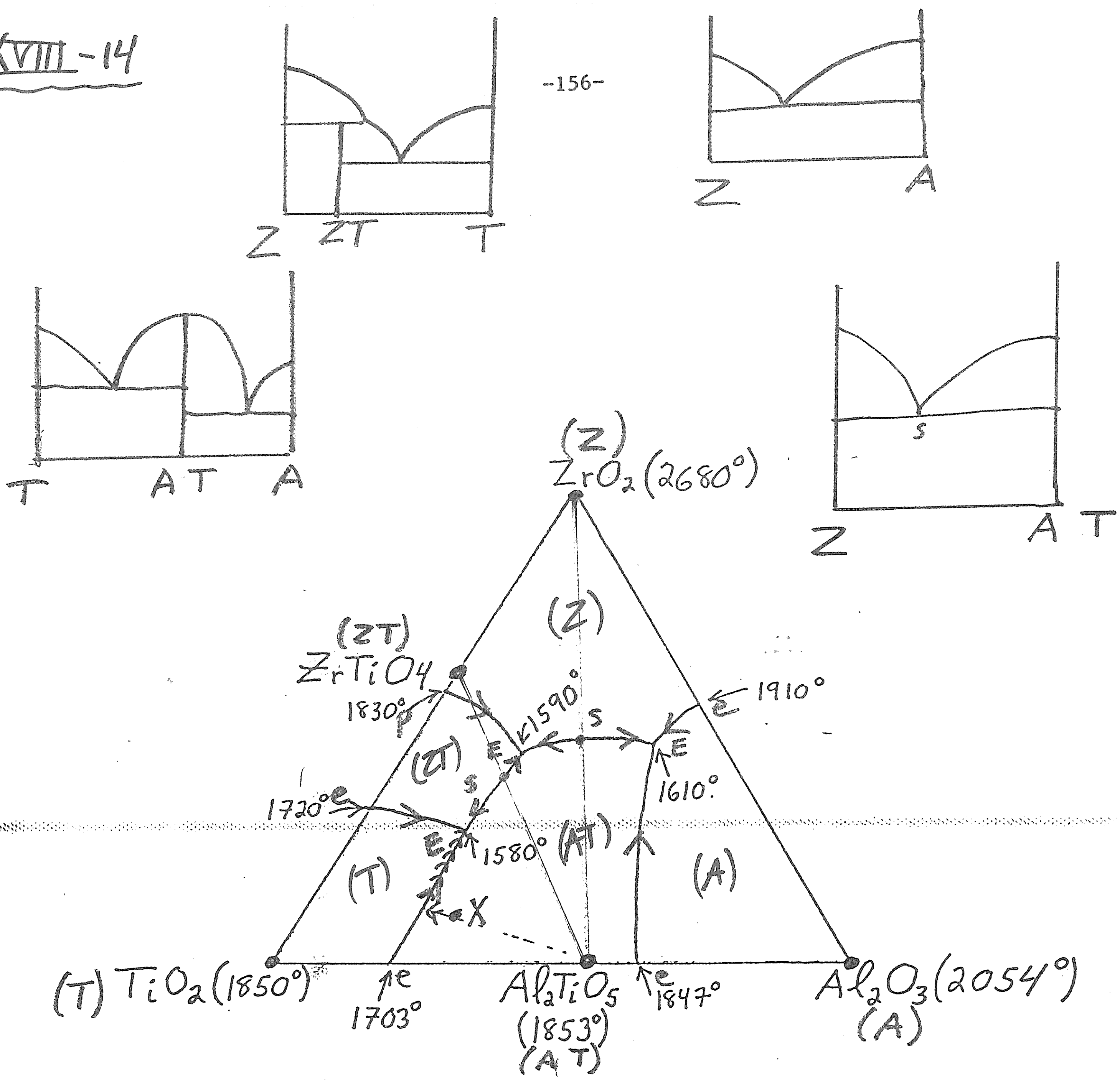


FIGURE XVIII-13

XVIII-14



(Température = °C)

(Composition = % poids)

(e) (i) Phases: ZT, T, AT

(ii) Constituents: AT (pro-eutectique)

FIGURE XVIII-14

AT+T (eutectique binaire)

AT+T+ZT (eutectique ternaire)

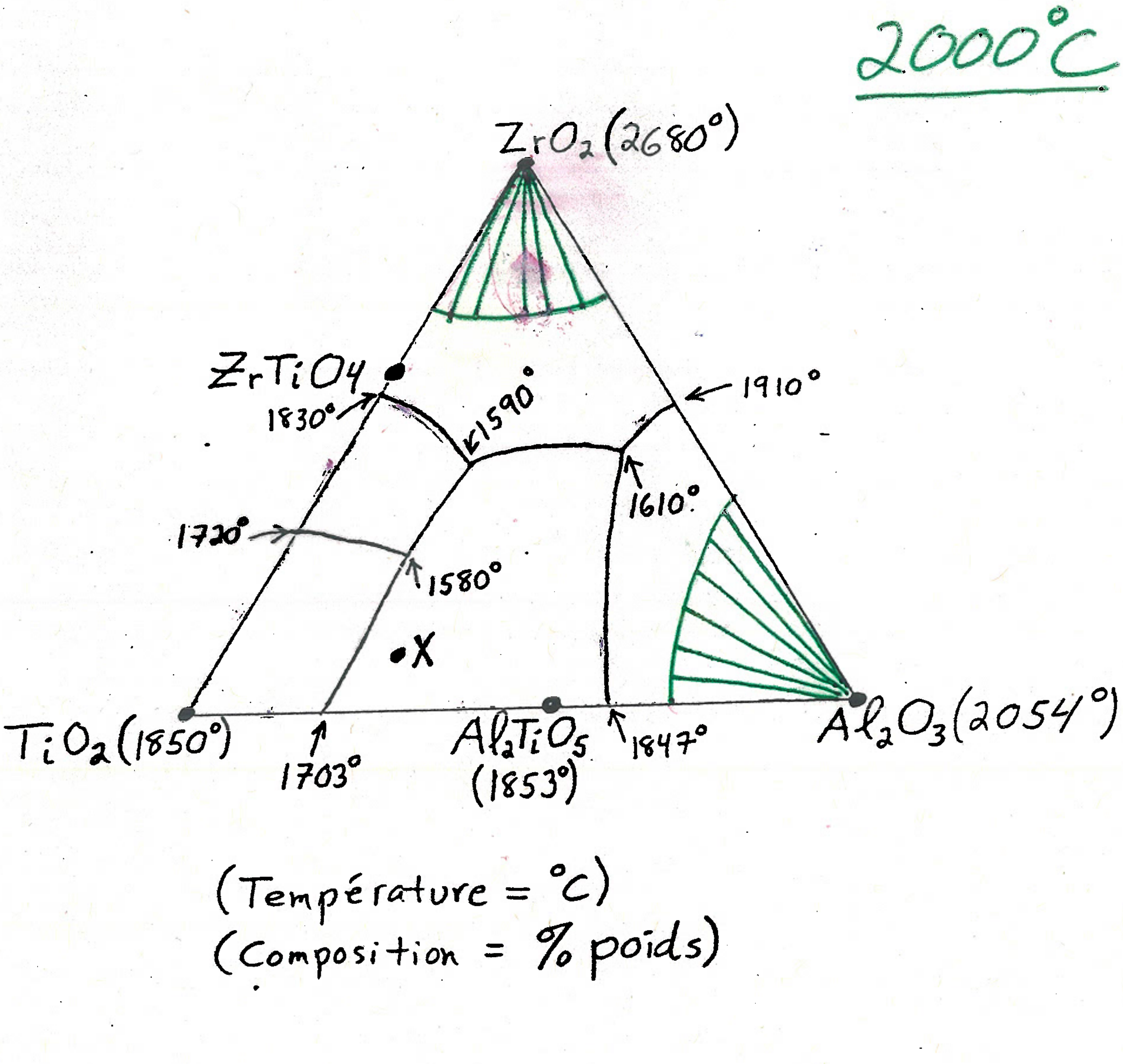
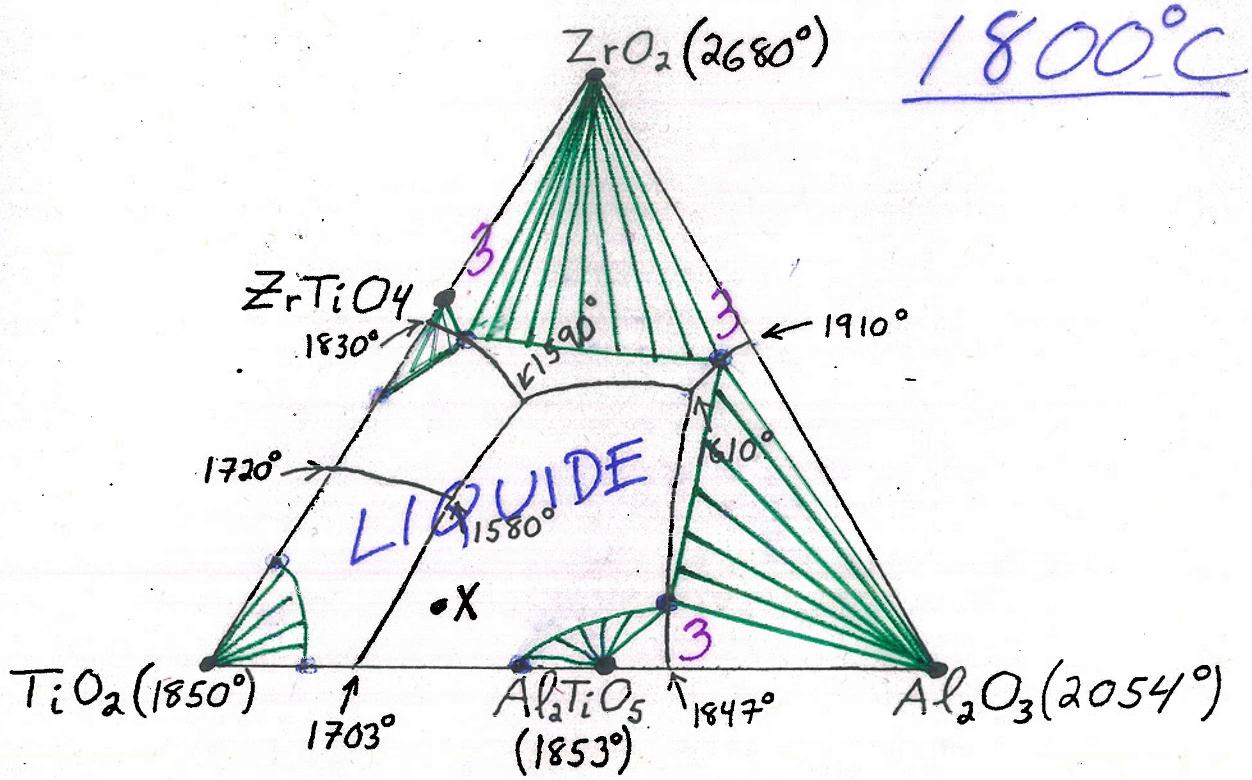


FIGURE XVIII-14



(Température = °C)
(Composition = % poids)

FIGURE XVIII-14

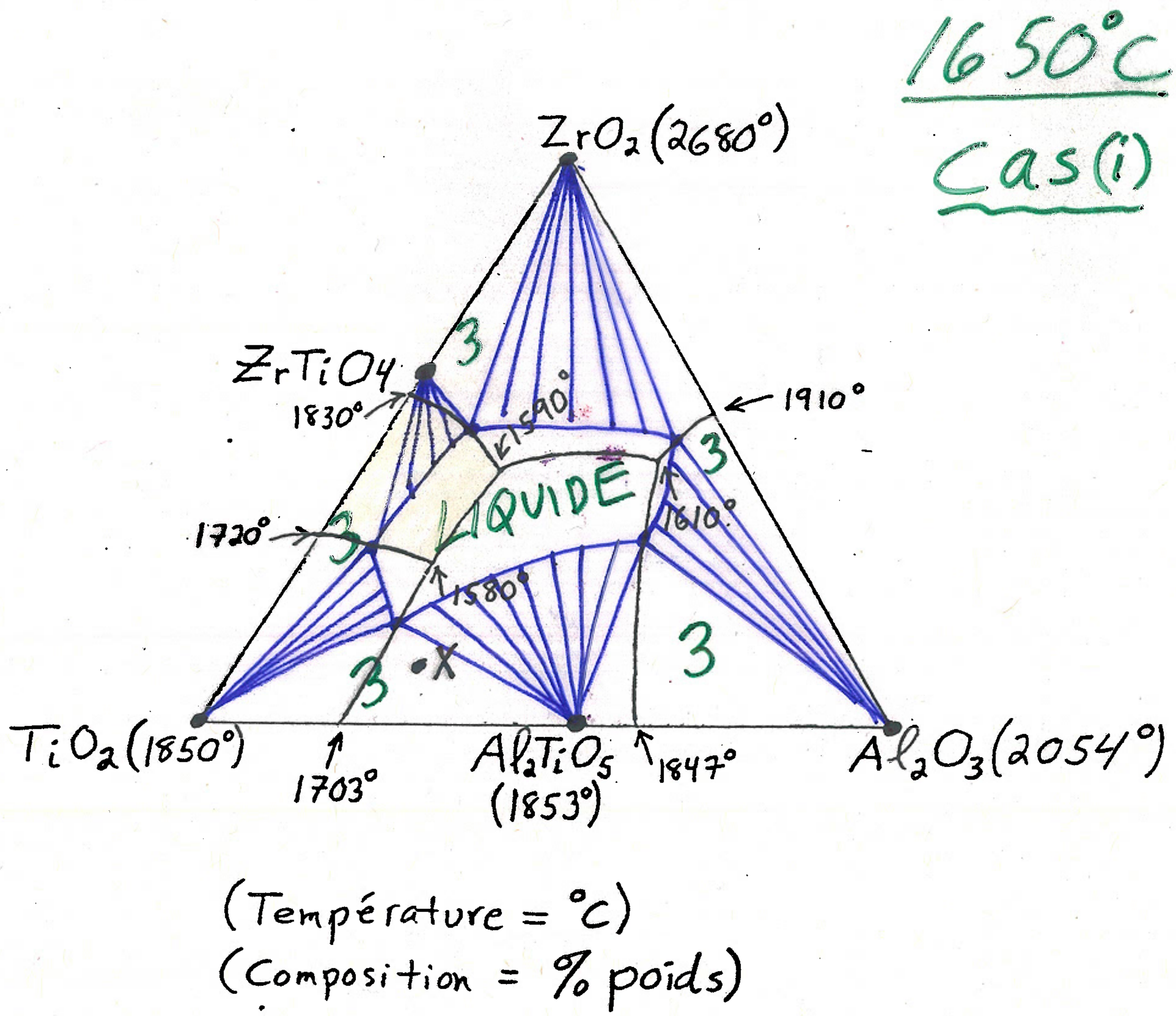


FIGURE XVIII-14

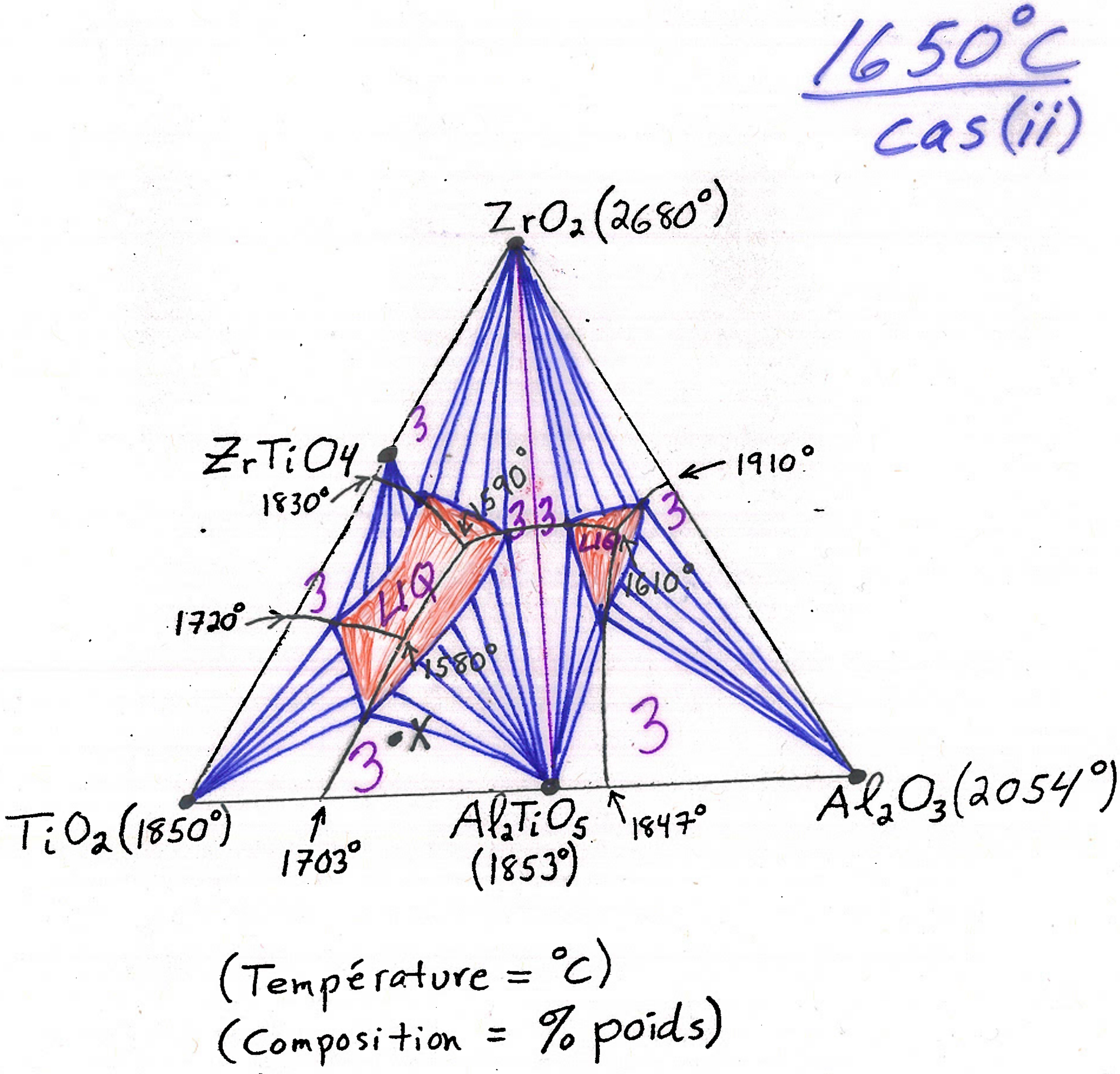


FIGURE XVIII-14

25°C

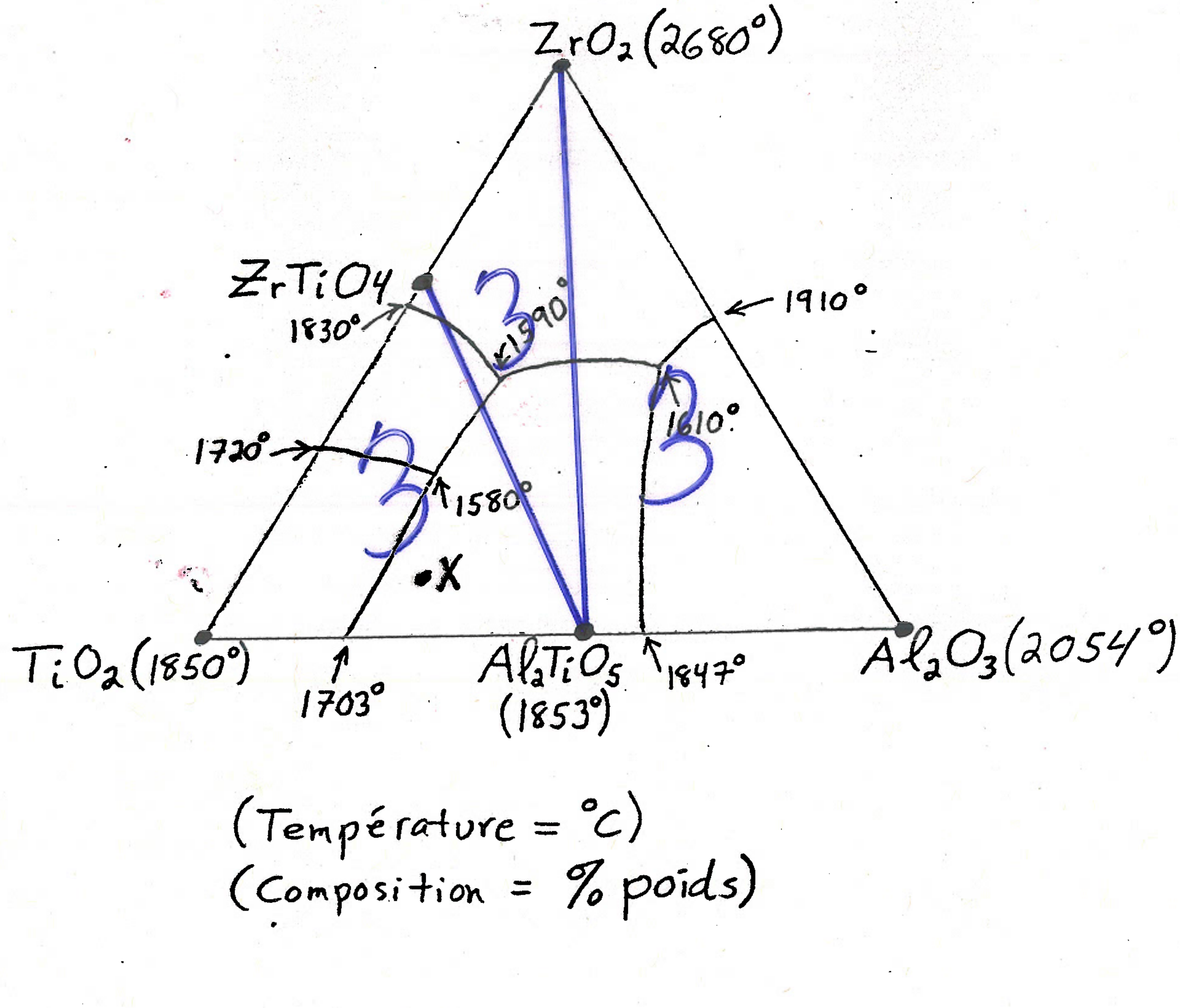


FIGURE XVIII-14

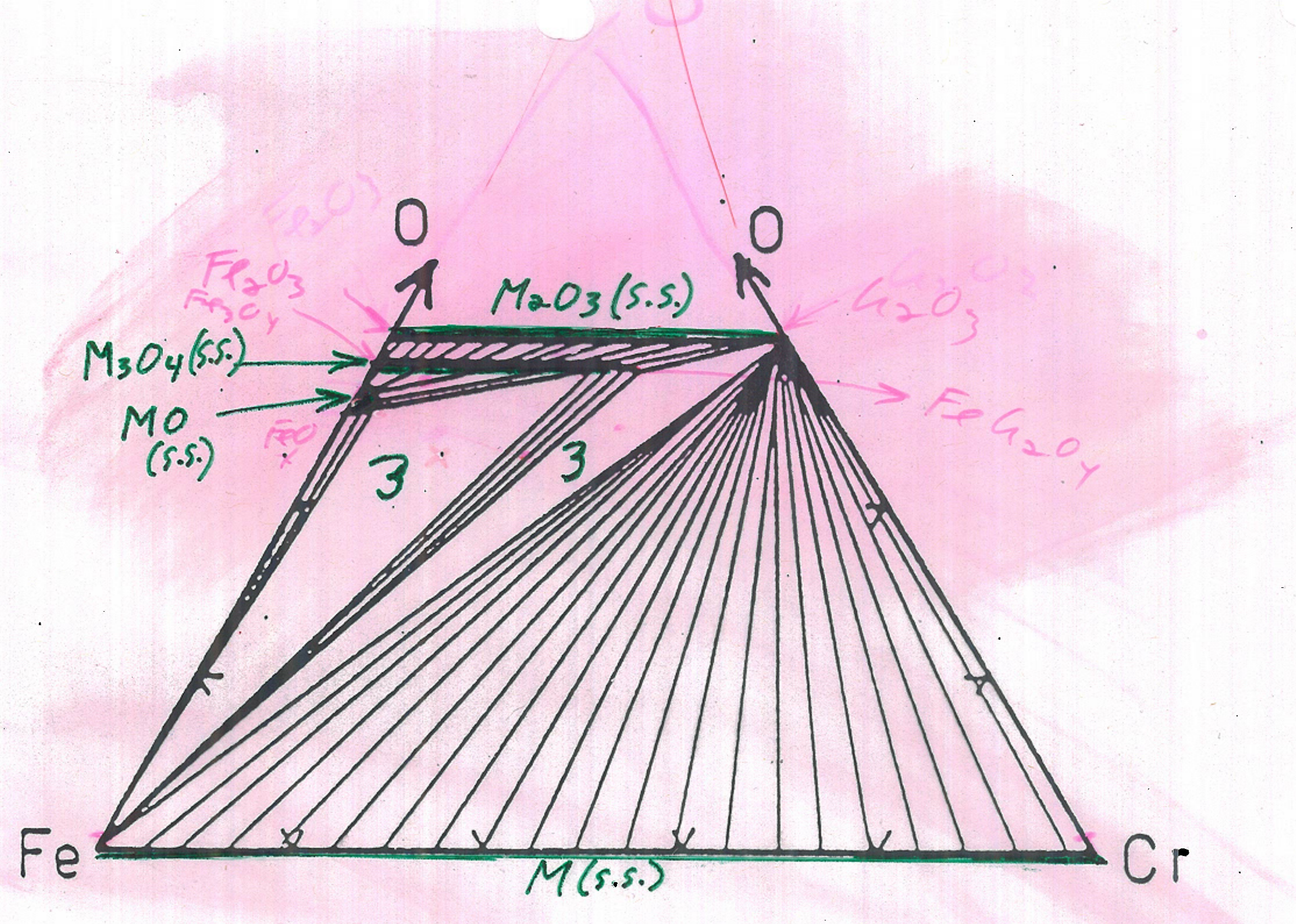


FIGURE XVIII-15

XVIII - 16

(i) Entre A et B — Évaporation de H_2O

(ii) Entre B et C — Précipitation de $(NH_4)_2SO_4$
+ Évaporation de H_2O
La solution suit la ligne BE

(iii) Entre C et D — Liquide reste constant au point E
Réaction péritectique:

$$LIQ\,(\text{au pt. } E) + (NH_4)_2SO_4 \rightarrow Li(NH_4)SO_4$$

+ Évaporation de H_2O

- Composition finale

$Li(NH_4)SO_4$ solide pur au point D.

XVIII - 17 $\quad v = C - P + 2$

Composants: O, N, S, Cu, Fe, Si $\quad C = 6$

Phases: Matte, laitier, gaz $\quad P = 3$

$$v = C - P + 2 = 6 - 3 + 2 = 5$$

Variables Connues:

$$\left.\begin{array}{l} T \\ P_{tot} \\ P_{SO_2}\ (\mu_{SO_2}) \\ P_{O_2}\ (\mu_{O_2}) \\ X_{Cu} \text{ du laitier} \end{array}\right\} 5$$

Donc: Oui, il a raison

XVIII - 16

(i) Entre A et B — Évaporation de H_2O

(ii) Entre B et C — Précipitation de $(NH_4)_2SO_4$

La solution suit la ligne BE

(iii) Entre C et D — Liquide reste constant au point E

Réaction péritectique:

$$LIQ\,(\text{au pt. E}) + (NH_4)_2SO_4 \rightarrow Li(NH_4)SO_4$$

- Composition finale

$Li(NH_4)SO_4$ solide pur au point D.

XVIII - 17 $\quad v = C - P + 2$

Composants: O, N, S, Cu, Fe, Si $\quad C = 6$

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$$v = C - P + 2 = 6 - 3 + 2 = 5$$

Variables Connues:

$$\left.\begin{array}{l} T \\ P_{tot} \\ P_{SO_2}\ (\mu_{SO_2}) \\ P_{O_2}\ (\mu_{O_2}) \\ X_{Cu} \text{ du laitier} \end{array}\right\} 5$$

Donc: Oui, il a raison