



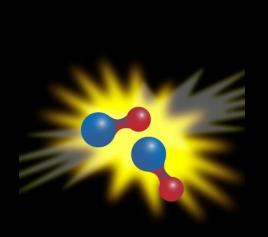


### **Chemical Reactions**

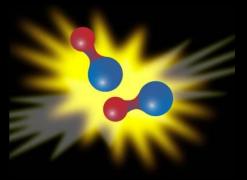


### **Collision Theory:**

Molecules react by colliding with each other Collisions may rearrange electron density



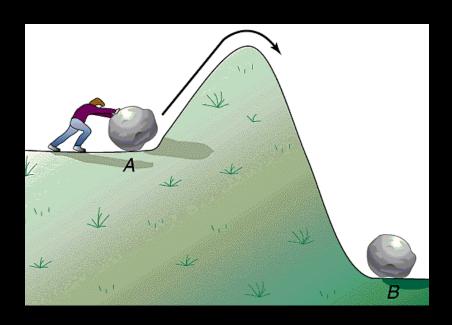


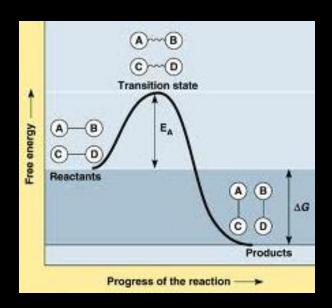


# **Chemical Reactions**

 $A + B \rightarrow C + D$  Requires Activation energy  $(E_A)$ 

**Energy to bring molecules together Energy to orient molecules to product geometry** 

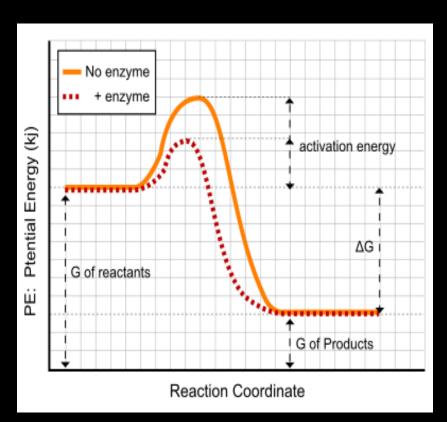




### **Chemical Reactions**

Catalyst: speeds up a chemical reaction without being consumed Changes rate only; equilibrium position unchanged

Enzymes are specialized protein catalysts



Substrate Binding Geometry  $\label{eq:approximates} \begin{substrate} Approximates Transition State \\ Lowers $E_A$ \end{substrate}$ 



Most chemical reactions are "reversible"

$$aA + bB \longrightarrow cC + dD$$

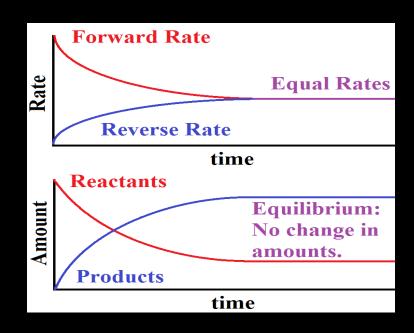
When forward rate = reverse rate

Overall concentrations remain constant

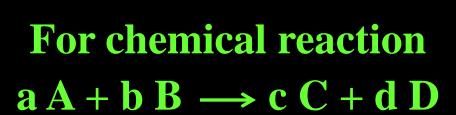
#### **Equilibrium:** Concentrations of all components stable



**Steady State** 



## Law of Equilibrium





### **K** = equilibrium constant:

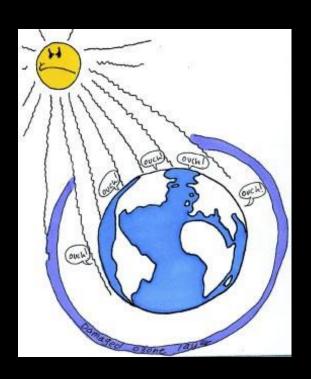
$$\mathbf{K} = \mathbf{[C]^c[D]^d}$$
$$\mathbf{[A]^a[B]^b}$$



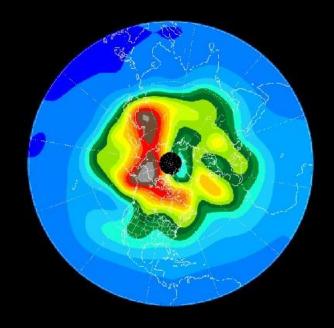


### For the conversion of oxygen to ozone:

$$3 O_{2(g)} \longrightarrow 2 O_{3(g)}$$



$$\mathbf{K} = \frac{[\mathbf{O}_3]^2}{[\mathbf{O}_2]^3}$$



Ammonia gas reacts with oxygen gas in a closed container to produce nitrogen monoxide gas and water vapor. Write the balanced equation and the equilibrium expression:

#### Write the equation:

$$NH_{3(g)} + O_{2(g)} \longrightarrow NO_{(g)} + H_2O_{(g)}$$



#### **Balance:**

$$4 \text{ NH}_{3(g)} + 5 \text{ O}_{2(g)} \longrightarrow 4 \text{ NO}_{(g)} + 6 \text{ H}_2\text{O}_{(g)}$$

#### Write equilibrium expression:



$$K = [NO]^{4}[H_{2}O]^{6}$$
$$[NH_{3}]^{4}[O_{2}]^{5}$$

Nitrogen gas in a closed container reacts with hydrogen gas to produce ammonia gas. Write the balanced equation and the equilibrium expression:

#### Write the equation:

$$N_{2(g)} + H_{2(g)} \longrightarrow NH_{3(g)}$$



#### **Balance:**

$$N_{2(g)} + 3 H_{2(g)} \longrightarrow 2 NH_{3(g)}$$

#### Write equilibrium expression:



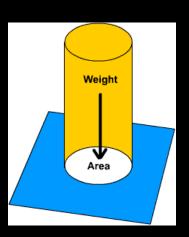
$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

**Equilibrium Position: A single set of concentration values** 

**Used to calculate K (equilibrium constant)** 

K value may change with alterations of temperature & pressure







For: 
$$2 SO_{2(g)} + O_{2(g)} \rightarrow 2 SO_{3(g)}$$

#### **Equilibrium Position Observed at 600 °C:**

$$[SO_2] = 0.590 M$$

$$[O_2] = 0.045 M$$

$$[SO_3] = 0.260 M$$

$$\mathbf{K} = \frac{[\mathbf{SO}_3]^2}{[\mathbf{SO}_2]^2[\mathbf{O}_2]}$$

$$K = \frac{(0.260 \text{ M})^2}{(0.590 \text{ M})^2(0.045 \text{ M})}$$

$$K = 4.32 M^{-1}$$



For: 
$$2 SO_{2(g)} + O_{2(g)} \longrightarrow 2 SO_{3(g)}$$

Given K, 4.32 M<sup>-1</sup>

Equilibrium Positions at same T & P can be calculated: For  $[SO_2] = 1.50 \text{ M}$  &  $[O_2] = 1.25 \text{ M}$ , Calculate  $[SO_3]$ 

$$\mathbf{K} = \frac{[\mathbf{SO}_3]^2}{[\mathbf{SO}_2]^2[\mathbf{O}_2]}$$

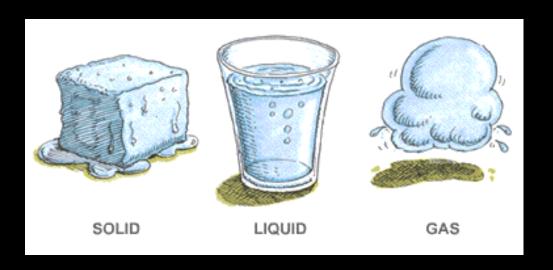
4.32 M<sup>-1</sup> = 
$$\frac{(x)^2}{(1.50 \text{ M})^2 (1.25 \text{ M})}$$
  
(4.32 M<sup>-1</sup>) (1.50 M)<sup>2</sup>(1.25 M) =  $x^2$   
12.15 M<sup>2</sup> =  $x^2$ 

 $x = [SO_3] = 3.49 M$ 

Solve with  $\sqrt{}$  Calculator Function

Homogeneous: All components in same phase

Heterogeneous: Components in different phases Solids and Liquids have no influence on K (Not involved in equilibrium equation)



# Heterogeneous Equilibrium

For: 
$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

$$K = [CO_2][CaO]$$

$$[CaCO_3]$$

But, CaCO<sub>3</sub> & CaO are solids (Constant Concentration):

$$K = [CO_2][Constant]$$
[Constant]

All constants combined:

$$K = [CO_2]$$

# Heterogeneous Equilibrium

**Equilibrium Expressions (K)** 

Depend only on the [species in solutions] and [gas phase]

**Pure Solids or Pure Liquids Not Considered** 





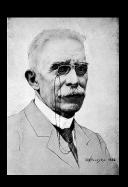
# Heterogeneous Equilibrium

For: 
$$NH_4NO_{3 (s)} \longrightarrow N_2O_{(g)} + 2 H_2O_{(g)}$$
  
 $K = [N_2O][H_2O]^2$ 

For: 
$$CO_{2(g)} + MgO_{(s)} \longrightarrow MgCO_{3(s)}$$

$$K = 1$$

$$[CO_2]$$



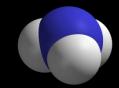
If a change is imposed on a system at equilibrium, the position of the equilibrium shifts to reduce the effect

### **Example - Changing Concentration:**

For: 
$$3 H_{2(g)} + N_{2(g)} \iff 2 NH_{3(g)}$$

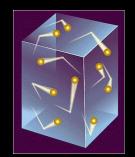
Increasing [N<sub>2</sub>]

$$3 H_{2(g)} + N_{2(g)} \longrightarrow 2 NH_{3(g)}$$



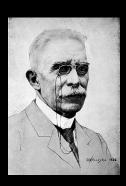
Reaction shifts to right

#### Increasing [NH<sub>3</sub>]



$$3 H_{2(g)} + N_{2(g)} \leftarrow 2 NH_{3(g)}$$

Reaction shifts to left



A change imposed on a system at equilibrium will shift equilibrium position to reduce the effect

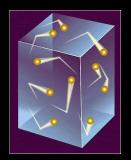
**Example - Changing Volume (Pressure):** 

For: 
$$3 H_{2(g)} + N_{2(g)} \stackrel{\longleftarrow}{\longrightarrow} 2 NH_{3(g)}$$

**Increasing Pressure (Lowers Volume)** 

$$3 H_{2(g)} + N_{2(g)}$$
  $2 NH_{3(g)}$ 

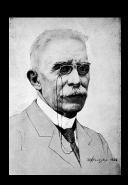
Reaction shifts to right (less molecules)



**Increasing Volume (Lowers Pressure)** 

$$3 H_{2(g)} + N_{2(g)} \leftarrow 2 NH_{3(g)}$$

Reaction shifts to left (more molecules)



If a change imposed on a system at equilibrium, the position of the equilibrium shifts to reduce the effect

**Example - Changing Volume (Pressure)** 

For: 
$$CaCO_{3(s)} \subseteq CaO_{(s)} + CO_{2(g)}$$

**Increasing Volume (Decreasing Pressure)** 

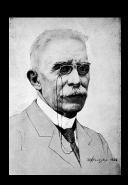
$$CaCO_{3(s)} \leftarrow CaO_{(s)} + CO_{2(g)}$$

Reaction shifts to right (more space)

**Decreasing Volume (Increasing Pressure)** 



$$CaCO_{3 (s)} \leftarrow \longrightarrow CaO_{(s)} + CO_{2 (g)}$$
Reaction *shifts* to left (less space)





If a change imposed on a system at equilibrium, the position of the equilibrium shifts to reduce the effect

**Example - Changing Temperature:** 

For: 
$$3 H_{2(g)} + N_{2(g)} \longrightarrow 2 NH_{3(g)} + 92 kJ$$

**Decreasing Temperature** 

$$3 H_{2(g)} + N_{2(g)} \stackrel{\longleftarrow}{\longrightarrow} 2 NH_{3(g)} + 92 kJ$$

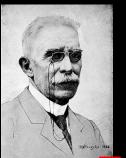
Reaction shifts to right (produce more product)



**Increasing Temperature** 

$$3 H_{2(g)} + N_{2(g)} \leftarrow 2 NH_{3(g)} + 92 kJ$$

Reaction shifts to left (consider heat a product)



If a change imposed on a system at equilibrium, the position of the equilibrium shifts to reduce the effect

Example - Changing Temperature:

For: 
$$CaCO_{3(s)} + 176.8 \text{ kJ} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

#### **Increasing Temperature**



$$CaCO_{3(s)} + 176.8 \text{ kJ} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

Reaction shifts to right (consider heat a reactant)



#### **Decreasing Temperature**

Reaction shifts to left (consider heat a reactant)

#### **Extent of reaction:**

K < 1.00 Reactants Dominate

**K** > 1.00 Products Dominate







Chemical manufacturing and research strive to "drive reactions to the right"

# Le Châtelier's Principle Driving Reaction to the Right



Industrial Tactic: Promote Product Formation

By Removing products as they form





#### For Dissociation of an ionic compound:

$$A_bB_{a\ (s)} \stackrel{\longleftarrow}{\longleftarrow} b A^+_{(ag)} + a B^-_{(aq)}$$

The Equilibrium Expression:

$$\mathbf{K} = \mathbf{A}^{+}\mathbf{B}^{-}\mathbf{B}^{-}\mathbf{A}$$

$$\mathbf{A}\mathbf{B}\mathbf{B}$$

For Saturated Solution [AB] (solid) ignored:

$$\mathbf{K}_{\mathrm{sp}} = [\mathbf{A}^{+}]^{\mathrm{b}} [\mathbf{B}^{-}]^{\mathrm{a}}$$



When  $K_{sp}$  exceeded, precipitation must occur

# Solubility Product (K<sub>sp</sub>)

Copper (I) bromide has a solubility of 2.0 x  $10^{-4}$  M at 25 °C. Calculate the  $K_{sp}$  for this compound.

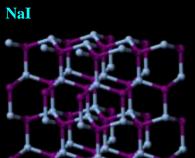
CuBr 
$$\iff$$
 Cu<sup>+</sup> + Br  
 $K_{sp} = [2.0 \times 10^{-4}] [2.0 \times 10^{-4}]$   
 $K_{sp} = 4.00 \times 10^{-8}$ 

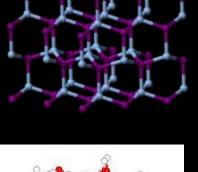


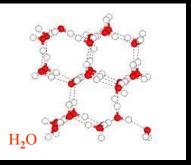
# Solubility Product (K<sub>sp</sub>)



Calculate the solubility of AgI  $(K_{sp} = 1.5 \times 10^{-16})$  at 25 °C







$$AgI \longrightarrow Ag^+ + I^-$$

$$\mathbf{K}_{\mathrm{sp}} = [\mathbf{A}\mathbf{g}^{+}] [\mathbf{I}^{-}]$$

$$1.5 \times 10^{-16} = x^2$$

$$x = \sqrt{1.5 \times 10^{-16} M^2}$$

$$x = 1.2 \times 10^{-8} M$$



Solve with  $\sqrt{}$  Calculator Function

AgI used to "Seed" Clouds to induce rain formation

