Winter 2012 Chem 1B Discussion Worksheet

Chapter 14: Equilibrium

The assignments are from: Chemistry by Raymond Chang; McGraw Hill Higher Education, 10th Edition, 2010

Goals

- Understand the concept of chemical equilibrium
- Write equilibrium constants for chemical reactions
- Understand different units used for equilibrium constants; $K_C$ and $K_P$
- Calculate equilibrium concentrations from equilibrium constants and vice versa
- Predict the direction of chemical reaction using reaction quotients
- Understand the way equilibrium systems respond to a stress

Exercises

1. Concentrations are usually measured in units of molarity (mol/L) for liquids and units of partial pressure [atm] are more common for gases. For problems dealing with gas-phase equilibria, you should be able to convert between different concentration units quickly. Make sure you are comfortable with the following problem before you proceed: If you are not – solve it!

   A small amount (0.44 grams) of dry ice is placed in a two liter bulb maintained at a room temperature (23 °C). Calculate the CO$_2$ concentration in [mol/L] and partial pressure in [atm] after the dry ice sublimes.

2. Equilibrium refers to a condition wherein the rates of forward reaction(s) are exactly balanced by the rates of reverse reaction(s). The forward and reverse reactions do not stop at equilibrium even though the concentrations of reactants and products stop changing.

   What processes are balanced in rates during the following equilibria:
   - Water vapor in equilibrium with liquid water
   - Gas-phase acetic acid in equilibrium with acetic acid dimer
   - A substance at its triple point
   - Blackbody radiator in equilibrium with its radiation field

3. The equilibrium constant depends on the reaction stoichiometric coefficients as well as the direction the reaction equation is written. Therefore, the equilibrium constants for the forward and reverse reactions are reciprocals of each other. i.e. $K_{forward} = 1/K_{reverse}$

   Problem 14.15: The equilibrium constant $K_c$ for the reaction:
   
   \[ 2 \text{HCl (g)} \rightleftharpoons \text{H}_2 \text{(g)} + \text{Cl}_2 \text{(g)} \]
   
   Is $4.17 \times 10^{-34}$ at 25 °C. What is the equilibrium constant for the reactions
   
   \[ \text{H}_2 \text{(g)} + \text{Cl}_2 \text{(g)} \rightleftharpoons 2 \text{HCl (g)} \]
   
   at the same temperature?

   Problem 14.20: A reaction vessel contains NH$_3$, N$_2$, and H$_2$ at equilibrium at a certain temperature. The equilibrium concentrations are $[\text{NH}_3] = 0.25 \text{ M}$, $[\text{N}_2] = 0.11 \text{ M}$, and $[\text{H}_2] = 1.91 \text{ M}$. Calculate the equilibrium constant $K_c$ if the reaction is represented as:

   (a) $\text{N}_2 \text{(g)} + 3 \text{H}_2 \text{(g)} \rightleftharpoons 2 \text{NH}_3 \text{(g)}$
4. Equilibrium constants $K_C$ and $K_P$ are related to each other via the ideal gas law. For example, for reaction $aA(g) \rightleftharpoons bB(g)$ the constants are $K_P = K_C \times (RT)^{\Delta n}$ where $\Delta n = b - a$. In general, $K_C$ and $K_P$ are equal only when the number of moles of gas-phase reactants and products are the same ($\Delta n = 0$).

**Problem 14.21:** The equilibrium constant $K_C$ for the reaction:

\[ \text{I}_2 (g) \rightleftharpoons 2 \text{I} (g) \]

is $3.8 \times 10^{-5}$ at 727 °C. Calculate both $K_C$ and $K_P$ for the equilibrium

\[ 2 \text{I} (g) \rightleftharpoons \text{I}_2 (g) \]

at the same temperature.

**Problem 14.22:** At equilibrium, the pressure of the following reaction mixture

\[ \text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g) \]

is 0.105 atm at 350 °C. Calculate both $K_C$ and $K_P$ for this reaction.

5. If a reaction can be represented as a sum of two other reactions, the equilibrium constant for the overall reaction is equal to the product of equilibrium constants of the individual sub-reactions.

**Problem 14.30:** Predict the equilibrium constant for the last reaction based on the information provided:

\[ \text{H}_2\text{C}_2\text{O}_4 (aq) \rightleftharpoons \text{H}^+ (aq) + \text{HC}_2\text{O}_4^- (aq) \quad K_c' = 6.5 \times 10^{-2} \]

\[ \text{HC}_2\text{O}_4^- (aq) \rightleftharpoons \text{H}^+ (aq) + \text{C}_2\text{O}_4^{2-} (aq) \quad K_c'' = 6.1 \times 10^{-5} \]

\[ \text{H}_2\text{C}_2\text{O}_4 (aq) \rightleftharpoons \text{C}_2\text{O}_4^{2-} (aq) + 2 \text{H}^+ (aq) \quad K_c = ???? \]

**Problem 14.31:** Predict the equilibrium constant for the last reaction based on the information provided:

\[ \text{C} (s) + \text{CO}_2 (g) \rightleftharpoons 2 \text{CO} (g) \quad K_p' = 1.3 \times 10^{14} \]

\[ \text{CO} (g) + \text{Cl}_2 (g) \rightleftharpoons \text{COCl}_2 (g) \quad K_p'' = 6.0 \times 10^{-3} \]

\[ \text{C} (s) + \text{CO}_2 (g) + 2\text{Cl}_2 (g) \rightleftharpoons 2 \text{COCl}_2 (g) \quad K_p = ???? \]

6. The reaction quotient, $Q$, is a useful quantity for predicting the direction of reactions in systems not at equilibrium. It has the same functional form as the equilibrium constant except that it is calculated from instantaneous concentrations, and not from the equilibrium ones. For example, for reaction $aA + bB \rightleftharpoons cC + dD$ the equilibrium constant is $K_C = \frac{[C]_e^c[D]_e^d}{[A]_e^a[B]_e^b}$ and the reaction quotient is $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$. If $Q<K_C$ the system will react to produce more products, $C$ and $D$. Conversely, if $Q>K_C$ the system will react to produce more reactants, $A$ and $B$.

**Problem 14.40:** For the synthesis of ammonia

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]
the equilibrium constant \( K_C \) at 375°C is 1.2. Starting with \([H_2]_0 = 0.76 \text{ M}, [N_2]_0 = 0.60 \text{ M}, \) and \([NH_3]_0 = 0.48 \text{ M}, \) which gases will have increased/decreased in concentration when the mixture comes to an equilibrium?

7. The concentrations of reactants and products at equilibrium can be calculated from the initial non-equilibrium concentrations by carefully tracking the molar amounts of reactants and products that are consumed or formed in the reactions.

**Problem 14.41:** For the reaction
\[ \text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{H}_2\text{O}(\text{g}) + \text{CO}(\text{g}) \]
at 700°C, \( K_C = 0.534 \). Calculate the number of moles of \( \text{H}_2 \) that will be present at equilibrium if a mixture of 0.300 mole of \( \text{CO} \) and 0.300 mole of \( \text{H}_2\text{O} \) is allowed to equilibrate at 700°C in a 10.0-L container.

**Problem 14.42:** At 1000 K, a sample of pure \( \text{NO}_2 \) decomposes
\[ 2 \text{NO}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \]
The equilibrium constant \( K_P \) is 158. The partial pressure of \( \text{O}_2 \) turns out to be 0.25 atm at equilibrium. What are equilibrium pressures of NO and \( \text{NO}_2 \) under the same conditions?

**Problem 14.44:** Molecular iodine dissociate at high temperatures as follows:
\[ \text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g}) \]
At 1000K, the equilibrium constant \( K_C \) is \( 3.80 \times 10^{-5} \). Starting with 0.0456 mole of pure \( \text{I}_2 \) in a 2.30-L flask maintained at 1000K calculate the equilibrium concentrations of \( \text{I} \) and \( \text{I}_2 \).

8. When a stress is applied to an equilibrium system, the equilibrium is shifted in the direction of relieving the stress.

**a). Problem 14.56:** What effect does an increase in pressure have on each of the following systems at equilibrium? Assume that the system is contained in cylinder with a movable piston maintained at a constant temperature:
\[ \text{A}(\text{s}) \rightleftharpoons 2 \text{B}(\text{s}) \]
\[ 2 \text{A}(\text{l}) \rightleftharpoons \text{B}(\text{l}) \]
\[ \text{A}(\text{s}) \rightleftharpoons \text{B}(\text{g}) \]
\[ \text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) \]
\[ \text{A}(\text{g}) \rightleftharpoons 2 \text{B}(\text{g}) \]

**b). Problem 14.61:** Consider the gas-phase reaction in a closed container:
\[ \text{O}_2(\text{g}) + 2 \text{CO}(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g}) \]
Predict the shift in the equilibrium position when inert gas helium is added to the system: (a) at constant pressure; (b) at constant volume. Assume that the addition of helium has no effect on the temperature of the container.