HOMEWORK 11

Handed out: Monday, 05 November 2007
Due: Monday, 12 November 2007 by 5 pm

Problem 1: Given the following expression for the internal energy U of a system in terms of S, V and N:

$$U = \frac{V_0\theta}{R^2}\frac{S^3}{NV}$$

a) Calculate the three corresponding equations of state:

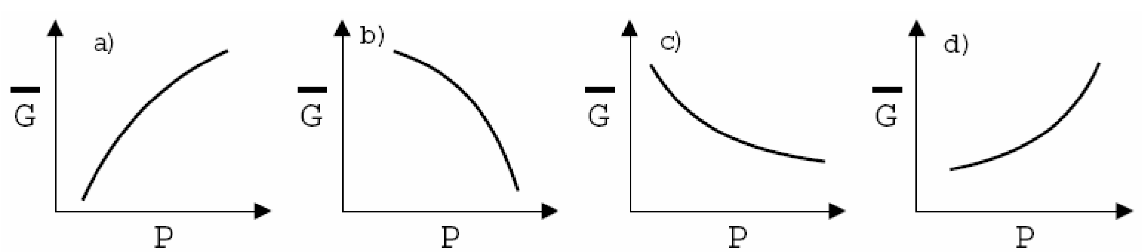
$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad \text{and} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$$

b) Show that P, T and μ are zeroth-order homogeneous (i.e. P, T and μ are intensive variables)

Note: For a zeroth order homogeneous state variable ξ when you increase the volume from V to λV, ξ(λV) = ξ(V) (ξ is an intensive variable).

c) Write down the differential form of the internal energy dU in terms of dV, dS and dN.

Problem 2: Select the figure below that illustrates the correct dependence of the molar Gibbs free energy $\overline{G}$, on pressure, P, at constant temperature for a single component solid. Explain your choice.



Problem 3: Diamond is metastable at atmospheric pressure. Sketch how the Gibbs free energies curve for diamond and graphite would look like as a function of pressure at constant temperature. Consider that the molar volume of a diamond is smaller than the molar volume of graphite. The sketch should be thermodynamically-sound. This means that you should pay attention to the slopes and curvatures of the curves.

Problem 4: Mixing two ideal gases in a tank: An insulated rigid tank is divided into two compartments by a partition. One compartment contains 7 kg of oxygen gas at 40 ^{o}C and 100 kPa and the other compartment contains 4 kg of nitrogen at 20 ^{o}C and 150 kPa. Now the partition is removed and the two gases are allowed to mix. Determine (a) the mixture temperature and (b) the mixture pressure after equilibrium has been established.

Problem 5: Read carefully the following statements and determine whether the following statements are true or false and indicate your thermodynamic reasoning. If the statement is false, indicate which laws of thermodynamics are violated and if possible amend the statement with a clarifying statement that makes it true.

a. The entropy of a material can never decrease.
b. The internal energy of a system and its surroundings is not conserved during an irreversible process.
c. A body in equilibrium and in thermal and mechanical contact with a reservoir at constant pressure and temperature will have the lowest possible value of Gibbs free energy for that body.
d. If two phases that are composed of the same kind of pure material are in equilibrium at constant pressure, then they must have the same value of the molar Gibbs free energy.
e. Melting of a fixed amount of a pure material at constant pressure is an endothermic process when the entropy of the liquid is greater than the entropy of the solid.
f. For a system composed of C components with chemical potentials μ_i for the i^{th} component and N_i the number of molecules of the i^{th} species, $\sum_{i=1}^{c} \mu_i N_i$ will always have its smallest possible value at equilibrium at fixed T and P.
g. If a system has no constraints other than being in equilibrium with a constant pressure reservoir and constant temperature reservoir, then that system is in equilibrium if there is at least one process that increases its Gibbs free energy.
h. The chemical potential of any species that can be exchanged between two phases will always be equal.

Problem 6 (*): Consider a binary alloy with components A and B, let X_A^α, X_A^β and X_A^γ represent the compositions of three phases α, β, γ, that coexist at a triple point at $P=P_{tp}$, $T=T_{tp}$.

Note that for each phase in a binary alloy the composition is given by one variable only because $X_A^\alpha = 1 - X_B^\alpha$, $X_A^\beta = 1 - X_B^\beta$ and $X_A^\gamma = 1 - X_B^\gamma$.

Starting with the Gibbs-Duhem expressions,

$$\begin{aligned}
-\bar{S}^\alpha dT^\alpha + \bar{V}^\alpha dP^\alpha - X_A^\alpha d\mu_A^\alpha - X_B^\alpha d\mu_B^\alpha &= 0 \\
-\bar{S}^\beta dT^\beta + \bar{V}^\beta dP^\beta - X_A^\beta d\mu_A^\beta - X_B^\beta d\mu_B^\beta &= 0 \\
-\bar{S}^\gamma dT^\gamma + \bar{V}^\gamma dP^\gamma - X_A^\gamma d\mu_A^\gamma - X_B^\gamma d\mu_B^\gamma &= 0
\end{aligned}$$

derive a relation for the change in the triple point dP_{tp} = (material properties) dT_{tp}.

Also for the triple point find a relation between the change in the chemical potential of A ($d\mu_A$) and the change in the chemical potential of B ($d\mu_B$).

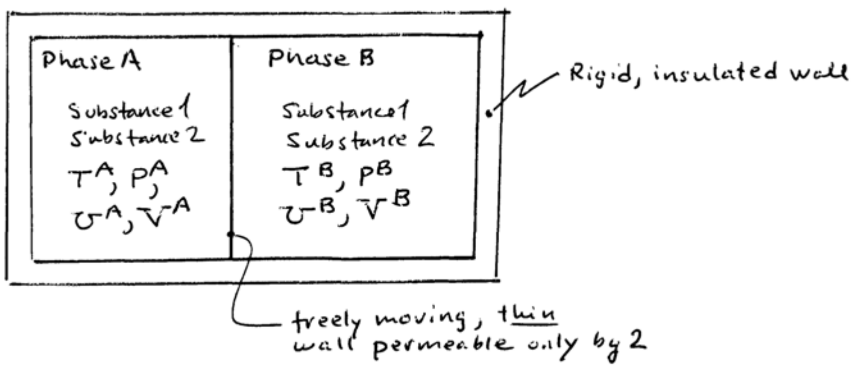
Problem 7: Starting with the Gibbs-Duhem expression for phases with fixed composition,

$$-S^{\alpha}dT^{\alpha} + V^{\alpha}dP^{\alpha} - \sum_i N_i^{\alpha} d\mu_i = 0$$
$$-S^{\beta}dT^{\beta} + V^{\beta}dP^{\beta} - \sum_i N_i^{\beta} d\mu_i = 0$$

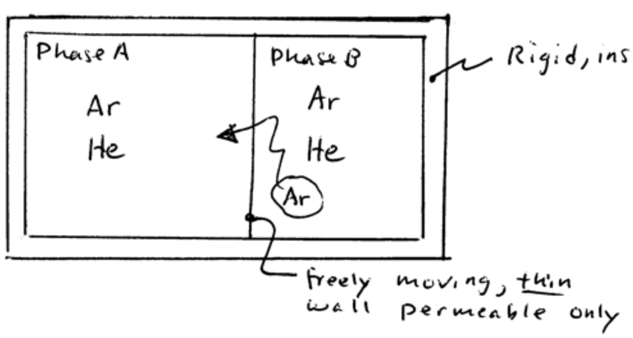
derive the Clausius-Clapeyron relation dP = $(\Delta \overline{S}/\Delta \overline{V})$ dT.

Use a carefully worded sentence to describe what this Clausius-Clapeyron expression means physically.

Problem 8 (*): An isolated system has two phases, A and B, each of which consists of the same two substances, 1 and 2. The phases are separated by a freely moving, thin wall permeable only by substance 2. Determine the necessary conditions for equilibrium.



Problem 9: Referring to the problem above, let each phase be a binary mixture of argon and helium and the wall be permeable only to argon. An isolated system has two gas phases, A and B, each of which consists of argon and helium. If the phases initially are at the equilibrium conditions tabulated below, determine the final equilibrium temperature, pressure and composition for the two phases.



Rigid, insulated wall

	T(K)	p(MPa)	n(kmol)	y_{AR}	y_{He}
A	300	0.2	6	0.5	0.5
B	400	0.1	5	0.8	0.2