ÉCOLE POLYTECHNIQUE

Département de génie chimique

Programme de métallurgie

MET 6208

ÉNERGÉTIQUE DES SOLUTIONS

Contrôle I

Vendredi, le 16 octobre, 2015

10:30 – 13:30

NOTES:
- All documentation permitted (open book exam)
- There are 5 questions and 3 figures

Le professeur: Arthur D. Pelton

Question 1 (4 points)

100 moles of a liquid Pb-Sn solution at 800°C with composition $X_{Sn} = 0.2$ is mixed with 200 moles of a liquid Pb-Sn solution, also at 800°C, with composition $X_{Sn} = 0.8$. How much heat must be added/removed (specify which) from the system in order to maintain the temperature at 800°C ?

Data: Enthalpy of liquid-liquid mixing: $\Delta h_m = 5520\, X_{Pb}X_{Sn}$ Joules/mol.

Question 2 (4 points)

The phase diagram of the Al-Li system is shown in Figure 1.

(a) Sketch the curves of Gibbs energy versus composition for all phases present at the eutectic temperature (874 K), and show all common tangent lines.

(b) Sketch the curves of Gibbs energy versus composition for all phases present at the peritectic temperature (793 K), and show all common tangent lines.

Question 3 (4 points)

The phase diagram of the Ag-Pb system is of the "simple eutectic" type with no intermediate compounds and no solubility in the terminal solid phases. The eutectic temperature is 576 K. Assuming that the liquid is a regular solution with an excess Gibbs energy

$g^E = \omega X_{Ag} X_{Pb}$

calculate the value of the parameter ω at 576 K as well as the eutectic liquid composition.

Data: Ag: $\Delta h^o_{fusion} = 11297$ J/mol at $T^o_{fusion} = 1234$ K
Pb: $\Delta h^o_{fusion} = 6109$ J/mol at $T^o_{fusion} = 594$ K

(Note: You will receive full marks for setting up the equations to be solved and indicating how you would go about solving them. It is not necessary to obtain an actual numerical solution unless you have time.)

Question 4 (4 points)

The liquidus projection of the "reciprocal ternary" system $NaCl$-$CaCl_2$-NaF-CaF_2 is shown in Figure 2. Because of the condition of charge neutrality, this is a ternary system in the sense of the Phase Rule. The vertical axis is the anionic molar ratio $F/(Cl + F)$ and the horizontal axis the cationic molar ("equivalent") ratio $2Ca/(Na + 2Ca)$. The four pure salts are at the corners of the square, and each side of the square represents a binary system. All solid phases are pure stoichiometric compounds (no solid solutions.)

(a) Indicate, by placing arrows on the diagram, the directioin of decreasing temperature along each of the univariant lines.

(b) Label all binary eutectic and peritectic points in the four binary sub-systems (that is, along the sides of the square) with "e" or "p".

(c) Label all ternary eutectic, peritectic and saddle points with "E", "P" or "S".

(d) Sketch the temperature-composition section along the join between NaCl and CaF_2. Is this a quasibinary system ?

(e) Sketch the isothermal reciprocal ternary section at room temperature. (At room temperature all phases are solid.)

(Note: Don't forget to put your name on the diagram and hand it in with your answer booklets.)

Question 5 (4 points)

A phase diagram is sketched in Figure 3. This is an isothermal diagram at 1600 K. The vertical axis is the partial pressure of oxygen, $P_{O2,}$ at equilibrium. The horizontal axis is the molar ratio $n_{Ni}/(n_{Ni} + n_{Co})$. That is, for the metallic solution the horizontal axis is the mole fraction X_{Ni}, and for the oxide solution this axis is the mole fraction X_{NiO}.

Calculate the compositions of the metallic and oxide solutions (at points B and A on Fig. 3) at equilibrium at 1600 K when the equilibrium oxygen pressure is $P_{O2} = 1.00 \text{ X } 10^{-7}$ bar, assuming that the metallic solution (Co-Ni) and the oxide solution (CoO-NiO) are ideal solutions.

(Note: You do not require any data other than that shown on the figure.)

Figure 1

Al - Li

Data from FTlite - FACT light alloy databases

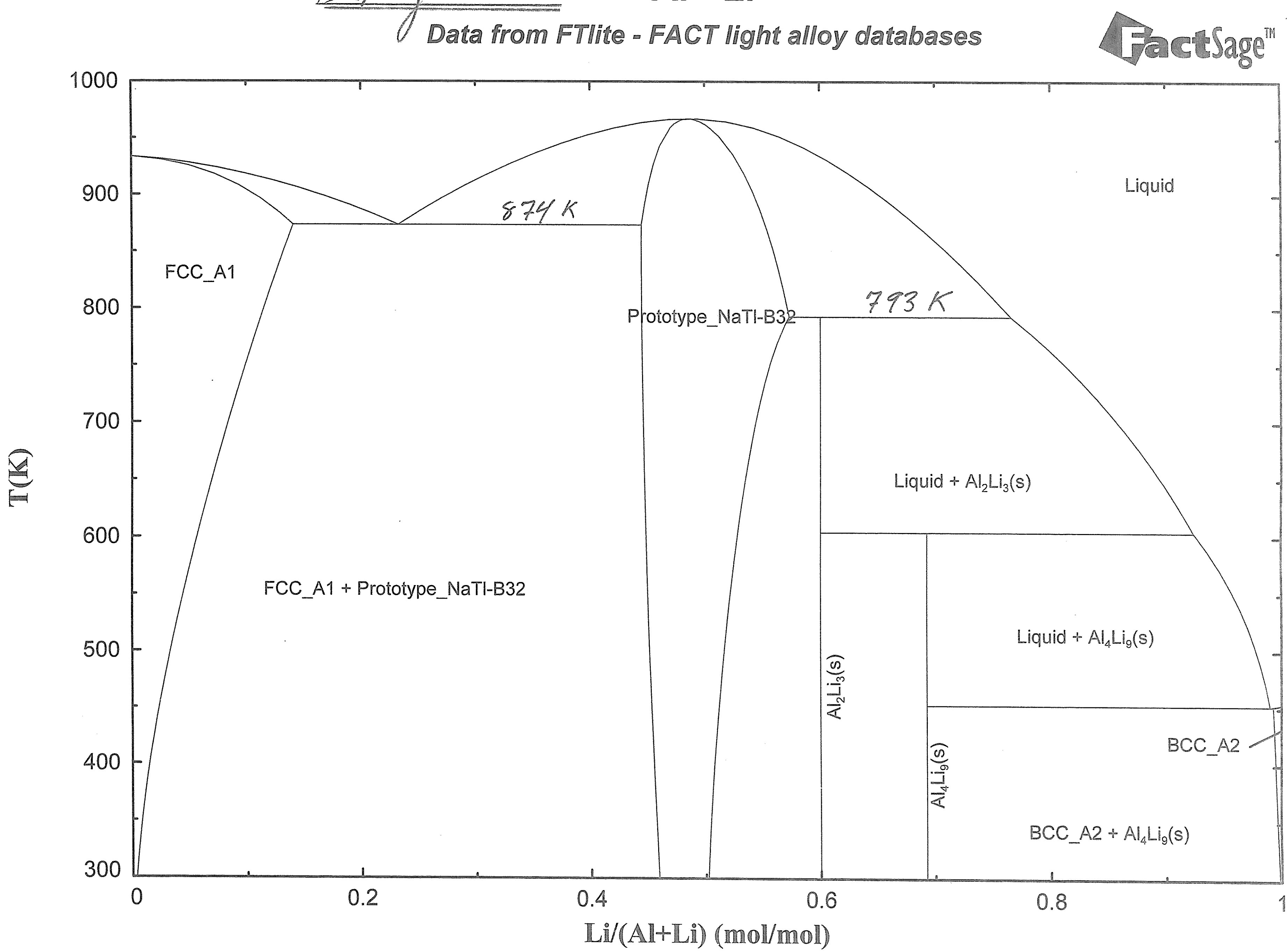
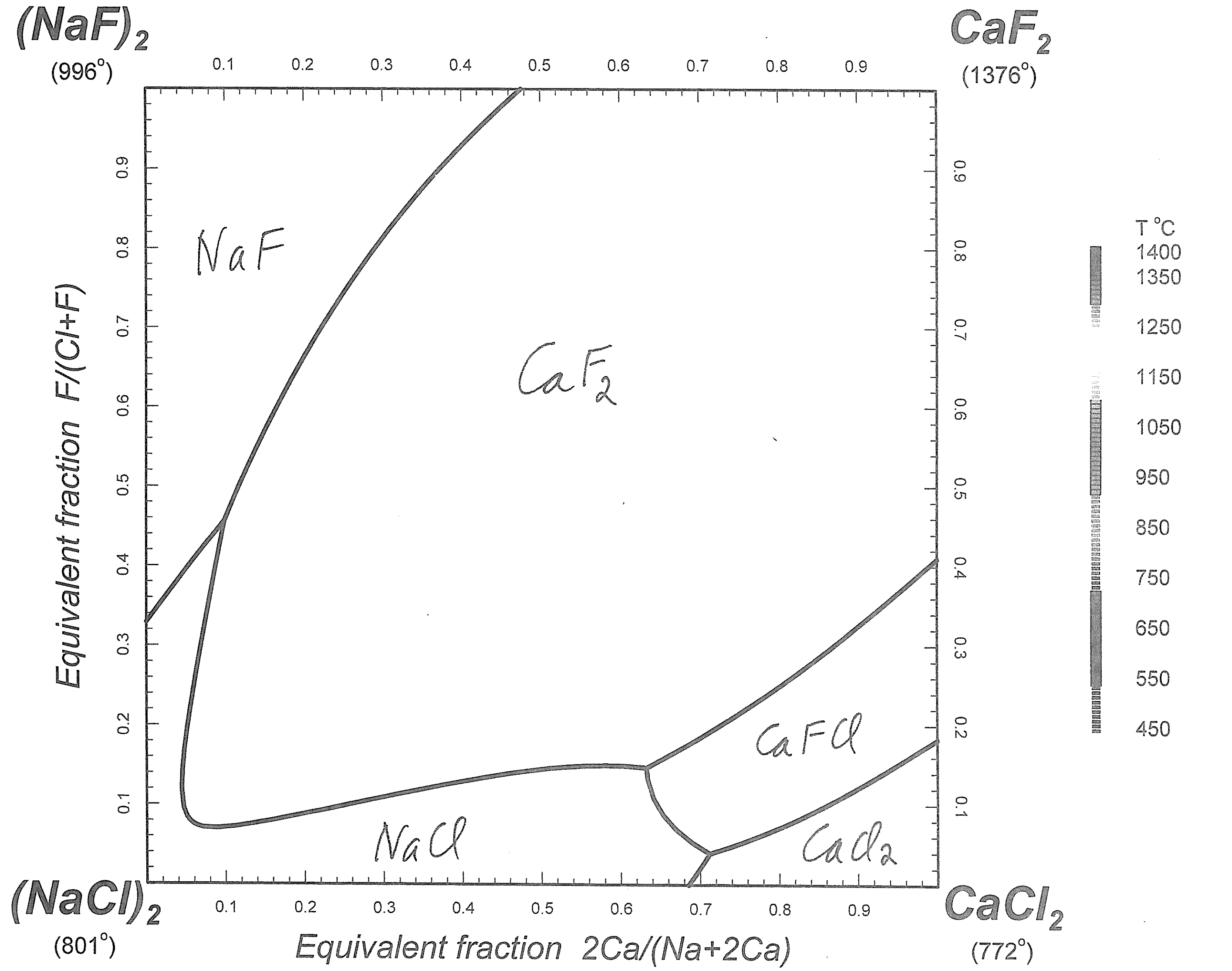


Figure 2

Na - Ca - Cl - F

(Na[+] + 2Ca[2+]) = (Cl[-] + F[-]), 1 atm



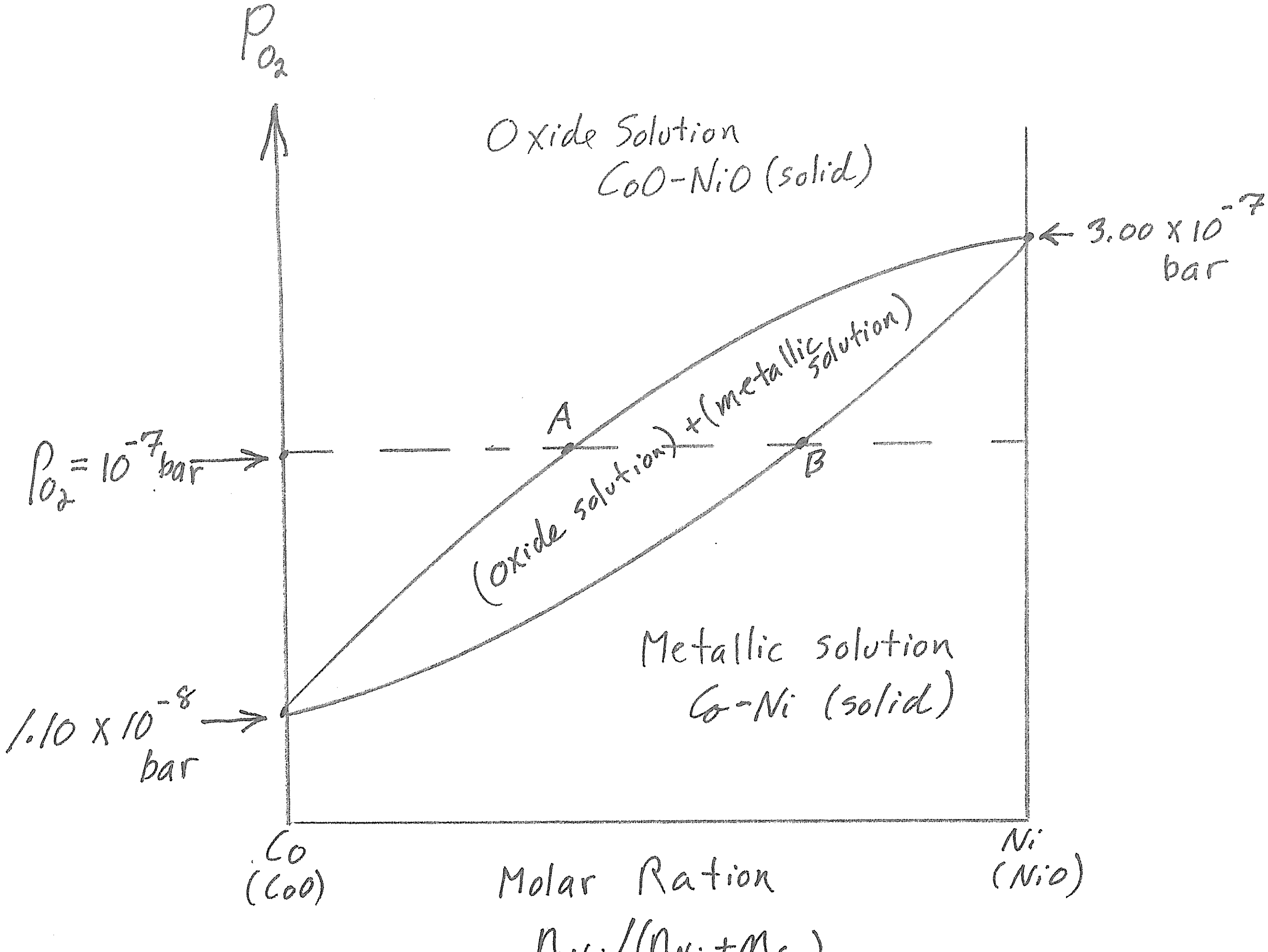


Figure 3 T = 1600 K

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Oct. 16, 2015

Solutionnaire

Question 1

$20Sn + 80Pb = \text{Solution 1}$ $\quad \Delta H = 100(5520)(0.2)(0.8)$
$= 88320$ joules

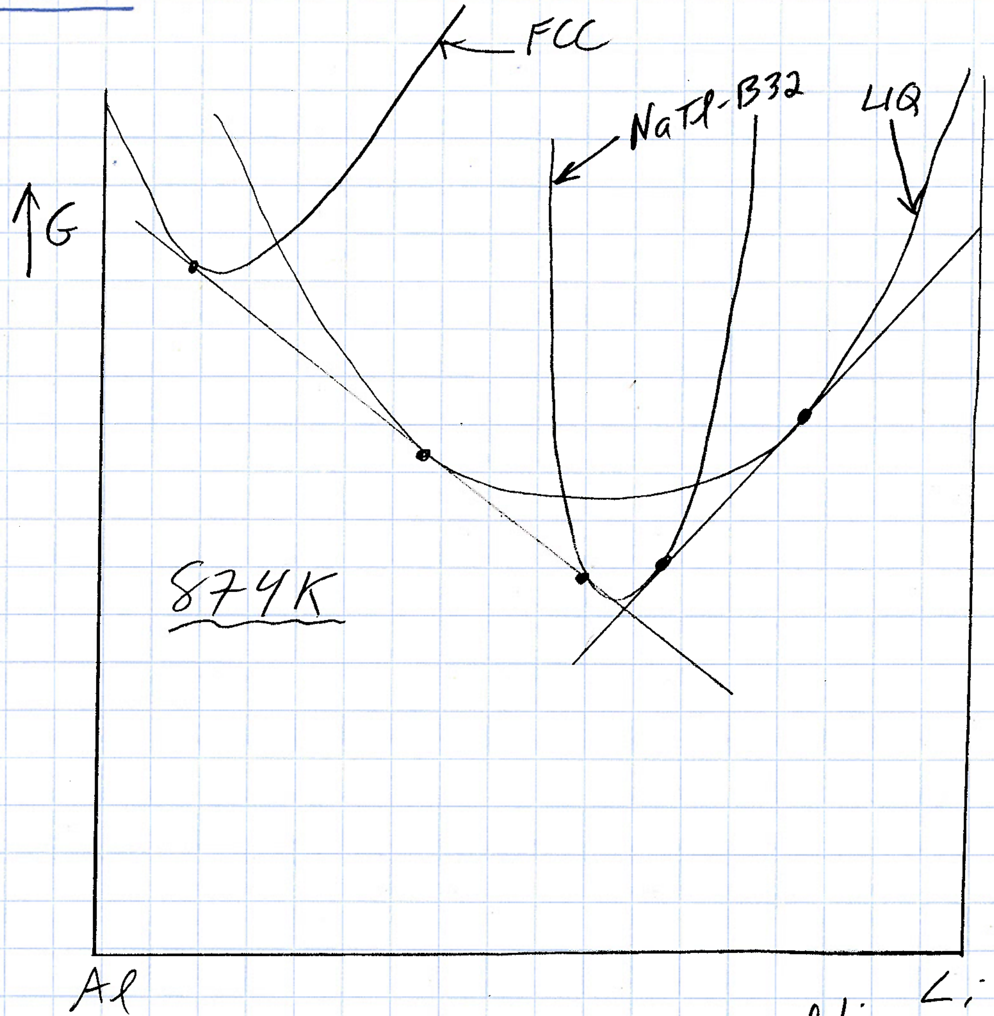
$160Sn + 40Pb = \text{Solution 2}$ $\quad \Delta H = 200(5520)(0.2)(0.8)$
$= 176640$ joules

$180Sn + 120Pb = \text{Solution 3}$ $\quad \Delta H = 300(5520)(0.4)(0.6)$
$= 397440$ joules

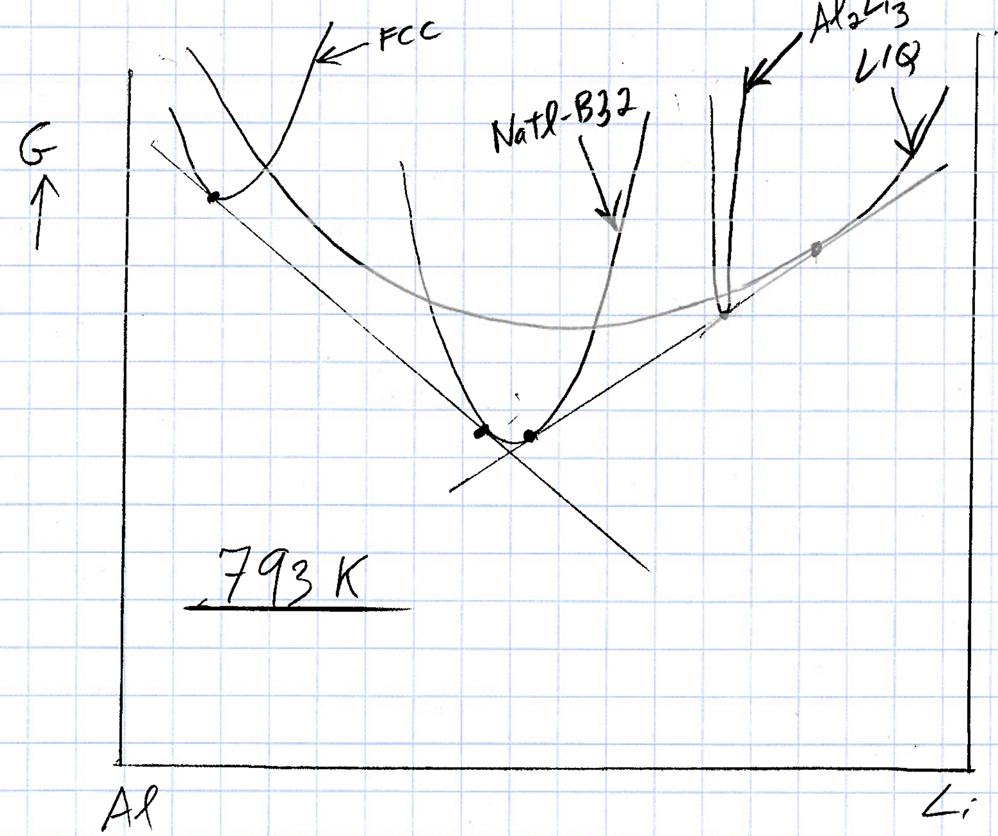
$\text{Solution 1} + \text{Solution 2} = \text{Solution 3}$ $\quad \Delta H = 397440 - 88320 - 176640$
$= \underline{132480 \text{ joules}}$.

$\Delta H > 0$ so must add heat

Question 2



FCC
NaTl-B32
LIQ
G
874K
Al
Li

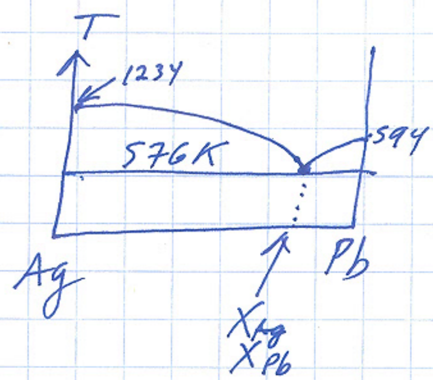


FCC
Al_2Li_3
LIQ
NaTl-B32
G
793 K
Al
Li

Question 3

$$g^E_{Pb} = X_{Ag}^2 \cdot \omega = RT\ln\gamma_{Pb}$$

$$g^E_{Ag} = X_{Pb}^2 \cdot \omega = RT\ln\gamma_{Ag}$$



$$RT\ln a_{Pb} = -\Delta h^\circ_{fus(Pb)}\left(1 - \frac{576}{594}\right) = -6109\,(0.03030)$$

$$8.315(576)(\ln X_{Pb}) + \omega X_{Ag}^2 = -185$$

$$4789 \ln X_{Pb} + \omega(1 - X_{Pb})^2 = -185 \quad (1)$$

$$RT\ln a_{Ag} = -11297\left(1 - \frac{576}{1234}\right) = -6024$$

$$8.315(576)\ln X_{Ag} + \omega X_{Pb}^2 = -6024$$

$$4789 \ln(1 - X_{Pb}) + \omega X_{Pb}^2 = -6024 \quad (2)$$

Solve (1) and (2) iteratively

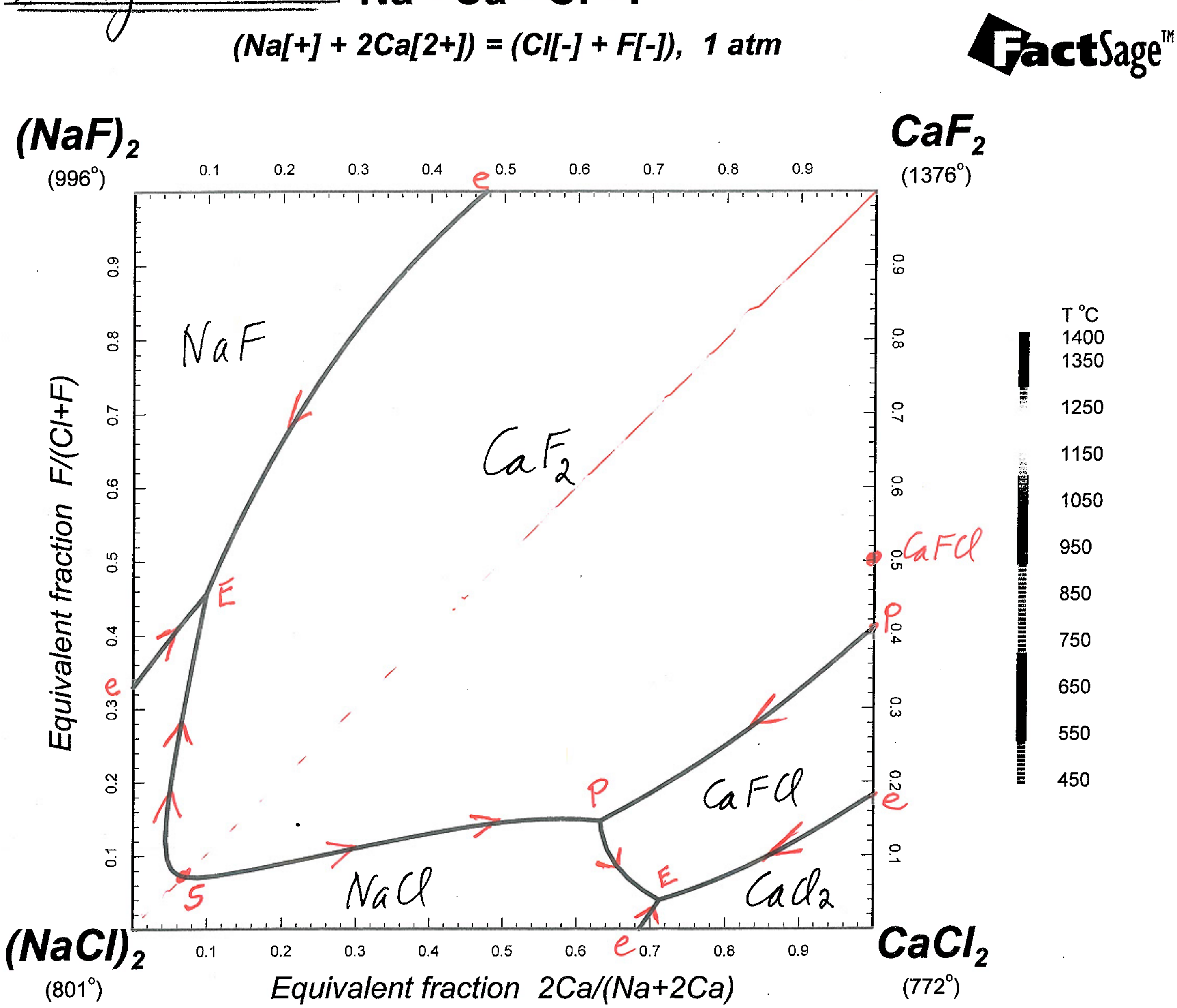
$X_{Pb} = 0.958(5)$

$\omega = 10200$ joules/mol

Question 4 (a, b, c)

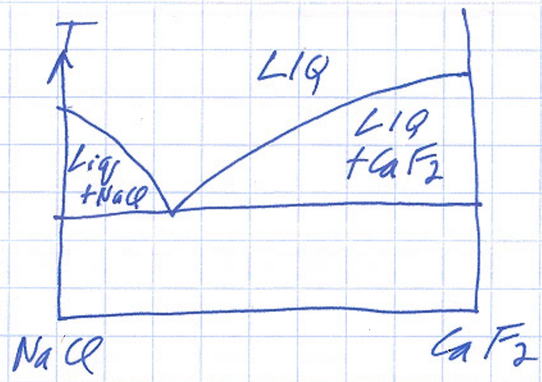
Figure 2 **Na - Ca - Cl - F**

(Na[+] + 2Ca[2+]) = (Cl[-] + F[-]), 1 atm



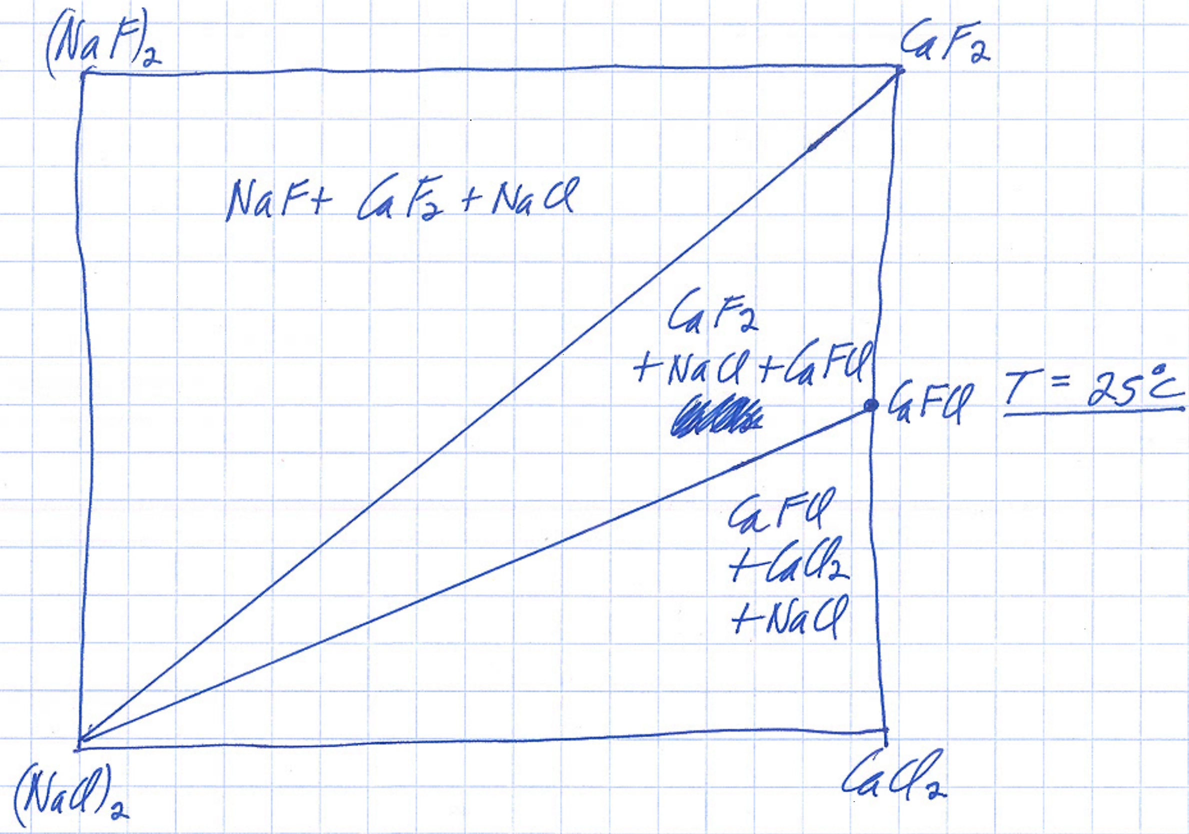
Question 4

(d)



This is a quasibinary

(e)



One compatibility triangle for each ternary invariant (P or E)

Question 5

$Co + \frac{1}{2}O_2 = CoO$

$$K = \frac{1}{(1.10\times10^{-8})^{1/2}} = \frac{X_{CoO}}{(10^{-7})^{1/2}\cdot X_{Co}}$$

$Ni + \frac{1}{2}O_2 = NiO$

$$K = \left(\frac{1}{(3.00\times10^{-7})^{1/2}}\right) = \frac{(1-X_{CoO})}{(10^{-7})^{1/2}\cdot(1-X_{Co})}$$

Solve the two equations:

$$\frac{X_{CoO}}{X_{Co}} = 3.01511$$

$$\frac{(1-X_{CoO})}{(1-X_{Co})} = 0.57735$$

$X_{Co} = 0.17358$ $\quad$ $X_{Ni} = 0.82642$

$X_{CoO} = 0.52275$ $\quad$ $X_{NiO} = 0.47725$