Chemistry 410B **Exam 5** **Spring 2012**

Solutions

1. **40 points.**

   (a) Calculate the entropy of mixing when we combine 0.100 mol of neon with 0.900 mol of argon at 298 K and 1.00 bar, assuming both are ideal gases. **Solution:**

$$\begin{aligned}\Delta S_{\text{mix}} &= -R(n_{\text{Ar}} \ln X_{\text{Ar}} + n_{\text{Ne}} \ln X_{\text{Ne}}) \\ &= -(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\,[(0.900\,\text{mol})\ln(0.900) + (0.100\,\text{mol})\ln(0.100)] = \boxed{2.70\,\text{J}\,\text{K}^{-1}.}\end{aligned}$$

   (b) In a dewar filled with liquid nitrogen, we have an equilibrium mixture of N_2, O_2, and argon, with each substance present in both liquid and vapor phases. Give any *complete* set of intensive parameters that can be independently adjusted while maintaining this equilibrium. **Solution:** $k = 3$ chemical components, $p = 2$ phases, so $d = k - p + 2 = 3$ degrees of freedom. For the intensive parameters, in addition to P and T, there are 6 mole fractions: $X_i(\text{g})$ and $X_i(\text{l})$ for each of the three components. $\boxed{\text{Any three}}$ of these is a valid answer.

   (c) Find $\Delta_{\text{fus}}H^\ominus$, $\Delta_{\text{fus}}S^\ominus$, and $\Delta_{\text{fus}}G^\ominus$ for water at its normal freezing point of 273.15 K. **Solution:** From Table 19.2, $\boxed{\Delta_{\text{fus}}H^\ominus = 6.008\,\text{kJ}\,\text{mol}^{-1}.}$ At constant T and P, $\boxed{\Delta_{\text{fus}}G^\ominus = 0,}$ which lets us set $\Delta_{\text{fus}}S^\ominus = \Delta_{\text{fus}}H^\ominus/T_f^\ominus = 6008\,\text{J}\,\text{mol}^{-1}/273.15\,\text{K} = \boxed{22.0\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}.}$

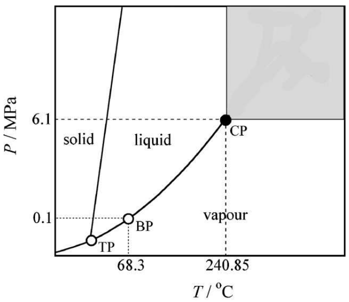
   (d) Find $\Delta_{\text{vap}}H^\ominus$ of n-pentane if $T_b^\ominus = 309.2\,\text{K}$ and the compound boils at a pressure of 0.680 bar at 298.15 K. **Solution:** We solve the Clausius-Clapeyron equation for $\Delta_{\text{vap}}H^\ominus$:

$$\begin{aligned}\ln P(\text{bar}) &= \frac{\Delta_{\text{vap}}H^\ominus}{R}\left(\frac{1}{T_b^\ominus} - \frac{1}{T}\right) \\ \Delta_{\text{vap}}H^\ominus &= R \ln P \left(\frac{1}{T_b^\ominus} - \frac{1}{T}\right)^{-1} \\ &= (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(\ln 0.680)\left(\frac{1}{309.2} - \frac{1}{298.15\,\text{K}}\right)^{-1} = \boxed{26.75\,\text{kJ}\,\text{mol}^{-1}.}\end{aligned}$$

2. Estimate $\Delta_{\text{vap}}E^\ominus$ for carbon tetrachloride at its standard boiling point. **Solution:** We already know $\Delta_{\text{vap}}H^\ominus$ at the standard boiling point, so we use the relation between H and E to get $\Delta_{\text{vap}}E^\ominus$. Along the way, we also apply the Clausius-Clapeyron approximation that the ΔV in vaporization is essentially the volume of the gas:

$$\begin{aligned}\Delta_{\text{vap}}E^\ominus &= \Delta_{\text{vap}}H^\ominus - \Delta(PV_m) = \Delta_{\text{vap}}H^\ominus - P^\ominus \Delta V_m \approx \Delta_{\text{vap}}H^\ominus - P^\ominus V_m(\text{gas}) \\ &= \Delta_{\text{vap}}H^\ominus - P^\ominus \frac{RT}{P^\ominus} = \Delta_{\text{vap}}H^\ominus - RT_b^\ominus \\ &= 29.82\,\text{kJ}\,\text{mol}^{-1} - (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})(349.9\,\text{K})(10^{-3}\,\text{kJ}/\,\text{J}) = \boxed{26.91\,\text{kJ}\,\text{mol}^{-1}.}\end{aligned}$$

3. Based on the phase diagram shown below for ethanol, estimate the ethanol-ethanol binding energy in cm^{-1} and the critical number density ρ_c in cm^{-3}. Pay close attention to all units, and note that $1\,\mathrm{MPa}{=}10^6\,\mathrm{Pa}$.



Solution: The critical temperature is $240.85\,\mathrm{C} + 273.15 = 514.00\,\mathrm{K}$, and is typically about 20-25% higher than the value of ϵ, so a good estimate here would be roughly

$$\epsilon \approx (1.23)T_c = (1.23)(514.00\,\mathrm{K})(0.6950\,\mathrm{cm}^{-1}/\,\mathrm{K}) = \boxed{440\mathrm{cm}^{-1}.}$$

Any value within about 10% of that would be reasonable. For the critical number density, we use $\rho = \mathcal{N}_A P/(RT)$ but with the critical pressure and temperature:

$$\rho_c = \frac{\mathcal{N}_A P_c}{RT_c} = \frac{(6.022\cdot 10^{23}\,\mathrm{mol}^{-1})(6.1\cdot 10^6\,\mathrm{Pa})}{(8.3145\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1})(514.00\,\mathrm{K})} = 8.6\cdot 10^{26}\,\mathrm{m}^{-3} = \boxed{8.6\cdot 10^{20}\,\mathrm{cm}^{-3}.}$$

4. If we mix 10.0 mol of water initially at 273.15 K with 10.0 mol of liquid nitrogen initially at 77.36 K and allow the mixture to come to equilibrium, what do we get? Give the phase or phases of each substance and how many moles in each phase, and the final temperature T_f. **Solution:** Since the $\Delta_{\mathrm{vap}}H^{\ominus}$ of N_2 and the $\Delta_{\mathrm{fus}}H^{\ominus}$ of water are similar, we can reasonably assume that the water will all freeze and the nitrogen will all vaporize as they exchange heat, giving for the final states $\boxed{10.0\,\mathrm{mol}\ \mathrm{N_2(g)}}$ and $\boxed{10.0\,\mathrm{mol}\ \mathrm{H_2O(s)}.}$ The only remaining question is: what is the final temperature? Note below that the enthalpy of freezing for the water is $-\Delta_{\mathrm{fus}}H^{\ominus}$. Call the inital temperatures of the water and N_2 T_w and T_n respectively, and similarly label the heat capacities C_w and C_n:

$$\begin{aligned} q_{\mathrm{N_2}} &= n_{\mathrm{N_2}}\left[\Delta_{\mathrm{vap}}H^{\ominus} + C_n\Delta T_{\mathrm{N_2}}\right] = n_{\mathrm{N_2}}\left[\left(\Delta_{\mathrm{vap}}H^{\ominus} - C_nT_n\right) + C_nT_f\right] \\ q_{\mathrm{H_2O}} &= n_{\mathrm{H_2O}}\left[-\Delta_{\mathrm{fus}}H^{\ominus} + C_w\Delta T_{\mathrm{H_2O}}\right] = n_{\mathrm{H_2O}}\left[\left(-\Delta_{\mathrm{fus}}H^{\ominus} - C_wT_w\right) + C_wT_f\right] \end{aligned}$$

Now set $q_{\mathrm{N_2}} = -q_{\mathrm{H_2O}}$, cancel the 10 mol from each side, and solve for T_f:

$$\begin{aligned} n_{\mathrm{N_2}}\left(\Delta_{\mathrm{vap}}H^{\ominus} - C_nT_n\right) + C_nT_f &= n_{\mathrm{H_2O}}\left(\Delta_{\mathrm{fus}}H^{\ominus} + C_wT_w\right) - C_nT_f \\ C_wT_f - C_nT_f &= \Delta_{\mathrm{fus}}H^{\ominus} - \Delta_{\mathrm{vap}}H^{\ominus} + C_wT_w + C_nT_n \end{aligned}$$

$$\begin{aligned} T_f &= \frac{\Delta_{\mathrm{fus}}H^{\ominus} - \Delta_{\mathrm{vap}}H^{\ominus} + C_nT_n + C_wT_w}{C_w + C_n} \\ &= \frac{(6.008 - 5.57)(10^3\,\mathrm{J\,mol}^{-1}) + [(29.088)(77.36) + (38.1)(273.15)]\,\mathrm{J\,mol}^{-1}}{38.1\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1} + 29.088\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1}} \\ &= \boxed{195\,\mathrm{K}} \end{aligned}$$