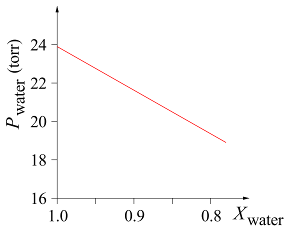
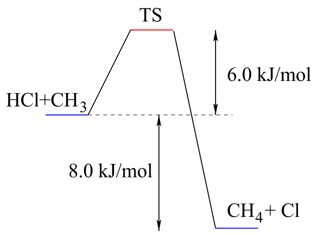
Chemistry 410B Exam 6 Spring 2012
Solutions

1. **40 points.**

   (a) Plot the vapor pressure of water over a solution of mannitol as a function of the mole fraction of mannitol. The vapor pressure of pure water at 298 K is 23.8 torr. **Solution:** According to Raoult's law, the vapor pressure of the solvent is proportional to its mole fraction, so the curve is a straight line starting at $P^\bullet_{\text{water}}$ for $X = 1$ and decreasing towards 0 at $X = 0$.





   (b) Sketch a reaction diagram for the reaction

$$\mathrm{CH_3}(g) + \mathrm{HCl}(g) \longrightarrow \mathrm{CH_4}(g) + \mathrm{Cl}(g)$$

   which has an activation energy of $6\,\mathrm{kJ\,mol^{-1}}$ and a $\Delta_{\text{rxn}}E$ of $-8\,\mathrm{kJ\,mol^{-1}}$.

   (c) Find the $\Delta_{\text{rxn}}G^\ominus$ and K_{eq} at 298 K for the reaction

$$\mathrm{N_2}(g) + 3\mathrm{H_2}(g) \longrightarrow 2\mathrm{NH_3}(g).$$

   Solution: This is the formation reaction for 2.00 mol of NH_3, so we use twice the free energy of formation: $\Delta_{\text{rxn}}G^\ominus = 2\Delta_f G^\ominus = \boxed{-32.90\,\mathrm{kJ.}}$ The equilibrium constant is therefore

$$K_{\text{eq}} = e^{-\Delta_{\text{rxn}}G^\ominus/(RT)} = e^{32900/[(8.3145)(298)]} = e^{13.3} = \boxed{5.97 \cdot 10^5.}$$

   (d) Write the expression for K_p for the above reaction. **Solution:** $\boxed{K_p = \frac{P^2_{\mathrm{NH_3}}}{P_{\mathrm{N_2}}P^3_{\mathrm{H_2}}}}$

2. Start with an osmotic cell where the volume of the cell is 10. ml and the volume of the bath is 100. ml. We first add 0.100 mmol B to the cell. Neither B nor C can penetrate the semipermeable membrane. What is the minimum number of moles C that must be added to the bath to get a pressure difference of 0.10 bar at 298 K? **Solution:** We can show that the pressure difference, as you might expect, is proportional to the difference

in concentrations:

$$\begin{aligned}
\mu_{\mathrm{A}}^{\mathrm{bath}} &= \mu_{\mathrm{A}}^{\bullet}(P^{\ominus}) + V_m(P + \Pi^{\mathrm{bath}} - P^{\ominus}) + RT\ln a_{\mathrm{A}}^{\mathrm{bath}} \\
\ln a_{\mathrm{A}}^{\mathrm{bath}} &= \ln X_{\mathrm{A}}^{\mathrm{bath}} = \ln(1 - X_{\mathrm{C}}) \approx -X_{\mathrm{C}} \\
\mu_{\mathrm{A}}^{\mathrm{bath}} &\approx \mu_{\mathrm{A}}^{\bullet}(P^{\ominus}) + V_m(P + \Pi^{\mathrm{bath}} - P^{\ominus}) - RTX_{\mathrm{C}} \\
\mu_{\mathrm{A}}^{\mathrm{cell}} &\approx \mu_{\mathrm{A}}^{\bullet}(P^{\ominus}) + V_m(P + \Pi^{\mathrm{cell}} - P^{\ominus}) - RTX_{\mathrm{B}} \\
\mu_{\mathrm{A}}^{\mathrm{bath}} &= \mu_{\mathrm{A}}^{\mathrm{cell}} \\
V_m\Pi^{\mathrm{bath}} - RTX_{\mathrm{C}} &= V_m\Pi^{\mathrm{cell}} - RTX_{\mathrm{B}} \\
\Delta\Pi = \Pi^{\mathrm{cell}} - \Pi^{\mathrm{bath}} &= \frac{RT(X_{\mathrm{B}} - X_{\mathrm{C}})}{V_m} = RT([\mathrm{B}] - [\mathrm{C}])
\end{aligned}$$

Then we solve for [C] and use that to find the number of moles C that have to be added to the bath:

$$\begin{aligned}
[\mathrm{C}] &= [\mathrm{B}] - \frac{\Delta\Pi}{RT} = \frac{n_{\mathrm{B}}}{V_{\mathrm{B}}} - \frac{\Delta\Pi}{RT} \\
n_{\mathrm{C}} &= V_{\mathrm{C}}[\mathrm{C}] = V_{\mathrm{C}}\left[\frac{n_{\mathrm{B}}}{V_{\mathrm{B}}} - \frac{\Delta\Pi}{RT}\right] \\
&= (0.100\,\mathrm{L})\left[\frac{1.00 \cdot 10^{-4}\,\mathrm{mol}}{0.010\,\mathrm{L}} - \frac{0.10\,\mathrm{bar}}{(0.083145\,\mathrm{bar\,L\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}\right] \\
&= 5.96 \cdot 10^{-4}\,\mathrm{mol} = \boxed{0.60\,\mathrm{mmol.}}
\end{aligned}$$

3. Write "+" or "−" or "0" to indicate whether $\Delta_{\mathrm{rxn}}S^{\ominus}$ of each of the following processes is likely to be positive, negative, or zero.

$2\mathrm{NO}(g) + \mathrm{O}_2(g) \longrightarrow 2\mathrm{NO}_2(g)$ n_{gas} decreases	$\boxed{-}$
formation reaction of NaCl(s) n_{gas} decreases $\mathrm{Na}(s) + \frac{1}{2}\mathrm{Cl}_2(g) \longrightarrow \mathrm{NaCl}(s)$	$\boxed{-}$
formation reaction of $\mathrm{Cl}_2(g)$ $\mathrm{Cl}_2(g) \longrightarrow \mathrm{Cl}_2(g)$	$\boxed{0}$
combustion of $\mathrm{CH}_4(g)$ n_{gas} decreases $\mathrm{CH}_4 + 3\mathrm{O}_2(g) \longrightarrow \mathrm{CO}_2(g) + 2\mathrm{H}_2\mathrm{O}(l)$	$\boxed{-}$
sublimation of $\mathrm{CO}_2(s)$ n_{gas} increases $\mathrm{CO}_2(s) \longrightarrow \mathrm{CO}_2(g)$	$\boxed{+}$

4. Calculate the overall change in volume of the gases for the reaction

$$\mathrm{N}_2\mathrm{O}_4(g) \longrightarrow \mathrm{N}_2(g) + 2\mathrm{O}_2(g)$$

carried out adiabatically at 1.00 bar, starting from 0.100 mol $\mathrm{N}_2\mathrm{O}_4$ at 298 K.

Solution: We can calculate the final temperature using the expression for the adiabatic flame temperature. The $\Delta_{\text{rxn}}H^{\ominus}$ is equal to -1 times the enthalpy of formation for N_2O_4:

$$T_2 = 298\,\text{K} - \frac{\Delta_{\text{rxn}}H}{C_P(\text{products})} = 298\,\text{K} - \frac{-(9.16\,\text{kJ}\,\text{mol}^{-1})(10^3\,\text{J}/\,\text{kJ})}{(29.088 + 2 \cdot 29.355)\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}} = 402\,\text{K}$$

Then we can use the ideal gas law to calculate the volume of the 0.3 moles of product at the final temperature and the volume of the 0.1 mole of reactant at the initial temperature. We want the difference:

$$\begin{aligned}
\Delta_{\text{rxn}}V^{\ominus} &= V_{\text{prod}} - V_{\text{react}} = \frac{n_{\text{prod}}RT_2}{P^{\ominus}} - \frac{n_{\text{react}}RT_1}{P^{\ominus}} \\
&= \frac{R}{P^{\ominus}}\left[n_{\text{prod}}T_2 - n_{\text{react}}T_1\right] \\
&= \frac{0.083145\,\text{bar}\,\text{L}\,\text{K}^{-1}\,\text{mol}^{-1}}{1.00\,\text{bar}}\left[(0.300\,\text{mol})(402\,\text{K}) - (0.100\,\text{mol})(298\,\text{K})\right] = \boxed{7.55\,\text{L}.}
\end{aligned}$$