ME-351 THERMODYNAMICS AND ENERGETICS II

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NAME : Solutions

SCIPER :

Question	Points	Score
1	10	
2	10	
3	10	
4	15	
5	15	
6	10	
7	15	
8	15	
Total:	100	

Answer the questions in the space provided. Please ensure you show all your work and your answers are legible. If you need additional space, continue on the back of the page. You have 3 hours to complete the exam. **Good Luck!**

Difficult to remember formulas

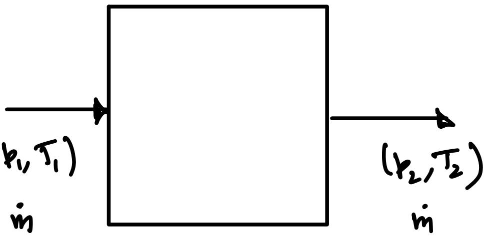
1. Reciprocal Rule : $\left(\frac{\partial x}{\partial y}\right) = \frac{1}{\left(\frac{\partial y}{\partial x}\right)}$
2. Cyclical Relation : $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$
3. Chain Rule : $\left(\frac{\partial x}{\partial z}\right)_\phi = \left(\frac{\partial x}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial z}\right)_\phi$
4. $\left(\frac{\partial x}{\partial \phi}\right)_z = \left(\frac{\partial x}{\partial \phi}\right)_y + \left(\frac{\partial x}{\partial y}\right)_\phi \left(\frac{\partial y}{\partial \phi}\right)_z$
5. Maxwell relations : $\left(\frac{\partial A}{\partial B}\right)_{\text{conjugate}(A)} = \pm \left(\frac{\partial(\text{conjugate}(B))}{\partial(\text{conjugate}(A))}\right)_B$

1. An engine is extracting work from an ideal gas in a steady state process. The gas enters the engine at a temperature and pressure of T_1, p_1 and exits from the engine at T_2, p_2. The inlet and outlet temperatures and pressure are such that $T_1 > T_2$ and $p_1 > p_2$. The gas flow rate into the engine is $\dot{m}$. The engine is adiabatically insulated from the environment.
   (a) (2 points) What is the rate of entropy change for the engine?
   (b) (6 points) What is the entropy change per mole of the gas?
   (c) (2 points) What is the rate of entropy change for the universe? You can ignore any entropy generated during the production of the steam.

   Heat capacity of one mole of an ideal gas is $C_p = \frac{5}{2}R$, $C_V = \frac{3}{2}R$

(a) Engine does not change and is adiabatic $\Rightarrow \Delta\dot{S}_{engine} = 0$

(b)



$$S(T,p) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp.$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \; ; \; \left(\frac{\partial S}{\partial p}\right)_T = \, ?$$

Consider: $du = TdS - pdV$

$dG = Vdp - SdT$ $[\because G = u - TS + pV]$

$\Rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$

for 1 mole of an ideal gas.

$pV = RT \Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$

$$dS = \frac{C_p}{T}dT - \frac{R}{p}dp$$

$$\Delta S = \int_{(p_1,T_1)}^{(p_2,T_2)} dS = \int_{T_1}^{T_2} \frac{C_p}{T}dT - \int_{p_1}^{p_2} \frac{R}{p}dp = C_p \log(T_2/T_1) - R\log(p_2/p_1) = R\left[\log\left[\left(\frac{T_2}{T_1}\right)^{5/2}\left(\frac{p_1}{p_2}\right)\right]\right]$$

for 1 mole.

$$\Delta\dot{S}_{gas} = R\dot{m}\log\left[\left(T_2/T_1\right)^{5/2}\left(\frac{p_1}{p_2}\right)\right]$$

c) $\Delta\dot{S}_{universe} = \Delta\dot{S}_{engine} + \Delta\dot{S}_{gas} = \Delta\dot{S}_{gas}$

2. A system has its characteristic potential given by:

$$\Lambda = C\frac{S^3 p}{N_A N_B}$$

where S, p, N_A, N_B are the entropy, pressure, number of A atoms, and number of B atoms respectively. C is a constant.

(a) (3 points) What are the natural variables of the characteristic potential? Express the characteristic potential as a Legendre transform of the internal energy

(b) (4 points) Compute all equations of state for the characteristic potential

(c) (3 points) Are the equations of state extensive or intensive? Justify your answer with mathematical arguments.

(a) Natural variables of $\Lambda(S, p, N_A, N_B)$

$$\Lambda = U + pV$$

(b) $d\Lambda = Vdp + TdS + \mu_A dN_A + \mu_B dN_B$

$$\left(\frac{\partial \Lambda}{\partial p}\right)_{S,N_A,N_B} = V = \frac{CS^3}{N_A N_B} \quad \text{—} ①$$

$$T = \left(\frac{\partial \Lambda}{\partial S}\right)_{p,N_A,N_B} = \frac{3CpS^2}{N_A N_B} \quad \text{—} ②$$

③

$$\left(\frac{\partial \Lambda}{\partial N_A}\right)_{S,p,N_B} = -\frac{CpS^3}{N_A^2 N_B} = \mu_A$$

$$\left(\frac{\partial \Lambda}{\partial N_B}\right)_{S,p,N_A} = -\frac{CpS^3}{N_B^2 N_A} = \mu_B$$

④

(c) ②, ③, ④ $\longrightarrow$ Intensive

① $\longrightarrow$ Extensive.

3. (a) (6 points) Derive the equilibrium criteria for two-phase coexistence (say between an α and β phase) in a binary A-B alloy at constant temperature, and pressure. The total number of A and B atoms, N_A and N_B are constant.

   (b) (4 points) Show that the chemical potential of A is equal to $\mu_A = G_m + (1 - x_A)\frac{\partial G_m}{\partial x_A}$, where $G_m = G/(N_A + N_B)$

a) Consider a system @ constant (T, p, N_A, N_B)

The characteristic potential is $G(T, p, N_A, N_B) = U - TS + pV$ ⇒ equilibrium is achieved when G is minimized

let there be 2-phases in the system: α & β

$G_{system} = G_\alpha + G_\beta$ → we have to minimize this to find equilibrium.

$dG_{system} = 0$ @ the minimum.

$$\Rightarrow \boxed{dG_\alpha + dG_\beta = 0} \text{ — ①}$$

$G = U - TS + pV \Rightarrow dG = dU - TdS - SdT + pdV + Vdp$

The fundamental equation of thermodynamics ⇒ $dU = TdS - pdV + \sum_i \mu_i dN_i$

$$\boxed{dG = Vdp - SdT + \sum_i \mu_i dN_i}$$

$$dG^\alpha = V^\alpha dp - S^\alpha dT + \sum_i \mu_i^\alpha dN_i^\alpha \text{ ②} \quad ; \quad dG^\beta = V^\beta dp - S^\beta dT + \sum_i \mu_i^\beta dN_i \text{ ③}$$

We are at constant T & p → drop the temperature & pressure terms

Substituting equations ②, ③ in ①

$$\Rightarrow \sum_i \mu_i^\alpha dN_i^\alpha + \sum_i \mu_i^\beta dN_i^\beta = 0$$

Mass conservation ⇒ $N_i^\alpha + N_i^\beta = N_i$

$$\Rightarrow dN_i^\alpha = -dN_i^\beta$$

$$\Rightarrow dG = \sum_i (\mu_i^\alpha - \mu_i^\beta) dN_i^\alpha = 0$$

$$\boxed{\text{At equilibrium } \mu_i^\alpha = \mu_i^\beta}$$

b) $dG = Vdp - SdT + \mu_A dN_A + \mu_B dN_B$

$$\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{p,T,N_B}$$

$$G^M = \frac{G}{N_A+N_B} \Rightarrow G = G^m (N_A + N_B)$$

$$\mu_A = \frac{\partial}{\partial N_A}\left(G^m (N_A+N_B)\right) = G_m + (N_A+N_B)\frac{\partial G_m}{\partial N_A} = G_m + (N_A+N_B)\left(\frac{\partial G_m}{\partial x_A}\right)_{T,p,N_B}\left(\frac{\partial x_A}{\partial N_A}\right)_{T,p,N_B}$$

$$\left(\frac{\partial x_A}{\partial N_A}\right)_{T,p,N_B} = \left[\frac{\partial}{\partial N_A}\left(N_A/N_A+N_B\right)\right]_{T,p,N_B} = \frac{1}{N_A+N_B} - \frac{N_A}{(N_A+N_B)^2} = \frac{1-x_A}{N_A+N_B}$$

$$\mu_A = G_m + \cancel{(N_A+N_B)} \times \frac{(1-x_A)}{\cancel{N_A+N_B}}\left(\frac{\partial G_m}{\partial x_A}\right) = G_m + (1-x_A)\left(\frac{\partial G_m}{\partial x_A}\right)_{T,p,N_B}$$

4. The phase diagram for a binary A-B alloy is shown in fig. 1

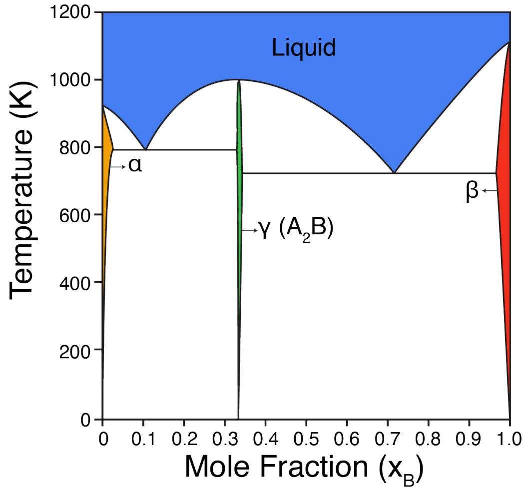
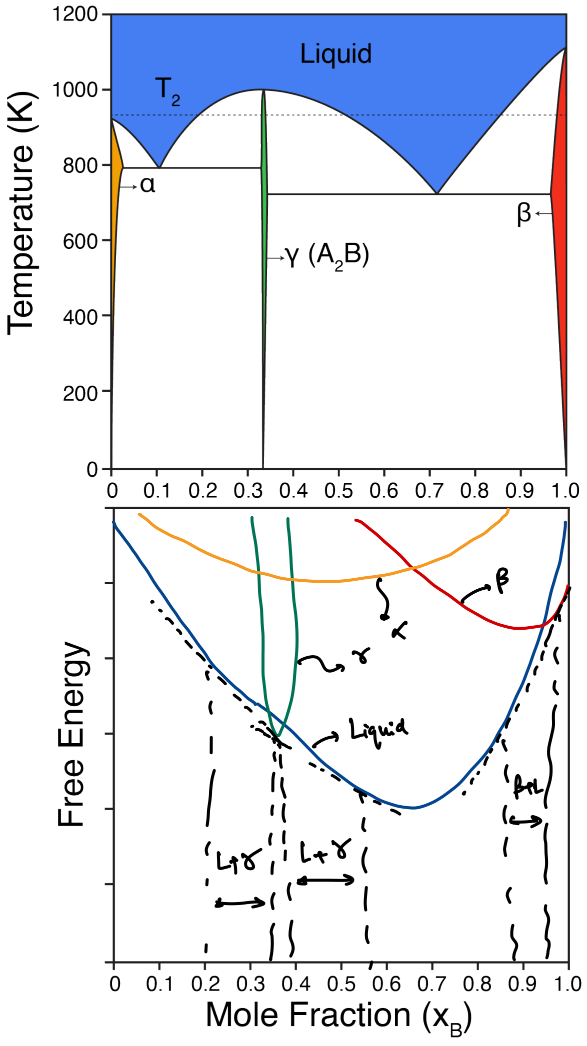
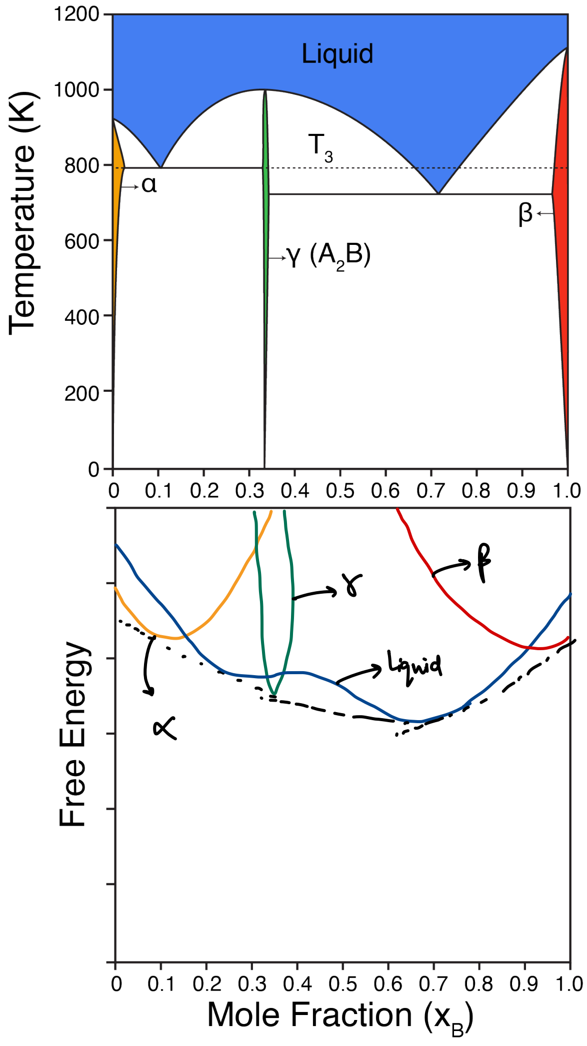


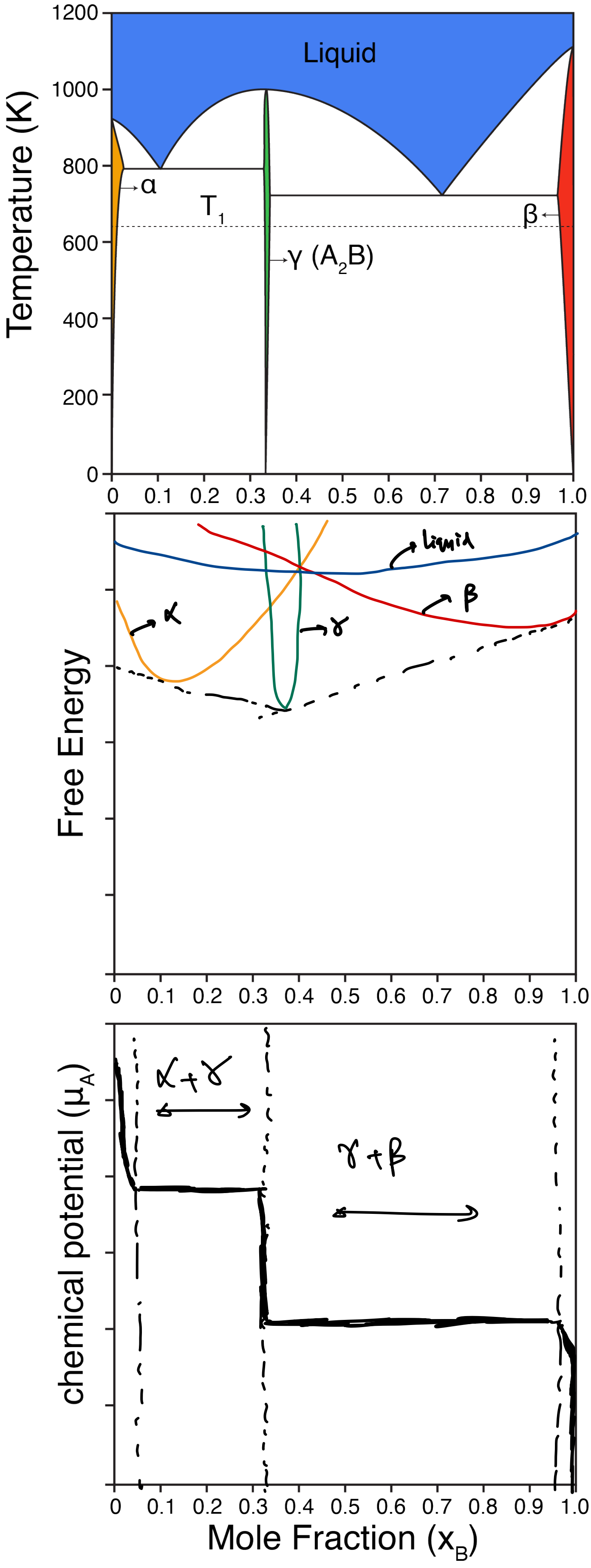
Figure 1

(a) (2 points) Consider an alloy with 50% A. If this alloy is held at 800K, which phases are present and what is their composition?

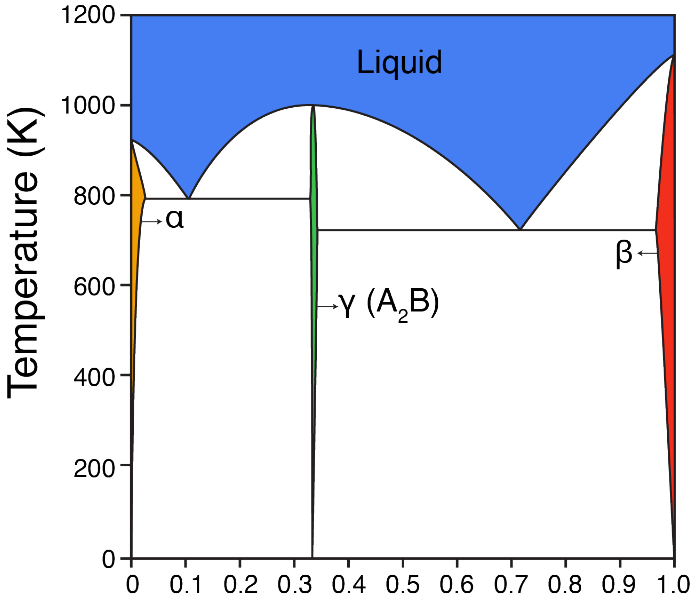
(b) (9 points) Sketch the free energies and chemical potentials of all the phases on the phase diagram at the indicated temperatures. Pay attention to the slopes, tangents, intercepts etc.

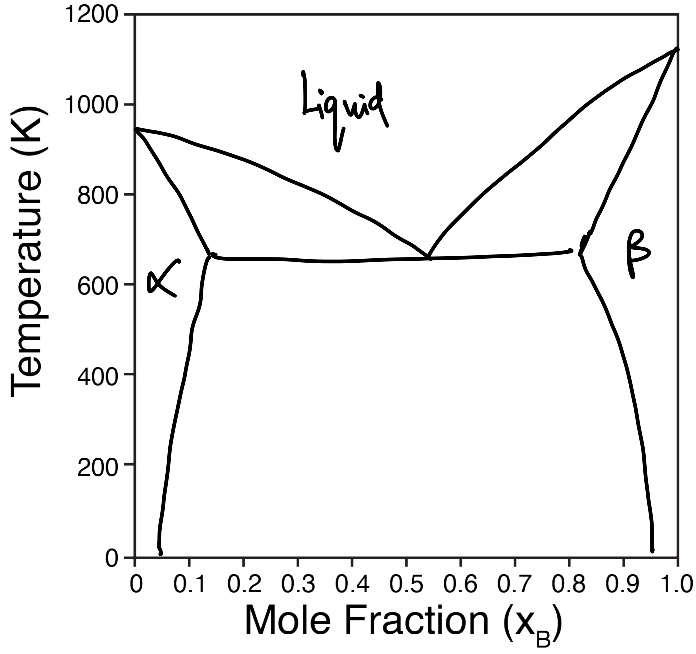





1200
1000
800
600
400
200
0
Temperature (K)
Liquid
α
T_1
γ (A_2B)
β
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Free Energy
liquid
β
α
γ
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
chemical potential (μ_A)
α + γ
γ + β
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0
Mole Fraction (x_B)

(c) (4 points) Schematically draw the phase diagram if the γ (A_2B) phase is prevented from forming.





5. A rod of length l and surface area A is stretched as shown in fig. 3.

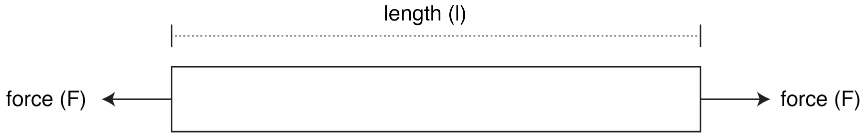


Figure 3

(a) (4 points) Write down an expression for the characteristic potential of the rod as a Legendre transform of the internal energy when the rod is placed in an isothermal environment. What is the characteristic potential when the rod is maintained in an isentropic environment?

(b) (8 points) The Young's modulus of the material is defined as $l\left(\frac{\partial \sigma}{\partial l}\right)$. Relate the isothermal Youngs modulus to the isentropic Young's modulus. Express your answer in terms of "well-known" material properties such as the thermal expansion, compressibility, and heat capacities of the material.

(c) (3 points) Based on the expression you derived in the previous part of the question, which of the modulii would you expect to be larger - the isentropic or isothermal modulus?

(a) Isothermal environment: constant $T, f \Rightarrow$ Characteristic potential $\Lambda = U - TS - fL$

Isentropic environment: constant $S, f \Rightarrow$ characteristic potential $\Theta = U - fL$

(b) $\sigma = f/A \Rightarrow Y =$ Youngs Modulus $= L\left(\frac{\partial \sigma}{\partial L}\right) = \frac{L}{A}\left(\frac{\partial f}{\partial L}\right)$

$Y_T =$ isothermal Youngs Modulus; $Y_S =$ isentropic Youngs Modulus.

$$d\Lambda = -S\,dT - L\,df \Rightarrow \left(\frac{\partial L}{\partial f}\right)_T = -\left(\frac{\partial^2 \Lambda}{\partial f^2}\right)_T = \left(Y_T A/L\right)^{-1}$$

$$d\Theta = T\,dS - L\,df$$

$$\Rightarrow \left(\frac{\partial L}{\partial f}\right)_S = -\left(\frac{\partial^2 \Theta}{\partial f^2}\right)_S = \left(\frac{Y_S A}{L}\right)^{-1}$$

Consider:

$$dL = \left(\frac{\partial L}{\partial f}\right)_T df + \left(\frac{\partial L}{\partial T}\right)_F dT$$

$$\Rightarrow \left(\frac{\partial L}{\partial f}\right)_S = \underbrace{\left(\frac{\partial L}{\partial f}\right)_T}_{\downarrow\ \left(Y_T A/L\right)^{-1}} + \underbrace{\left(\frac{\partial L}{\partial T}\right)_f}_{\text{Thermal expansion coefficient.}} \overbrace{\left(\frac{\partial T}{\partial f}\right)_S}^{\to \text{ we need to simplify this term.}}$$

$$\alpha_f = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_f$$

$$\left(\frac{\partial T}{\partial f}\right)_S \left(\frac{\partial S}{\partial T}\right)_f \left(\frac{\partial f}{\partial S}\right)_T = -1$$

$$\Rightarrow \left(\frac{\partial T}{\partial f}\right)_S = \frac{-\left(\frac{\partial S}{\partial f}\right)_T}{\underbrace{\left(\frac{\partial S}{\partial T}\right)_f}_{\hookrightarrow C_f/T \text{ (heat capacity)}}}$$

$$\left(\frac{\partial S}{\partial f}\right)_T = \left(\frac{\partial L}{\partial T}\right)_f = \alpha_f L \left[\text{from Maxwell relation on } \Lambda\right]$$

$$\left(\frac{\partial L}{\partial f}\right)_S = \left(\frac{Y_S A}{L}\right)^{-1} = \left(\frac{Y_T A}{L}\right)^{-1} + \alpha_f L \times \left(-\frac{\alpha_f L}{C_f/T}\right)$$

$$\Rightarrow \frac{L}{AY_S} = \frac{L}{AY_T} - \frac{L^2 \alpha_f^2 T}{C_f}$$

$$\Rightarrow \boxed{\frac{1}{Y_S} = \frac{1}{Y_T} - \frac{LA\alpha_f^2 T}{C_f}}$$

$$\Rightarrow \boxed{\frac{LA\alpha_f^2 T}{C_f} = \frac{1}{Y_T} - \frac{1}{Y_S}}$$

(c) L, A, α_f^2, T, C_f are all positive numbers.

$$\Rightarrow \frac{1}{Y_T} - \frac{1}{Y_S} > 0$$

$$\Rightarrow \boxed{Y_S > Y_T}$$

6. (10 points) A colleague has asked you to verify a phase diagram (fig. 4) that they constructed based on some experiments that they conducted on a metal substrate. The metal substrate was exposed to a gaseous environment of oxygen and your collaborator ran a series of experiments to construct the phase diagram shown in fig. 4. The α phase is found to be a *disordered* phase where that oxygen atoms are randomly distributed on the surface of the metal while the β phase is an ordered phase comprising of a well-defined arrangement of oxygen atoms on the surface of the metal. You also know that the ordered β phase is not tolerant to any defects - leading to very high energies for any arrangement other than the ordered state. Could the phase diagram in fig. 4 be correct? Justify your answer with thermodynamic arguments.

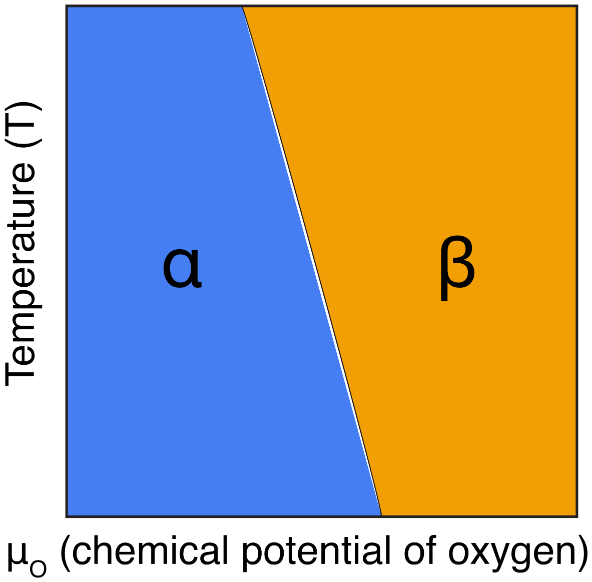


Figure 4

Experimentally controlled parameters:

(T, μ_0)

Characteristic potential under these boundary conditions:

$$\Lambda(T,\mu_0) = U - TS - \mu_0 N_0 \Rightarrow d\Lambda = -S\,dT - N_0\,d\mu_0$$

Clausius-Clapeyron relation under these conditions:

$$\Lambda^\alpha(T^*, \mu_0^*) = \Lambda^\beta(T^*, \mu_0^*) \longrightarrow$$ Note: T^*, μ_0^* is the phase transition temperature and chemical potential.

$$\Rightarrow -S^\alpha dT^* - N_0^\alpha d\mu_0^* = -S^\beta dT^* - N_0^\beta d\mu_0^*$$

$$\Rightarrow dT^*(S^\beta - S^\alpha) = -d\mu_0^*(N_0^\beta - N^\alpha) \Rightarrow \boxed{\frac{dT^*}{d\mu_0^*} = -\frac{(N_0^\beta - N_0^\alpha)}{S^\beta - S^\alpha}}$$

$$N_0^\beta > N_0^\alpha \Rightarrow N_0^\beta - N_0^\alpha > 0$$

$$\boxed{S^\beta - S^\alpha \gtrless 0 \; ?}$$

$\alpha \rightarrow$ is a disordered phase

$\beta \rightarrow$ ordered phase where any arrangement other than the lowest energy ordering is very high in energy.

$$\Rightarrow S^\beta \approx P_\beta \log P_\beta \ll S^\alpha$$ $\rightarrow$ can tolerate more "disorder" $\Rightarrow S^\beta - S^\alpha < 0$

$$\frac{dT^*}{d\mu_0^*} = -\left[\frac{N_0^\beta - N_0^\alpha > 0}{S^\beta - S^\alpha < 0}\right] > 0$$

$\Rightarrow$ PHASE DIAGRAM IS INCORRECT

7. (15 points) Polymers are substances that consist of repeating subunits called *monomers*. Consider a one-dimensional polymer chain with M monomers. Each monomer can exist in two states. The lowest energy state has energy ϵ_0, and length l_0 while the higher energy state has energy ϵ_1 and length l_1. The polymer chain is held at fixed temperature (T), force (F) and number of monomer units (M). Each monomer unit and bond between neighboring monomer units are inifinitely stiff. This means that the length of the monomer units do not change elastically under the application of a force. Derive an expression for the average length of the chain as a function of the external force F.

controlled variables:

(T, f, M)

$\Rightarrow$ characteristic potential = $\Lambda = U - TS - fL$

$$Z(f,T,M) = \sum_{\nu} \exp\left(-\frac{E_\nu - fL_\nu}{k_B T}\right)$$

Consider a microstate with n monomers in the lowest energy state:

- $E_\nu = n\varepsilon_0 + (M-n)\varepsilon_1$
- $L_\nu = n l_0 + (M-n) l_1$
- # of such microstates = $\Omega(E) = \dfrac{M!}{n!\,(M-n)!}$

The partition function can then be written as:

$$Z = \sum_{n=0}^{M} \frac{M!}{n!\,(M-n)!} \left(\exp\left(-\beta\left[\varepsilon_0 - f l_0\right]\right)\right)^{n} \left(\exp\left(-\beta\left[\varepsilon_1 - f l_1\right]\right)\right)^{M-n}$$

Using the binomial expansion.

$$Z = \left[\exp\left(-\beta(\varepsilon_0 - f l_0)\right) + \exp\left(-\beta(\varepsilon_1 - f l_1)\right)\right]^{M}$$

$$\Lambda = -k_B T \log Z$$

$$d\Lambda = -S\,dT - L\,dF + \mu\,dM$$

$$\Rightarrow \left(\frac{\partial \Lambda}{\partial F}\right)_{T,M} = -L \Rightarrow k_B T \left(\frac{\partial \log Z}{\partial f}\right)_{T,M} = L \Rightarrow \frac{k_B T}{Z} \left(\frac{\partial Z}{\partial F}\right)_{T,M} = L$$

$$L = \frac{k_B T}{Z} \left[\frac{MZ \times \left\{ +\beta\left(L_0 \exp(-\beta(\varepsilon_0 - f L_0)) + l_1 \exp(-\beta(\varepsilon_1 - f l_1))\right)\right\}}{\left(\exp\left(\beta(\varepsilon_0 - f l_0)\right) + \exp\left(\beta(\varepsilon_1 - f l_1)\right)\right)} \right]$$

$$L = \frac{M\left(l_0 \exp\left(-\beta(\varepsilon_0 - f l_0)\right) + l_1 \exp\left(-\beta(\varepsilon_1 - f l_1)\right)\right)}{\exp\left(-\beta(\varepsilon_0 - f l_0)\right) + \exp\left(-\beta(\varepsilon_1 - f l_1)\right)}$$

8. Two elements (A and B) form an ideal solid solution in the liquid phase. They are also found to form a compound with stoichiometry AB The Gibbs free energy of the AB compound, relative to solid A and solid B is given by:

$$\Delta G_{AB} = C_1 + TC_2$$

where $C_1 < 0, C_2 < 0$ are constants and T is the temperature. The free energies of liquid A and liquid B relative to the solid phases is given by:

$$\Delta G^l_A = \alpha_1 + T\alpha_2$$

$$\Delta G^l_B = \beta_1 + T\beta_2$$

where $\alpha_1, \alpha_2, \beta_1, \beta_2$ are all constants. The units of all free energies are J/mole. The liquid phase is found at high temperatures, while the solid phases are stable at lower temperatures

(a) (4 points) What are the signs of the constants, $\alpha_1, \alpha_2, \beta_1, \beta_2$? Use thermodynamic arguments to justify your answer.

(b) (2 points) Compute the melting temperature of pure A and pure B. Express your answer in terms of $\alpha_1, \alpha_2, \beta_1, \beta_2$.

(c) (2 points) Draw a schematic (one-dimensional) phase diagram at 0K with respect to the composition (x_A) of the A-B mixture.

(d) (4 points) Compute the melting point of the AB compound.

(e) (3 points) Experimental measurements in this A-B alloy show that the liquid phase is better described as a regular solution with a negative mixing enthalpy. Will the melting temperature you computed for the AB compound in the previous question be higher or lower than the experimentally measured melting point in a real system?

The entropy of mixing of an ideal solid solution is given by:

$$\Delta S = -R(x_A \log(x_A) + x_B \log(x_B))$$

(a) $\Delta G^l_A = G^l_A(T,p) - G^s_A(T,p) = \alpha_1 + T\alpha_2$

@ low temperatures the solid phase is stable

$\Rightarrow G^l_A(0,p) > G^s_A(0,p) \Rightarrow \Delta G^l_A(0,p) = \alpha_1 > 0$

liquid is stable at higher temperatures $\Rightarrow G^l_A(T>T_m) < G^s_A(T>T_m$

$\Rightarrow \alpha_2 < 0$

Similarly for β_1 & β_2

$$\boxed{\alpha_1, \beta_1 > 0 \text{ and } \alpha_2, \beta_2 < 0}$$

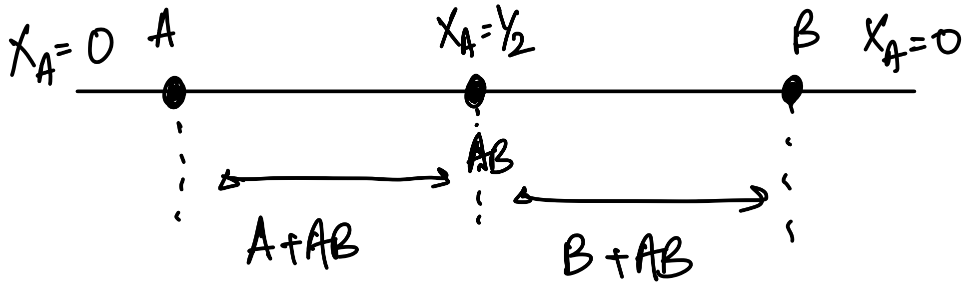
(b) Melting temperature of pure A

$\Delta G^l_A(T) = 0 \Rightarrow \alpha_1 + T\alpha_2 = 0 \Rightarrow \boxed{T^m_A = -\alpha_1/\alpha_2}$

Similarly $\boxed{T_B^m = -\beta_1/\beta_2}$

(c) @ 0K

$$\Delta G_{AB} = G_{AB} - G_A - G_B = C_1 < 0$$



(d) melting point of AB:

$$\Delta G_{solid} = C_1 + C_2 T$$

$$\Delta G_{liquid}(T, x=\tfrac{1}{2}) = \Delta G_A^l + \Delta G_B^l + 2RT\left[\tfrac{1}{2}\log \tfrac{1}{2} + \tfrac{1}{2}\log(\tfrac{1}{2})\right]$$

$$= (\alpha_1 + \beta_1) + (\alpha_2 + \beta_2)T - 2RT\log 2$$

@ eq^n: $\Delta G_{solid} = \Delta G_{liquid}$

$$\Rightarrow (\alpha_1 + \beta_1 - C_1) = T\left[C_2 + 2R\log 2 - \alpha_2 - \beta_2\right]$$

$$\Rightarrow \boxed{T_{AB}^m = \frac{\alpha_1 + \beta_1 - C_1}{C_2 + 2R\log 2 - \alpha_2 - \beta_2}}$$

(e) In real systems $\Delta G_{liquid} = \Delta G_A + \Delta G_B + 2\Omega \frac{1}{2} \times \frac{1}{2} - 2RT\log 2$

$$\Rightarrow T_{AB}^{m,real} = \frac{\alpha_1 + \beta_1 - C_1 + \frac{\Omega}{2}}{C_2 + 2R\log 2}$$

$$\Omega < 0 \Rightarrow \boxed{T_{AB}^{m,real} < T_{AB}^m}$$