

HW 7 key

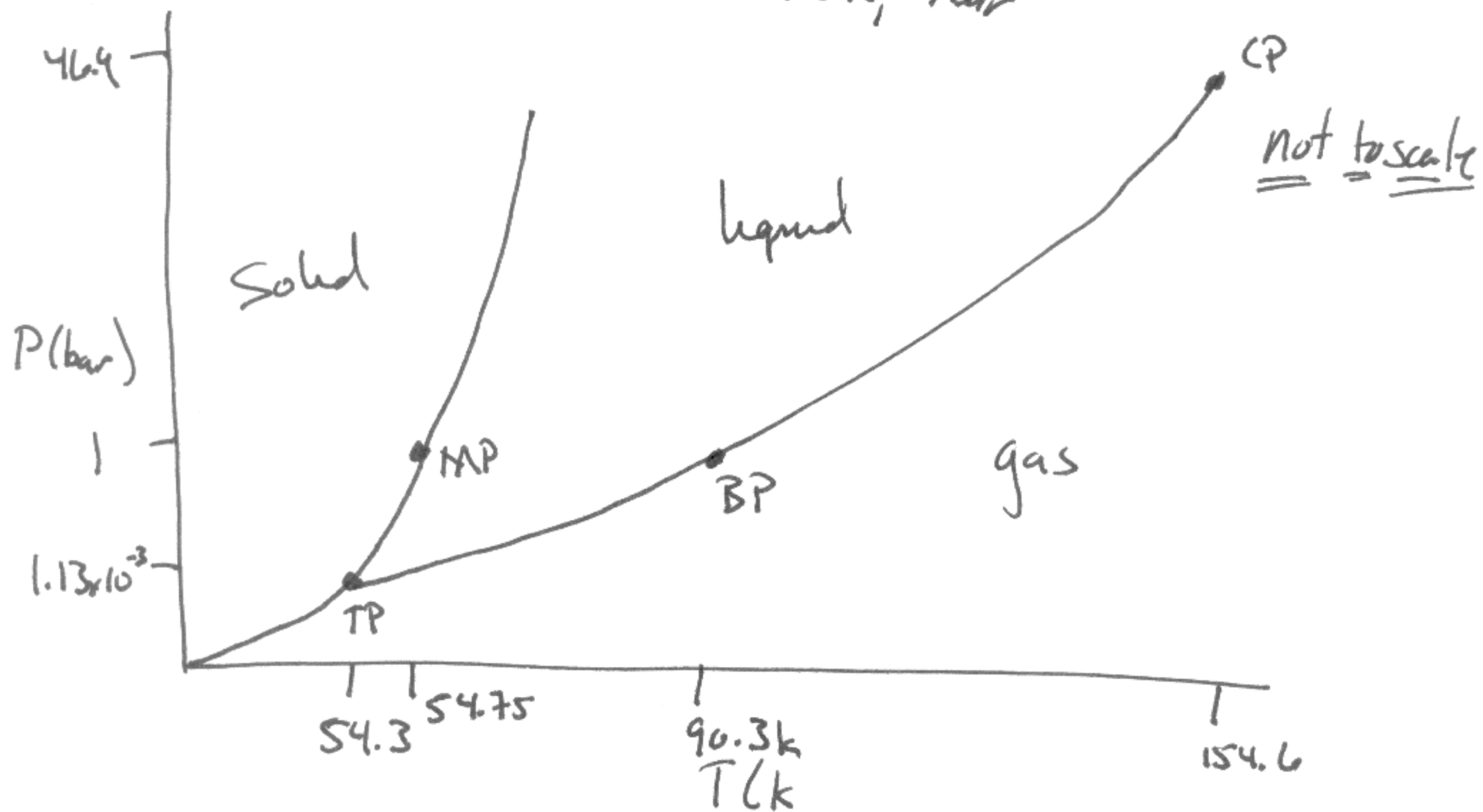
1. In this problem, sig figs matter

Triplepoint:  $54.3\text{ k}$ ,  $1.129 \times 10^{-3}\text{ bar}$

CP:  $154.6\text{ k}$ ,  $46.86\text{ bar}$

$T_m = 273.15 - 218.4^\circ\text{C} = 54.75\text{ k}$ ,  $1\text{ bar}$

$T_b = 273.15 - 182.9^\circ\text{C} = 90.25\text{ k}$ ,  $1\text{ bar}$



The melting point occurs at higher  $T$  &  $P$  than the triple point, so the slope between the TP and the MP is positive. Therefore, between these two points, solid oxygen does not melt as pressure increases. We have no information about what happens above the melting point, so in the absence of other information, I have drawn a positive slope for the boundary between the solid + liquid phases.

$$2. \Delta H_{\text{vap}} = 40.65 \text{ kJ/mol}$$

$$T_{\text{vap}} = 100^\circ\text{C} = 373 \text{ K}$$

$$\ln\left(\frac{P_f}{P_i}\right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{T_f - T_i}{T_f T_i} \right)$$

$$\ln\left(\frac{P_f}{1 \text{ atm}}\right) = \frac{40650 \text{ J/mol}}{8.315 \text{ J/kmol}} \left( \frac{10 \text{ K}}{(373 \text{ K})(383 \text{ K})} \right)$$

$$\ln P_f = 0.342 ; \boxed{P_f = 1.41 \text{ atm} = 1070 \text{ Torr}}$$

This is pretty close to the experimental value; any differences are probably due to the Clausius-Clapeyron equation.

$$3. T_c^* = 24.1^\circ\text{C} = 297.2 \text{ K}$$

$$P^* = 53.3 \text{ kPa}$$

$$\Delta H_{\text{vap}} = 28.7 \text{ kJ/mol}$$

$$P = 70.0 \text{ kPa}$$

$$T_f = ?$$

$$P = P^* e^{-\chi}$$

$$\chi = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_f} - \frac{1}{T^*} \right)$$

$$\frac{P}{P^*} = e^{-\chi} ; \ln\left(\frac{P}{P^*}\right) = -\chi$$

$$\ln\left(\frac{P^*}{P}\right) = \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \quad \ln\left(\frac{P^*}{P}\right) = \chi$$

$$\frac{1}{T} = \frac{1}{T^*} + \frac{R}{\Delta H_{\text{vap}}} \ln\left(\frac{P^*}{P}\right)$$

$$T = \left( \frac{1}{T} \right)^{-1} = \left( \frac{1}{297.25 \text{ K}} + \frac{8.315 \text{ J/kmol}}{28.7 \times 10^3 \text{ J/mol}} \ln\left(\frac{53.3 \text{ kPa}}{70.0 \text{ kPa}}\right) \right)^{-1}$$

$$\boxed{T = 304 \text{ K}}$$

4.  $P = 50 \text{ atm}$

$\rho_{ice} = 0.92 \text{ g/cm}^3$

$\rho_L = 1.00 \text{ g/cm}^3$

$\Delta H_{fus} = 6.01 \times 10^3 \text{ J/mol}$

$\Delta T = T_f + (50 \text{ atm}) - T_f (1 \text{ atm})$

$= \frac{T_f \Delta P (FW)}{\Delta H_{fus}} \left( \frac{L}{\rho} \right)$

$\Delta T = -0.35 \text{ K}$

$T_f (50 \text{ atm}) = 272.65 \text{ K}$

5.  $T_{vap} = -29.2^\circ\text{C} = 243.95 \text{ K}$

$\Delta H_{vap} = 20.25 \text{ kJ/mol}$

$T_2 = 40^\circ\text{C} = 313 \text{ K}$

$\ln \left( \frac{P_2}{P_{atm}} \right) = \frac{\Delta H_{vap}}{R} \left( \frac{1}{T_{vap}} - \frac{1}{T_2} \right)$

$P_2 = \exp \left[ \frac{\Delta H_{vap}}{R} \left( \frac{1}{T_{vap}} - \frac{1}{T_2} \right) \right] = \exp \left[ \frac{20.25 \times 10^3 \text{ J/mol}}{8.315 \text{ J/mol}\cdot\text{K}} \left( \frac{1}{243.95 \text{ K}} - \frac{1}{313 \text{ K}} \right) \right]$

$P_2 = 9.08 \text{ atm}$

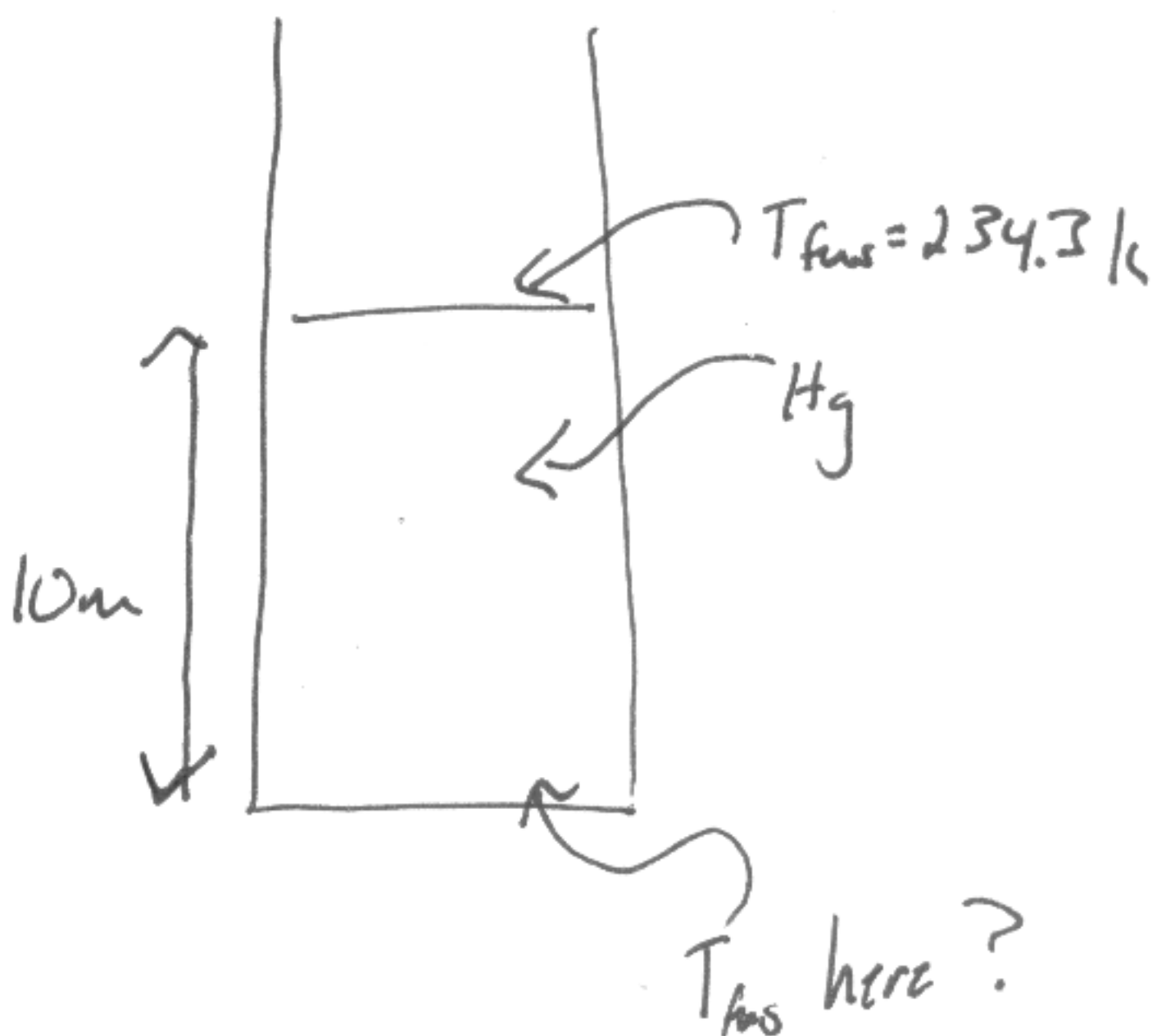
6.  $\Delta H_{fus} (\text{Hg}) = 2.92 \text{ kJ/mol}$

$T_{fus} = 234.3 \text{ K}$

$\Delta V_{fus} = 0.517 \text{ cm}^3/\text{mol}$

$\rho = 13.6 \text{ g/cm}^3$

$h = 10.0 \text{ cm}$



$$\frac{dP}{dT} = \frac{\Delta H_{fus}}{T \Delta V_{fus}} \quad dT = \frac{dP (T \Delta V_{fus})}{\Delta H_{fus}}$$

$$\Delta T = \int_{T_{top}}^{T_{bottom}} dT = \int_{P_{top}}^{P_{bottom}} \frac{T_{fus} \Delta V_{fus} dP}{\Delta H_{fus}}$$

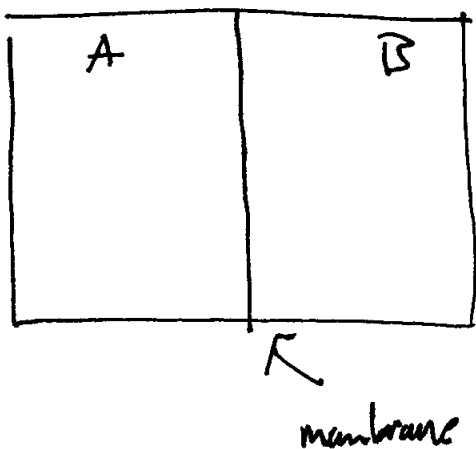
assume  $T_{fus}$ ,  $\Delta V_{fus}$ ,  $\Delta H_{fus}$   
 VC remains constant

$$\Delta T = \frac{T_{fus} \Delta V_{fus}}{\Delta H_{fus}} \Delta P \quad ; \quad \Delta P = P_{bottom} - P_{top} = \rho g h$$

$$\Delta T = 0.071 \text{ K}$$

$T_{fus} = 234.4 \text{ K}$  at the bottom of the column

7.



if  $\Delta T, \Delta V, \Delta P = 0$ ,  
the only contribution to entropy  
will be from chemical potentials

$$\Delta V = 0 \Rightarrow w = 0$$

$$\text{adiabatic} \Rightarrow q = 0$$

$$\Delta U = w + q = 0$$

$$n_A + n_B = n_{\text{TOT}} = \text{constant at all times}$$

$$dG = dU - TdS + PdV$$

$$\text{but } \mu = \frac{dG}{dn} \Rightarrow dG = \mu dn$$

$$\frac{\mu dn}{T} = \frac{dU}{T} - dS + \frac{P}{T} dV$$

$$dS = \frac{dU}{T} + \frac{P}{T} dV - \frac{\mu}{T} dn$$

$$dU = dV = 0$$

$$dS = \frac{\mu}{T} dn \quad |$$

$$dS_A = -\frac{\mu_A}{T} dn_A$$

$$dS_B = -\frac{\mu_B}{T} dn_B$$

$$dS_{\text{sys}} = dS_A + dS_B = -\frac{\mu_A}{T} dn_A - \frac{\mu_B}{T} dn_B$$

$$dn_A = -dn_B$$

$$dS_{\text{sys}} = -\frac{\mu_A}{T} dn_A - \frac{\mu_B}{T} (-dn_A)$$

$$dS_{\text{sys}} = \left( \frac{\mu_B}{T} - \frac{\mu_A}{T} \right) dn_A$$

$$\text{if } \mu_A > \mu_B, \Rightarrow dn_A < 0, dn_B > 0 \Rightarrow dS_{\text{sys}} > 0$$

$$\text{if } \mu_A < \mu_B \Rightarrow dn_A > 0, dn_B < 0 \Rightarrow dS_{\text{sys}} > 0$$

$$\text{if } \mu_A = \mu_B, dn_A = -dn_B, \Rightarrow dS_{\text{sys}} = 0$$

So no matter which solution has a higher chemical potential,  $dS_{\text{sys}} > 0$  always. This is a derivative of our previous finding that  $\Delta S_{\text{mix}} > 0$  always.