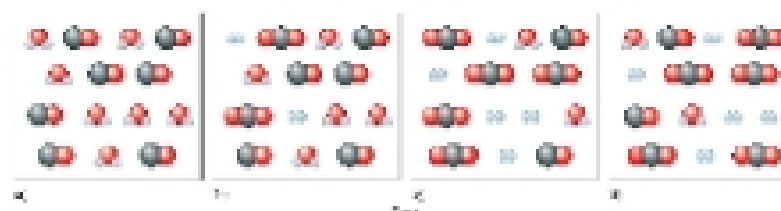


Chapter 6: Chemical Equilibrium

- 6.1 The Equilibrium Condition
- 6.4 The Concept of Activity
- 6.2 The Equilibrium Constant
- 6.3 Equilibrium Expressions Involving Pressures
- 6.5 Heterogeneous Equilibria
- 6.6 Applications of the Equilibrium Constant
- 6.7 Solving Equilibrium Problems
- 6.8 Le Châtelier's Principle

Molecular Picture of Establishment of Equilibrium



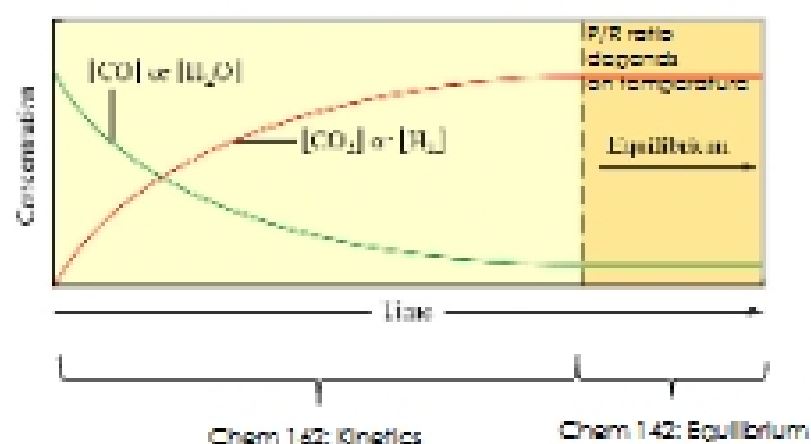
Initial amounts



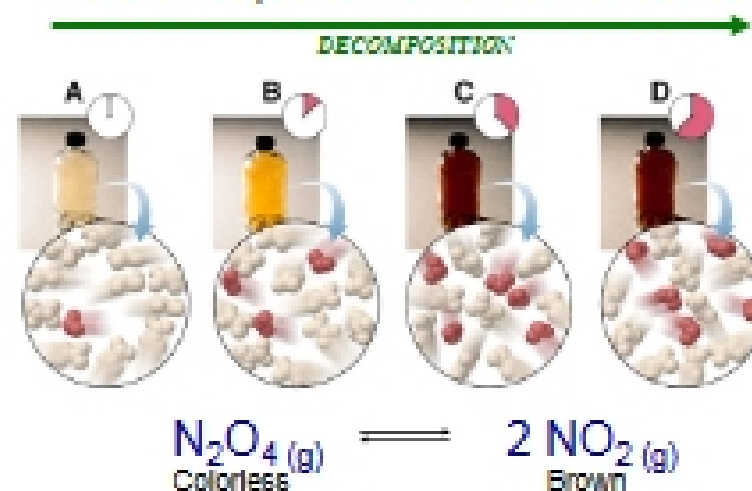
At equilibrium



Concentration vs. Time



Reaching Equilibrium on the Macroscopic and Molecular Levels



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:

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

The Equilibrium Constant



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

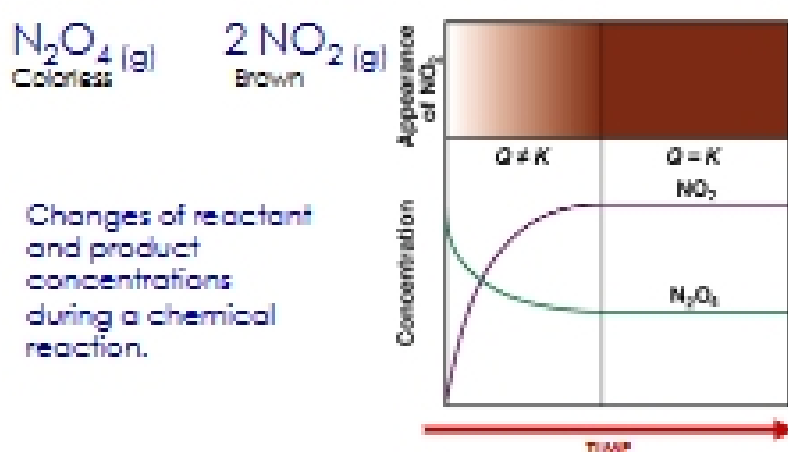
Example

At equilibrium $[\text{NH}_3] = 3.1 \times 10^{-4} \text{ M}$, $[\text{N}_2] = 8.5 \times 10^{-1} \text{ M}$, and $[\text{H}_2] = 3.1 \times 10^{-2} \text{ M}$. 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: $K_{\text{reverse}} = (K_{\text{forward}})^{-1}$
 - 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: $K_{\text{new}} = (K_{\text{original}})^n$
- 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

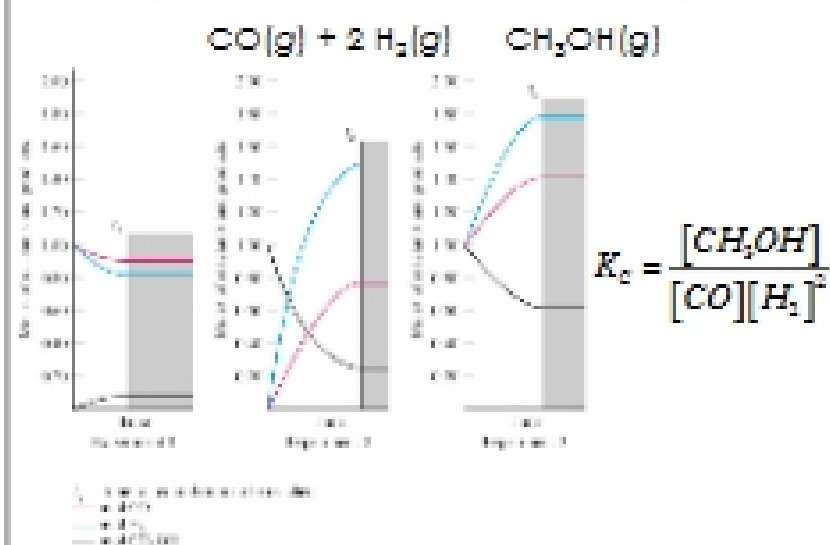


Initial and Equilibrium Concentrations for the N_2O_4 - NO_2 System at 100°C

Initial		Equilibrium		Ratio
$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$
0.1000	0.0000	0.0491	0.1018	0.211
0.0000	0.1000	0.0185	0.0627	0.212
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



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)