Chemical Equilibrium:

Chemical Reactions reach a state of dynamic equilibrium in which "*The rate of the forward and reverse reaction are equal"* and there is no net change in composition.

Reversible Reactions

Consider the following reaction in the gas phase:

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

Let's graph the reaction rates:

Let's graph the concentrations:

Le Chatelier's Principle

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

Consider adding and removing certain species.

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

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

Consider changing things other than the concentrations of reactants and products.

$$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g) + \text{Energy}$$

a) The volume is increased

b) The pressure is decreased

c) The temperature is increased

d) The system is compressed

e) It is placed into an ice bath

f) A catalyst is added

A classic example of Le Chatelier's Principle is the iron (III) thiocyante equilibrium:

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

By starting with a dilute solution of $Fe^{3+}(aq)$ and adding a drop or two of $SCN^{-}(aq)$ you get a "Brick Red" solution. The equilibrium system can be "Stressed" by adding solutions that contain common ions.

Laboratory Data

Solution Added	What two ions are in this solution?	Did it get darker or lighter?	How does the $[FeSCN^{2+}]$ Change?	What ion caused the change?
$FeCl_3$		Darker		
KSCN		Darker		
NaSCN		Darker		
NaCl		Little Change		
$Fe(NO_3)_3$		Darker		
NH_4NO_3		Little Change		
Na_2CO_3		Substantially Lighter		
KBr		Little Change		
NH_4SCN		Darker		
NaOH		Substantially Lighter		
$CaCl_2$		Substantially Lighter		

What are the spectator ions?

How does solubility play a role in this?

Classic Equilibrium Demonstrations

Consider the reaction:

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

We have seen previously that N_2O_4 is a dimer held together with a bond between two NO_2 molecules. NO_2 is brown and N_2O_4 is clear.

Draw a picture of two beakers:

Is this reaction exothermic or endothermic as written above?

Now consider the reaction of Cobalt Chloride

$$Co(H_2O)_6^{2+}(aq) + 4Cl^-(aq) \leftrightarrows CoCl_4^{2-}(aq) + 6H_2O(l)$$

Draw a picture of three beakers:

Is this reaction exothermic or endothermic as written above?

Equilibrium Constants

What is an equilibrium constant?

How do you write an equilibrium constant?

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

What is included in an equilibrium constant?

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

Rate Laws

What are the special cases of the equilibrium constant?

K_{eq} K_c K_p K_a K_b K_w K_{sp} K_f

Write the equilibrium constant expression for the following reactions:

1) $2NO_2(g) \leftrightarrows N_2O_4(g)$ $K_{eq} =$

2) $H_2(g) + I_2(g) \leftrightarrows 2HI(g)$ $K_{eq} =$

3) $SO_3(g) + H_2(g) \leftrightarrows SO_2(g) + H_2O(g)$ $K_{eq} =$

4) $PCl_5(g) \leftrightarrows PCl_3(g) + Cl_2(g)$ $K_{eq} =$

5) $6CO_2(g) + 6H_2O(l) \leftrightarrows C_6H_{12}O_6(s) + 6O_2(g)$ $K_c =$

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

7) $NH_3(aq) + H_2O(l) \leftrightarrows NH_4^+(aq) + OH^-(aq)$ $K_b =$

8) $2H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$ $K_w =$

9) $AgCl(s) \leftrightarrows Ag^+(aq) + Cl^-(aq)$ $K_{sp} =$

10) $AsF_5(g) \leftrightarrows AsF_3(g) + F_2(g)$ $K_p =$

11) $Ag^+(aq) + 2NH_3(aq) \leftrightarrows Ag(NH_3)_2^+(aq)$ $K_f =$

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

$K_1=$ =

$K_2=$ =

$K_3=$ =

Manipulating the equilibrium constant

1) For the following reaction:

$Br_2(g) \leftrightarrows 2Br(g)$ $K_p = 2250$

Write the following reactions and their equilibrium constants:

Reverse Reaction

Twice the forward reaction

Half the forward reaction

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

$H_2(g) + F_2(g) \leftrightarrows 2HF(g)$ $K = 100$

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

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

c. $HF(g) \leftrightarrows \frac{1}{2}H_2(g) + \frac{1}{2}F_2(g)$ c. ______________

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

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

3) Consider the following reactions:

$2BrCl(g) \leftrightarrows Br_2(g) + Cl_2(g)$ $K = 0.45$

$2IBr(g) \leftrightarrows Br_2(g) + I_2(g)$ $K = 20$

Find the equilibrium constant for:

$2BrCl(g) + I_2(g) \leftrightarrows 2IBr(g) + Cl_2(g)$ $K = ?$

K_p versus K_c

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

Now apply this to the idea of equilibrium constants:

Consider the reaction:

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

In an isolated flask the total pressure of the equilibrium mixture at 110°C is 1.648 atm. What is the value of K_p and K_c for this reaction?

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?

ICE Boxes

2) The K_a for the reaction of HCN in water is $6.3x10^{-10}$, as in 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) For the reaction of acetic acid in water the K_{eq} is 1.75×10^{-5}. What is the remaining concentration of acetic acid if the original concentration was 0.10 M?

$$HC_2H_3O_2\ (aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + C_2H_3O_2^-(aq)$$

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

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

K_p and K_c

5) 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 K_p and K_c at for this system at 289 Kelvin.

6) Given

$Br_2(g) \leftrightarrows 2Br(g)$ $K_p = 2250$

Find the value of K_c at 2000 K.

7) What is the ratio of K_c/K_p for the reaction at 25°C:

$$CO(g) + 2H_2(g) \leftrightarrows CH_3OH(g)$$

Reaction Quotients

8) 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 tetroxide. Is this system at equilibrium? Which direction will it shift to reach equilibrium?

9) At some unspecified temperature

$Br_2(g) \leftrightarrows 2Br(g)$ $K_c = 150$

Which way will the system shift to achieve equilibrium if the concentration of Br is 0.100 M and the concentration of Br_2 is also 0.100 M?

10) For the reaction

$2BrCl(g) \leftrightarrows Br_2(g) + Cl_2(g)$ $K = 0.45$

Which way will the equilibrium shift if you start with $[Br_2] = [Cl_2] = 0.0100$ M and $[BrCl] = 10.0$ M?

11)

$$Cl_2(g) + H_2(g) \leftrightarrows 2HCl\ (g)$$

For the reaction above, the value of the equilibrium constant, K_p is 193 at 2500. K.

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

b) Assume the initial partial pressures of the gases are as follows:

$P\ H_2 = 0.766$ atm, $P\ Cl_2 = 0.393$ atm, and $P\ HCl = 0.921$ 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 2500. K if the initial partial pressures are those given above. Justify your answer.

c) The value of K_p for the reaction represented below is 1.5×10^3 at 2500. K.

$$NH_3(g) + HCl(g) \leftrightarrows NH_4Cl(g)$$

Calculate the value of K_p at 2500. K for each of the reactions represented below:

(i) $NH_4Cl\ (g) \leftrightarrows NH_3\ (g) + HCl\ (g)$

(ii) $H_2(g) + Cl_2(g) + 2NH_3(g) \leftrightarrows 2NH_4Cl(g)$