5.111 Principles of Chemical Science
Fall 2008

CHEMICAL EQUILIBRIUM (Chapter 9 Section 9.0-9.9)

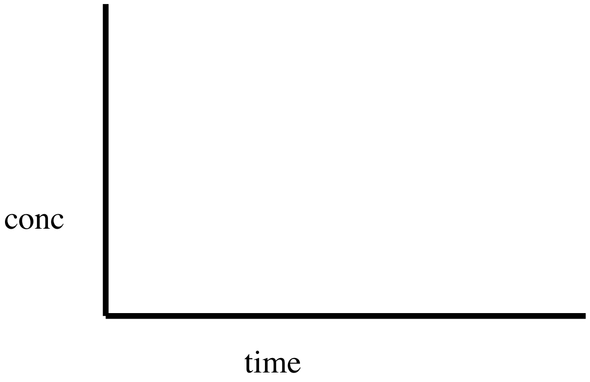
Topics

Nature of Chemical Equilibrium
Meaning of K
Relationship between Equilibrium Expressions
External Effects on K

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

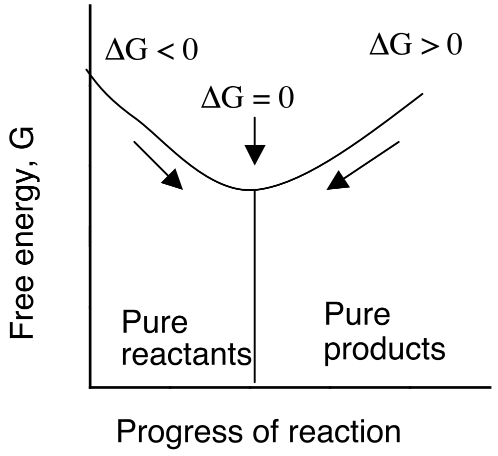
Consider:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta G° = -32.90$ kJ/mol



When the reaction mixture has not produced enough products to have reached equilibrium, the spontaneous direction of change is toward more products ($\Delta G_{\text{forward reaction}}$ ______ 0).

When excess products are present (ex. pure ammonia), the reverse reaction is spontaneous ($\Delta G_{\text{forward reaction}}$ ______ 0).



The reaction free energy (ΔG) changes as the proportion of reactants and products change. To find out how ΔG changes with composition of reactants and products, we need to know how the molar free energy of each substance varies with its partial pressure (if gas), or with its concentration (if solute).

$\Delta G = \Delta G° + RT \ln Q$

Where

ΔG = reaction free energy at any definite, fixed composition of the reaction mixture.

$\Delta G°$ = is the difference in molar free energy of the products and reactants in their standard states.

R = universal gas constant, T = Temperature, and Q = reaction quotient

For $aA + bB \rightleftharpoons cC + dD$

in gaseous phase

$$\Delta G = \Delta G° + RT \ln \underbrace{\left[\frac{(P_C/P_{ref})^c\,(P_D/P_{ref})^d}{(P_A/P_{ref})^a\,(P_B/P_{ref})^b}\right]}_{Q}$$

$P_{ref} = 1$ bar

$$Q = \frac{P_C{}^c\,P_D{}^d}{P_A{}^a\,P_B{}^b}$$

in solution

$$\Delta G = \Delta G° + RT \ln \underbrace{\left[\frac{([C]/C_{ref})^c\,([D]/C_{ref})^d}{([A]/C_{ref})^a\,([B]/C_{ref})^b}\right]}_{Q}$$

$C_{ref} = 1$ M and [C] in M

$$Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

At equilibrium $\Delta G = 0$ and $Q = K$ (the equilibrium constant),

$0 = \Delta G° + RT \ln K$

$\Delta G° = -RT \ln K$

K = is the equilibrium constant. It has the same form as Q, but only uses the amounts of products and reactants at equilibrium.

$$K = \left\{\frac{P_C{}^c\,P_D{}^d}{P_A{}^a\,P_B{}^b}\right\}_{eq.}$$

$$K = \left\{\frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}\right\}_{eq.}$$

We can rewrite $\Delta G = \Delta G° + RT \ln Q$ as
$\Delta G = -RT \ln K + RT \ln Q$ or $\Delta G = RT \ln (Q/K)$

Relationship between K and Q:

If $Q < K$, ΔG is ___________ and the forward reaction will occur

If $Q > K$, ΔG is ___________and the reverse reaction will occur

Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

If $K=1.9 \times 10^{-4}$ at 400°C, and $P_{N2} = 5.5$ bar $P_{H2}=2.2$ bar $P_{NH3} = 1.1$ bar at 400°C, which direction will the reaction go?

Q =

WHAT DOES K TELL US?

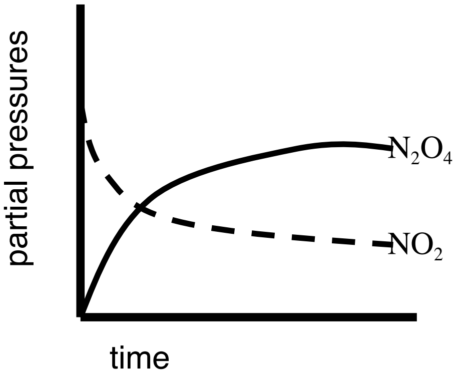
K tells us about the mixture of products and reactants at equilibrium, whether we can expect high or low concentration of products at equilibrium.

when $K > 1$, __________ products

when $K < 1$, _________ products

For K >1
$2NO_2 \rightleftharpoons N_2O_4$ $\Delta G° = -4.76$ kJ/mol and $K = 6.84$ at 298 K

Start with 1.000 bar of NO_2 (reactant) and no N_2O_4 (product)
so $Q < K$ and $\Delta G < 0$, and the reaction goes forward



	$2NO_2$	$\rightleftharpoons$	N_2O_4
initial partial pressure (bar)	1.000		0
change partial pressure			+X
equilibrium partial pressure			+X

K =

For K >1, more products at equilibrium. Large K results from very spontaneous reaction (very negative ΔG°)

Relationship between ΔG° and the magnitude of K:

rewrite $\Delta G° = -RT \ln K$ as

$K = \exp [-\Delta G° / RT]$

K is large if ΔG° is ???

Relationship among equilibrium expressions

If the equilibrium constant for the overall reaction can be written as the *sum* of two or more chemical equations, the equilibrium constant for the overall reaction is the *product* of the equilibrium constant for the component reactions.

$2P\ (g) + 3Cl_2\ (g) \rightleftharpoons 2\ PCl_3\ (g) \qquad K_1$

$\underline{PCl_3\ (g) + Cl_2\ (g) \rightleftharpoons PCl_5\ (g)} \qquad K_2$

$2P\ (g) + 5\ Cl_2\ (g) \rightleftharpoons 2PCl_5\ (g) \qquad K_3$

$K_3 =$

When a balanced equation is multiplied by a constant factor, K is raised to the power of that constant factor.

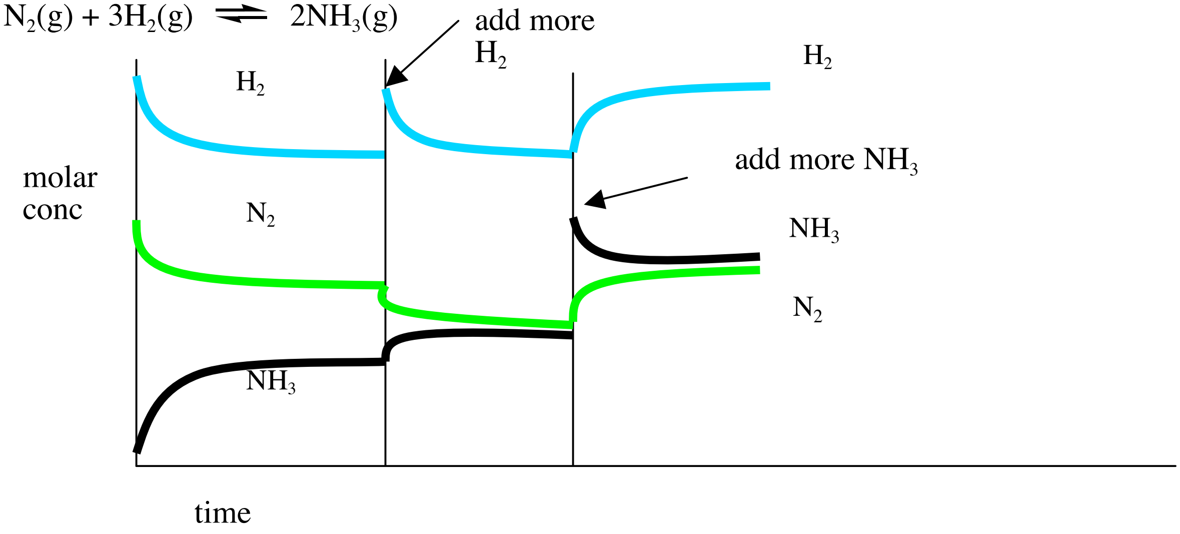
EXTERNAL EFFECTS ON K

Principle of Le Châtelier: A system in equilibrium that is subjected to stress will react in a way that tends to minimize the effect of the stress.

Le Châtelier's principle provides a way to predict qualitatively the direction of change of a system under an external perturbation.

ADDING AND REMOVING REAGENTS

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



1) ADDING MORE REACTANT
If you are at equilibrium and then add more hydrogen, according to Le Châtelier's principle, the system will tend to minimize the increase in the number of hydrogen molecules. Reaction shifts to the right toward product.

This can be explained in terms of Q and K. When reactants are added, Q falls below K momentarily, because the reactant concentration term appears in the denominator.

Q = [products]/[reactants] K= {[products]/[reactant]}$_{\text{equilibrium}}$

With Q<K, the system responds by making more products (reaction proceeds in the forward direction).

2) ADDING MORE PRODUCT

Q rises above K. Q is larger because product term is in numerator (K is unchanged). With Q>K, reaction goes toward reactants (reaction proceeds in the reverse direction).

3) REMOVING PRODUCT
What happens?