Due: Friday, 10-February-2006 by the beginning of class. I will get answers up shortly after class, and try to grade and return them before close of business Friday. Remember this is really meant to be your own work. Sorry for the somewhat shorter time, but I wanted you to be able to ask questions, and get ready for the first exam. (Note that the problem set is 2 pages.)

1) Refining petroleum involves cracking large hydrocarbon molecules into smaller, more volatile pieces. A simple example of hydrocarbon cracking is the thermal gas-phase decomposition of butane to give ethane and ethylene

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{CH}_3 + \quad \text{CH}_2 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{butane} & \quad \text{ethane} + \quad \text{ethylene} \\
\text{C}_4\text{H}_{10} & \quad \text{C}_2\text{H}_6 \quad \text{C}_2\text{H}_4
\end{align*}
\]

a) Write the equilibrium constant expressions for \( K_c \) and \( K_p \).

b) The value of \( K_p \) at 500ºC is 12. What is the value of \( K_c \)?

c) A sample of butane having a pressure of 50 atm is heated at 500ºC in a closed container at constant volume. When equilibrium is reached, what percentage of the butane has been converted to ethane and ethylene?

d) What is the total pressure at equilibrium?

2) The equilibrium constant \( K_p \) for the reaction

\[
P\text{Cl}_5(g) \rightleftharpoons P\text{Cl}_3(g) + Cl_2(g)
\]

is 23.6 at 500 K and 380 at 600 K

a) Is the reaction endothermic or exothermic? Justify your answer.

b) How are the equilibrium concentrations affected by each of the following changes? (Hint: you must do both reactants and products.)

i) An increase in the volume of the vessel.

ii) Addition of an inert gas

iii) Addition of a catalysts
3) Gaseous acetic acid molecules have a certain tendency to form dimers. (We saw this last term on the last problem set.) (A dimer is a molecule formed by the association of two identical, simpler molecules.) The equilibrium constant $K_p$ at 25°C for this reaction is $1.3 \times 10^3$.

   a) If the initial pressure of CH$_3$COOH monomer (the simpler molecule) is $7.5 \times 10^{-3}$ atm, what are the pressures of the monomer and dimer when the system comes to equilibrium? (The simpler quadratic is obtained by assuming that all the molecules have dimerized, and then some dissociates to monomer.)

   b) Why do the acetic acid molecules dimerize? What type of structure would you draw for the dimer? (This is asking for a drawing of the dimer!)

   c) As the temperature increases, would you expect the percentage of dimer to increase or decrease? Explain.

4) A 79.2 g chunk of dry ice (CO$_2$(s)) and 30.0 g of graphite (C(s)) were placed in an empty 5.00 L container, and the mixture was heated to achieve equilibrium. The reaction is:

   \[ \text{CO}_2(\text{g}) + \text{C}(\text{s}) \rightleftharpoons 2 \text{CO}(\text{g}) \]

   a) What is the value of $K_p$ at 1000 K if the gas density at 1000 K is 16.3 g/L?

   b) What is the value of $K_p$ at 1100 K if the gas density at 1100 K is 16.9 g/L?

   c) Is the reaction endothermic or exothermic? Justify your answer.

5) Given the Arrhenius equation, $k = Ae^{-\frac{E_a}{RT}}$ and the relation between the equilibrium constant and the forward and reverse rate constants, $K = \frac{k_f}{k_r}$, explain why $K_c$ for an exothermic reaction decreases with increasing temperature.