Chemistry 230
Problem Set # 10 -- Answers

1. The plot of ln P vs $^1/_T$ is very linear in this T region, so there is no indication of a T dependence in $\Delta H_{m,vap}$.

2. Consider this 3-step process at 100.0˚C: $\text{Hg}(l,P^\circ) \xrightarrow{1} \text{Hg}(l,P) \xrightarrow{2} \text{Hg}(id.gas,P) \xrightarrow{3} \text{Hg}(id.gas,P^\circ)$.
ΔH_m°, ΔG_m°, and ΔS_m° can all be expressed as sums of terms for these three steps.

$(\partial H/\partial P)_T = V(1-\alpha T)$ $\quad \Delta H_{m,1} \approx V_m\,(0.933)\,\Delta P = -13.8\ \text{cm}^3\ \text{atm mol}^{-1} = -1.40$ J/mol;
$\Delta H_{m,2} = \Delta H_{vap} = 61.34$ kJ/mol; $\Delta H_{m,3} = 0$ (ideal gas).

$\Delta G_{m,1} = \int_{P^\circ}^{\sim 0} V_m\ dP = -V_m P^\circ = -1.50$ J/mol; $\Delta G_{m,2} = 0$; $\Delta G_{m,3} = \int V_m\, dP = RT \ln (P^\circ/0.2729\ \text{torr})$

$\Delta G_m^\circ = 24.57$ kJ/mol; $\Delta H_m^\circ = 61.34$ kJ/mol; $\Delta S_m^\circ = 98.54$ J mol^{-1} K^{-1}.

3. $\dfrac{dP}{dT} = \dfrac{\Delta S}{\Delta V} = \dfrac{\Delta H}{T\Delta V}$ $\qquad \dfrac{\Delta T}{\Delta P} \approx \dfrac{1\ \text{K}}{192\ \text{atm}}$

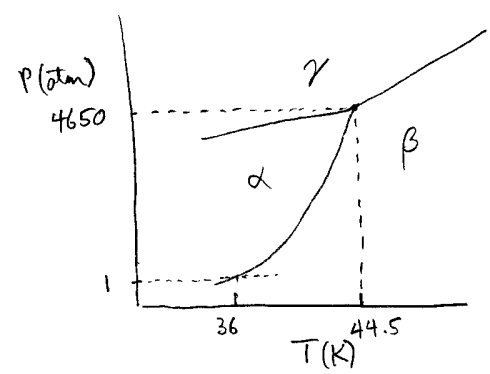
(a) –38.57˚C. (b) –36.48˚C.

4. (a) 1.12_3 g of gas and 0.86_7 g of liquid.
(b) Now <u>all</u> of the ethanol is present in the gas phase.

5. $d\mu_s = dG_{m,s} = V_{m,s}\,dP_s = d\mu_g = V_{m,g}\,dP_g$ $\qquad V_{m,s}\,dP_s = \dfrac{RT}{P_g}\,dP_g$

$\ln\left(\dfrac{P_{g,2}}{P_{g,1}}\right) \approx \dfrac{V_{m,s}\ \Delta P_s}{RT}$ $\qquad P_{g,2} = 2.1_3$ torr.

6. $\dfrac{dP}{dT} = \dfrac{\Delta S}{\Delta V} = \dfrac{\Delta S_m}{\Delta V_m} = 74.8$ atm/K ($\gamma \rightarrow \alpha$ @ T.P.)
279 " ($\gamma \rightarrow \beta$ @ T.P.)
1053 " ($\alpha \rightarrow \beta$ @ T.P.)
292 " ($\alpha \rightarrow \beta$ @ 1 atm & 36 K).



7. <u>Path</u>: l (–10˚C, 1 atm) $\xrightarrow{1}$ l (–10˚C, 2.149 torr) $\xrightarrow{2}$ g (–10˚C, 2.149 torr) $\xrightarrow{3}$
g (–10˚C, 1.950 torr) $\xrightarrow{4}$ s (–10˚C, 1.950 torr) $\xrightarrow{5}$ s (–10˚C, 1 atm).

$$\Delta G_m = \Sigma\, \Delta G_{m,i} = \int_{760}^{2.149} V_{m,l}\, dP + 0 + \int_{2.149}^{1.950} \frac{RT}{P}\, dP + 0 + \int_{1.950}^{760} V_{m,s}\, dP$$

$= (-0.0179 - 2.093 + 0.0196)$ L atm/mol $= -212.4$ J/mol $= -50.7_8$ cal/mol.

$\Delta S_m = T^{-1}(\Delta H_m - \Delta G_m) = 263.15^{-1}(-5620 + 212.4)$ J mol^{-1} K^{-1} $= -4.91_1$ cal mol^{-1} K^{-1}.

<u>Previous results</u>: $\Delta G_m = -50.6_8$ cal/mol & $\Delta S_m = -4.914$ cal mol^{-1} K^{-1}.

As we previously concluded, the process is indeed spontaneous.