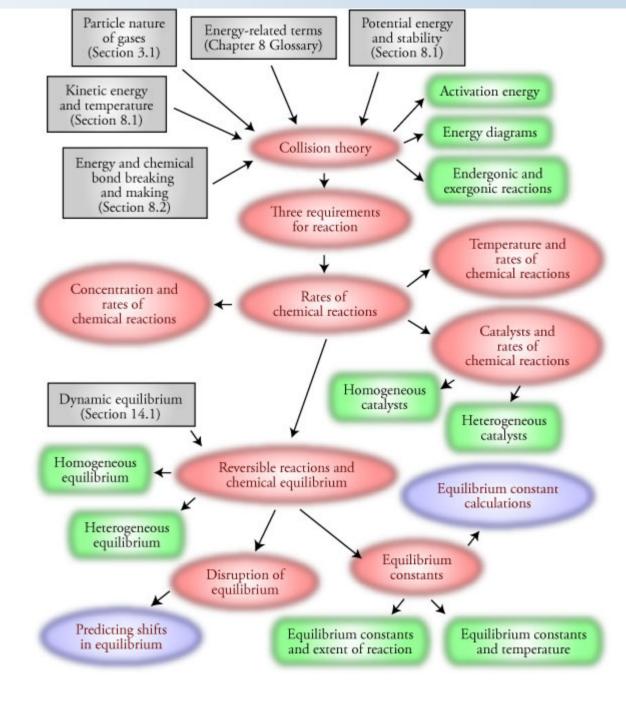


### Chapter 16

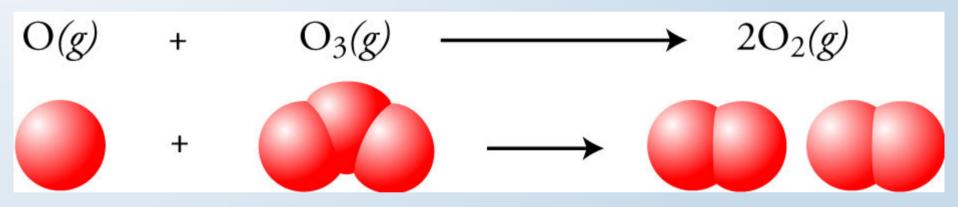
The Process of Chemical Reactions

## **Chapter Map**



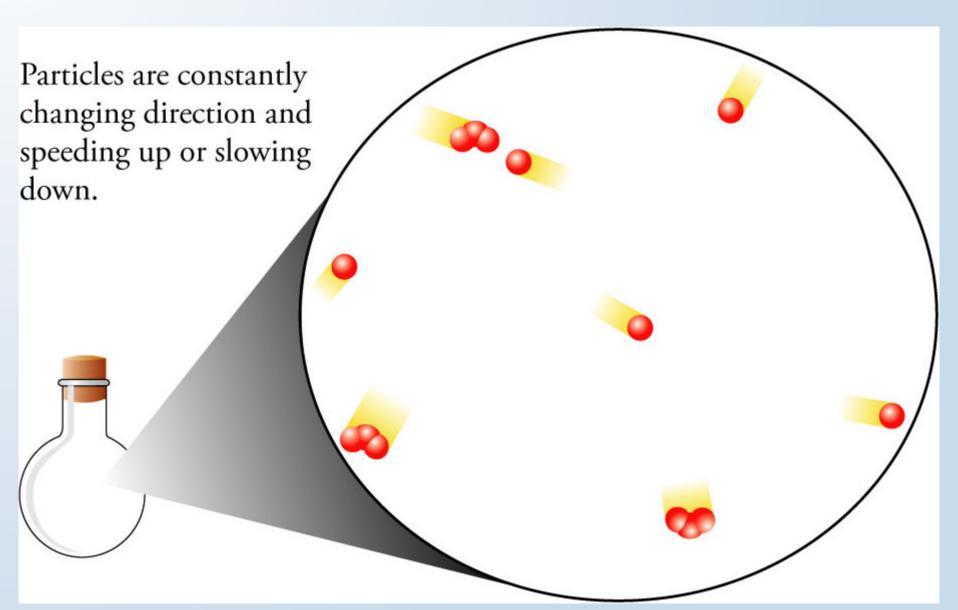
#### **Collision Theory**

Reactants must collide

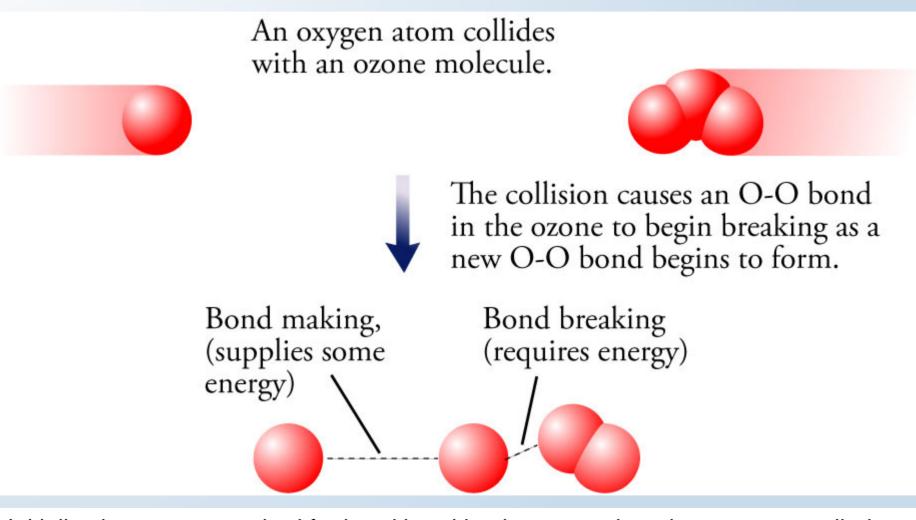


- collision brings contact between reactants
- collision provides energy to break bonds

$$O(g) + O_3(g) \rightarrow 2O_2(g)$$

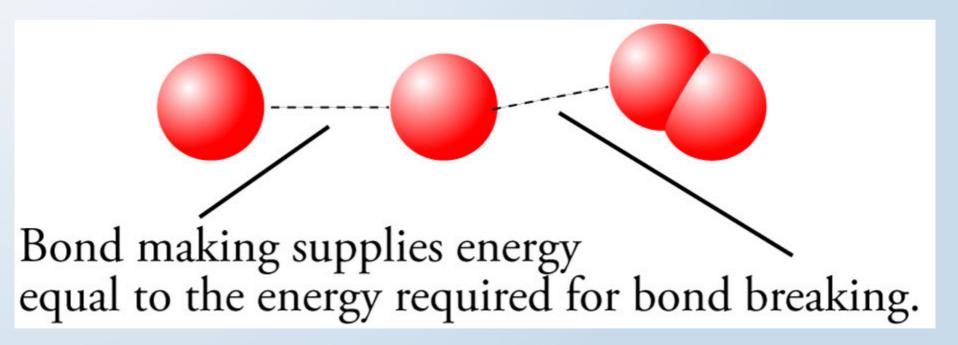


### **Bond Breaking and Making**



Initially, the energy required for bond breaking is greater than the energy supplied from bond making. The extra energy necessary for the reaction comes from the kinetic energy of the colliding particles.

## Formation of Activated Complex



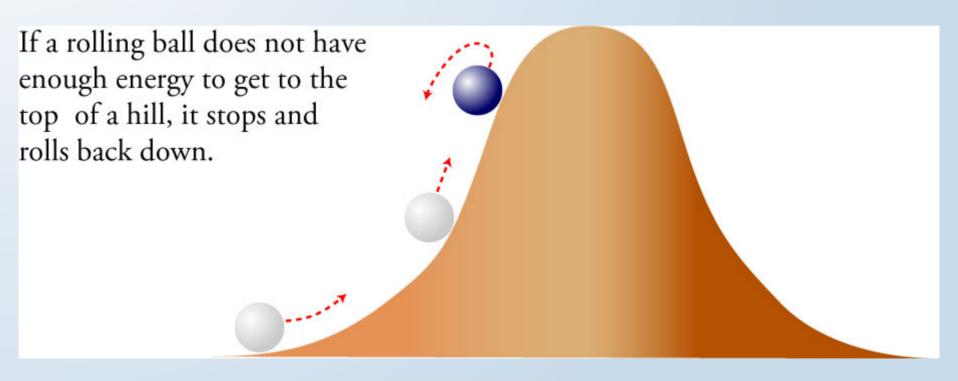
#### **Formation of Product**

Beyond some point in the reaction, bond making predominates over bond breaking.

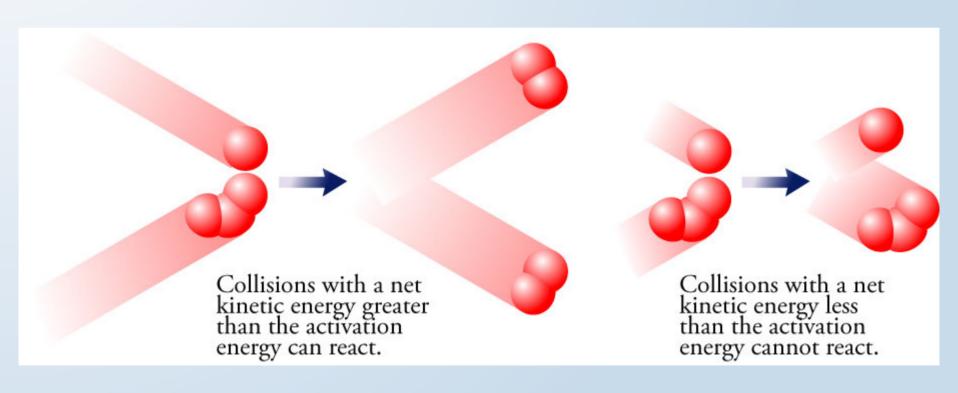
+ Energy

Bond making supplies more energy than is necessary for bond breaking... so energy is released

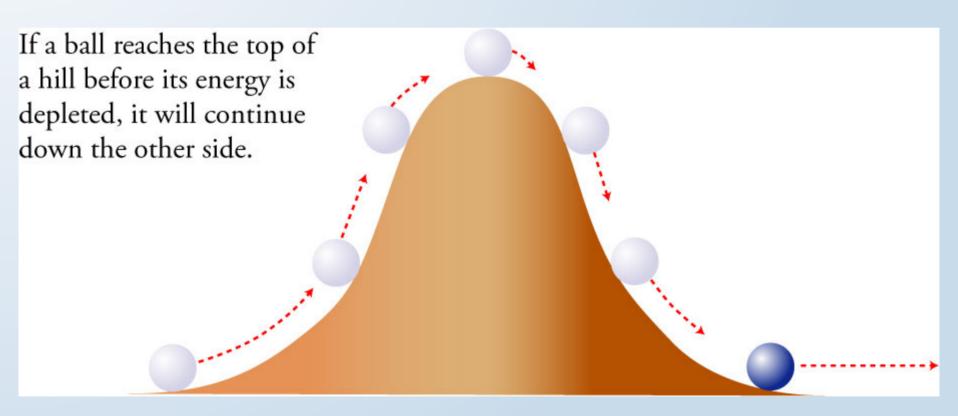
# Reactions must have a minimum activation energy...if too little, no change



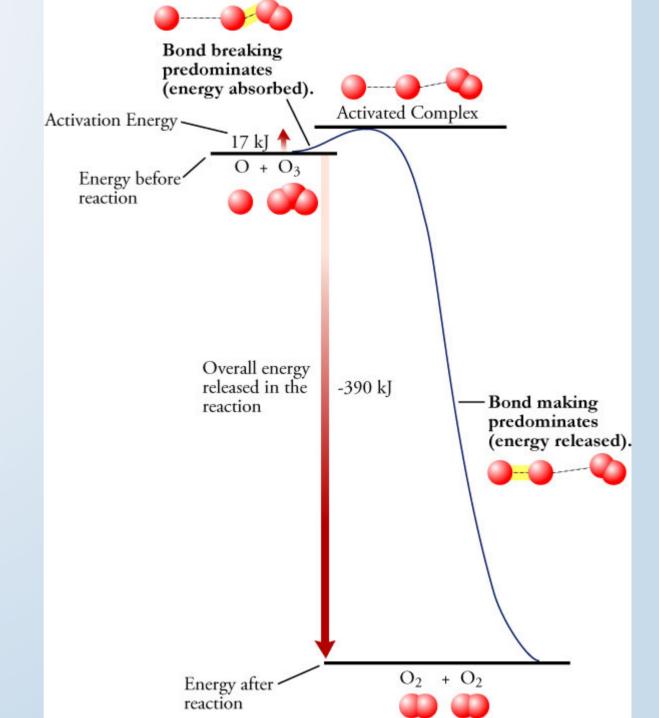
# Collision Energy and Activation Energy



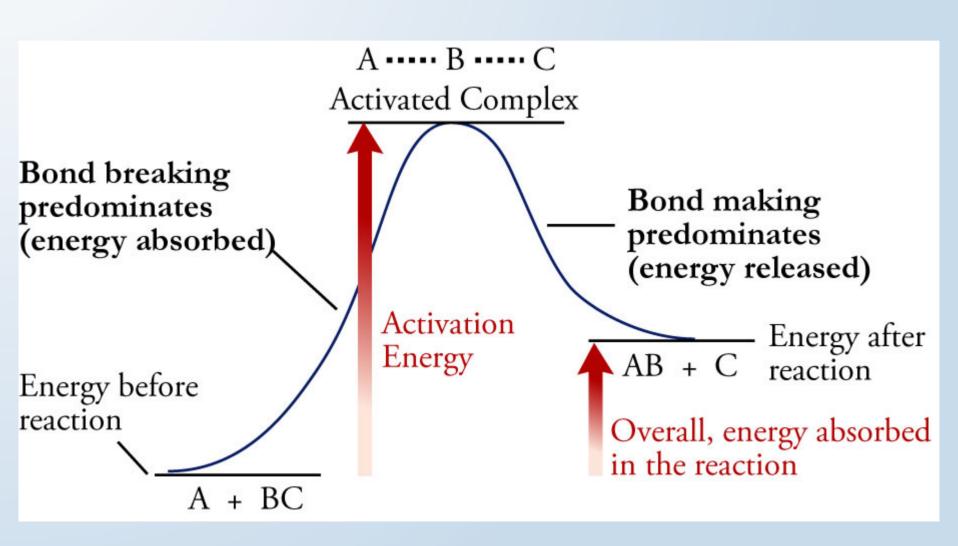
# Reactions must have a minimum activation energy...if enough, change



# Energy Diagram for O/O<sub>3</sub> Reaction



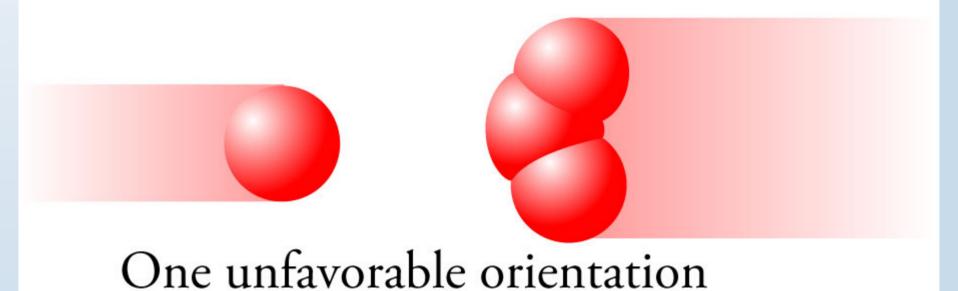
### **Endogonic Reactions**



#### Orientation



One favorable orientation





- The reactant particles must collide.
  - The collision brings together the atoms that will form the new bonds, and the kinetic energy of the particles provides energy for the reaction to proceed.

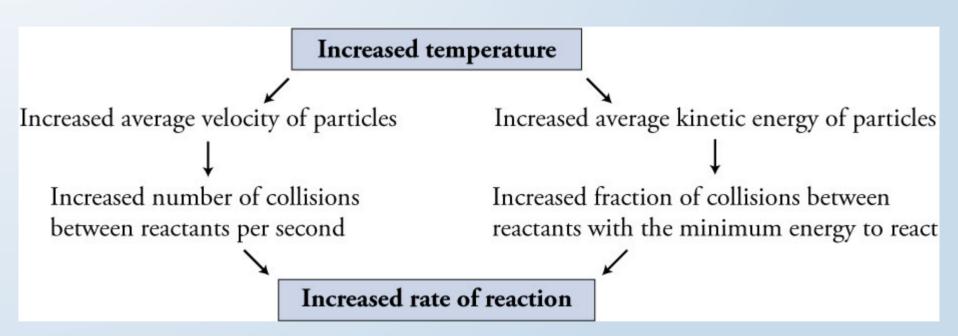


- The collision must provide at least the minimum energy necessary to produce the activated complex.
  - It takes energy to initiate the reaction by converting the reactants into the activated complex. If the collision does not provide this energy, products cannot form.

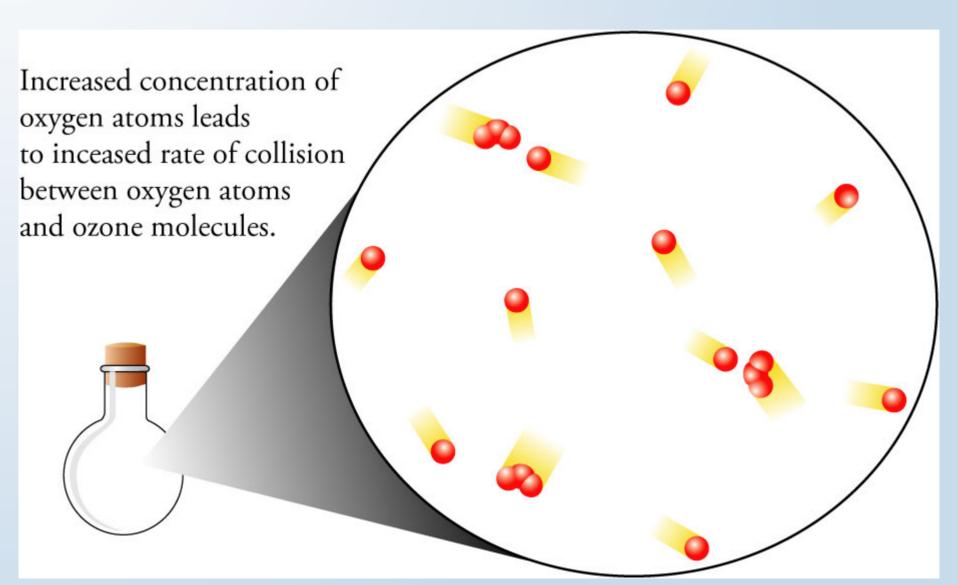


- The orientation of the colliding particles must favor the formation of the activated complex, in which the new bond or bonds are able to form as the old bond or bonds break.
  - Because the formation of the new bonds provides some of the energy necessary to break the old bonds, the making and breaking of bonds must occur more or less simultaneously. This is only possible when the particles collide in such a way that the bond-forming atoms are close to each other.

## Temperature and Rate of Reaction



### Increased Concentration of One Reactant



## Concentration and Rates of Reaction

Increased concentration of reactant (Increased number of particles per unit volume)

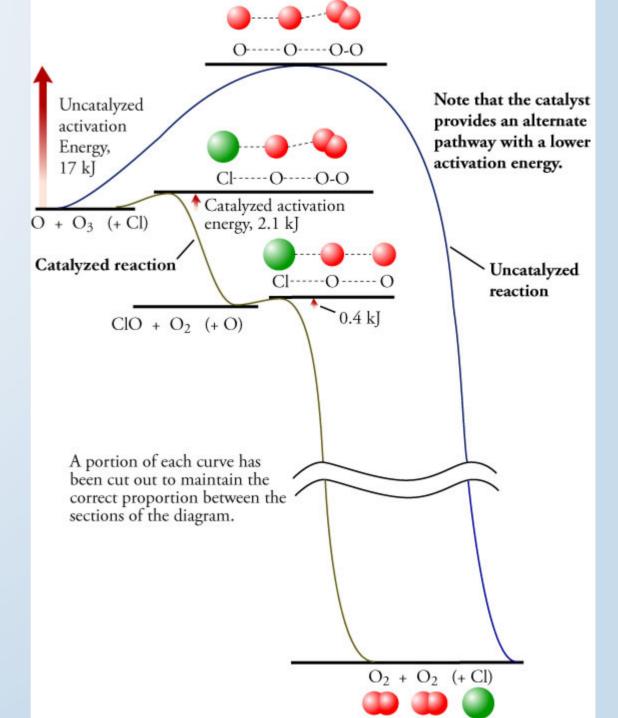
Decreased average distance between particles and decreased volume available in which to move without colliding

Increased number of collisions between reactants per liter per second

Increased number of particles fulfilling the requirements for reaction

Increased rate of reaction

# Catalyzed O/O<sub>3</sub> Reaction



## Catalysts and Rate of Reactions

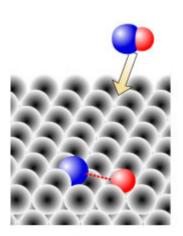
The catalyst provides an alternate pathway with a lower activation energy.

A greater fraction of collisions have the activation energy.

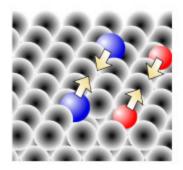
A greater fraction of collisions lead to products.

Increased rate of reaction

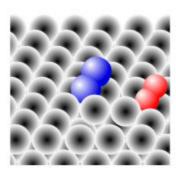
#### Heterogeneous Catalysis



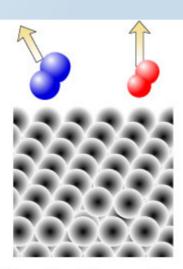
Step 1 - The reactant molecules are adsorbed, and the bonds are weakened.



Step 2 - The atoms migrate across the catalyst.



Step 3 - New bonds form.



**Step 4** - The products leave the catalyst.

# Production and Uses of Hydrogen Gas

Chemical plants make a mixture of hydrogen gas and carbon monoxide gas called synthesis gas.

Ammonia for fertilizers, explosives, plastics, and fibers Hydrogen gas

Reduction of metal oxides to form pure metals

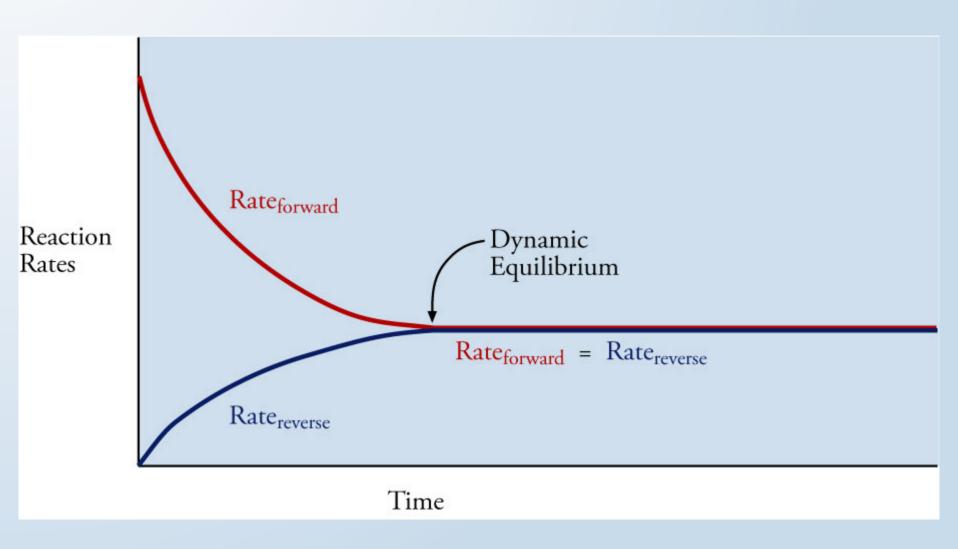
A shift converter converts carbon monoxide and water into more hydrogen gas and carbon dioxide.



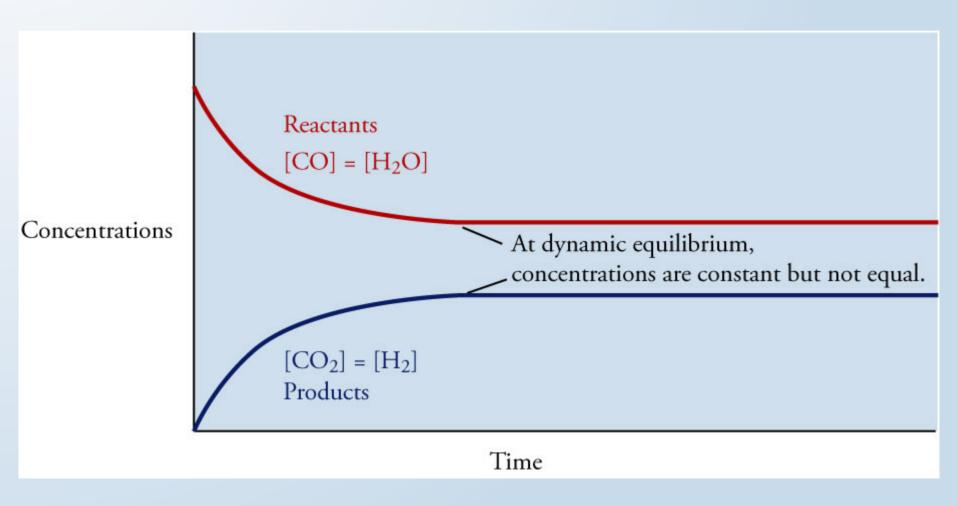
HCl for cleaning metals acidifying oil wells, food processing, and the manufacture of many other chemicals

Methanol, used to make formaldehyde, acetic acid, MTBE, and many other chemicals

## Rates of Reaction for Reversible Reactions

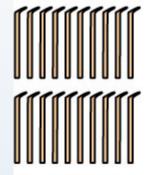


## Changes in Concentrations for a Reversible Reaction



#### Ski Shop Analogy for Equilibrium

#### Early morning







No skis on the slope

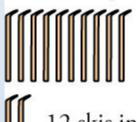
Initially, there are 20 skis in the shop.

0 pairs of skis return per hour

#### Later in the day

(Fewer skis available so fewer

are rented per hour)



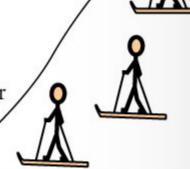
12 skis in the shop.



3 pairs of skis on the slope (More skis on the slope so more skis are returned)

3 pairs of skis leave per hour

3 pairs of skis return per hour



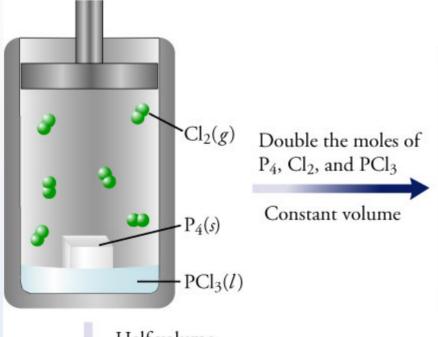
**Equilibrium** (No change in the number of skis in the shop and on the slope)

# Equilibrium Constant Expression

$$CH_4(g) + H_2O(g) \iff CO(g) + 3H_2(g)$$

The coefficient before  $H_2$  is 3, so we raise the concentration or pressure to the third power.

$$K_C = \frac{[CO] [H_2]^3}{[CH_4] [H_2O]}$$
  $K_P = \frac{P_{CO} P_{H_2}^3}{P_{CH_4} P_{H_2O}}$ 



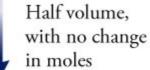


Concentration of gas doubles.

Double 
$$\frac{\text{mol } \text{Cl}_2}{\text{L}}$$

Concentrations of solid and liquid remain constant.

Same 
$$\frac{\text{mol } P_4}{L}$$
Same 
$$\frac{\text{mol } PCl_3}{L}$$





#### Heterogeneous Equilibrium

Concentration of gas doubles.

Double 
$$\frac{\text{mol } Cl_2}{L}$$

Concentrations of solid and liquid remain constant.

Same 
$$\frac{\text{mol P}_4}{\text{L}}$$
 and  $\frac{\text{mol PCl}_3}{\text{L}}$ 

# Equilibrium Constant Expressions for Heterogeneous Equilibria

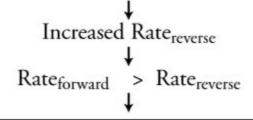
$$SO_2(g) + 2H_2S(g) \Longrightarrow 3S(s) + H_2O(g)$$

The solid does not appear in the  $K_C$  and  $K_P$  expressions.

$$K_C = \frac{[H_2O]}{[SO_2] [H_2S]^2}$$
  $K_P = \frac{P_{H_2O}}{P_{SO_2} P_{H_2S}^2}$ 

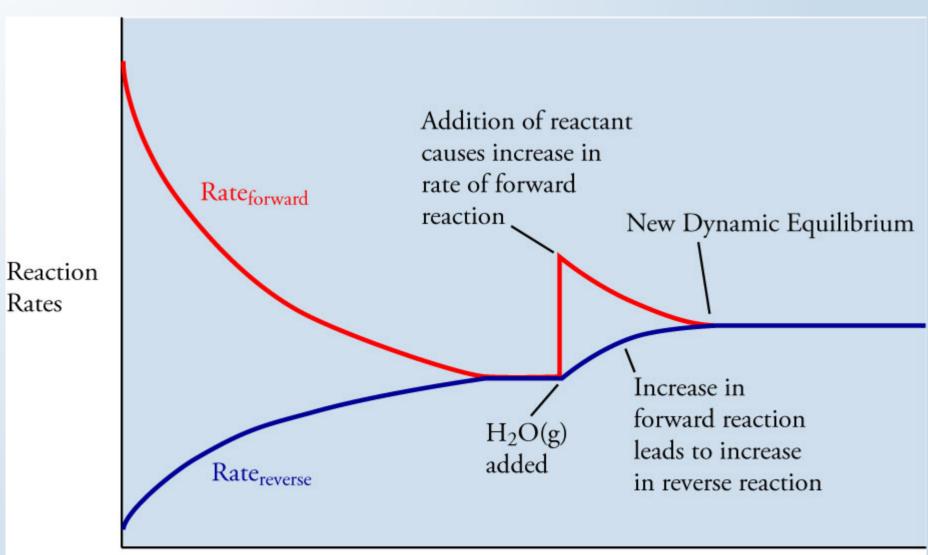
# Effect of Increased Concentration on Equilibrium

Increased concentration of reactant for a system at equilibrium with Rate<sub>forward</sub> = Rate<sub>reverse</sub>



System shifts toward products

## Change in Rates When Reactant Added



Time

### Ski Shop **Analogy 2**



There are 12 skis in the shop.







3 pairs of skis on the slope

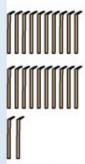


3 pairs of skis return per hour

Equilibrium (No change in the number of skis in the shop and on the slope)

#### Immediately after buying more skis

There are 22 skis in the shop. (With more skis in the shop, more are rented per hour.)







3 pairs of skis on the slope



3 pairs of skis return per hour

More skis leave than return, so the equilibrium is disrupted.

#### Later

There are 18 skis in the shop. (This is more skis than before the purchase but fewer than immediately after the purchase.).







4 pairs of skis leave per hour

4 pairs of skis return per hour

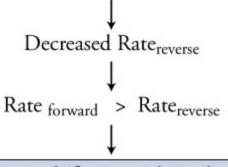


5 pairs of skis on the slope

New equilibrium (No change in the number of skis in the shop and on the slope)

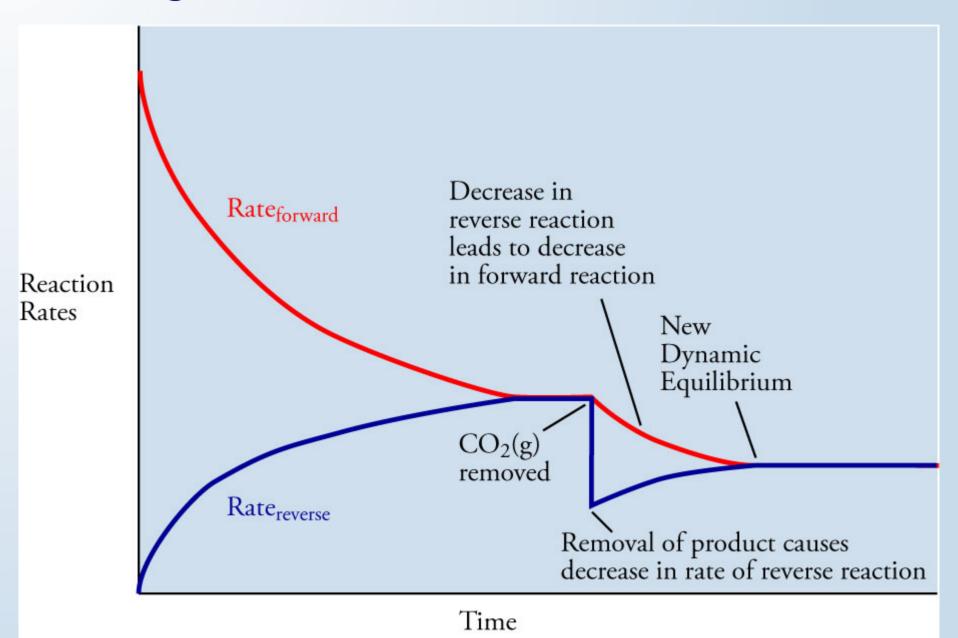
# Effect of Decreased Concentration on Equilibrium

Decreased concentration of one product for a system at equilibrium with Rateforward = Ratereverse



System shifts toward products

#### **Change in Rates When Product Removed**





## Le Chatelier's Principle

 If a system at equilibrium is altered in a way that disrupts the equilibrium, the system will shift in such a way as to counter the change.