

Question 1:

Consider a closed system at constant volume composed of a very large number N of distinguishable subsystem which do not interact with each other upon forming the larger system. The subsystem can be only be in one of two energy states: $E = 0$, or $E = \epsilon$.

- What is the maximum possible value of the energy per subsystem (E_{tot}/N) when the system is in equilibrium (at any thermodynamic condition) ?
- In this condition of maximum energy, what is the entropy of the systems (S_{tot}/N) ?
- Sketch the heat capacity ^{c_v} of the system as function of temperature. Pay particular attention to limiting values (e.g. what is the value of the heat capacity at $T = 0$ and how is that value approached; value at high temperature, etc.)

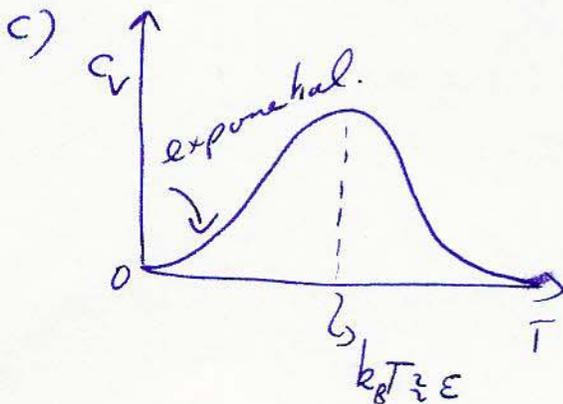
$$a) P_0 = P_\epsilon = \frac{1}{2} \rightarrow \text{high } T \text{ limit} \Rightarrow E_{max}/N = \epsilon/2$$

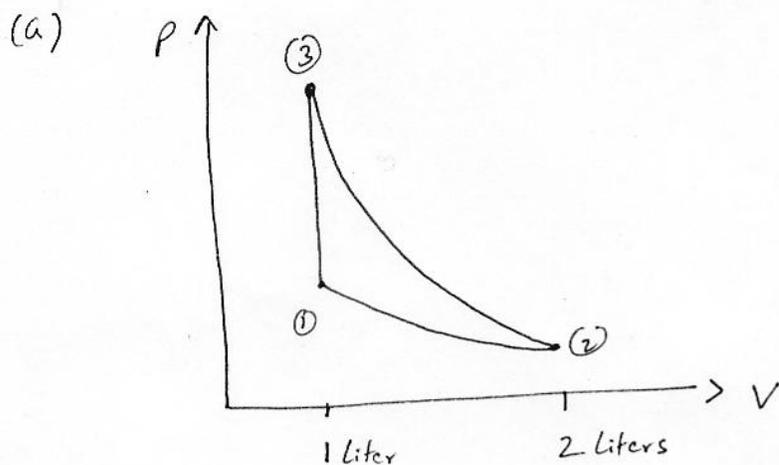
$$b) \text{ Entropy per subsystem} = k_B \ln 2 \rightarrow S_{tot}/N = k_B \ln 2$$

$$\text{or think of} \rightarrow \Omega = \binom{N}{N/2} \rightarrow \Omega \text{ for total system}$$

$$\begin{aligned} \frac{S}{k_B} &= \frac{N!}{N/2! N/2!} = N \ln N - N - N/2 \ln N/2 - N/2 \ln N/2 + \cancel{N/2} + \cancel{N/2} \\ &= N [\ln N - \ln N/2] = N \ln 2 \end{aligned}$$

$$S_{tot}/N = k_B \ln 2$$





(b) $V_1 = 1\text{L} = 10^{-3}\text{m}^3$
 $T_1 = 800\text{K}$

$$\Rightarrow P_1 = \frac{nRT_1}{V_1} = \frac{1 \times 8.314 \times 800}{10^{-3}} = 6.69 \times 10^6 \text{ Pa} = 66 \text{ atm}$$

$$V_2 = 2\text{L} = 2 \times 10^{-3}\text{m}^3$$

$$T_2 = 800\text{K}$$

$$\Rightarrow P_2 = \frac{nRT_2}{V_2} = \frac{1 \times 8.314 \times 800}{2 \times 10^{-3}} = 3.34 \times 10^6 \text{ Pa} = 33 \text{ atm}$$

$$V_3 = 1\text{L} = 1 \times 10^{-3}\text{m}^3$$

$$T_3 = ?$$

$$P_3 = ?$$

For $2 \rightarrow 3$, the path is adiabatic

$$\therefore dU = \delta Q + \delta W = \delta W \quad \Rightarrow \quad dU = -PdV$$

$\delta Q = 0$

For an ideal gas, $dU = nC_v dT$

$$\Rightarrow nC_v dT = -PdV$$

$$nC_v dT = -\frac{nRT}{V} dV$$

$$\frac{C_V}{R} \frac{dT}{T} = - \frac{dV}{V}$$

$$\Rightarrow \frac{C_V}{R} \ln \frac{T_3}{T_2} = \ln \frac{V_2}{V_3} \quad \text{for } 2 \rightarrow 3$$

$$\text{or } \left(\frac{T_3}{T_2} \right)^{C_V/R} = \frac{V_2}{V_3}$$

$$\left(\frac{T_3}{800} \right)^{C_V/R} = \frac{2}{1}$$

$$\text{Now } \frac{C_V}{R} = \frac{\frac{5}{2} R}{R} = \frac{5}{2}$$

$$\Rightarrow T_3 = (2)^{2/5} \times 800 \Rightarrow T_3 = 1056 \text{ K}$$

$$P_3 = \frac{nRT_3}{V_3} = \frac{1 \times 8.314 \times 1056}{10^{-3}} = \del{8.78 \times 10^6} \text{ Pa} = 86.6 \text{ atm}$$

Summary:

①	$P_1 = 66 \text{ atm}$	$T_1 = 800 \text{ K}$	$V_1 = 1 \text{ L}$
②	$P_2 = 33 \text{ atm}$	$T_2 = 800 \text{ K}$	$V_2 = 2 \text{ L}$
③	$P_3 = 86.6 \text{ atm}$	$T_3 = 1056 \text{ K}$	$V_3 = 1 \text{ L}$

$$(c) \quad dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP = \frac{nC_p dT}{T} - nR \frac{dP}{P}$$

work: ~~isobaric~~ (Note: $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} dP$)

$$1 \rightarrow 2: \quad \underline{\Delta S_{1 \rightarrow 2}} = -nR \ln \frac{P_2}{P_1} = nR \ln 2 = \underline{5.76 \text{ J/K}}$$

$$2 \rightarrow 3: \quad \underline{\Delta S_{2 \rightarrow 3}} = 0 \quad \text{since the process is adiabatic}$$

$$3 \rightarrow 1: \quad \underline{\Delta S_{3 \rightarrow 1}} = -nR \ln 2 = \underline{-5.76 \text{ J/K}}$$

↓
 (because the path is circular,
 $\Delta S_{1 \rightarrow 2} + \Delta S_{2 \rightarrow 3} + \Delta S_{3 \rightarrow 1}$ must be = 0)

(d) If the compression is irreversible but still adiabatic, more work would have to be put in

$$\Rightarrow \Delta U_{\text{irrev}} > \Delta U_{\text{rev}}$$

⇓ (for ideal gas)

$$T_{\text{irrev}} > T_{\text{rev}} \Rightarrow$$

$$\boxed{P_{\text{irrev}} > P_{\text{rev}}}$$

3.20 FALL 2002

FINAL EXAM SOLUTION PROBLEM 3

$$dF = -SdT - PdV \quad - (1)$$

$$dF = \left(\frac{\partial F}{\partial P}\right)_T dP + \left(\frac{\partial F}{\partial T}\right)_P dT \quad - (2)$$

comparing (1) and (2)

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

Need $\left(\frac{\partial F}{\partial P}\right)_T$ and $\left(\frac{\partial F}{\partial T}\right)_P$

$$\begin{aligned} \left(\frac{\partial F}{\partial T}\right)_P &= \left(\frac{\partial F}{\partial T}\right)_V + \left(\frac{\partial F}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \\ &= -S + (-P)(V\alpha_V) \\ &= -S - PV\alpha_V \end{aligned}$$

$$\left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial F}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = (-P)(-V/\beta_T) = \underline{PV/\beta_T}$$

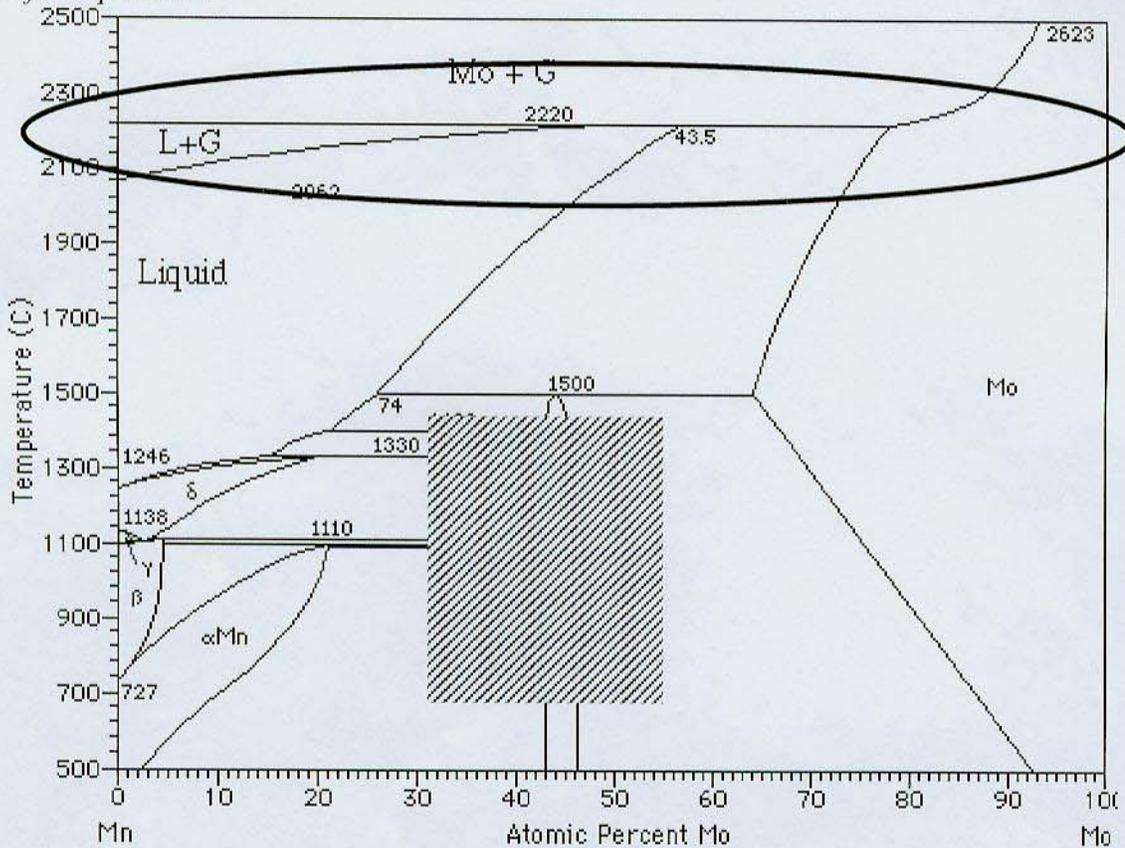
$$\Rightarrow dF = (-S - PV\alpha_V)dT + (PV/\beta_T)dP$$

Question 4:

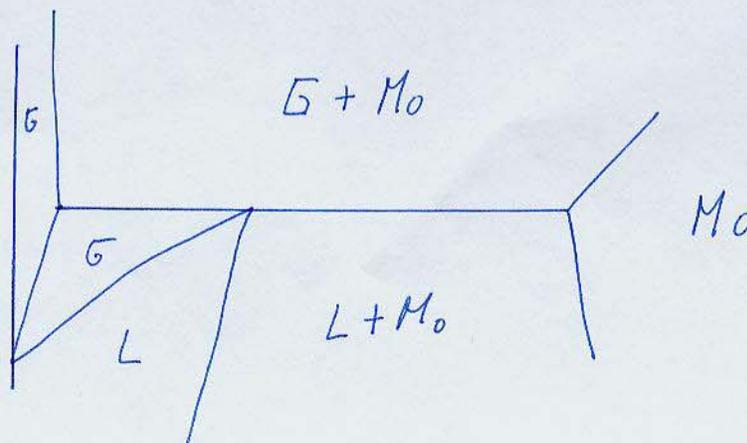
Do not draw more than one solution. Clearly specify your answer

Below is the Mn-Mo phase diagram.

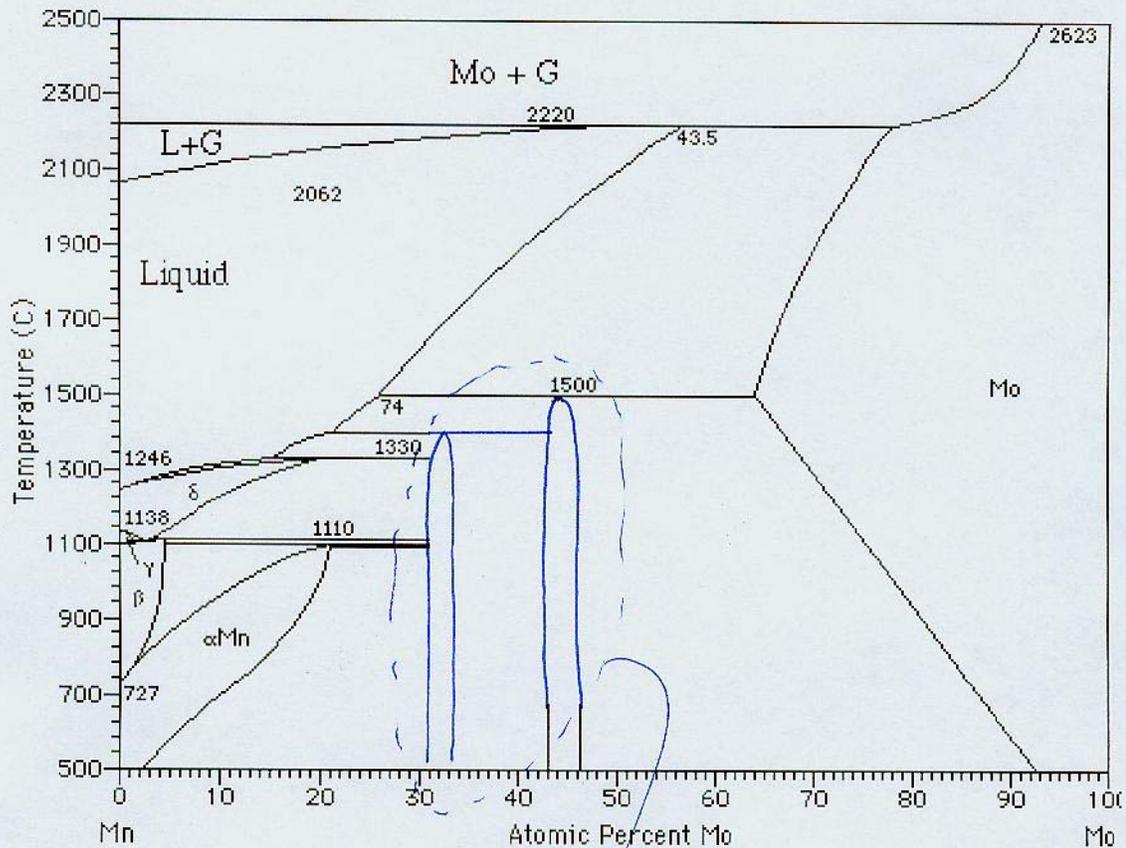
a) The phase boundaries in the area that is circled (near 2220°C) are somewhat unclear. Please draw a possible (but thermodynamically correct) solution for the three-phase equilibria near 2220°C showing clearly how all single phase regions connect to the invariant three-phase equilibrium. If necessary, exaggerate the width of single phase regions. Please do not draw on the phase diagram, but make a clear drawing below. You do not need to draw the complete phase diagram, only the relevant section involving Mo, G and L near 2220°C. Do not yet worry about the hashed rectangle, which is for part b of the question.



A Solution



b) Your advisor spilled beer over part of the phase diagram, and as a result the region that is hashed on the previous page became illegible. On the diagram, below, please sketch a plausible solution for the missing region.



A possible solution
 Note that every invariant
 (horizontal line) needs to
 involve a three-phase
 reaction.

Question 5:

$Y_2O_3-ZrO_2$ is a material of interest for sensors and solid oxide fuel cells. At the relevant temperature and composition range ZrO_2 forms a simple fluorite structure with an fcc array of Zr cations, and the oxygen ions occupying all the tetrahedral interstitials of this array.

As Y_2O_3 is added to ZrO_2 , the Y cations substitute on the Zr sublattice. For charge compensation reasons, a vacancy needs to exist on the oxygen sublattice for each 2 Y cations added

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a) Assuming an ideal solution of Y and Zr on the cation sublattice, and oxygen and vacancies on the anion sublattice, write down the entropy of mixing as function of the mole fraction of Y cations on the cation sublattice.

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b) In the real material, oxygen vacancies may be attracted to the Y cation, for electrostatic reasons or due to size effects. Describe how the entropy in part a) will change when such attractive interaction occurs.

Zr sublattice \rightarrow standard B-W $\left[X_Y \ln X_Y + (1-X_Y) \ln(1-X_Y) \right]$
 O sublattice \rightarrow $2N$ sites, $\frac{N_Y}{2}$ vacancies, $(2N - \frac{N_Y}{2})$ oxygen

$$\begin{aligned} \ln \frac{2N!}{\left(\frac{N_Y}{2}\right)! \left(2N - \frac{N_Y}{2}\right)!} &= 2N \ln 2N - \frac{N_Y}{2} \ln \frac{N_Y}{2} + \frac{N_Y}{2} - \left(2N - \frac{N_Y}{2}\right) \ln \left(2N - \frac{N_Y}{2}\right) + 2N - \frac{N_Y}{2} \\ &= \frac{N_Y}{2} \ln 2N + \left(2N - \frac{N_Y}{2}\right) \ln 2N - \frac{N_Y}{2} \ln \frac{N_Y}{2} - \left(2N - \frac{N_Y}{2}\right) \ln \left(2N - \frac{N_Y}{2}\right) \\ &= \frac{N_Y}{2} \ln \frac{4N}{N_Y} + \left(2N - \frac{N_Y}{2}\right) \ln \frac{2N}{2N - \frac{N_Y}{2}} \\ &= \frac{N_Y}{2} \ln \frac{4}{X_Y} + \left(2N - \frac{N_Y}{2}\right) \ln \frac{1}{1 - \frac{N_Y}{4N}} \\ &= - \left[\frac{N_Y}{2} \ln \frac{X_Y}{4} + \left(2N - \frac{N_Y}{2}\right) \ln \left(1 - \frac{X_Y}{4}\right) \right] \end{aligned}$$

divide by $2N$

$$- \left[\frac{X_Y}{4} \ln \frac{X_Y}{4} + \left(1 - \frac{X_Y}{4}\right) \ln \left(1 - \frac{X_Y}{4}\right) \right]$$

b. goes down

QUESTION 6

• AT CONSTANT T, P , THE HEAT THAT EVOLVES DURING A CHANGE OF STATE IS EQUAL TO THE CHANGE OF THE ENTHALPY BETWEEN THE FINAL & INITIAL STATE.

• THE FINAL STATE IS A SOLID SOLUTION ON THE FCC LATTICE BUT PURE A AT 1200 K IS A LIQUID

• THEREFORE, FIRST NEED ENTHALPY DIFFERENCE BETWEEN THE SOLID & LIQUID STATE OF PURE A AT 1200 K

$$* \quad \frac{\Delta H^{l \rightarrow s}}{\text{mole}} \text{ of } A_{1200, \text{liquid}} \rightarrow A_{1200, \text{solid}} = -\left(\Delta H_{\text{melt}}^{l \rightarrow s}(1750) + \int_{1750}^{1200} \Delta C_p^{s \rightarrow l} dT \right)$$

$\Delta C_p^{s \rightarrow l} = 0$ for pure A

$$\Rightarrow \frac{\Delta H^{l \rightarrow s}}{\text{mole}} = -4 \text{ kJ/mole}$$

$$3 \text{ mole of A} \Rightarrow \Delta H^{l \rightarrow s} = -12 \text{ kJ}$$

* ENTHALPY CHANGE UPON MIXING SOLID A & SOLID B

$$\frac{\Delta H_{\text{mix}}}{\text{mole}} = X_A X_B (-12600) = (0.3)(0.7)(-12600) = -2646 \text{ J/mol}$$

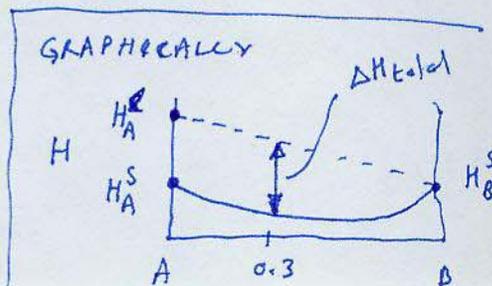
a total of 10 moles

$$\Rightarrow \Delta H_{\text{mix}} = 10(-2646) = -26460 \text{ J} = -26.460 \text{ kJ}$$

$$Q = \Delta H_{\text{total}} = -12 \text{ kJ} - 26.460 \text{ kJ}$$

$$= -38.46 \text{ kJ}$$

or -38.46 kJ of heat is released upon mixing



$$ds = \frac{1}{T} du + \frac{p}{T} dv$$

Question 7 (Short questions):

a) Define the Legendre transform of the **entropy** that gives a function with natural variables $1/T$ and p/T .

b) A material (closed system) at constant pressure undergoes a reversible phase transition with temperature at $T = T_0$. Please indicate whether the following statements are always true, true only part of the time, or never true.

At the phase transition temperature the high temperature phase has a higher volume than the low-temperature phase:

NEVER TRUE ALWAYS TRUE TRUE PART OF THE TIME

At the phase transition temperature T_0 , the high temperature phase has a higher entropy than the low-temperature phase:

NEVER TRUE ALWAYS TRUE TRUE PART OF THE TIME

At the phase transition temperature T_0 the high temperature phase has a higher enthalpy than the low-temperature phase:

NEVER TRUE ALWAYS TRUE TRUE PART OF THE TIME

At the phase transition temperature T_0 the high temperature phase has a higher Gibbs free energy than the low-temperature phase:

NEVER TRUE ALWAYS TRUE TRUE PART OF THE TIME

c) A metal always has a higher electronic entropy than an oxide

TRUE FALSE

d) For a system with only pdV work, in an environment under constant pressure and temperature, the condition that $\Delta S_{\text{universe}} > 0$ is equivalent to:

_____ $\Delta G > 0$ ~~_____ $\Delta G < 0$~~ _____ $\Delta H < 0$ _____ $\Delta H > 0$ _____ $\Delta S < 0$
_____ $\Delta S > 0$

In the above, the state functions (G, H, S) refer to properties of the system.

e) At constant composition, does the free energy increase or decrease with increasing temperature?

_____ INCREASE ~~_____ DECREASE~~

QUESTION 8

a) ~~$\frac{1}{Z_A}$~~ Energy spectrum of a harmonic oscillator

$$E_n = (n + \frac{1}{2}) h\nu$$

$$\frac{q_A^\lambda}{Z_A} = \sum_{n=0}^{\infty} e^{-\beta h\nu(n + \frac{1}{2})} = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \quad \text{with } \nu = \frac{v_A^\lambda}{A}$$

↑
geometric series

b) Free energy for α -phase (pure A, all atoms are NON-INTERACTING) AND LOCALISED ON A LATTICE

$$Q_\alpha = \left(\frac{q_A^\lambda}{Z_A}\right)^{N_A^\lambda}$$

N_A^λ = total number of A atoms in α

$$F_\alpha = -kT \ln Q_\alpha$$

(remember, α only has A atoms)

$$= -N_A^\lambda kT \ln \frac{q_A^\lambda}{Z_A}$$

Free energy for β -phase

$$Q_\beta = \frac{N^\beta!}{(N_A^\beta!)(N_B^\beta!)} \left(\frac{q_A^\beta}{Z_A}\right)^{N_A^\beta} \left(\frac{q_B^\beta}{Z_B}\right)^{N_B^\beta}$$

N^β = total number of atoms in β

N_A^β = # of A atoms in β

N_B^β = # of B atoms in β

→ arises due to configurational degrees of freedom

$$G_\beta = -kT \ln Q_\beta$$

$$= -N_A^\beta kT \ln \frac{q_A^\beta}{Z_A} - N_B^\beta kT \ln \frac{q_B^\beta}{Z_B} + N^\beta kT \{x_A \ln x_A + x_B \ln x_B\}$$

$$\left\{ \begin{aligned} x_A &= \frac{N_A^\beta}{N^\beta} \\ x_B &= \frac{N_B^\beta}{N^\beta} \end{aligned} \right.$$

QUESTION 8 CONTINUED

c) Solubility ~~of~~ limit of A in β

comes from 2-phase equilibrium between α & β

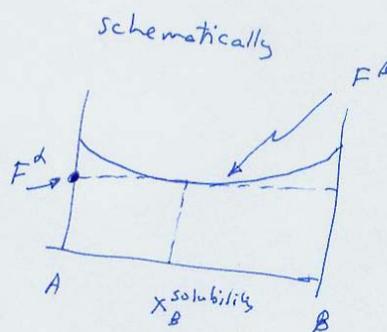
α	β
pure A	mixture of A & B

Equilibrium: $\mu_A^\alpha = \mu_A^\beta$

$$\mu_A^\alpha = \frac{\partial F^\alpha}{\partial N_A^\alpha} = -kT \ln q_A^\alpha$$

$$\mu_A^\beta = \frac{\partial F^\beta}{\partial N_A^\beta} = -kT \ln q_A^\beta + kT \ln X_A^\beta$$

$$X_A^{\beta \text{ solubility}} = \left(\frac{q_A^\beta}{q_A^\alpha} \right)$$



(NOTICE SIMILARITY TO $\mu_A^\beta + kT \ln X_A^\beta$)