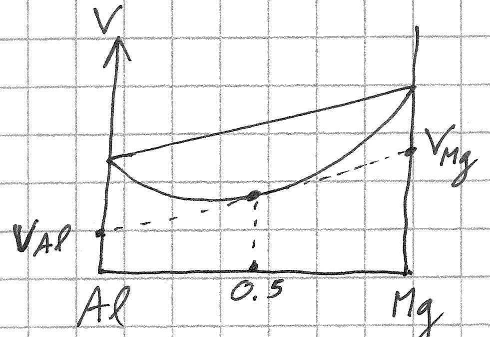
MET6208 - Contrôle I, 15 oct. 2014

Solutionnaire

Question 1



$$V_{Mg} = \left(\frac{\partial V}{\partial n_{Mg}}\right) \approx \frac{0.0139341 - 0.0137728}{0.01}$$

$$= 0.01613 \ \ell/mol$$

$$V = n_{Mg} V_{Mg} + n_{Al} V_{Al}$$

$$0.0137728 = 0.5\,(0.01613) + 0.5\,V_{Al}$$

$$V_{Al} = 0.01141 \ \ell/mol = (\partial V/\partial n_{Al})$$

$$V_{final} = 0.0139341 + 0.01\,(0.01141)$$

$$= \underline{\underline{0.0140482 \ \ell}}$$

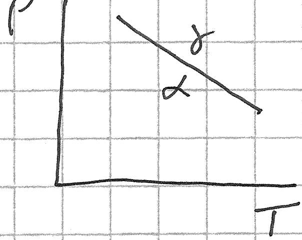
Alternate Solution:

After adding 0.01 mol Mg and 0.01 mol Al, the solution is at the same composition ($X_{Mg} = X_{Al} = 0.50$) as initially and so it has the same properties. Hence

$$V_{final} = \frac{0.51}{0.50}(0.0137728)$$

$$= \underline{\underline{0.0140482 \ \ell}}$$

Question 2



Increasing P at constant T favors the denser phase.
γ(fcc) is denser than α(bcc) [fcc is close-packed]
Therefore higher P favors γ. ⇒ Slope is negative.

or: $dG = VdP - SdT \qquad (dG/dP)_T = V$

Consider $\alpha \rightarrow \gamma \qquad (d\Delta G/dP)_T = V_\gamma - V_\alpha < 0$

Therefore high P favors γ

or: Clausius - Clapeyron equation

$$dP/dT = \frac{\Delta S_{\alpha\rightarrow\gamma}}{\Delta V_{\alpha\rightarrow\gamma}}$$

Since $\Delta S_{\alpha\rightarrow\gamma} > 0$ and $\Delta V_{\alpha\rightarrow\gamma} < 0$ the slope is negative

Question 3

The reactions which occur upon cooling at the ternary eutectic, peritectic and quasi-peritectic points are, respectively:

$$L \to \alpha + \beta + \gamma$$
$$L + \gamma \to \alpha + \beta$$
$$L + \beta + \gamma \to \alpha$$

In each case, if the overall system composition is in the tie-triangle $(\alpha+\beta+\gamma)$, the liquid phase will be completely consumed by the invariant reaction, leaving the 3 solid phases $(\alpha+\beta+\gamma)$ at lower temperatures.

Hence, the 25°C section will consist of a tie-triangle (also called compatability triangle) for each ternary invariant.

- See figure on next page.
- Example: Invariant P_1' involves the 3 solids δ, ϵ, ξ. Therefore, there is a 25°C tie-triangle whose corners are the compositions of these 3 phases.

Question 4

(See figure, page 4)

(a) 800°C → 700°C

At 800°C, (AB+C) is more stable than (AC+B)

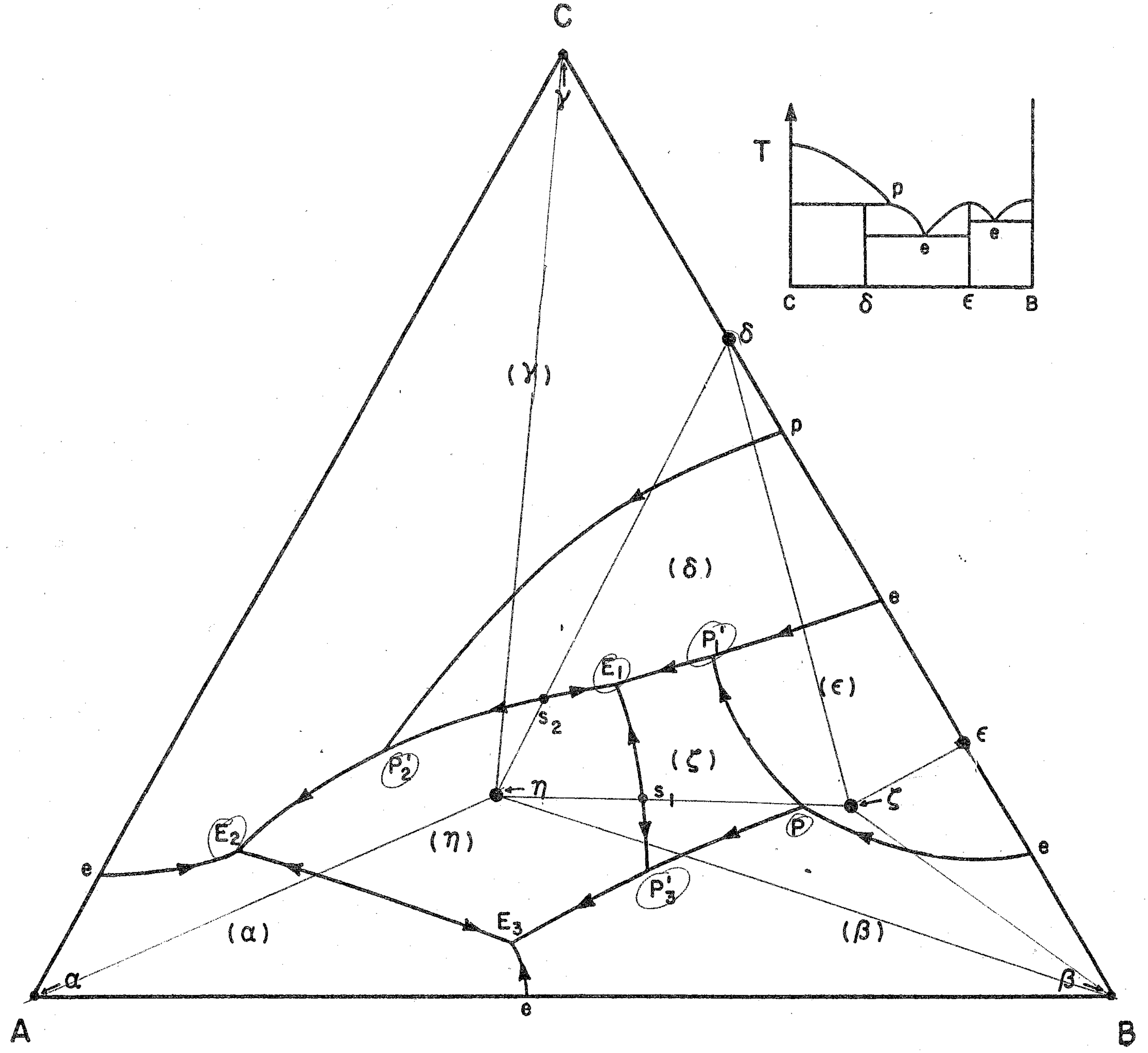
Therefore, the reaction is (upon cooling):

$$(AB + C) \to (AC + B)$$

(b) 700°C → 600°C

The reaction upon cooling is:

$$B + C \to BC$$


C
(γ)
γ
δ
p
(δ)
e
P'1
E1
(ε)
s2
P'2
(ζ)
ε
η
s1
ζ
E2
(η)
P
e
e
P'3
E3
(α)
(β)
α
β
e
A
B
T
p
e
e
C
δ
ε
B

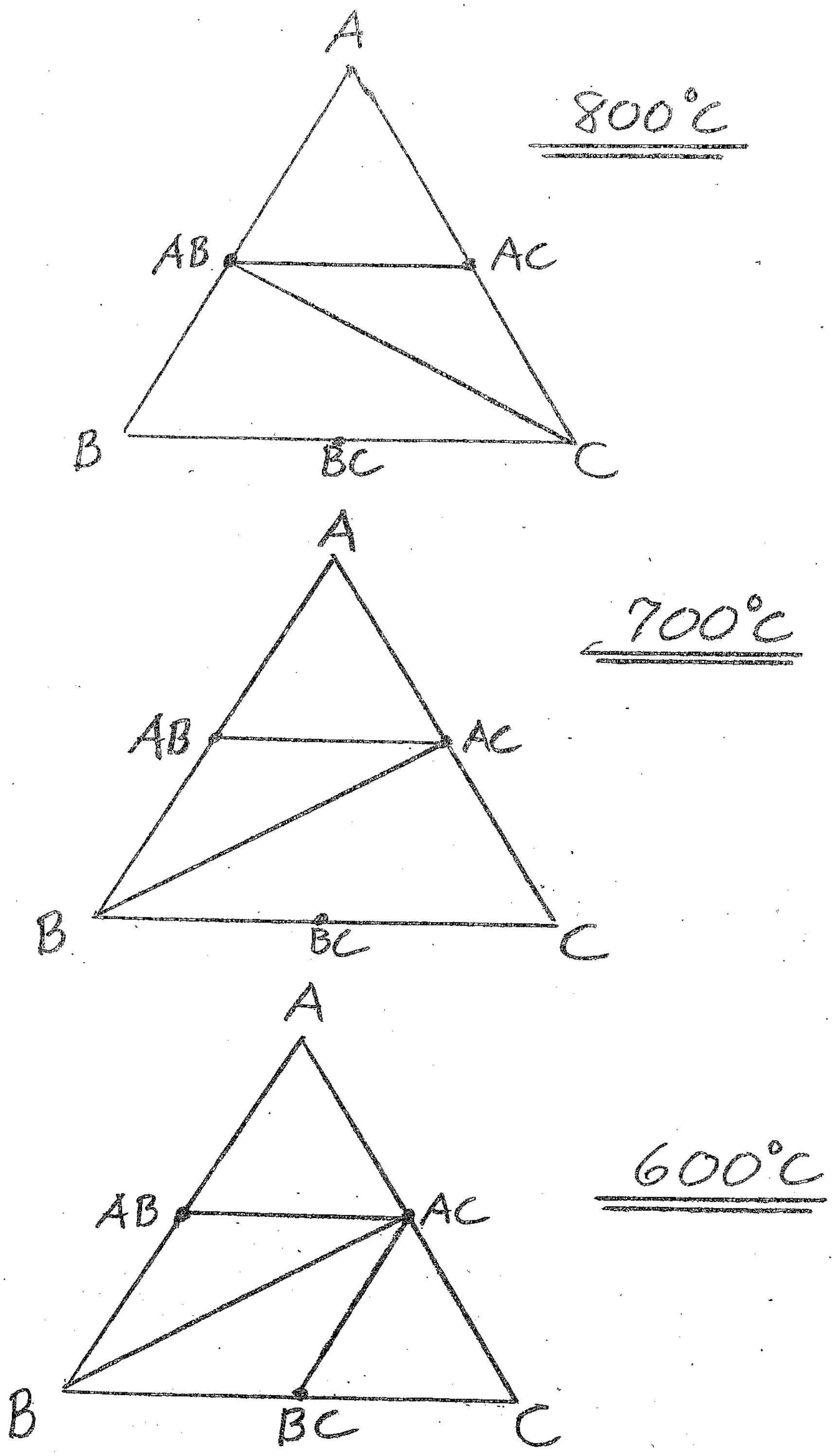


Figure 3

Question 5 See figure, page 6

Along the Cu-liquidus

$$RT\ln a_{Cu}^{liq} - RT\ln a_{Cu}^{sol} = -\Delta h_{fusion}^{o}\left(1-\frac{T}{T_{fus}^{o}}\right)$$

The solid phase is Raoultian. Hence: $a_{Cu}^{sol} = X_{Cu}^{sol} = (1-0.009) = 0.991$

$$T_{fus}^{o} = 1085+273 = 1358K$$
$$T_{monotectic} = 983+273 = 1256K$$

$$(8.315)1256\ln a_{Cu}^{liq} - 8.315(1256)\ln(0.991) = -13128\left(1-\frac{1256}{1358}\right)$$

$$a_{Cu}^{liq} = \underline{\underline{0.9017}}$$

The activity is the same at points A and B because these two liquid solutions are in equilibrium.

Question 6

From the Gibbs-Helmholtz equation: $\frac{d\Delta H}{dT} = T\frac{dS^E}{dT}$

Hence, if ΔH depends on T, then S^E cannot be constant.

Alternatively: If $\Delta H = a+bT$
and $S^E = 0$

Then $g^E = \Delta H - TS^E = (a+bT) - T(0.0) = a+bT$

But then $\Delta H = a$ and $S^E = -b$

Cu - Pb

Data from FScopp - FactSage copper alloy database

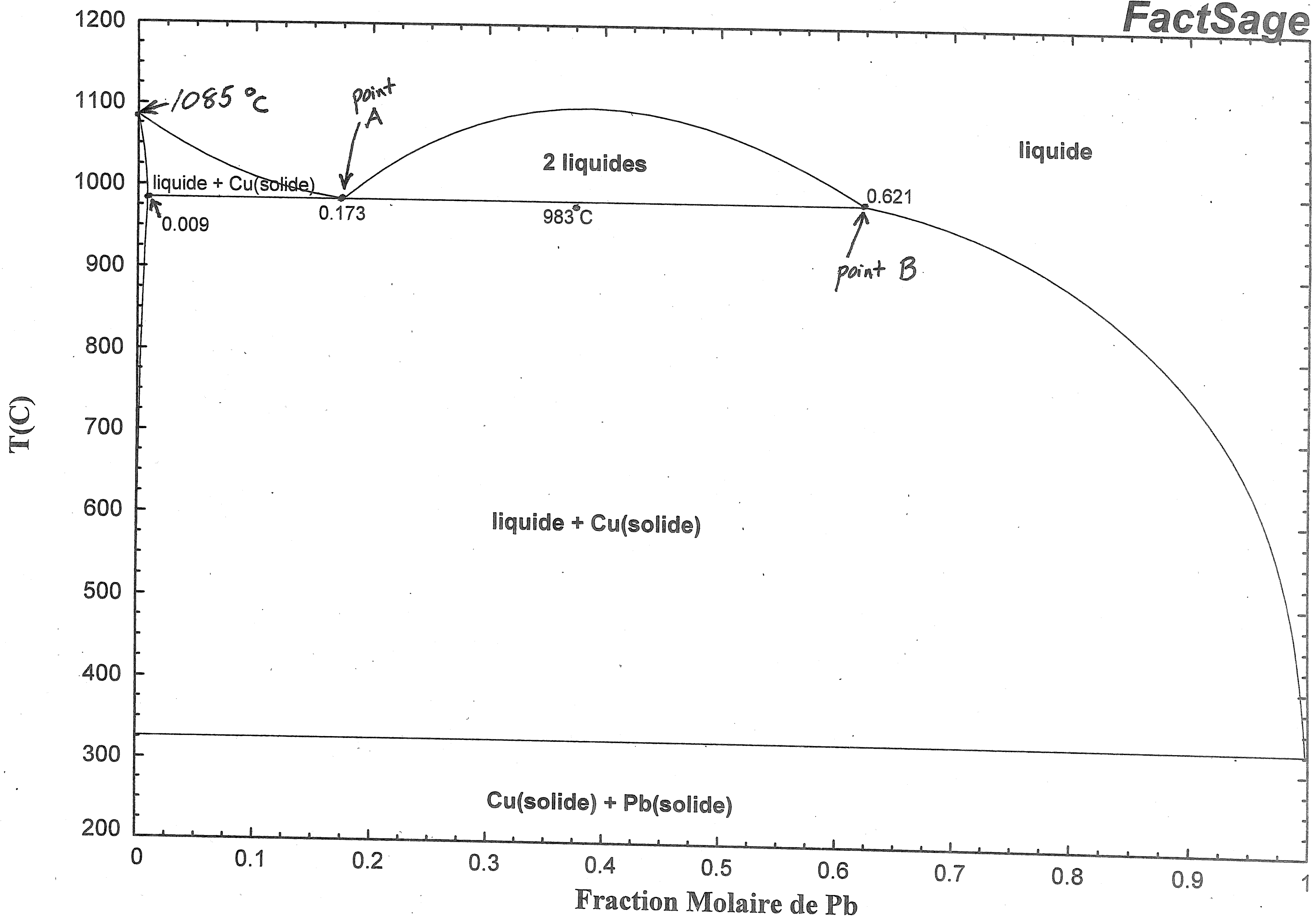


Figure 4

Question 7:

Treat the components of the system as $Fe-Cr-O_2-SO_2$

$\underline{q_i}$	$\underline{\Phi_i}$
S	$\underline{T}$
$-V$	$\underline{P}$
$\underline{n_{Cr}}$	μ_{Cr}
$\underline{n_{Fe}}$	μ_{Fe}
n_{O_2}	$\underline{\mu_{O_2}}$
n_{SO_2}	$\underline{\mu_{SO_2}}$

Choose one variable from each pair as shown by underlines

Set Size of system $= n_{Fe}$

Normalize extensive variables: (n_{Cr}/n_{Fe})

Final list of variables: $T, P, (n_{Cr}/n_{Fe}), \mu_{O_2}, \mu_{SO_2}$

At constant T: $\begin{cases} \mu_{O_2} = \mu^{\circ}_{O_2} + RT\ln p_{O_2} \\ \mu_{SO_2} = \mu^{\circ}_{SO_2} + RT\ln p_{SO_2} \end{cases}$

Set; T, P, p_{O_2} constant

Plot: p_{SO_2} versus (n_{Cr}/n_{Fe})

Therefore, all the rules are obeyed and the diagram $\underline{\text{is}}$ a true single-valued section