AP CHEMISTRY NOTES 8-1

CHEMICAL EQUILIBRIUM: AN INTRODUCTION

Chemical Equilibrium – a dynamic state in which the rate of the forward reaction and the rate of the reverse reaction in a system are equal (the concentration of the products and reactants remains ***constant*** but ***not equal***)

EQUILIBRIUM EXPRESSIONS

Equilibrium Constant (K_{eq}) – a value which relates the concentration of products with the concentration of reactants in a chemical reaction (units depend on the reaction and are usually not used)

Also known as **"K_c"** (concentration equilibrium constant)

and **"K_p"** (pressure equilibrium constant)

or simply **"K"**

For the reaction:

$$wA + xB \leftrightarrow yC + zD$$

the ***equilibrium constant expression*** would be:

$$K_c = \frac{[C]^y\,[D]^z}{[A]^w\,[B]^x}$$

If the ***reverse reaction*** occurs:

$$K_c' = \frac{1}{K_c}$$

If the original reaction is ***multiplied by some factor "n"***:

$$K_c' = K_c^{\,n}$$

For a ***2-step reaction*** with K_{c1} and K_{c2} as equilibrium constants for each step:

$$K_{c-overall} = K_{c1} \times K_{c2}$$

Pressures can also be used in equilibrium expressions:

$$K_p = \frac{(P_C)^y\,(P_D)^z}{(P_A)^w\,(P_B)^x}$$

NOTE:

$$K_c = K_p$$

if the # of moles of gaseous reactant = the # of moles of gaseous product

OTHERWISE:

$$K_p = K_c\,(RT)^{\Delta n}$$

where ***"Δn"*** = # moles gaseous products – # moles gaseous reactants

Also note: Concentrations of pure solids and pure liquids are not included in equilibrium expressions because they are constant

In addition: If ***K>>1***, then the equilibrium is shifted to the right (favoring ***products***)

If ***K<<1***, then the equilibrium is shifted to the left (favoring ***reactants***)

EXAMPLE: Give the equilibrium constant expressions for the following reactions:

$$4NH_{3(g)} \quad + \quad 7O_{2(g)} \quad \leftrightarrow \quad 4NO_{2(g)} \quad + \quad 6H_2O_{(g)}$$

$$CaCO_{3(s)} \quad \leftrightarrow \quad CaO_{(s)} \quad + \quad CO_{2(g)}$$

EXAMPLE: Consider the reaction

$$2NOCl_{(g)} \leftrightarrow 2NO_{(g)} + Cl_{2(g)}$$

3.00 mol NOCl, 1.00 mol NO, and 2.00 mol Cl_2 are mixed in a 10.0-L flask. After the system has reached equilibrium, the concentrations at 35°C are observed to be:

$[Cl_2] = 1.52 \times 10^{-1}$ <u>M</u>
$[NO] = 4.00 \times 10^{-3}$ <u>M</u>
$[NOCl] = 3.96 \times 10^{-1}$ <u>M</u>

Calculate the value of "K" for this reaction at 35°C:

Calculate the value of "K" for the reverse reaction:

Calculate the value of "K" for the reaction: $4NOCl_{(g)} \leftrightarrow 4NO_{(g)} + 2Cl_{2(g)}$

Calculate the value of "K_p" for the reaction in part "a":

http://www.chm.davidson.edu/ronutt/che115/EquKin/EquKin.htm

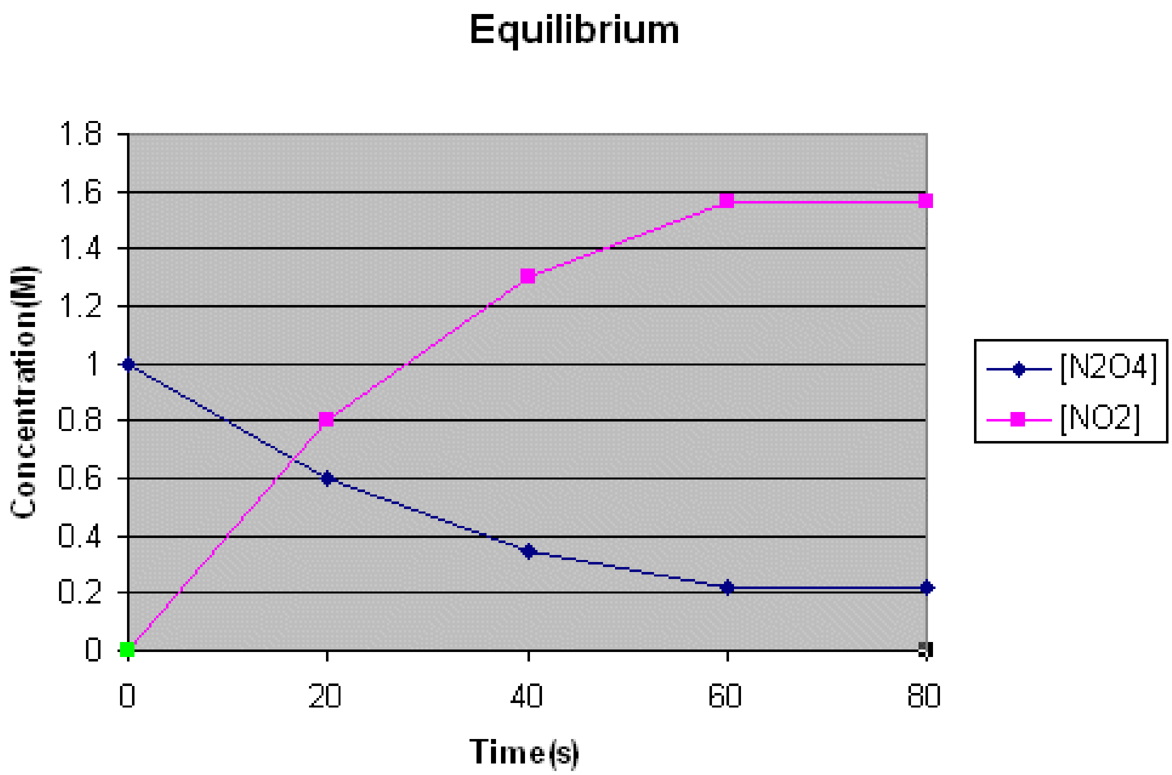

Fig. 1

$NO_{2(g)}$ ↔ $N_2O_{4(g)}$

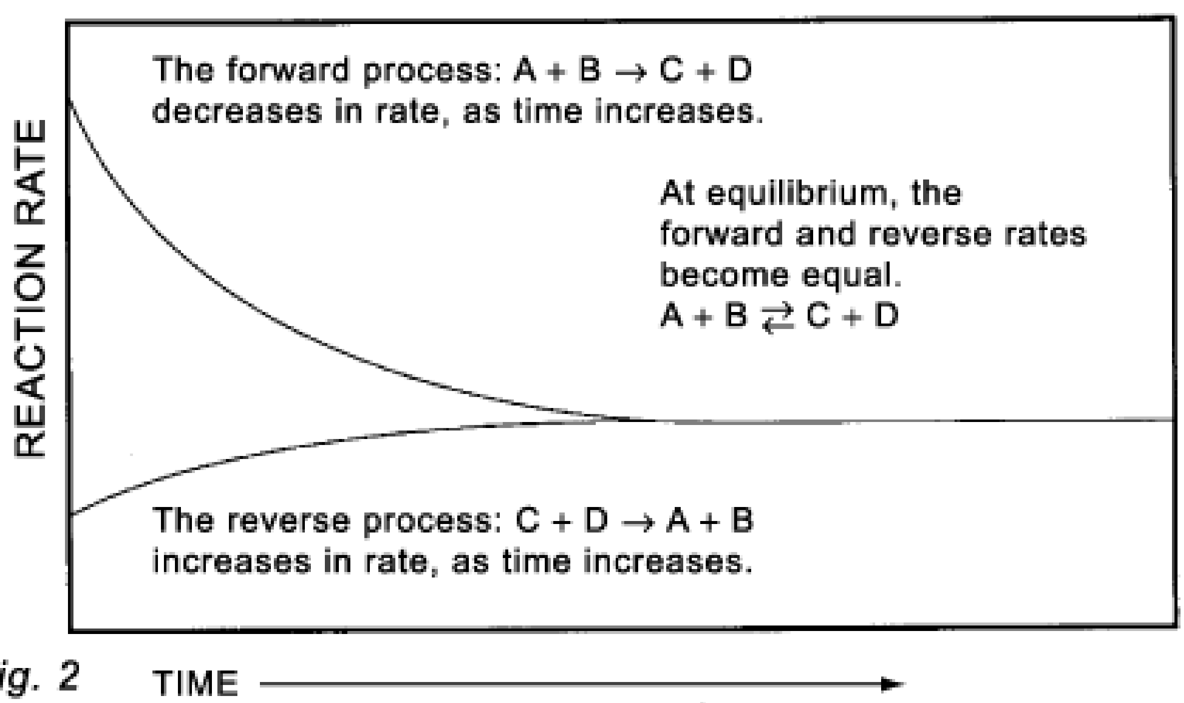

Fig. 2

EQUILIBRIUM: Le CHATELIER'S PRINCIPLE

Le Chatelier's Principle – When a stress is applied to a system the equilibrium will shift in the direction that will relieve that stress.

$$2NH_3 \leftrightarrow N_2 + 3H_2$$

If a reaction shifts in the direction that ***favors the products*** as written in a chemical equation, it is referred to as a ***shift right*** (ie. the reaction proceeds in the forward direction):

If a reaction shifts in the direction that ***favors the reactants*** as written in a chemical equation, it is referred to as a ***shift left*** (ie. the reaction proceeds in the reverse direction):

Changes in Concentration

*Increasing the concentration of a reactant will shift the reaction to the right (ie. to the opposite side)
*Increasing the concentration of a product will sift the reaction to the left (ie. to the opposite side)

*A change in concentration of a reactant or product will not change the value of "K_c"

*A change in the concentration of a pure solid or a pure liquid will not affect equilibrium

$$H_2CO_{3(aq)} + \text{heat} \leftrightarrow H_2O_{(l)} + CO_{2(g)}$$

Changes in Temperature

*Increasing the T^o of an exothermic reaction will shift the react to the left ("K_c" will decrease)
*Decreasing the T^o of an exothermic reaction will shift the reaction to the right ("K_c" will increase)

*Increasing the T^o of an endothermic reaction will shift the reaction to the right ("K_c" will increase)
*Decreasing the T^o of an endothermic reaction will shift the reaction to the left ("K_c" will decrease)

$$H_2CO_{3(aq)} + \text{heat} \leftrightarrow H_2O_{(l)} + CO_{2(g)}$$

Changes in Pressure

*Only affects systems having a gaseous reactant and/or product

*Increasing pressure shifts the reaction to the side with the fewest number of moles of gas
*Decreasing pressure shifts the reaction to the side with the greatest number of moles of gas
*Pressure change has ***no effect*** on reactions in which #moles gaseous reactant = #moles gaseous product

*Adding an inert gas does not affect equilibrium

*Pressure changes will ***not*** affect the value of "K_c"

$$H_2CO_{3(aq)} + \text{heat} \leftrightarrow H_2O_{(l)} + CO_{2(g)}$$

Addition of a Catalyst

*Adding a catalyst has ***no effect*** on equilibrium (it just causes the reaction to reach equilibrium faster)

EXAMPLE: Consider the reaction

$$2NO_{2(g)} \leftrightarrow N_{2(g)} + 2O_{2(g)} + \text{heat}$$

A vessel contains nitrogen dioxide, nitrogen, and oxygen at equilibrium. Predict how each of the following stresses will shift the reaction. In addition, determine the effect on the concentration of oxygen in the container as well as the value of "K_c".

	Direction of shift	Δ [oxygen]	Δ K_c
*nitrogen dioxide is added			
*nitrogen is removed			
*helium is added			
*the temperature is increased			
*the pressure is decreased			
*a catalyst is added			
*the volume of the container is halved			

EQUILIBRIUM: THE REACTION QUOTIENT

The ***Reaction Quotient*** **(Q)** is determined in the same manner as **“K_c”**, but is not at equilibrium.

The reaction quotient used values for concentrations of substances at points other than equilibrium.

The reaction quotient can determine which way a reaction needs to shift in order to reach equilibrium.

*If **Q > K** . . . . the concentration of products is too high; the reaction will shift left to reach equilibrium

*If **Q < K** . . . . the concentration of products is too low; the reaction will shift right to reach equilibrium

*If **Q = K** . . . . the system is at equilibrium

EXAMPLE: For the synthesis of ammonia, the value of “K” is 6×10^{-2} at $500^{o}C$. In an experiment, 0.50 mol of nitrogen, 1.0×10^{-2} mol of hydrogen, and 1.0×10^{-4} mol of ammonia are mixed at $500^{o}C$ in a 1.0-L flask. In which direction will the system proceed to reach equilibrium?

$$N_{2(g)} + 3H_{2(g)} \leftrightarrow 2NH_{3(g)}$$

EQUILIBRIUM: THE RICE METHOD

SOLVING EQUILIBRIUM PROBLEMS

Use the ***RICE Method:***

1. Write the balanced **"Reaction"** with the corresponding equilibrium expression.

2. Set up a chart that includes **"Initial Concentrations"** (all values ***must*** be in mol/L)

3. Add the **"Changes in Concentration"** in terms of "x" to the chart.

4. Add the **"Equilibrium Concentration"** in terms of "x" to the chart.

5. Substitute the equilibrium concentration terms into the equilibrium expression and solve.

PROBLEMS WITH SMALL EQUILIBRIUM CONSTANTS ("Neglecting x")

EXAMPLE: Consider the reaction

$$2NOCl_{(g)} \leftrightarrow 2NO_{(g)} + Cl_{2(g)}$$

At 35°C the equilibrium constant is 1.6×10^{-5}. In an experiment in which 1.0 mol of NOCl is placed in a 2.0-liter flask, what are the equilibrium concentrations? How many grams of NOCl remain in the flask?

EXAMPLE: Calculate the number of moles of chlorine produced at equilibrium in a 10.0-L flask when 2.0 mol of phosphorus pentachloride is heated to 150°C. ($K_c = 4.10 \times 10^{-6}$)

$$PCl_{5(g)} \leftrightarrow PCl_{3(g)} + Cl_{2(g)}$$

EQUILIBRIUM: THE RICE METHOD REVISITED

OTHER TYPES OF EQUILIBRIUM PROBLEMS

EXAMPLE: At 700 K, carbon monoxide reacts with water to form carbon dioxide and hydrogen. The equilibrium constant for this reaction is 5.10. Consider an experiment in which 0.500 mol of carbon monoxide and 0.500 mol of water vapor are mixed together in a 0.500-L flask. Calculate the concentrations of all species at equilibrium.

EXAMPLE: When solid ammonium carbamate sublimes, it dissociates completely into ammonia and carbon dioxide according to the equation

$$N_2H_6CO_{2\,(s)} \leftrightarrow 2NH_{3\,(g)} + CO_{2\,(g)}$$

At 25^{o}C, experiment shows that the total pressure of the gases in equilibrium with the solid is 0.116 atm. What is the equilibrium constant for the reaction?

EXAMPLE: The equilibrium constant, K_p, for $N_2O_{4(g)} \leftrightarrow 2NO_{2(g)}$

is 0.15 at 25°C. If the pressure of N_2O_4 at equilibrium is 0.85 atm, what is the total pressure of the gas mixture (N_2O_4 + NO_2) at equilibrium?

PROBLEMS WITH LARGER EQUILIBRIUM CONSTANTS ("The Quadratic Equation")

EXAMPLE: For the synthesis of hydrogen fluoride from hydrogen and fluorine, 3.000 mol of hydrogen and 6.000 mol of fluorine are mixed in a 3.000-L flask. The equilibrium constant for the reaction at this temperature is 1.15×10^2. Calculate the equilibrium concentration of each component.