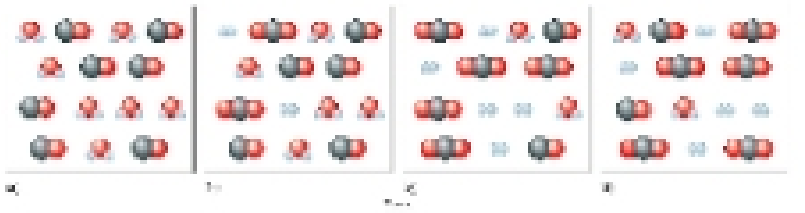
Chapter 6: Chemical Equilibrium

Molecular Picture of Establishment of Equilibrium

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



Initial amounts

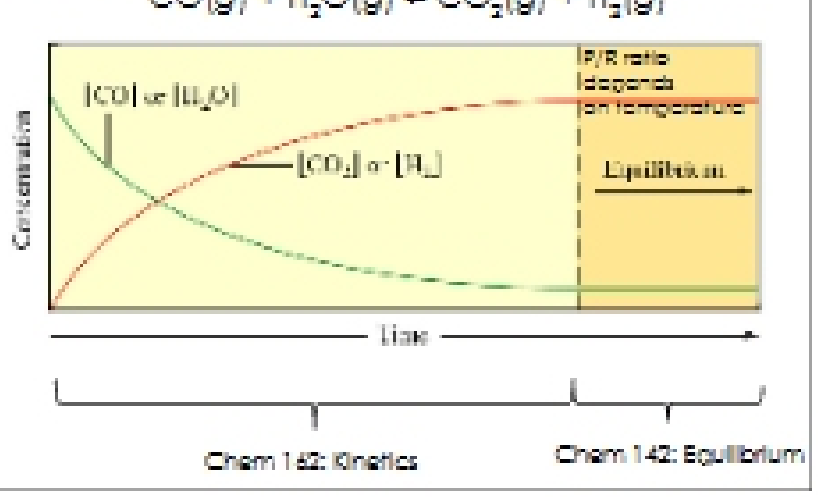
7 CO + 7 H_2O + 0 CO_2 + 0 H_2

At equilibrium

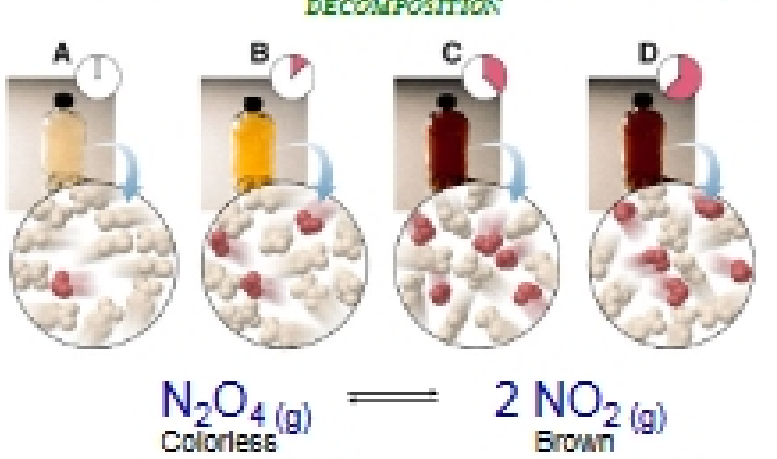
2 CO + 2 H_2O + 5 CO_2 + 5 H_2

Concentration vs. Time

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



Reaching Equilibrium on the Macroscopic and Molecular Levels



N_2O_4 (g) ⇌ 2 NO_2 (g)

Colorless — Brown

Activity (cont'd.)

- When performing a proper thermodynamic description of equilibrium, one considers the activity of substances, not simply the concentrations.
- For our purposes, we will simply refer all of our concentrations (or pressures) to a standard state:
  - For gases: 1 atm
  - For solutions: 1 M
  - For pure liquids: the state of the liquid itself
  - For solids: the state of the solid itself
- Given these definitions, we define activity (a_i) for the species *i* as:

$$a_i = \frac{[i]}{1M} \quad \text{or} \quad = \frac{P_i}{1atm}$$

The Equilibrium Constant

$$bB + cC \leftrightarrow dD + eE$$

$$K = \frac{(a_D)^d (a_E)^e}{(a_B)^b (a_C)^c}$$

Example

At equilibrium $[NH_3] = 3.1 \times 10^{-3}$ M, $[N_2] = 8.5 \times 10^{-1}$ M, and $[H_2] = 3.1 \times 10^{-3}$ M. What is the equilibrium constant?

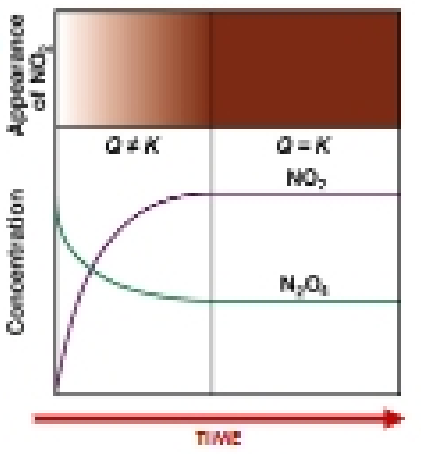
The Equilibrium Constant

- Properties of the equilibrium constant:
  - *K* for a reaction written in reverse is the reciprocal of the original K expression: $K_{reverse} = (K_{forward})^{-1}$
  - If you multiply a chemical equation by a factor, n, the new K is simply the old *K* raised to the power of the factor: $K_{new} = (K_{original})^n$
- The equilibrium constant is always unitless.
- When calculating *K*, you must use **equilibrium** concentrations.
- ***K* depends only on *T***, not on initial concentrations.

The Equilibrium Constant

N_2O_4 (g) Colorless $2\ NO_2$ (g) Brown

Changes of reactant and product concentrations during a chemical reaction.



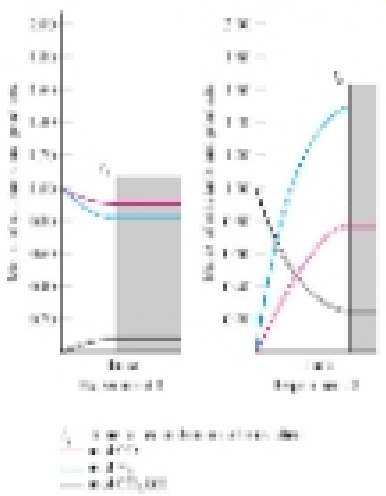
Initial and Equilibrium Concentrations for the N_2O_4-NO_2 System at 100°C

Initial		Equilibrium		Ratio	
$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[NO_2]^2/[N_2O_4]$	
0.1000	0.0000	0.0491	0.1018	0.211	
0.0000	0.1000	0.0185	0.0627	0.212	=K
0.0500	0.0500	0.0332	0.0837	0.211	
0.0750	0.0250	0.0411	0.0930	0.210	

Experiments carried out at a certain temperature, but with different initial concentrations, yield the same value for the equilibrium constant, K.

Reaching Equilibrium from Different Starting Points

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



$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2}$$

Types of Equilibrium Constants

Dissociation constant (acids, bases, salts; Chs 7/8)

Solubility product (precipitation reactions; Ch 8)

Formation constant (complexation reactions; Ch 8)

Standard potentials (redox reactions; Ch 11)