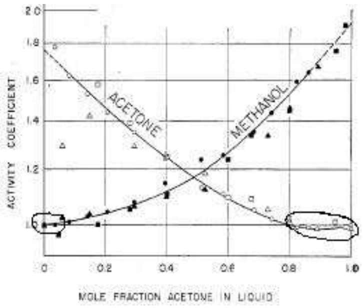
Chemistry 410B Exam 6 Spring 2009
Solutions

1. **40 points.**

   (a) In the graph of the activity coefficients γ for methanol and acetone, circle the region or regions where either liquid obeys Raoult's law. **Solution:** Raoult's law will be obeyed in the region where the activity is equal to the mole fraction, where γ is close to one. As expected, this is in the region where the mole fraction of the liquid is high (close to one).



   (b) On the F+H_2 reaction surface, determine the energy, relative to H+HF, when the F atom is 2.5 Å from the nearest H atom, and the H atoms are separated by 1.5 Å. **Solution:** About $\boxed{360\,\text{kJ}\,\text{mol}^{-1}}$.

   (c) Fill in the table. **Solution:** The number of translational degrees of freedom goes down, so $\Delta S < 0$.

	$9O_2(g)$	+	$2HC_4H(g)$	$\longrightarrow$	$8CO_2(g)$	+	$2H_2O(g)$
translational	$9 \times 3 = 27$		$2 \times 3 = 6$		$8 \times 3 = 24$		$2 \times 3 = 6$
rotational	$9 \times 2 = 18$		$2 \times 2 = 4$		$8 \times 2 = 16$		$2 \times 3 = 6$
vibrational	$9 \times 1 = 9$		$2 \times 13 = 26$		$8 \times 4 = 32$		$2 \times 3 = 6$
$\Delta_{\text{rxn}}S$ + or $\boxed{-}$							

   (d) For the metabolism of methylamine to formaldehyde and ammonia, the enthalpy of reaction is $-201.8\,\text{kJ}\,\text{mol}^{-1}$ and the entropy of reaction is $148.8\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$. Find the value of the equilibrium constant at 325 K. **Solution:**

$$K_{\text{eq}} = e^{-\Delta_{\text{rxn}}G^{\ominus}/(RT)} = \exp\left[-\frac{\Delta_{\text{rxn}}H^{\ominus}}{RT} + \frac{\Delta_{\text{rxn}}S^{\ominus}}{R}\right]$$
$$= \exp\left[\frac{201800}{(8.3145)(325)} + \frac{148.8}{8.3145}\right] = e^{92.6} = \boxed{1.6 \cdot 10^{40}}.$$

2. If $k_X = 8.64 \cdot 10^4$ bar, estimate the molarity of $N_2(g)$ in water at 298 K when the water is in equilibrium with 1.20 bar of air, 78% N_2 by volume. **Solution:** To get the molarity, use the concentration of liquid water ($55.6\,\text{mol}\,\text{L}^{-1}$) to get the total number of moles, and use Henry's law to find the mole fraction of N_2:

$$[N_2] = \frac{n_{N_2}}{V_{\text{soln}}} = \frac{n_{N_2}}{n_{\text{soln}}/(55.6\,\text{mol}\,\text{L}^{-1})}$$
$$= X_{N_2}(55.6\,\text{mol}\,\text{L}^{-1}) = \frac{\text{P}_{N_2}}{\text{k}_\text{X}}(55.6\,\text{mol}\,\text{L}^{-1})$$
$$= \frac{(0.78)(1.10)}{8.64 \cdot 10^4}(55.6\,\text{mol}\,\text{L}^{-1}) = \boxed{5.5 \cdot 10^{-4}\,M}.$$

3. Calculate $\Delta_{\text{rxn}}F^{\circ}$ for the formation of 1.00 mol $IF_5(g)$ from solid iodine and fluorine gas at 320 K and 1.00 bar. **Solution:** The chemical reaction is

$$\frac{1}{2}\mathrm{I_2}(s) + \frac{5}{2}\mathrm{F_2}(g) \longrightarrow \mathrm{IF_5}(g).$$

$$\begin{aligned}
\Delta_{\text{rxn}}F^{\circ}(T_2) &= \Delta_{\text{rxn}}(G-PV) = \Delta_{\text{rxn}}G^{\circ}(T_2) - \Delta_{\text{rxn}}(PV) \\
&= \left[\Delta_{\text{rxn}}H^{\circ}(T_2) - T_2\Delta_{\text{rxn}}S(T_2)\right] - RT_2\Delta_{\text{rxn}}n_{\text{gas}} \\
&= \left[\Delta_{\text{rxn}}H^{\circ}(T_1) + \Delta_{\text{rxn}}C_P\Delta T\right] - T_2\left[\Delta_{\text{rxn}}S^{\circ}(T_1) + \Delta_{\text{rxn}}C_P \ln\frac{T_2}{T_1}\right] - RT_2\Delta_{\text{rxn}}n_{\text{gas}} \\
&= \left[-822.49\,\text{kJ mol}^{-1} + (-6.27\,\text{J K}^{-1}\,\text{mol}^{-1})(22\,\text{K})(10^{-3}\,\text{kJ/ J})\right] \\
&\quad - (320\,\text{K})\left[-237.32\,\text{J K}^{-1}\,\text{mol}^{-1} + (-6.27\,\text{J K}^{-1}\,\text{mol}^{-1})\ln\frac{320}{298}\right](10^{-3}\,\text{kJ/ J}) \\
&\quad - (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(320\,\text{K})(-3/2)(10^{-3}\,\text{kJ/ J}) \\
&= -822.628 + 76.085 + 3.991 = \boxed{-742.55\,\text{kJ mol}^{-1}}.
\end{aligned}$$

4. (a) Write the chemical reaction for the combustion of $H_2C{=}C{=}O$ at 298 K. **Solution:**

$$\mathrm{H_2C{=}C{=}O}(g) + 2\mathrm{O_2}(g) \longrightarrow 2\mathrm{CO_2}(g) + \mathrm{H_2O}(l)$$

(b) The enthalpy of combustion for ketene is $-1025.3\,\text{kJ mol}^{-1}$. Find $\Delta_f H[\mathrm{H_2C_2O}]$. **Solution:**

$$\begin{aligned}
\Delta_{\text{comb}}H^{\circ} &= 2\Delta_f H^{\circ}[\mathrm{CO_2}] + \Delta_f H^{\circ}[\mathrm{H_2O}] - \Delta_f H[\mathrm{H_2C_2O}] - 2\Delta_f H^{\circ}[\mathrm{O_2}] \\
\Delta_f H[\mathrm{H_2C_2O}] &= 2\Delta_f H^{\circ}[\mathrm{CO_2}] + \Delta_f H^{\circ}[\mathrm{H_2O}] - \Delta_{\text{comb}}H^{\circ} - 2\Delta_f H^{\circ}[\mathrm{O_2}] \\
&= 2(-393.509\,\text{kJ mol}^{-1}) + (-285.830\,\text{kJ mol}^{-1}) - (-1025.3\,\text{kJ mol}^{-1}) - 2(0) \\
&= \boxed{-47.5\,\text{kJ mol}^{-1}}.
\end{aligned}$$

(c) Estimate the adiabatic flame temperature. **Solution:**

$$\begin{aligned}
C_P(\text{prod}) &= [2(37.11) + 33.577]\ \text{J K}^{-1}\,\text{mol}^{-1} = 107.80\,\text{J K}^{-1}\,\text{mol}^{-1} \\
T_{\text{ad}} &= T_1 - \frac{\Delta_{\text{comb}}H(T_1)}{C_P(\text{prod})} = 298\,\text{K} - \frac{-1025.3\,\text{kJ mol}^{-1}}{(107.80\,\text{J K}^{-1}\,\text{mol}^{-1})(10^{-3}\,\text{kJ/ J})} = \boxed{9809\,\text{K}}.
\end{aligned}$$