Chemistry 410B Exam 6 Fall 2016
Solutions

1. **40 points.**

   (a) The vapor pressure of THF at 293 K is 0.173 bar. Use Raoult's law to estimate the partial pressure at equilibrium of THF over a solution of 5.0 M $LiBH_4$ in THF. (The molarity of pure THF is 12.33 M. Assume the molarity is not affected by the solute.) **Solution:**

$$P_\mathrm{A} = P^\bullet_\mathrm{A}\, X_\mathrm{A} = (0.173\,\mathrm{bar})\left(\frac{12.33}{12.33+5.0}\right) = \boxed{0.123\,\mathrm{bar.}}$$

   (b) Calculate the osmotic pressure **in bar** across the membrane when the concentration inside the osmotic cell is 0.100 M at 298 K. **Solution:**

$$\Pi = RT[\mathrm{B}] = (0.083145\,\mathrm{bar\,L\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})(0.100\,\mathrm{mol\,L^{-1}}) = \boxed{2.48\,\mathrm{bar.}}$$

   (c) Indicate whether each of the following reactions has a $\Delta_\mathrm{rxn}S$ value that is large (**L**) or small (**S**) in magnitude, where large is $> 80\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and small is $< 40\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Also indicate whether the value is positive (+) or negative (−). **Solution:** If $|\Delta_\mathrm{rxn}n_\mathrm{gas}| \geq 1$, then we expect large $|\Delta_\mathrm{rxn}S|$, with the greater entropy on the side of the reaction with more moles of gas. If $\Delta_\mathrm{rxn}n_\mathrm{gas} = 0$, then the magnitude should be small. To find the sign of $\Delta_\mathrm{rxn}S$, we check first the rotational degrees of freedom, and then the vibrations:

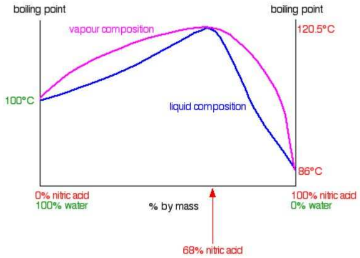
$$\begin{aligned}
\mathrm{I_2}(s) &\longrightarrow 2\mathrm{I}(g) && \boxed{+\mathrm{L}}\\
2\mathrm{CH_3OH}(g) + 3\mathrm{O_2}(g) &\longrightarrow 2\mathrm{CO_2}(g) + 4\mathrm{H_2O}(g) && \boxed{+\mathrm{L}}\\
2\mathrm{H_2CCO}(g) + 4\mathrm{O_2}(g) &\longrightarrow 4\mathrm{CO_2}(g) + 2\mathrm{H_2O}(g) && \boxed{+\mathrm{S}}
\end{aligned}$$

   For the third reaction, both sides of the reaction have the same number of rotations (because both sides have 4 linear and 2 non-linear molecules). But because the product side of the reaction has more vibrational modes in the linear molecules, it has the higher entropy.

   (d) In a calorimetry experiment, 0.100 mol of $Br_2(l)$ evaporates with ΔH° of 3.091 kJ. Find the final temperature of the 1.00 L ($c_P = 4.184\,\mathrm{J\,K^{-1}\,g^{-1}}$, $C_{Pm} = 75.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$) water bath if the initial temperature was 298.15 K. **Solution:**

$$\Delta T = -\frac{\Delta H^\circ}{C_{P,\mathrm{water}}} = -\frac{3091\,\mathrm{J}}{(4.184\,\mathrm{J\,K^{-1}\,g^{-1}})(1000\,\mathrm{g})} = -0.739\,\mathrm{K}$$

$$T_f = T_i + \Delta T = (298.15 - 0.739)\,\mathrm{K} = \boxed{297.41\,\mathrm{K.}}$$



2.

   (a) What is the boiling point of pure nitric acid? **Solution:** The boiling point is the vapor pressure where $X_{\mathrm{HNO_3}} = 1$: $\boxed{86^o\mathrm{C.}}$

(b) At what temperature is the azeotrope? **Solution:** The azeotrope is the point where both species are present (so neither X is zero) and both phases (liquid and gas) have the same composition: $\boxed{120.5^o\text{C.}}$

(c) Would this mixture show a positive, negative, or zero deviation from Raoult's law? **Solution:** The diagram shows that at any composition other than at the azeotrope, the mole fraction of the solvent (water to the left of the azeotrope, HNO_3 to the right) is *lower* than its mole fraction in the liquid. According to Raoult's law, the solvent vapor pressure above the solution should always be proportional to the mole fraction in the solution, so this is a $\boxed{\text{negative}}$ deviation.

(d) In one sentence, explain what process or structure at the molecular scale would justify your answer to the previous question. **Solution:** A negative deviation arises when the particles are more stable in the solution than in the gas phase, in this case because HNO_3 dissociates into ions in water, stabilizing the particles through ion-dipole attractions and hydrogen bonding.

3. Let the reaction $2\text{F}(g) \longrightarrow \text{F}_2(g)$ occur adiabatically, starting at an initial temperature of 298 K. Use the properties in the attached table of thermodynamic properties (including the heat capacities) to calculate the final temperature *and* the value of K_{eq} at the final temperature. **Solution:**

$$\begin{aligned}
\Delta_{\text{rxn}}H^{\circ} &= \Delta_f H^{\circ}(\text{F}_2) - 2\Delta_f H^{\circ}(\text{F}) = [0 - 2(78.99)]\ \text{kJ} = -157.98\,\text{kJ} \\
\Delta_{\text{rxn}}S^{\circ} &= S^{\circ}(\text{F}_2) - 2S^{\circ}(\text{F}) = [202.78 - 2(158.754)]\ \text{J K}^{-1}\,\text{mol}^{-1} = -114.73\,\text{J K}^{-1}\,\text{mol}^{-1} \\
C_P(\text{prod}) &= C_P(\text{F}_2) = 31.30\,\text{J K}^{-1} \\
\Delta T_{\text{ad}} &= -\frac{\Delta_{\text{rxn}}H^{\circ}}{C_P(\text{prod})} = -\frac{(-157.98\,\text{kJ})(10^3\,\text{J/kJ})}{31.30\,\text{J K}^{-1}} = 5047\,\text{K} \\
T_f &= T_i + \Delta T = (298 + 5047)\,\text{K} = \boxed{5345\,\text{K.}} \\
\Delta_{\text{rxn}}G^{\circ} &= \Delta_{\text{rxn}}H^{\circ} - T\Delta_{\text{rxn}}S^{\circ} = -157.98\,\text{kJ mol}^{-1} - (5345\,\text{K})(-114.73\,\text{J K}^{-1}\,\text{mol}^{-1})(10^{-3}\,\text{kJ/J}) = 455\,\text{kJ mol}^{-1} \\
\ln K_{\text{eq}} &= -\frac{\Delta_{\text{rxn}}G^{\circ}}{RT} = -\frac{455\,\text{kJ mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(5345\,\text{K})(10^{-3}\,\text{J/kJ})} = 10.24 \\
K_{\text{eq}} &= e^{10.24} = \boxed{2.81 \cdot 10^4.}
\end{aligned}$$

4. The two reaction surfaces drawn below describe the two reactions shown. There is no transition state for either reaction. The contour lines are drawn every $3\,\text{kJ mol}^{-1}$. The H atoms are labeled in half of each reaction. The CO bond axis is always perpendicular to and bisects the H_aH_b bond.

(a) R_2 in surface (a) is measuring the distance between what two atoms? **Solution:** $\boxed{\text{H}_a \text{ and C.}}$

(b) Find $\Delta_{\text{rxn}}E$ for reaction (a): $\text{H}_3^+ + \text{CO} \longrightarrow \text{H}_2 + \text{HCO}^+$. **Solution:** Crossing 15 contour lines to get to lower energy = $\boxed{-45\,\text{kJ mol}^{-1}.}$

(c) Find $\Delta_{\text{rxn}}E$ for the reaction $\text{HCO}^+ \longrightarrow \text{HOC}^+$. **Solution:** From the same reactants, the $\Delta_{\text{rxn}}E$ for reaction (b) is $-21\,\text{kJ mol}^{-1}$ (crossing 7 contour lines). Therefore, the $\Delta_{\text{rxn}}E$ for $\text{HCO}^+ \longrightarrow \text{HOC}^+$ is

$$E(\text{HOC}^+) - E(\text{HCO}^+) = \Delta_{\text{rxn}}E(\text{b}) - \Delta_{\text{rxn}}E(\text{a}) = [-21 - (-45)]\ \text{kJ mol}^{-1} = \boxed{+24\,\text{kJ mol}^{-1}.}$$

(d) How many vibrational coordinates would we need to describe the *entire* reaction surface? **Solution:** There are a total of 5 atoms in the system, so $3N_{\text{atom}} - 6 = \boxed{9}$ vibrational modes.