SOLUTIONS TO HOMEWORK 11

Problem 1: a) The equations of state are given by

$$-\left(\frac{\partial U}{\partial V}\right)_{S,N} = P = \frac{V_0\theta}{R^2}\frac{S^3}{N}\frac{1}{V^2} \qquad \left(\frac{\partial U}{\partial S}\right)_{V,N} = T = \frac{V_0\theta}{R^2}\frac{3S^2}{NV}$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,N} = \mu = -\frac{V_0\theta}{R^2}\frac{S^3}{N^2V}$$

b) Intensive quatities are independent of the size of a system. We know that N, S and V are extensive properties and additive. If one system is characterized by N, S and V, then λ systems joined together to form a super-system are characterized by λN, λS and λV. For this new system, we have

$$P(\lambda) = \frac{V_0\theta}{R^2}\frac{(\lambda S)^3}{\lambda N}\frac{1}{(\lambda V)^2} = \frac{V_0\theta}{R^2}\frac{S^3}{N}\frac{1}{V^2} \qquad T(\lambda) = \frac{V_0\theta}{R^2}\frac{3(\lambda S)^2}{\lambda N}\frac{1}{\lambda V} = \frac{V_0\theta}{R^2}\frac{3S^2}{NV}$$

$$\mu(\lambda) = \frac{V_0\theta}{R^2}\frac{(\lambda S)^3}{\lambda V}\frac{1}{(\lambda N)^2} = -\frac{V_0\theta}{R^2}\frac{S^3}{VN^2}$$

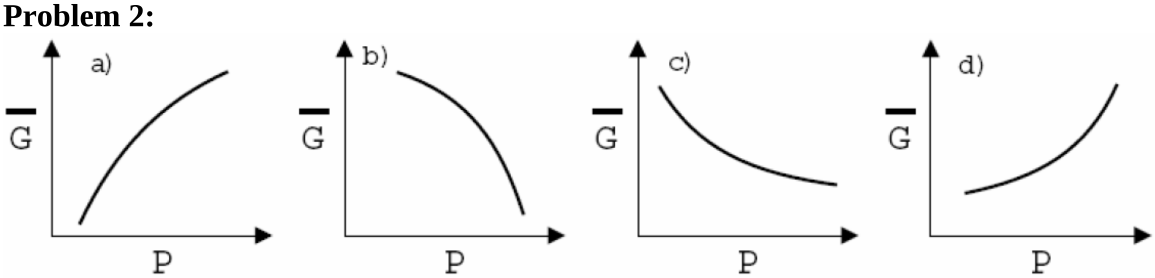
By inspection of these terms it is apparent that P, T and μ are independent of the size of the system (note that S, V and N double as for example the size of the system doubles!).

c) $$dU(S,N,V) = \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial S}\right)_{N,V} dS + \left(\frac{\partial U}{\partial N}\right)_{V,S} dN$$

$$dU(S,N,V) = -PdV + TdS + \mu dN$$

$$dU(S,N,V) = \frac{V_0\theta}{R^2}\frac{S^3}{NV^2}dV + \frac{V_0\theta}{R^2}\frac{3S^2}{NV}dS - \frac{V_0\theta}{R^2}\frac{S^3}{VN^2}dN$$

Problem 2:



Starting from the differential expression for $\bar{G}$, we can write expressions for slope and curvature.

$$d\bar{G} = -\bar{S}dT + \bar{V}dp \quad \Rightarrow \quad \left(\frac{\partial \bar{G}}{\partial \mathrm{P}}\right)_T = \bar{V} \quad \text{and} \quad \left(\frac{\partial^2 \bar{G}}{\partial \mathrm{P}^2}\right)_T = \left(\frac{\partial \bar{V}}{\partial P}\right)_T = -\beta_T V$$

where β_T denotes the isothermal compressibility and is given by, $\beta_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. The molar volume $\bar{V}$ is a positive quantity and therefore the slope is positive. This eliminates (b) and (c). The definition of β_T ensures that $\beta_T > 0$ and therefore the curvature is negative. This eliminates choice (d). Therefore, curve (a) is the right answer since it gives the correct slope and curvature.

Problem 3

Let's have a look at the expression for a differential change in the Gibbs free energy at constant temperature:

$$\mathrm{d}\bar{\mathrm{G}} = -\bar{\mathrm{S}}\mathrm{dT} + \bar{\mathrm{V}}\mathrm{dP}$$

The slope of the Gibbs Free energy vs. Pressure should thus be:

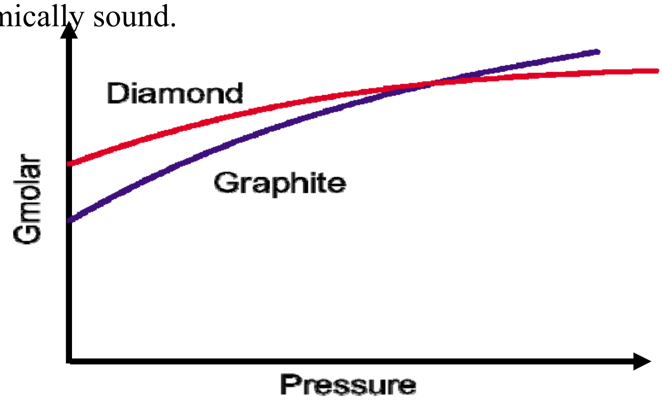
$$\frac{d\bar{G}}{dP} = \bar{V}$$

This means that the slope should always be positive, since a negative volume would be physically irrelevant. The curvature of the same plot should be given by:

$$\frac{\mathrm{d}^2\bar{\mathrm{G}}}{\mathrm{dP}^2} = \frac{\mathrm{d}\bar{\mathrm{V}}}{\mathrm{dP}} = -\bar{\mathrm{V}}\beta$$

So the curvature of the plots should be negative, since we expect the compressibility coefficient β to be positive for these systems.

Note that since the molar volume of graphite is larger than that of diamond, the slope of the Gibbs free energy curve for graphite is larger. As you can see, the sketch is thermodynamically sound.



Problem 4

Assumptions: 1) We assume both gasses to be ideal gases, and their mixture to be an ideal-gas mixture. This assumption is reasonable since both the oxygen and nitrogen are well above their critical temperatures and well below their critical pressures

2) The tank is insulated and thus there is no heat transfer
3) There are no other forms of work involved

(a) Noting that there is no energy transfer to or from the tank, the energy balance for the system can be expressed as:

$$E_{in} - E_{out} = \Delta E_{system}$$

$$0 = \Delta U = \Delta U_{N_2} + \Delta U_{O_2}$$

$$\left[mC_v\left(T_f - T_1\right)\right]_{N_2} + \left[mC_v\left(T_f - T_1\right)\right]_{O_2} = 0$$

Using values of C_v from the back of Moran and Shapiro for N_2 and O_2 you can solve for T_f

$$(4kg)(0.743kJ/kg\cdot{}^oC)(T_f - 20^oC) + (7kg)(0.658kJ/kg\cdot{}^oC)(T_f - 40^oC) = 0$$

$T_f = 32.2\ ^oC$

(b) The final pressure of the mixture is determined from the ideal-gas law PV=NRT Solve for the moles of each gas so that you can solve for the volume that each gas occupies. With the two initial volumes you can solve for the total volume and thus the final pressure

$$N_{O_2} = \frac{m_{O_2}}{M_{O_2}} = \frac{7kg}{32kg/kmol} = 0.219kmol$$

$$N_{N_2} = \frac{m_{N_2}}{M_{N_2}} = \frac{4kg}{28kg/kmol} = 0.143kmol$$

$$N_m = N_{O_2} + N_{N_2} = 0.219 + 0.143 = 0.362kmol$$

$$V_{O_2} = \left(\frac{NRT_1}{P_1}\right)_{O_2} = \frac{0.219kmol(8.314kPa\cdot m^3/kmol\cdot K)(313K)}{100kPa} = 5.70m^3$$

$$V_{N_2} = \left(\frac{NRT_1}{P_1}\right)_{N_2} = \frac{0.143kmol(8.314kPa\cdot m^3/kmol\cdot K)(293K)}{150kPa} = 2.32m^3$$

$$V_{Tot} = V_{O_2} + V_{N_2} = 5.70 + 2.32 = 8.02m^3$$

$$P = \frac{NRT}{V} = \frac{0.362kmol(8.314kPa\cdot m^3/kmol\cdot K)(305.2K)}{8.02m^3}$$

P=114.5kPa

Problem 5: (a) False. The second law applies to a material and its surroundings. For example when water freezes to ice that has a lower entropy.

(b) False. The first law states that internal energy is conserved for any process.

(c) True. The change in Gibb's free energy for a body in equilibrium at constant T and P must be positive as a condition of equilibrium. The body could have a lower value of Gibb's free energy if the equilibrium at that T and P is not the absolute equilibrium.

(d) True. They will have the same value of Gibb's free energy if the bodies have the same extent (i.e. the same number of moles). This is stated here by requiring that they have the same molar Gibbs free energy.

(e) True. $\Delta\bar{G} = 0 = \Delta\bar{H} - T\Delta\bar{S}$. Therefore, $\Delta\bar{H}$ has the same sign as $\Delta\bar{S}$

(f) True. $G=\sum_{i=1}^{C}\mu_i N_i$ and G approaches its smallest value subject to the constraints of fixed T and P as the system approaches equilibrium.

(g) The statement is not necessarily true. At equilibrium, all imaginable processes would have a positive change in the Gibb's free energy at equilibrium. The existence of a single process is not sufficient to specify equilibrium.

(h) False. The statement would be true if it were specified that the system was in equilibrium. Chemical potentials can vary spatially if the system is not in equilibrium.

Problem 6 (*):

At the tri-critical point all three phases are at equilibrium. The equilibrium conditions on thermodynamic potentials are $\mu_i^\alpha=\mu_i^\beta=\mu_i^\gamma=\mu_i, T^\alpha=T^\beta=T^\gamma$, and $P^\alpha=P^\beta=P^\gamma$. It is also given that $X_A^\alpha=1-X_B^\alpha, X_A^\beta=1-X_B^\beta$, and $X_A^\gamma=1-X_B^\gamma$.

The Clausius-Clapeyron equation for the system at equilibrium,

$$-\overline{S}^\alpha dT^\alpha+\overline{V}^\alpha dP^\alpha-X_A^\alpha d\mu_A^\alpha-X_B^\alpha d\mu_B^\alpha=0 \qquad (1)$$

$$-\overline{S}^\beta dT^\beta+\overline{V}^\beta dP^\beta-X_A^\beta d\mu_A^\beta-X_B^\beta d\mu_B^\beta=0 \qquad (2)$$

$$-\overline{S}^\gamma dT^\gamma+\overline{V}^\gamma dP^\gamma-X_A^\gamma d\mu_A^\gamma-X_B^\gamma d\mu_B^\gamma=0 \qquad (3)$$

Applying the conditions on thermodynamic potentials and rearranging the terms,

$$-\overline{S}^\alpha dT+\overline{V}^\alpha dP-X_A^\alpha(d\mu_A-d\mu_B)=d\mu_B \qquad (3)$$

$$-\overline{S}^\beta dT+\overline{V}^\beta dP-X_A^\beta(d\mu_A-d\mu_B)=d\mu_B \qquad (4)$$

$$-\overline{S}^\gamma dT+\overline{V}^\gamma dP-X_A^\gamma(d\mu_A-d\mu_B)=d\mu_B \qquad (5)$$

Since RHS of the above equations are same, they can be compared with each other. Equating Eqs. 3 and 5 with Eq. 4 gives,

$$d\mu_A-d\mu_B=\frac{-(S^\beta-S^\gamma)dT+(V^\beta-V^\gamma)dP}{(X_A^\beta-X_A^\gamma)} \qquad (6)$$

$$d\mu_A-d\mu_B=\frac{-(S^\alpha-S^\beta)dT+(V^\alpha-V^\beta)dP}{(X_A^\alpha-X_A^\beta)} \qquad (7)$$

On simplification the above two equations give,

$$dP=\left(\frac{\Delta V^{\beta\to\gamma}}{\Delta X^{\beta\to\gamma}}-\frac{\Delta V^{\alpha\to\beta}}{\Delta X^{\alpha\to\beta}}\right)^{-1}\left(\frac{\Delta S^{\beta\to\gamma}}{\Delta X^{\beta\to\gamma}}-\frac{\Delta S^{\alpha\to\beta}}{\Delta X^{\alpha\to\beta}}\right)dT \qquad (8)$$

Where $\Delta(.)^{\alpha\rightarrow\beta} = (.)^{\alpha} - (.)^{\beta}$. Also, $\Delta S^{\alpha\rightarrow\beta}$ can be written in terms of enthalpy of transformation and the equilibrium transformation temperature.

To find the relation between $d\mu_A$ and $d\mu_B$, we first start from Eqs. 3 and 4 as follows:

$$\overline{S}^{\beta} * (\text{Eq.3}) \Rightarrow -\overline{S}^{\alpha}\overline{S}^{\beta}dT + \overline{S}^{\beta}\overline{V}^{\alpha}dP - \overline{S}^{\beta}X_A^{\alpha}d\mu_A - \overline{S}^{\beta}X_B^{\alpha}d\mu_B = 0$$

$$(-\overline{S}^{\alpha}) * (\text{Eq.4}) \Rightarrow \overline{S}^{\alpha}\overline{S}^{\beta}dT - \overline{S}^{\alpha}\overline{V}^{\beta}dP + \overline{S}^{\alpha}X_A^{\beta}d\mu_A + \overline{S}^{\alpha}X_B^{\beta}d\mu_B = 0$$

Adding the above two equations gives:

$$(\overline{S}^{\beta}\overline{V}^{\alpha} - \overline{S}^{\alpha}\overline{V}^{\beta})dP + (\overline{S}^{\alpha}X_A^{\beta} - \overline{S}^{\beta}X_A^{\alpha})d\mu_A + (\overline{S}^{\alpha}X_B^{\beta} - \overline{S}^{\beta}X_B^{\alpha})d\mu_B = 0 \quad (9)$$

Similarly from Eqs. 4 and. 5 we can write:

$$\overline{S}^{\gamma} * (4) \Rightarrow -\overline{S}^{\beta}\overline{S}^{\gamma}dT + \overline{S}^{\gamma}\overline{V}^{\beta}dP - \overline{S}^{\gamma}X_A^{\beta}d\mu_A - \overline{S}^{\gamma}X_B^{\beta}d\mu_B = 0$$

$$(-\overline{S}^{\beta}) * (5) \Rightarrow \overline{S}^{\beta}\overline{S}^{\gamma}dT - \overline{S}^{\beta}\overline{V}^{\gamma}dP + \overline{S}^{\beta}X_A^{\gamma}d\mu_A + \overline{S}^{\beta}X_B^{\gamma}d\mu_B = 0$$

Adding the above two equations gives:

$$(\overline{S}^{\gamma}\overline{V}^{\beta} - \overline{S}^{\beta}\overline{V}^{\gamma})dP + (\overline{S}^{\beta}X_A^{\gamma} - \overline{S}^{\gamma}X_A^{\beta})d\mu_A + (\overline{S}^{\beta}X_B^{\gamma} - \overline{S}^{\gamma}X_B^{\beta})d\mu_B = 0 \quad (10)$$

Basically we have eliminated dT from the picture. We now need to eliminate dP as well. From Eqs. 9 and 10 we can solve for dP as follows:

$$dP = \frac{(\overline{S}^{\alpha}X_A^{\beta} - \overline{S}^{\beta}X_A^{\alpha})}{(\overline{S}^{\alpha}\overline{V}^{\beta} - \overline{S}^{\beta}\overline{V}^{\alpha})}d\mu_A - \frac{(\overline{S}^{\alpha}X_B^{\beta} - \overline{S}^{\beta}X_B^{\alpha})}{(\overline{S}^{\alpha}\overline{V}^{\beta} - \overline{S}^{\beta}\overline{V}^{\alpha})}d\mu_B$$

$$dP = \frac{(\overline{S}^{\beta}X_A^{\gamma} - \overline{S}^{\gamma}X_A^{\beta})}{(\overline{S}^{\beta}\overline{V}^{\gamma} - \overline{S}^{\gamma}\overline{V}^{\beta})}d\mu_A - \frac{(\overline{S}^{\beta}X_B^{\gamma} - \overline{S}^{\gamma}X_B^{\beta})}{(\overline{S}^{\beta}\overline{V}^{\gamma} - \overline{S}^{\gamma}\overline{V}^{\beta})}d\mu_B$$

Equating the right hand side of the above two equations gives the following:

$$\left[\frac{(\overline{S}^{\alpha}X_A^{\beta} - \overline{S}^{\beta}X_A^{\alpha})}{(\overline{S}^{\alpha}\overline{V}^{\beta} - \overline{S}^{\beta}\overline{V}^{\alpha})} - \frac{(\overline{S}^{\beta}X_A^{\gamma} - \overline{S}^{\gamma}X_A^{\beta})}{(\overline{S}^{\beta}\overline{V}^{\gamma} - \overline{S}^{\gamma}\overline{V}^{\beta})}\right]d\mu_A = \left[\frac{(\overline{S}^{\alpha}X_B^{\beta} - \overline{S}^{\beta}X_B^{\alpha})}{(\overline{S}^{\alpha}\overline{V}^{\beta} - \overline{S}^{\beta}\overline{V}^{\alpha})} - \frac{(\overline{S}^{\beta}X_B^{\gamma} - \overline{S}^{\gamma}X_B^{\beta})}{(\overline{S}^{\beta}\overline{V}^{\gamma} - \overline{S}^{\gamma}\overline{V}^{\beta})}\right]d\mu_B$$

$$\frac{d\mu_A}{d\mu_B}=\frac{(\overline{S}^{\beta}X_B^{\gamma}-\overline{S}^{\gamma}X_B^{\beta})(\overline{S}^{\alpha}\overline{V}^{\beta}-\overline{S}^{\beta}\overline{V}^{\alpha})-(\overline{S}^{\alpha}X_B^{\beta}-\overline{S}^{\beta}X_B^{\alpha})(\overline{S}^{\beta}\overline{V}^{\gamma}-\overline{S}^{\gamma}\overline{V}^{\beta})}{(\overline{S}^{\alpha}X_A^{\beta}-\overline{S}^{\beta}X_A^{\alpha})(\overline{S}^{\beta}\overline{V}^{\gamma}-\overline{S}^{\gamma}\overline{V}^{\beta})-(\overline{S}^{\beta}X_A^{\gamma}-\overline{S}^{\gamma}X_A^{\beta})(\overline{S}^{\alpha}\overline{V}^{\beta}-\overline{S}^{\beta}\overline{V}^{\alpha})}$$

$$\frac{d\mu_A}{d\mu_B}=\frac{\overline{S}^{\gamma}(\overline{V}^{\beta}-\overline{V}^{\beta}X_A^{\alpha}+\overline{V}^{\alpha}(-1+X_A^{\beta}))+\overline{S}^{\alpha}(\overline{V}^{\gamma}-\overline{V}^{\gamma}X_A^{\beta}+\overline{V}^{\beta}(-1+X_A^{\gamma}))+\overline{S}^{\beta}(\overline{V}^{\alpha}-\overline{V}^{\alpha}X_A^{\gamma}+\overline{V}^{\gamma}(-1+X_A^{\alpha}))}{(-\overline{S}^{\gamma}\overline{V}^{\beta}X_A^{\alpha}+\overline{S}^{\beta}\overline{V}^{\gamma}X_A^{\alpha}+\overline{S}^{\gamma}\overline{V}^{\alpha}X_A^{\beta}-\overline{S}^{\alpha}\overline{V}^{\chi}X_A^{\beta}-\overline{S}^{\beta}\overline{V}^{\alpha}X_A^{\gamma}+\overline{S}^{\alpha}\overline{V}^{\beta}X_A^{\gamma})}$$

Problem 7 : Starting with the Gibbs-Duhem expression for phases with fixed composition, derive the Clausius-Clapeyron relation dP = $(\Delta\overline{S}/\Delta\overline{V})$ dT.

Using a carefully worded sentence or two describe what this Clausius-Clapeyron expression means physically.

The Gibbs-Duhem expression for two phases in equilibrium with fixed composition is given by,

$$-S^{\alpha}dT^{\alpha}+V^{\alpha}dP^{\alpha}-\sum_i N_i^{\alpha}d\mu_i=0 \quad (10)$$
$$-S^{\beta}dT^{\beta}+V^{\beta}dP^{\beta}-\sum_i N_i^{\beta}d\mu_i=0 \quad (11)$$

For equilibrium between the phases, at the coexistence curve, the chemical potential, consequently change in chemical potential, of any species in these phases need to be equal, i.e. $d\mu_i^{\alpha}=d\mu_i^{\beta}=d\mu$. Similarly $dP^{\alpha}=dP^{\beta}=dP$ and $dT^{\alpha}=dT^{\beta}=dT$.

$$-S^{\alpha}dT+V^{\alpha}dP-\sum_i N_i^{\alpha}d\mu_i=0 \quad (12)$$
$$-S^{\beta}dT+V^{\beta}dP-\sum_i N_i^{\beta}d\mu_i=0 \quad (13)$$

For a single component system, the compositions are fixed, leading to the relations,

$$-\overline{S}^{\alpha}dT+\overline{V}^{\alpha}dP-d\mu=0 \quad (14)$$
$$-\overline{S}^{\beta}dT+\overline{V}^{\beta}dP-d\mu=0 \quad (15)$$

Subtracting the above relations from the previous one, and rearranging,

$$\frac{dP}{dT}=\frac{\overline{S}^{\alpha}-\overline{S}^{\beta}}{\overline{V}^{\alpha}-\overline{V}^{\beta}}=\frac{\Delta\overline{S}^{\alpha\to\beta}}{\Delta\overline{V}^{\alpha\to\beta}} \quad (16)$$

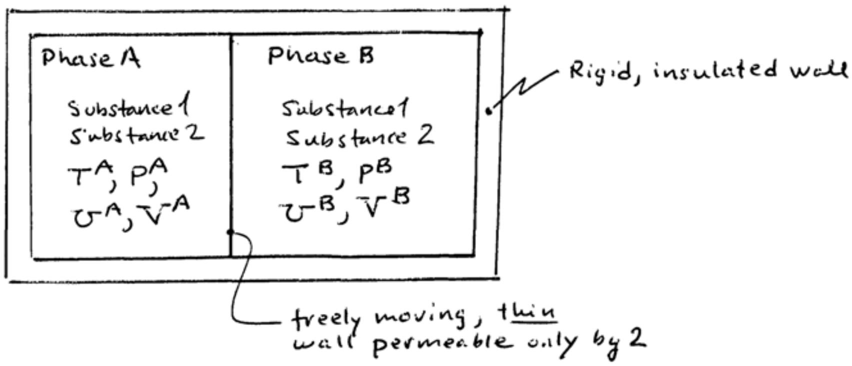
Physically Clausius Clapeyron equation provides relation between thermodynamic potentials for the phases at equilibrium.

Problem 8 (*)

Known: 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.

Find: Determine the necessary conditions for equilibrium.

Schematic:



Assumptions:
(1) The system consists of phase A plus Phase B.
(2) For the system, Q = W = 0 and there are no kinetic/potential energy effects.
(3) The phases are separated by a freely moving, thin wall permeable only by 2.

Analysis: The appropriate equilibrium criteria for this case is obtained via Equation 14.3 as $dS]_{U,V} = 0$, where the equality is used in place of the inequality for equilibrium and $dS = dS^A + dS^B$.
Using Eq. 11.114a, $dU = TdS - pdV + \sum_i \mu_i dn_i$:

$$dU^A = T^A dS^A - p^A dV^A + \mu_1^A dn_1^A + \mu_2^A dn_2^A$$
$$dU^B = T^B dS^B - p^B dV^B + \mu_1^B dn_1^B + \mu_2^B dn_2^B$$

Where the dn_1 terms drop out of each equation since the wall is impermeable to substance 1, so the amount of substance 1 in each of the phases cannot change.

Since the container is rigid and insulated,
Total volume is constant: $dV^B = -dV^A$
Total energy is constant: $dU^B = -dU^A$
Since substance B is conserved:
$dn_2^B = -dn_2^A$

Collecting results:

$$dS]_{U,V} = \left[\frac{dU^A}{T^A} + \frac{p^A}{T^A}dV^A - \frac{\mu_2^A}{T^A}dn_2^A\right] + \left[\frac{dU^B}{T^B} + \frac{p^B}{T^B}dV^B - \frac{\mu_2^B}{T^B}dn_2^B\right]$$

Since substance B is conserved:

$dn_2^B = -dn_2^A$

So:

$$dS]_{U,V} = dU^A\left[\frac{1}{T^A} - \frac{1}{T^B}\right] + dV^A\left[\frac{p^A}{T^A} - \frac{p^B}{T^B}\right] - dn_2^A\left[\frac{\mu_2^A}{T^A} - \frac{\mu_2^B}{T^B}\right]$$

Since U^A, V^A, and n_2^A can all be varied independently, for $dS]_{U,V} = 0$ to be term true, all of the terms in parentheses must equal 0. Therefore, the criteria of equilibrium are:

$$\frac{1}{T^A} - \frac{1}{T^B} = 0 \Rightarrow T^A = T^B$$ (temperature is the same in each phase)

$$\frac{p^A}{T^A} - \frac{p^B}{T^B} = 0 \Rightarrow \frac{p^A - p^B}{T} = 0 \Rightarrow p^A = p^B$$ (pressure is the same in each phase)

$$\frac{\mu_2^A}{T^A} - \frac{\mu_2^B}{T^B} = 0 \Rightarrow \frac{\mu_2^A - \mu_2^B}{T} = 0 \Rightarrow \mu_2^A = \mu_2^B$$ (chemical potential of substance 2 is the same in each phase)

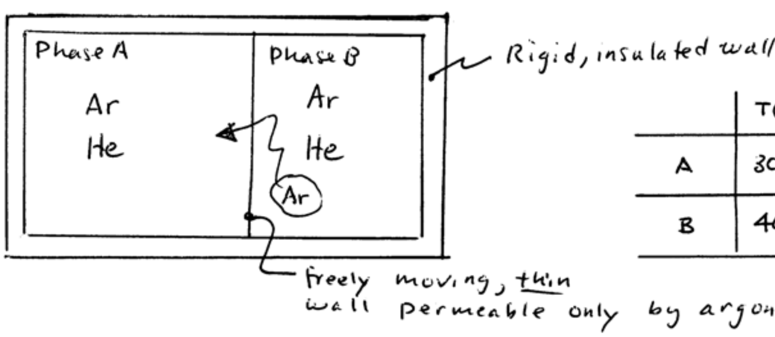
Note: There is no restriction on μ_1^A or μ_1^B

Problem 9

Known: An isolated system has two gas phases, A and B, each of which consists of argon and helium. The phases are separated by a freely moving, thin wall permeable only to argon. Initial data is provided.

Find: Using the result of Problem 12, determine the final equilibrium temperature, pressure, and composition in the two phases.

Schematic & Given Data:



	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

Assumptions:

(1) The idealizations of Problem 12 apply

(2) Ideal gas principles apply to the gas mixtures

Analysis: An energy balance requires $\Delta U = \Delta U^A + \Delta U^B = 0$, since we are assuming that $Q = W = 0$. Writing this in terms of molar internal energy results in:

$$\Delta U^A = \left[n^A_{Ar,f}\bar{u}_{Ar}\left(T_f\right) + n^A_{He}\bar{u}_{He}\left(T_f\right)\right] - \left[n^A_{Ar,i}\bar{u}_{Ar}\left(T^A\right) + n^A_{He}\bar{u}_{He}\left(T^A\right)\right]$$
$$\Delta U^B = \left[n^B_{Ar,f}\bar{u}_{Ar}\left(T_f\right) + n^B_{He}\bar{u}_{He}\left(T_f\right)\right] - \left[n^B_{Ar,i}\bar{u}_{Ar}\left(T^B\right) + n^B_{He}\bar{u}_{He}\left(T^B\right)\right]$$

Where T_f is constant throughout the container by the results from problem 12, so

$$\begin{aligned}\Delta U^A + \Delta U^B = 0 = &\left[n^A_{Ar,f}\bar{u}_{Ar}\left(T_f\right) + n^A_{He}\bar{u}_{He}\left(T_f\right)\right] - \left[n^A_{Ar,i}\bar{u}_{Ar}\left(T^A\right) + n^A_{He}\bar{u}_{He}\left(T^A\right)\right] \\ &+ \left[n^B_{Ar,f}\bar{u}_{Ar}\left(T_f\right) + n^B_{He}\bar{u}_{He}\left(T_f\right)\right] - \left[n^B_{Ar,i}\bar{u}_{Ar}\left(T^B\right) + n^B_{He}\bar{u}_{He}\left(T^B\right)\right]\end{aligned} \quad (1)$$

Since the total amount of argon must remain constant:
$n^A_{Ar,f} + n^B_{Ar,f} = n^A_{Ar,i} + n^B_{Ar,i}$, where $n^A_{Ar,i} = 3$ and $n^B_{Ar,i} = 4$, so $n^{Tot}_{Ar} = 7$

Substituting $n^A_{Ar,f} + n^B_{Ar,f} = n^A_{Ar,i} + n^B_{Ar,i}$ into Eq. (1) results in:

$$\begin{aligned}0 = &\, n^A_{Ar,i}\left[\bar{u}_{Ar}\left(T_f\right) - \bar{u}_{Ar}\left(T^A\right)\right] + n^B_{Ar,i}\left[\bar{u}_{Ar}\left(T_f\right) - \bar{u}_{Ar}\left(T^B\right)\right] \\ &+ n^A_{He}\left[\bar{u}_{He}\left(T_f\right) - \bar{u}_{He}\left(T^A\right)\right] + n^B_{He}\left[\bar{u}_{He}\left(T_f\right) - \bar{u}_{He}\left(T^B\right)\right]\end{aligned}$$

For monatomic gases, $\Delta\bar{u} = c_v \Delta T$, where c_v is constant. Further arrangement leads to:

$$T_f = \frac{\left(n^A_{Ar,i} + n^A_{He}\right)T^A + \left(n^B_{Ar,i} + n^B_{He}\right)T^B}{\left(n^A_{Ar,i} + n^A_{He}\right) + \left(n^B_{Ar,i} + n^B_{He}\right)} = \frac{6\left(300K\right) + 5\left(400K\right)}{11} = 345.5K$$

The total volume is unchanged, so $\left(V^A + V^B\right)_f = \left(V^A + V^B\right)_i$, and applying the ideal gas equation:

$$n_{TOT}\frac{\bar{R}T_f}{p_f} = \frac{n^A\bar{R}T^A}{p^A} + \frac{n^B\bar{R}T^B}{p^B} \Rightarrow p_f = \frac{n_{TOT}T_f}{\dfrac{n^A\bar{R}T^A}{p^A} + \dfrac{n^B\bar{R}T^B}{p^B}} = \frac{11\left(345.5\right)}{\dfrac{6\left(300\right)}{0.2} + \dfrac{5\left(400\right)}{0.1}} = 0.131MPa = p_f$$

The final constraint is $\mu^A_{Ar} = \mu^B_{Ar}$ at the final state. With Eq. 14.17, this becomes
$y^A_{Ar,f} = y^B_{Ar,f}$
Writing out the mole fractions:

$$\frac{n^A_{Ar,f}}{n^A_{Ar,f} + n^A_{He,f}} = \frac{n^B_{Ar,f}}{n^B_{Ar,f} + n^B_{He,f}} \Rightarrow \frac{n^A_{Ar,f}}{n^A_{Ar,f} + 3} = \frac{\left(7 - n^A_{Ar,f}\right)}{\left(7 - n^A_{Ar,f}\right) + 1} \Rightarrow 4n^A_{Ar,f} = 21 \Rightarrow n^A_{Ar,f} = 5.25$$

So at the final equilibrium state phase A contains 5.25 kmol of Argon and 3.0 kmol of Helium, and phase B contains 7 - 5.25 = 1.75 kmol of Argon and 1.0 kmol of Helium.