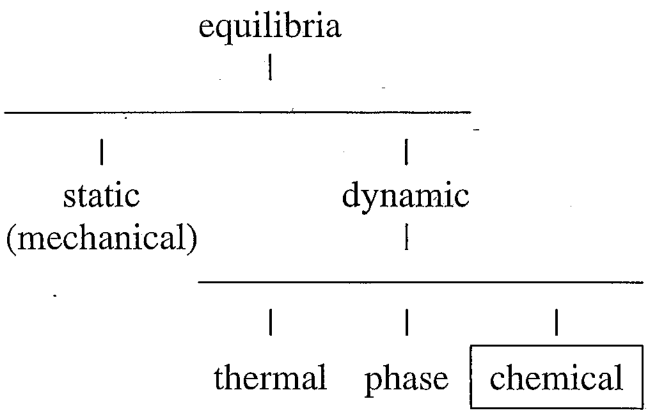
CHEMICAL EQUILIBRIUM

"When a system is in chemical equilibrium, a change in one of the parameters of the equilibrium produces a shift in such a direction that, were no other factors involved in this shift, it would lead to a change of opposite sign in the parameter involved." Henri Louis Le Châtelier, 1888

Nature of Equilibrium



attributes of equilibrium

isolated from outside interference
macroscopic properties constant
spontaneously reach equilibrium state
forward rate = reverse rate
(dynamically balanced)
reached from products or reactants

Arrows of Chemistry

reaction:

$Ag^{+}(aq)$ + $Cl^{-}(aq)$ --> $AgCl(s)$

resonance:

O = S – O <--> O – S = O

equilibrium:

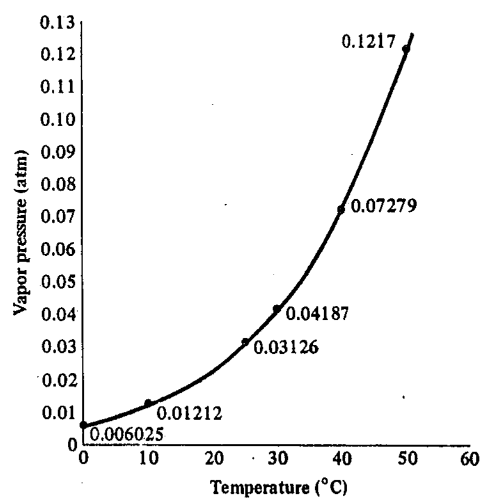
$H_2O(l)$ <=> $H_2O(g)$

$N_2O_4(g)$ <=> 2 $NO_2(g)$

equilibrium constant, K

K_p - pressure
K_c - concentration
K_a - ionization of weak acid
K_b - ionization of weak base
K_{sp} - dissolution of slightly soluble salt

FIG I. Equilibrium vapor pressure of water



Phase Equilibrium

$H_2O(l)$ <=> $H_2O(g)$

$CO_2(s)$ <=> $CO_2(g)$

Form of Equilibrium Constant Expressions

Law of Mass Action

for a A + b B <=> c C + d D the equilibrium constants K_p and K_c are

$$K_p = \frac{(P_C)^c_{EQ}(P_D)^d_{EQ}}{(P_A)^a_{EQ}(P_B)^b_{EQ}} \qquad K_c = \frac{[C]^c_{EQ}[D]^d_{EQ}}{[A]^a_{EQ}[B]^b_{EQ}}$$

where pure solids and pure liquids are represented by the number 1

EX 1. Write the equilibrium constant expression for each of the following reactions.

$CaCO_3(s)$ <=> $CaO(s)$ + $CO_2(g)$

$H_2O(l)$ <=> $H_2(g)$ + 1/2 $O_2(g)$

$Fe_2O_3(s)$ + 3 $H_2(g)$ <=> $Fe(s)$ + 3 $H_2O(g)$

$Cl_2(g)$ + 2 $HgO(s)$ + $H_2O(l)$ <=> $HgO \cdot HgCl_2(s)$ + 2 $HOCl(aq)$

Determining Equilibrium Constants (table of changes on pp. 70-71 - ICE)

EX 2. At 1000 K the equilibrium gas mixture contains 0.562 atm SO_2, 0.101 atm O_2, and 0.332 atm SO_3. What is K?

	4 $SO_2(g)$	+	$O_2(g)$	<=>	2 $SO_3(g)$
EQ					

EX 3. What is the value of K_c if an equilibrium mixture contains 1.0 mol Fe, 1.0×10^{-3} mol O_2, and 2.0 mol $Fe_2O_3(s)$ in a 2.0-L container?

	4 $Fe(s)$	+	3 $O_2(g)$	<=>	2 $Fe_2O_3(s)$
EQ					

EX 4. 4.00 atm of $H_2(g)$ and 2.00 atm of $I_2(g)$ are mixed and allowed to react. When equilibrium is reached 3.76 atm of $HI(g)$ is formed. What is K_p for the reaction?

	$H_2(g)$	+	$I_2(g)$	<=>	$2\ HI(g)$
I	4 atm		2 atm		
C					
E					3.76 atm

Relationship of K's of Related Reactions

$K_p = 55.6$ at a temperature where the equilibrium partial pressures are: $P_{H_2} = 2.12$, $P_{I_2} = 0.12$, $P_{HI} = 3.76$ for

$$H_2(g) + I_2(g) \iff 2\ HI(g) \quad \text{with } K_p = \frac{P_{HI}^2}{P_{H_2} P_{I_2}}$$

EX 5. For the above reaction what is K_p for:

a) $2\ HI(g) \iff H_2(g) + I_2(g)$

b) $2\ H_2(g) + 2\ I_2(g) \iff 4\ HI(g)$

c) $1/2\ H_2(g) + 1/2\ I_2(g) \iff HI(g)$

EX 6. In terms of K_1 and K_2, find K, the equilibrium constant for

$$SO_2(g) + CO_2(g) \iff SO_3(g) + CO(g) \qquad K = \frac{P_{SO_3}P_{CO}}{P_{SO_2}P_{CO_2}}$$

if you know

1) $SO_2(g) + 1/2\ O_2(g) \iff SO_3(g) \qquad K_1 = \dfrac{P_{SO_3}}{P_{SO_2}P_{O_2}^{1/2}}$

2) $CO_2(g) \iff CO(g) + 1/2\ O_2(g) \qquad K_2 = \dfrac{P_{CO}P_{O_2}^{1/2}}{P_{CO_2}}$

EX 7. Given

K_1 for $PCl_5(s) \iff PCl_3(g) + Cl_2(g)$
and K_2 for $PCl_5(s) \iff PCl_5(g)$

Find K for $PCl_5(g) \iff PCl_3(g) + Cl_2(g)$

summary

adding reactions: a + b => multiply K's => K_aK_b

subtracting reactions: a - b => divide K's => $\dfrac{K_a}{K_b}$

(reversing reaction b)

Equilibrium Constant and **Reaction Quotient**

Want to tell how far a reaction has gone (reactions seldom go to completion)

- reactions eventually reach a state of equilibrium
- want a number which defines this equilibrium situation
- no net change => some fixed relationship between reactants and products
- **equilibrium constant** gives the relationship, some examples at 25°C)

$$H_2(g) + 1/2\ O_2(g) \ \Leftrightarrow\ H_2O(g) \qquad K_c = \frac{[H_2O]}{[H_2][O_2]^{1/2}} = 5.6 \times 10^{40}$$

$$Cl_2O(g) + H_2O(g) \ \Leftrightarrow\ 2\ HOCl(g) \qquad K_p = \frac{P^2_{HOCl}}{P_{Cl_2O}P_{H_2O}} = 0.0900$$

$$N_2(g) + O_2(g) \ \Leftrightarrow\ 2\ NO_2(g) \qquad K_p = \frac{P^2_{NO_2}}{P_{N_2}P_{O_2}} = 4.7 \times 10^{-31}$$

1) $K > 1$ => product-favored; $K >> 1$ => reaction essentially complete
2) $K < 1$ => reactant-favored; $K << 1$ => essentially no reaction

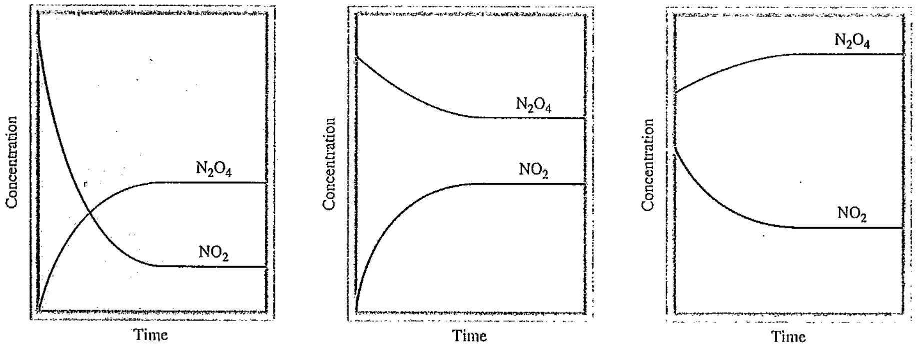
- **reaction quotient**, Q, tells how reaction approaches equilibrium:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad \text{or} \qquad Q = \frac{P^c_C P^d_D}{P^a_A P^b_B}$$

1) $Q < K$ => reaction proceeds left to right
2) $Q = K$ => reaction is at equilibrium
3) $Q > K$ => reaction proceeds right to left

Example: $N_2O_4(g) \Leftrightarrow 2\ NO_2(g)$

	initial		equilibrium	
exp	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$
1	0.25	0	0.10	0.30
2	0	0.50	0.10	0.30
3	0.25	0.50	0.26	0.48



Equilibrium Calculations

1. Using K to Determine Equilibrium Amounts of Reactants and Products

Given K and all equilibrium partial pressures but one, find the missing pressure.

EX 8. At 425°C $K_p = 55.6$ for the following reaction. If $P_{H_2} = 2.12$ atm and $P_{I_2} = 0.12$ atm at 425°C what is the equilibrium partial pressure of HI?

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

Given K find the equilibrium partial pressures of the gaseous products from decomposition of a solid.

EX 9. If $K_p = 2.9 \times 10^{-3}$ at 25°C what are the equilibrium partial pressures of NH_3 and CO_2?

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

Given K find the equilibrium concentration of the ions from a sparingly soluble salt. (Chapter 9 - Dissolution and Precipitation Equilibria)

EX 10. What are the equilibrium concentration of the ions at 25°C if $K_{sp} = 3.2 \times 10^{-25}$?

	$AuCl_3(s)$	<=>	$Au^{3+}(aq)$	+	$3\ Cl^-(aq)$
EQ					

2. Using Initial and Equilibrium Amounts

EX 11. The equilibrium concentration of gaseous chlorine is 0.030 M when 0.075 and 0.033 M hydrogen chloride and oxygen gas, respectively, are initially placed in a reaction vessel. How much hydrogen chloride and oxygen gas are left unreacted at equilibrium?

$$4\,HCl(g) \quad + \quad O_2(g) \quad <=> \quad 2\,Cl_2(g) \quad + \quad 2\,H_2O(g)$$

I

C

E

3. Using *K* and Initial Amounts

EX 12. If 2.00 mol of HBr were introduced into a 1.00 L vessel at 1495 K what would be the equilibrium concentration of all species if $K_c = 2.86 \times 10^{-5}$?

$$2\,HBr(g) \quad <=> \quad H_2(g) \quad + \quad Br_2(g)$$

I

C

E

4. Equilibrium Calculations Involving the **Quadratic Equation**

for $ax^2 + bx + c = 0$ the solution is $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

EX 13. At a particular temperature $K_c = 9.1 \times 10^{-4}$. Determine the concentration of all ions in a solution that is initially 2.0 M $FeSCN^{2+}$.

	$FeSCN^{2+}(aq)$	<=>	$Fe^{3+}(aq)$	+	$SCN^{-}(aq)$
I					
C					
E					

EX 14. If 1.00×10^{-3} M H_2 and 2.00×10^{-3} M I_2 are mixed and allowed to react at 425°C what are the equilibrium concentrations if $K_c = 55.6$?

	$H_2(g)$	+	$I_2(g)$	<=>	$2\ HI(g)$
I					
C					
E					

EX 15. What is the concentration of $[H_3O^+]$ in a 1.00 M solution of acetic acid at 25°C if $K_a = 1.8 \times 10^{-5}$? (Chapter 8 - Acid-Base Equilibria)

	$CH_3COOH(aq)$	+	$H_2O(l)$	<=>	$H_3O^+(aq)$	+	$CH_3COO^-(aq)$
I							
C							
E							

5. The Relation between K_c and K_p

EX 16. At 250°C the equilibrium concentrations are $[PCl_3] = [Cl_2] = 0.280$ M and $[PCl_5] =$ 1.885 M for

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

a) What is K_c?

b) What is K_p?

Le Châtelier'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 counteract the effects of the change.

I. change of **temperature**

II. change of total **pressure**

a) add or remove gaseous reactant or product
b) change volume of container
c) add inert gas (one not involved in the reaction)

III. change of **concentration/partial pressure**

Le Châtelier's Principle predicts

effect on K
direction of equilibrium shift
effect on concentrations/partial pressures

I. **temperature** - only stress that can change value of K

1) phase equilibria

$$H_2O(l) \quad \text{<=>} \quad H_2O(g), \quad K = P_{H_2O(g)}, \quad P_{H_2O(g)}(T)$$

2) exothermic and endothermic reactions - sign of ΔH^o

EX 17. For each of the following reactions determine whether the value of K would be larger or smaller at a higher temperature.

a) At 500 K $K = 90$ for the following exothermic reaction.

$$N_2(g) + 3\,H_2(g) \text{ <=> } 2\,NH_3(g)$$

b) At 25°C $K = 10^{-31}$ for the following endothermic reaction.

$$N_2(g) + O_2(g) \text{ <=> } 2\,NO(g)$$

II. total **pressure**

1) pressure induced phase transition

$$\underset{d = 0.917}{H_2O(s)} \quad \text{<=>} \quad \underset{d = 0.999}{H_2O(l)}$$

2) increase of P_{TOT} by decreasing volume

$$N_2(g) + 3\,H_2(g) \text{ <=> } 2\,NH_3(g)$$

EX 18. For the above chemical reaction what would be the effect on the equilibrium if the volume were changed so that the total pressure were increased 10-fold?

III. **concentration**

EX 19. For the following reaction if 0.500 M of each reactant were initially present what would be the equilibrium concentrations if $K_c = 24$?

	$PCl_3(g)$	+	$Cl_2(g)$	<=>	$PCl_5(g)$
I	0.500 M		0.500 M		0 M
C					
E					

a) add PCl_5 to double molarity; $Q = \frac{[PCl_5]_o}{[PCl_3]_o[Cl_2]_o} =$

I

C

E

b) then decrease V by 25%; $Q = \frac{[PCl_5]_o}{[PCl_3]_o[Cl_2]_o} =$

I

C

E