Chemical Equilibrium:

Chemical Reactions reach a state of dynamic equilibrium in which the rates of the forward and reverse reactions are equal and there is no net change in composition.

$$CO(g) + H_2O(g) \leftrightarrows CO_2(g) + H_2(g)$$

Le Chatelier's Principle

When a system at equilibrium is subjected to a stress, the equilibrium will shift to relieve the stress.

Consider:

$$CO(g) + H_2O(g) \leftrightarrows CO_2(g) + H_2(g)$$

Which direction does the equilibrium shift if we:

a) Add CO

b) Add water

c) Add carbon dioxide

d) Remove Hydrogen gas

e) Remove CO

Now consider

$$2CrO_4^{2-}(aq) + 2H^+(aq) \leftrightarrows Cr_2O_7^{2-}(aq) + H_2O(l) + \text{heat}$$

yellow orange

Which direction does the equilibrium shift if we:

a) K_2CrO_4 is added

b) $K_2Cr_2O_7$ is added

c) HCl is added

d) It is placed in an ice bath.

e) What color will predominate if we remove water?

$$NH_4HS_{(s)} \leftrightarrows NH_{3(g)} + H_2S_{(g)} \qquad \Delta H^\circ = +93 \text{ kilojoules}$$

The equilibrium above is established by placing solid NH_4HS in an evacuated container at 25°C. At equilibrium, some solid NH_4HS remains in the container. Predict each of the following.

a) The effect on the equilibrium partial pressure of NH_3 gas when additional solid NH_4HS is introduced into the container

b) The effect on the equilibrium partial pressure of NH_3 gas when additional solid H_2S is introduced into the container

c) The effect on the mass of solid NH_4HS present when the volume of the container is decreased

d) The effect on the mass of solid NH_4HS present when the temperature is increased.

In this unit you did a lab that dealt with the following equilibrium:

$$Fe^{3+}(aq) + SCN^-(aq) \leftrightarrows FeSCN^{2+}(aq)$$

Fill in the following table based upon what you observed during the lab.

Solution Added	What two ions are in this solution?	Will it get darker or lighter?	How will the $[FeSCN^{2+}]$ Change?
Potassium carbonate			
Calcium thiocyanate			
Sodium bromide			
Potassium hydroxide			
Potassium nitrate			
Iron (III) bromide			
Ammonium bromide			

What is an equilibrium constant?

How do you write an equilibrium constant?

$aA(g) + bB(g) \leftrightarrows cC(g) + dD(g)$

Who is included in an equilibrium constant?

Why not solids and pure liquids? What is the physical difference?

What are the special cases of the equilibrium constant?

Kc

Kp

Ka

Kb

Kw

Ksp

Write the equilibrium constant expression for the following reactions:

1) $2NO_2(g) \leftrightarrows N_2O_4(g)$ K=

2) $aA(g) \leftrightarrows bB(g)$ K=

3) $H_2(g) + I_2(g) \leftrightarrows 2HI(g)$ K=

4) $SO_3(g) + H_2(g) \leftrightarrows SO_2(g) + H_2O(g)$ K=

5) $PCl_5(g) \leftrightarrows PCl_3(g) + Cl_2(g)$ K=

6) $6CO_2(g) + 6H_2O(l) \leftrightarrows C_6H_{12}O_6(s) + 6O_2(g)$ K=

7) $HCN(aq) + H_2O(l) \leftrightarrows H_3O^+(g) + CN^-(aq)$ K=

8) $NH_3(aq) + H_2O(l) \leftrightarrows NH_4^+(aq) + OH^-(aq)$ K=

9) $H_2O(l) \leftrightarrows H^+(aq) + OH^-(aq)$ K=

10) $AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$ K=

How do you calculate an equilibrium constant?
Calculate the equilibrium constants for the following reactions:

$2NO_2(g) \leftrightarrows N_2O_4(g)$ K=

Experiment	$[NO_2]$	$[N_2O_4]$
1.	0.052	0.595
2.	0.024	0.127
3.	0.068	1.02

Show work here Show answers here

K_1= =

K_2= =

K_3= =

$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$ K=

Experiment	$[N_2]$	$[H_2]$	$[NH_3]$
1.	0.921	0.763	0.157
2.	0.399	1.197	0.203
3.	2.59	2.77	1.82

Show work here Show answers here

K_1= =

K_2= =

K_3= =

This equation:

$$CO_2(g) + H_2(g) \leftrightarrows CO(g) + H_2O(g)$$

describes a reaction that was carried out at 900 Celsius with the following results:

Partial Pressure(atm) at equilibrium

Trial	CO	H_2O	CO_2	H_2
1	0.352	0.352	0.648	0.148
2	0.266	0.266	0.234	0.234
3	0.186	0.686	0.314	0.314

a) Write the equilibrium expression for this reaction

b) Verify that the constant for this expression is constant by calculating the value for all three trials.

Manipulating the equilibrium constant
For the following reaction:

$H_2(g) + 1/2O_2(g) \leftrightarrows H_2O(g)$ K =

Write the following reactions and their equilibrium constants:

Reverse Reaction

Twice the forward reaction

Half the forward reaction

Give numerical values for K in the following situations dealing with:

$$H_2(g) + F_2(g) \leftrightarrows 2HF(g) \qquad K = 115$$

a. $2HF(g) \leftrightarrows H_2(g) + F_2(g)$ a. _____

b. $4HF(g) \leftrightarrows 2H_2(g) + 2F_2(g)$ b. _____

c. $HF(g) \leftrightarrows 1/2H_2(g) + 1/2F_2(g)$ c. _____

d. $2H_2(g) + 2F_2(g) \leftrightarrows 4HF(g)$ d. _____

e. $3H_2(g) + 3F_2(g) \leftrightarrows 6HF(g)$ e. _____

Kp versus Kc

Let's think about how we measure the concentration using the ideal gas law.

Now apply this to the idea of equilibrium constants:

The Reaction Quotient

Solving Equilibrium Problems

Steps to solving an equilibrium problem.
1)

2)

3)

4)

5)

6)

7)

The Quadratic Equation.

For an equation of the form:
$ax^2+bx+c=0$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

1. For the reaction:

$$A \leftrightarrows B + C$$

the equilibrium constant is 3.0×10^{-6}. What is the concentration of B at equilibrium if A was originally 0.10 M?

2. The K for the reaction of HCN is 6.3×10^{-10} for the following reaction:

$$HCN(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CN^-(aq)$$

What is the concentration of cyanide ion at equilibrium if you start with 0.100 M HCN?

3. An equilibrium mixture contains oxygen gas at 2.9 atm and carbon dioxide at 2.6 atm.

$$C(s) + O_2(g) \leftrightarrows CO_2(g)$$

Calculate Kp and Kc at for this system at 289 Kelvin.

4 . If a 0.10 M solution of an acid HA has an H_3O^+ concentration of 4.0×10^{-4} what is the equilibrium constant Ka for the reaction?

$$HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$$

5. For the equilibrium system:

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

the equilibrium constant is 170 at room temperature. Assume a 1.00 liter container contains 0.005 moles of nitrogen dioxide and 0.005 moles of dinitrogen tetraoxide. Is this system at equilibrium? Which direction will it shift to reach equilibrium?

6. The K for the following reaction is 1.9×10^{-3}.

$$PbF_2(s) \leftrightarrows Pb^{2+}(aq) + 2F^-(aq)$$

What is the concentration of lead ion at equilibrium?

7. Phosphoric acid undergoes three reactions in succession:

$$H_3PO_4(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + H_2PO_4^-(aq) \qquad K_{a1} = 7.5 \times 10^{-3}$$
$$H_2PO_4^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HPO_4^{2-}(aq) \qquad K_{a2} = 6.2 \times 10^{-8}$$
$$HPO_4^{2-}(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + PO_4^{3-}(aq) \qquad K_{a3} = 3.6 \times 10^{-13}$$

What is K for the overall reaction:

$$H_3PO_4(aq) + 3H_2O(l) \leftrightarrows 3H_3O^+(aq) + PO_4^{3-}(aq) \qquad K_a = ?$$

From the 2000 Exam

$$2H_2S(g) \leftrightarrows 2H_2(g) + S_2(g)$$

When heated, hydrogen sulfide gas decomposes according to the equation above. A 3.40 g sample of H_2S (g) is introduced into an evacuated rigid 1.25 L container. The sealed container is heated to 483 K and 3.72 x 10^{-2} mole of S_2 (g) is present at equilibrium.

(a) Write the expression for the equilibrium constant, Kc, for the decomposition reaction represented above.

(b) Calculate the equilibrium concentration, in mole per L, of the following gases in the container at 483 K.

(i) H_2 (g)

(ii) H_2S (g)

(c) Calculate the value of the equilibrium constant, Kc, for the decomposition reaction at 483 K.

(d) Calculate the partial pressure of S_2 (g) in the container at equilibrium at 483 K.

(e) For the reaction H_2 (g) + $1/2S_2$(g) $\leftrightarrows$ H_2S (g) at 483 K, calculate the value of the equilibrium constant Kc.

From the 1992 Exam

$$2\ NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + H_2O_{(g)} + CO_{2(g)}$$

Solid sodium hydrogen carbonate, $NaHCO_3$, decomposes on heating according to the equation above.

(a) A sample of 100. grams of solid $NaHCO_3$ was placed in a previously evacuated rigid 5.00-liter container and heated to 160°C. Some of the original solid remained and the total pressure in the container was 7.76 atmospheres when equilibrium was reached. Calculate the number of moles of $H_2O_{(g)}$ present at equilibrium.

(b) How many grams of the original solid remain in the container under the conditions described in (a)?

(c) Write the equilibrium expression for the equilibrium constant, K_P, and calculate its value for the reaction under the conditions in (a).

(d) If 110. grams of solid $NaHCO_3$ had been placed in the 5.00-liter container and heated to 160°C, what would the total pressure have been at equilibrium? Explain.