Ch 13:

<u>Chemical Equilibrium</u> exists when 2 opposing reactions occur simultaneously at the same rate (dynamic rather than static)

Forward rate = reverse rate

https://www.youtube.com/watch?v=wlD_ImYQAgQ

The equilibrium constant (K) is defined as the product of the equilibrium concentrations of the products, each raised to the power that corresponds to its coefficient in the balanced equation, divided by the product of the equilibrium concentrations of reactants, each raised to the power that corresponds to its coefficient in the balanced equation.

$$aA + bB <=> cC + dD$$

The magnitude of the K_c is a measure of the extent to which reaction occurs.
For any balanced chemical equation, the value of K_c

1) is constant at a given temperature
2) changes if the temperature changes
3) does not depend on the initial concentrations

Give the equilibrium expressions for each of the following reactions:

1) $N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$

2) $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$

3) $NH_3(g) + HCl(g) \Leftrightarrow NH_4Cl(s)$

4) $Ca_3(PO_4)_2(s) \Leftrightarrow 3Ca^{+2}(aq) + 2PO_4^{-3}(aq)$

<u>More facts about equilibrium:</u>

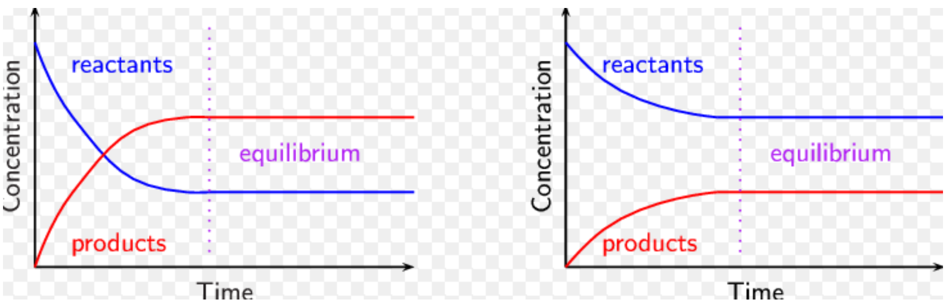
A) When <u>Equilibrium point</u> is reached, molecular level is still reacting and decomposing, just at = rates (like a bridge to an island, with same number of people leaving as coming each hour)

B) Equilibrium point is determined by

1) Initial concentrations of reactants

2) Relative energies of reactants vs products

3) Relative "organization" of reactants to products



K values - of concentration (Kc) and pressure (Kp)

A) When using K values, only gases and solutions go in K expressions

B) Partial pressures are plugged into Kp

C) Molarities are plugged into Kc

D) If necessary, Kc and Kp can be converted

$K_p = K (RT)^{\Delta n}$ Δn = change in sum of gaseous **products - reactants**

Examples:

1) Calculate K_p for 2NO(g) + Cl2(g) <===> 2NOCl(g)

if the partial press are P_{NOCl} = 1.2 atm, P_{NO} = .050 atm, P_{Cl2} = .30 atm

2) For the reaction above, determine K from Kp if reaction is at 25 C

Example 1:

Some N_2 and H_2 are placed in an empty 5.00-L container at 500 °C. When equilibrium is established, 3.01-mol N_2, 2.10-mol H_2, and 0.565-mol NH_3 are present. Evaluate K_c for the following reaction at 500°C:

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$$

Part (II)

Now calculate K_c for the opposite reaction (NH_3 decomp. in this reaction)

Part (III) Now find K_c for $1/2N_2 + 3/2H_2 \Leftrightarrow NH_3$

Example 2: We put 10.0-mol of N_2O into a 2.00-L container at some temperature, where it decomposes according to:

$$2N_2O(g) \iff 2N_2(g) + O_2(g)$$

At equilibrium, 2.20 moles N_2O remain. Calculate the value of K_c for the reaction.

Ex 3: At a certain temperature a 1.00-L flask initially contained 0.298 mol $PCl_3(g)$ and 8.70 x 10^{-3} mol $PCl_5(g)$. After the system had reached equilibrium,
2.00 x 10^{-3} mol $Cl_2(g)$ was found in the flask. Gaseous PCl_5 decomposes according to the reaction:

$$PCl_5(g) \Leftrightarrow PCl_3(g) + Cl_2(g)$$

Calculate the equilibrium concentrations and the value of K.

Ex 4: A mixture of CO and Cl_2 is placed in a reaction flask:

[CO] = 0.0102M and [Cl_2] = 0.00609M. When the reaction comes to equilibrium at 600K, [Cl_2] = 0.00301M.

$$CO(g) + Cl_2(g) \longleftrightarrow COCl_2(g)$$

a) Calculate the concentrations of CO and $COCl_2$ at equilibrium

b) Calculate K

Ex 5: You place 3.00-mol of pure $SO_3(g)$ in an 8.00-L at 1150K. At equilibrium, 0.58-mol of O_2 has been formed. Calculate K for the reaction at 1150K

$2SO_3(g)$ <--> $2SO_2(g)$ + $O_2(g)$

$2SO_3(g)$ <--> $2SO_2(g)$ + $O_2(g)$

Using K to see if we are at equilbrium:

By knowing K:

A) We know the tendency of a reaction to occur

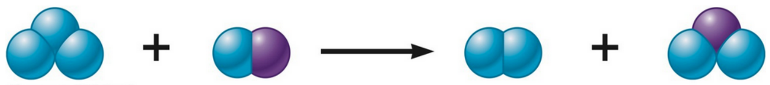
K > 1 = favored in forward direction (products)

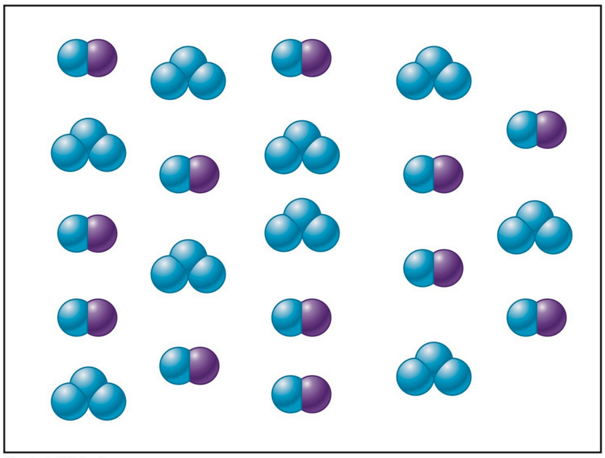
K<1 = favored in reverse direction (reactants)

B) Determine if a given set of concentrations represents equilibrium

C) The final position achieved by reactants and products based on K and the initial concentrations

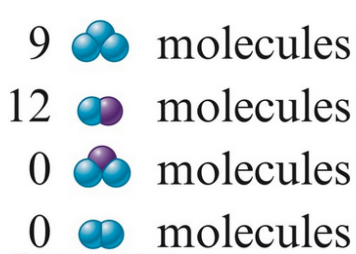
EX: In the following equation, K = 16. Use the given amount of each reactant and product to see if system is at equilibrium.





If 5 molecules of each product form, will we be at equilibrium?

Initial Conditions



New Conditions

How do we mathematically determine amount of reactants and products when system *is* at equilibrium?

REACTION QUOTIENT:

A) If either reactants or product initial values are 0, the rxn equilibrium shifts to this side

B) If both sides of reaction start with values (of product and reactant)
- find Q (reaction quotient)
- IF Q IS:
  - $Q = K$ - system is at equilibrium
  - $Q > K$ - system shifts to the left
  - $Q < K$ - system shifts to the right

(shifts to the left/right →) quantity of numerator and denominator to make $Q = K$

Reaction Quotient:

If K_c = 65.0 for 2HI(g) <=> H_2(g) + I_2(g) , the following concentrations were detected in the mixture. Is the system at equilibrium? If not, in which direction must the reaction proceed for equilibrium to be established?

[HI] = 0.500M, [H_2] = 2.80M, [I_2] = 3.40M

For the synthesis of ammonia at 500^{o}C, the equilibrium constant is 6.0 x 10^{-2}. Predict the direction in which the system will shift to reach equilibrium in each of the following cases:

A) $[NH_3]_o$ = 1.0 x 10^{-3}M; $[N_2]_o$ = 1.0 x 10^{-5}M; $[H_2]_o$ = 2.0 x 10^{-3}M

B) $[NH_3]_o$ = 2.0 x 10^{-4}M; $[N_2]_o$ = 1.50 x 10^{-5}M; $[H_2]_o$ = 3.54 x 10^{-1}M

C) $[NH_3]_o$ = 1.0 x 10^{-4}M; $[N_2]_o$ = 5.0M; $[H_2]_o$ = 1.0 x 10^{-2}M

SUMMARY STATEMENTS-1

1) K_{eq} is temperature dependent

2) $K_c = \frac{[Products]^{coefficients}}{[Reactants]^{coefficients}}$

3) No liquids or solids in the K_{eq} expression

4) [ ] = molarity = moles/liters

5) $K_c >> 1$ => product favored

6) K_p : partial pressures are used

7) Q = using initial concentrations in the IK_{eq} expression

8) If $Q = K_{eq}$, at equilibrium
$Q > K_{eq}$, shift left (towards reactants)
$Q < K_{eq}$, shift right (toward products)

PROCEDURE FOR SOLVING EQUILIBRIUM PROBLEMS:

1) Write the balanced equation.
2) Write the equilibrium expression using the law of mass action.
3) List the initial concentrations.
4) If necessary, calculate Q, and determine the direction of the shift to equilibrium.
5) Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations (ICE)
6) Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.
7) Check your calculated equilibrium concentrations by making sure they give the correct value of K.

(1) Determine the equilibrium concentration of NH_3 after 2.0-mol of N_2 and 3.0-mol of H_2 are placed in a 1.0-L vessel and are allowed to achieve equilibrium. K_c = .444

(2) Calculate the equilibrium concentration of T after 1.00-mol of G, 2.00-mol of J, and 0.500-mol of D are put into a 1.00-L vessel and allowed to come to equilibrium.

$$2G + J \rightleftharpoons D + 2T \quad K = 1.5 \times 10^{-3}$$

3) Carbon monoxide reacts with steam to produce CO_2 and H_2. At 700K the equilibrium constant is 5.10. Calculate the equilibrium concentrations of all species if 1.000 mol of each component is mixed in a 1.000-L flask.

4) Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 115 at a certain temperature. In a particular experiment, 3.000-mol of each component was added to a 1.500-L. Calculate the equilibrium concentrations of all the species.

5) At a particular temperature, K_c = 100. for the reaction

$$H_2(g) \quad + \quad I_2(g) \ <=> \ 2HI(g)$$

In an experiment, 1.00-mol H_2, 1.00-mol I_2, and 1.00-mol HI are introduced into a 2.00-L container. Calculate the concentrations of all species when equilibrium is reached.

6) At a given temperature, $K = 1.3 \times 10^{-2}$ for the reaction

$$N_2(g) + 3H_2(g) <=> 2NH_3(g)$$

Calculate K for the following reactions:

A) $1/2N_2(g) + 3/2H_2(g) <=> NH_3(g)$

B) $2NH_3(g) <=> N_2(g) + 3H_2(g)$

C) $NH_3(g) <=> 1/2N_2(g) + 3/2H_2(g)$

D) $2N_2(g) + 6H_2(g) <=> 4NH_3(g)$

7) A mixture of 1.374-g of H_2 and 70.31-g Br_2 is heated in a 2.00-l vessel at 700K. These substances react as follows:

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$$

At equilibrium the vessel is found to contain 0.566-g H_2.

a) Calculate K_c

b) Calculate the equilibrium partial pressure of H_2, Br_2, and HBr

c) Calculate K_p.

8) Solid NH_4HS is introduced into an evacuated 2-L flask at 24 ^oC. The following reaction takes place:

$$NH_4HS(s) <=> NH_3(g) + H_2S(g)$$

At equilibrium the total pressure in the container is 0.614-atm. What is the K_p for this equilibrium at 24 ^oC? What is the K_c?

9) At 2000°C, the K_p for the reaction

$$2NO(g) \;<=>\; N_2(g) \quad + \quad O_2(g) \qquad \text{is } 2.4 \times 10^{3}$$

If the initial partial pressure of NO is 37.3-atm, what are the equilibrium partial pressures of NO, N_2, and O_2? What is the total pressure?

10) At 25°C, $K_p = 2.9 \times 10^{-3}$ for the reaction

$NH_4OCONH_2(s) <=> 2NH_3(g) + CO_2(g)$

In an experiment carried out at 25°C, a certain amount of NH_4OCONH_2 is placed in an evacuated rigid container and allowed to come to equilibrium. Calculate the total pressure in the container at equilibrium. Calculate the minimum mass of the solid necessary to reach equilibrium.

11) At 25^{o}C, K_p = 0.25 for the reaction

$$2NaHCO_3(s) \Leftrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

A 1.00-L flask containing 10.0-g $NaHCO_3$ is evacuated and heated to 125^{o}C.

a) Calculate the partial pressures of CO_2 and H_2O after equilibrium is established

b) Calculate the masses of $NaHCO_3$ and Na_2CO_3 present at equilibrium

c) What is the total pressure at equilibrium?

12) The partial pressures of an equilibrium mixture of $N_2O_4(g)$ and $NO_2(g)$ are P_{N2O4} = 0.34-atm and P_{NO2} = 1.20-atm at a certain temperature. The volume of the container is doubled. Find the partial pressures of the 2 gases when a new equilibrium is established.

Treating systems with small equilibrium constants (K values)

Ex 13) 1.0 mol $NOCl_{(g)}$ is placed into a 2.0 L flask where decomposition into $NO_{(g)}$ and $Cl_{2(g)}$ results until equilibrium is reached. The K = 1.6×10^{-5} . Determine the concentrations of all reactants and products at equilibrium.

LE CHATELIER'S PRINCIPLE:

If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

1) The Effect of a Change in Concentration (remember solids and liquids DO NOT affect equilibrium)

2) The Effect of a Change in Pressure
   a) Add or remove a gaseous reactant or product (concentration change)
   b) Add an inert gas (one not involved in the reaction)
   c) Change the volume of the container (inc. or dec pressure)

3) The Effect of a Change in Temperature

4) Adding a Catalyst

EX 1:

Predict the shift in the equilibrium position for the reaction:

$$58kJ + N_2O_4(g) <=> 2NO_2(g)$$

a) Addition of $N_2O_4(g)$
b) Addition of $NO_2(g)$
c) Removal of $N_2O_4(g)$
d) Removal of $NO_2(g)$
e) Addition of He(g)

f) Decrease container volume

g) Increase container volume

h) Decrease temperature

i) Increase temperature

EX 2:

Suppose the following **exothermic** reaction is allowed to reach equilibrium.

$$A(s) + 3B(g) <=> 2C(g) + 3D(g)$$

The following changes are made and then allow the reaction to reestablish equilibrium. Tell whether the amount of B present at the new equilibrium will be greater than, less than, or the same as the amount of B before the change was imposed.

a) the temperature is increased at constant volume
b) more A is added
c) more C is added
d) a small amount of D is removed
e) The pressure is increased by decreasing the volume

EX 3:

For the following reaction: $3H_2\,(g) + N_2\,(g) \;<=>\; 2NH_3\,(g) + \text{heat}$

What conditions would be best to obtain the greatest amount of NH_3?

Ex 4) For the following reaction at a certain temperature

$H_2(g)$ + $F_2(g)$ --> $2HF(g)$ K = 320.

Initially 0.500-mol each of hydrogen gas and fluorine gas are placed in a 5.00-L container and equilibrium occurs. Then 0.200-mol of F_2 is added to this equilibrium mixture.

a) Calculate the concentrations all the species before addition fluorine is added.

b) Calculate the concentrations of all gases once equilibrium is reestablished.

c) Draw a graph showing the what occurred.

Ex 5) $N_2(g) + 3H_2(g) <=> 2NH_3(g)$

For the reaction above, the value of the equilibrium constant, K_p, is 3.1×10^{-4} at 700.K

a) Write the expression for the equilibrium constant, K_p, for the reaction

b) Assume that the initial partial pressures of the gases are as follows: p_{N2} = 0.411-atm, p_{H2} = 0.903-atm, and p_{NH3} = 0.224-atm

i) Calculate the value of the reaction quotient, Q, at these initial conditions

ii) Predict the direction in which the reaction will proceed at 700.K if the initial partial pressures are those given above. Justify your answer.

c) Calculate the value of the equilibrium, K_c, given that the value of K_p for the reaction at 700K is 3.1×10^{-4}.

d) The value of K_p for the reaction below is 8.3×10^{-3} at 700.K

$$NH_3(g) + H_2S(g) <=> NH_4HS(g)$$

Calculate the value of K_p at 700.K for each of the reactions below:

i) $NH_4HS(s) <=> NH_3(g) + H_2S(g)$

ii) $2H_2S(g) + N_2(g) + 3H_2(g) <=> 2NH_4HS(g)$

Ex 6) For the following reaction at a certain temperature

$H_2(g)$ + $F_2(g)$ --> $2HF(g)$

It is found that the equilibrium concentrations in a 5.00-L rigid container are $[H_2]$ = 0.0500M, $[F_2]$ = 0.0100M, and [HF] = 0.400M. If 0.200mol of F_2 is added to this equilibrium mixture, calculate the concentrations of all gases once equilibrium is reestablished.

Ex 7) For the reaction below the $K_c = 5.84 \times 10^{-3}$ at 25°C.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

a) Calculate the equilibrium concentrations of both gases when 3.50-g N_2O_4 is placed in a 2.00-L flask.

b) What will be the new equilibrium concentrations if the volume of the system is suddenly increased to 3.00-L at 25°C

Ex 8) Given A(g) +B(g) <=> C(g) + D(g)

a) At equilibrium a 1.00-L container was found to contain 0.400-mol of A,0.400-mol of B, 1.60-mol of D, and 1.60-mol of C. Calculate the equilibrium constant for this reaction.

b) If 0.20-mol of B and 1.20-mol of C are added to this system, what will the new equilibrium concentration of A be?

Equilibrium Graphs:

1) Beginning with NO_2 in a container, show the graph that would result with the reaction reaching equilibrium and then show the results of adding some O_2 to the system.

$$2NO_2(g) \; <=> \; O_2(g) \; + \; 2NO(g)$$

2) Beginning with only SO_3(0.5M) and no SO_2 or O_2