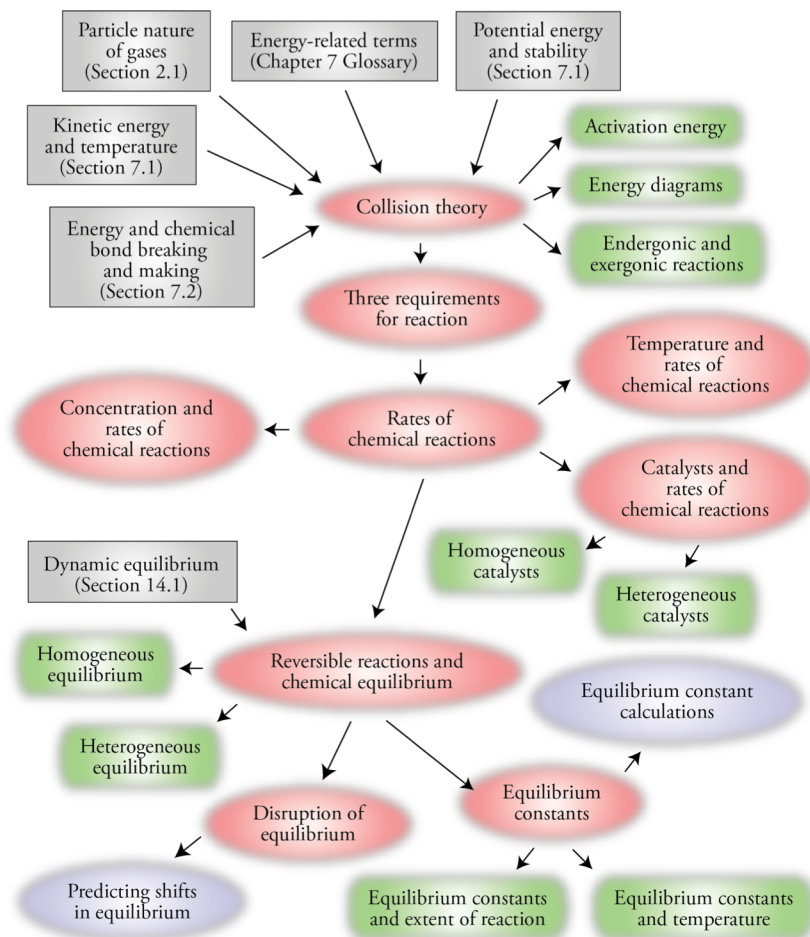


# Chapter 14

## The Process of Chemical Reactions

*An Introduction to Chemistry*  
by Mark Bishop

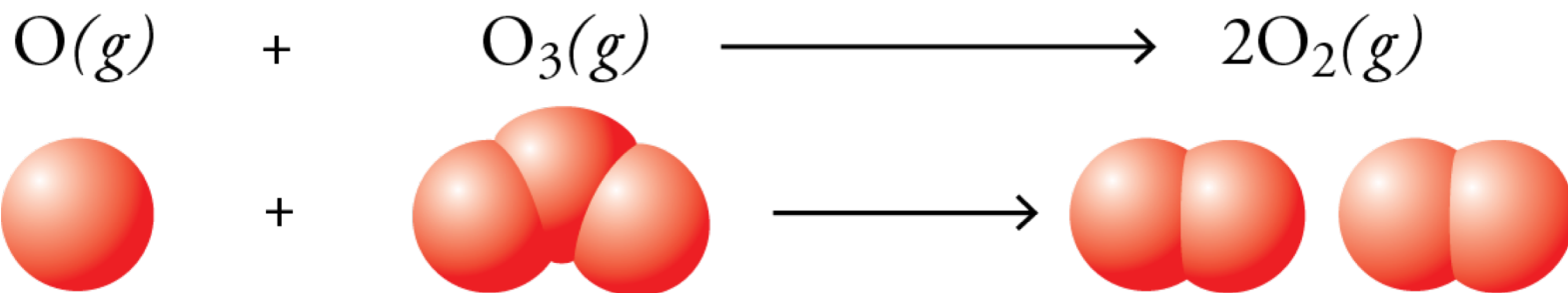
# Chapter Map



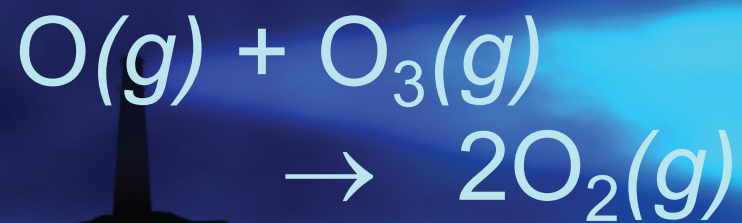


# Collision Theory

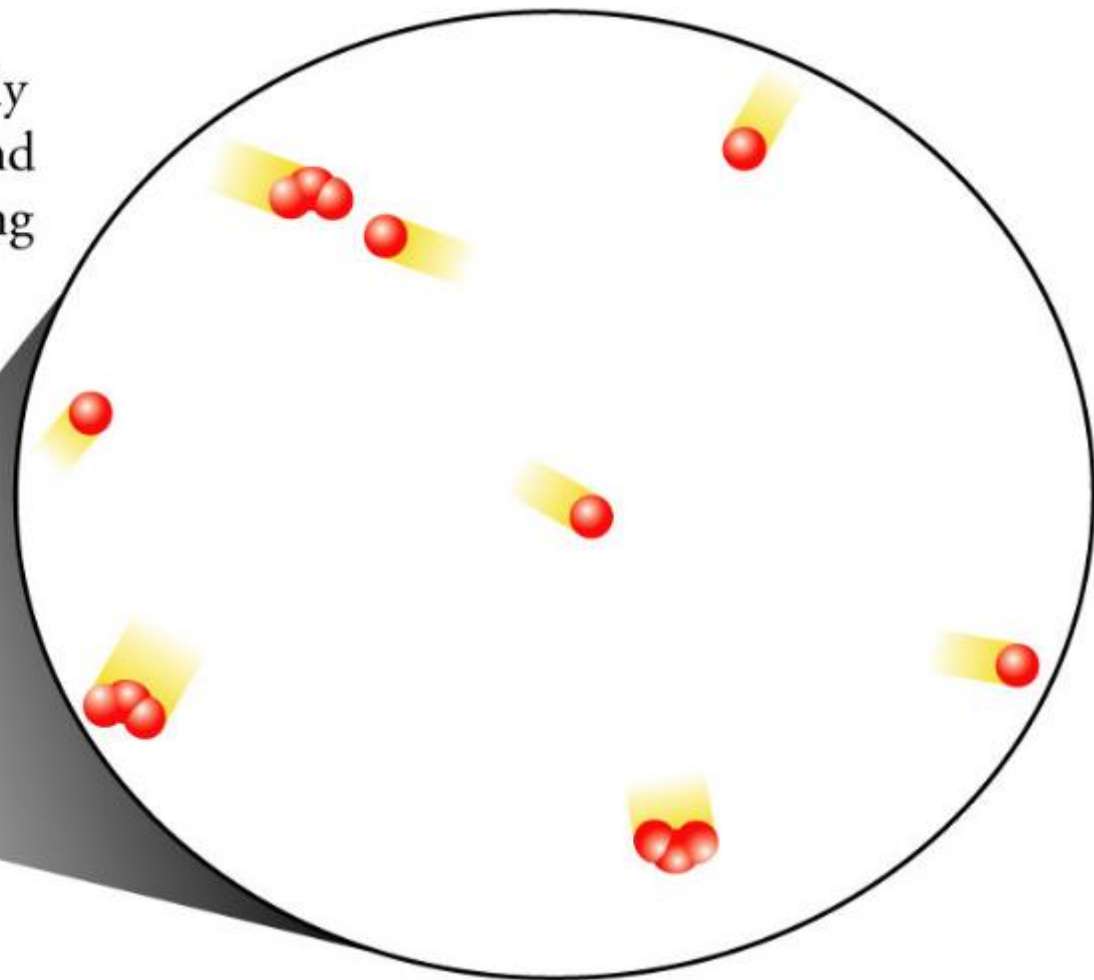
- Reactants must collide



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



Particles are constantly changing direction and speeding up or slowing down.



# Endergonic Change

more stable + **energy** → less stable system

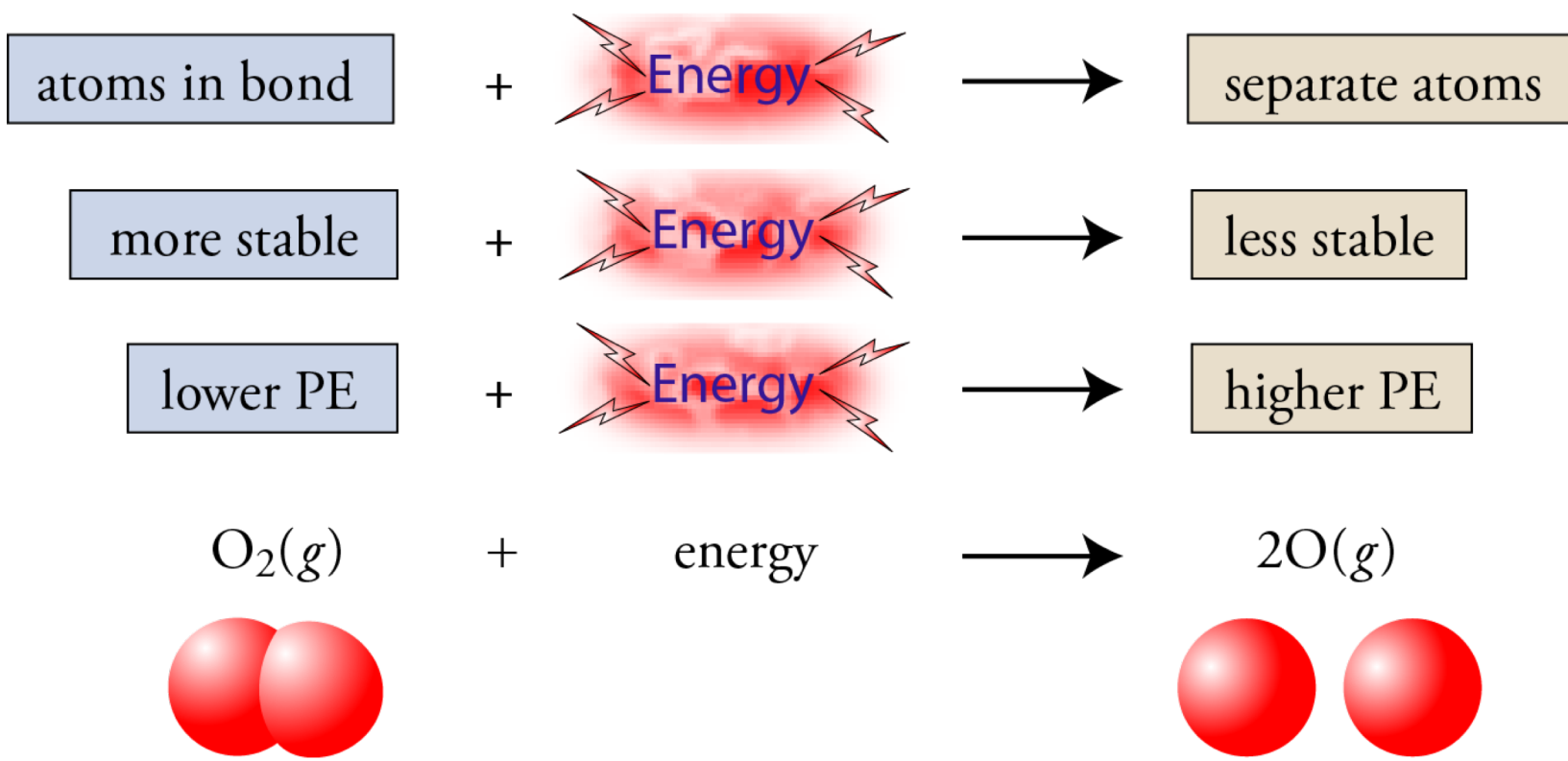
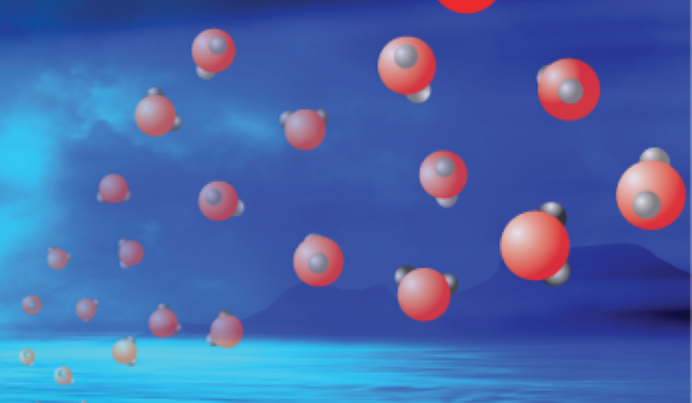
lesser capacity  
to do work + **energy** → greater capacity  
to do work

lower PE + **energy** → higher PE

# Exergonic Change

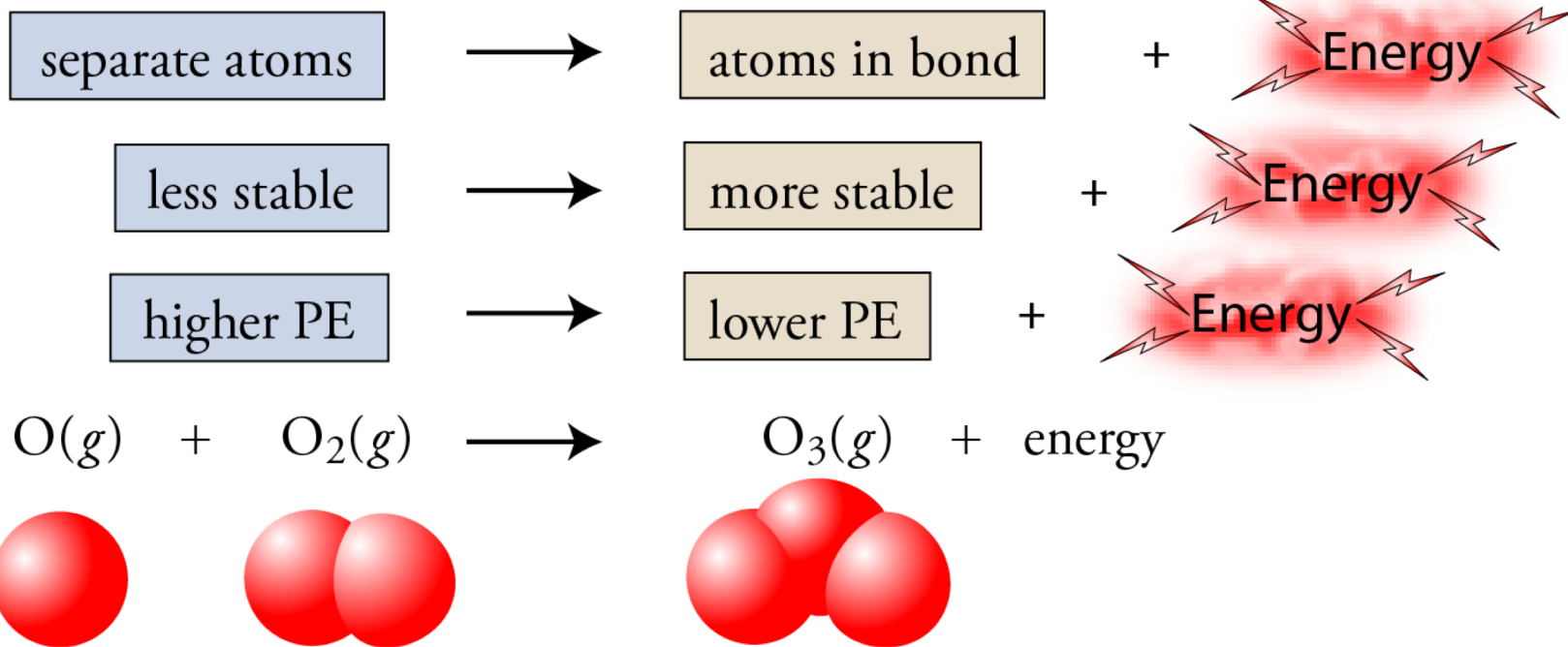
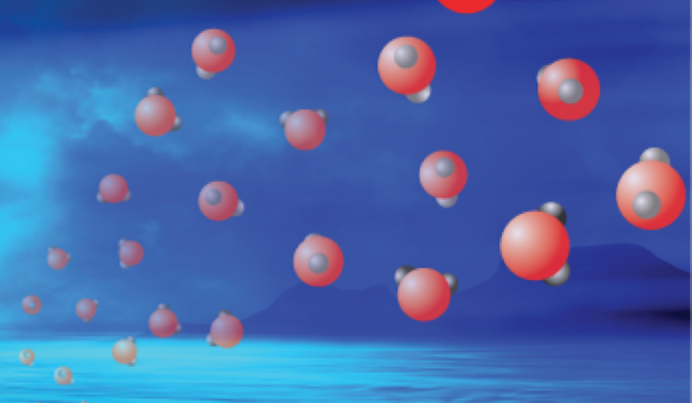
- less stable system → more stable + energy
- greater capacity to do work → lesser capacity to do work + energy
- higher PE → lower PE + energy

# Bond Breaking and Potential Energy





# Bond Making and Potential Energy



# Bond Breaking and Making

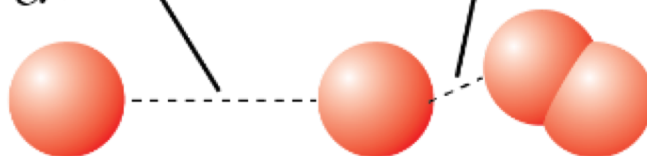
An oxygen atom collides with an ozone molecule.



The collision causes an O-O bond in the ozone to begin breaking as a new O-O bond begins to form.

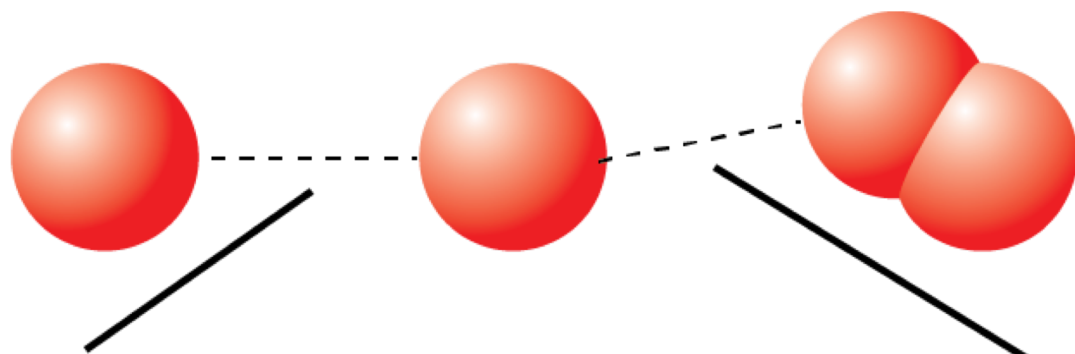
Bond making,  
(supplies some  
energy)

Bond breaking  
(requires energy)



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.

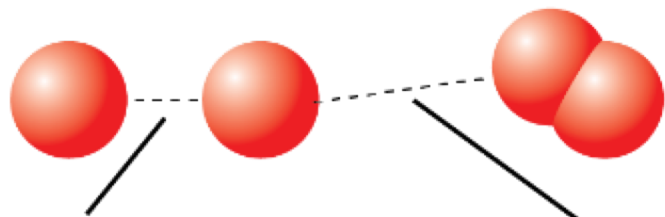
# Formation of Activated Complex



Bond making supplies energy  
equal to the energy required for bond breaking.

# Formation of Product

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



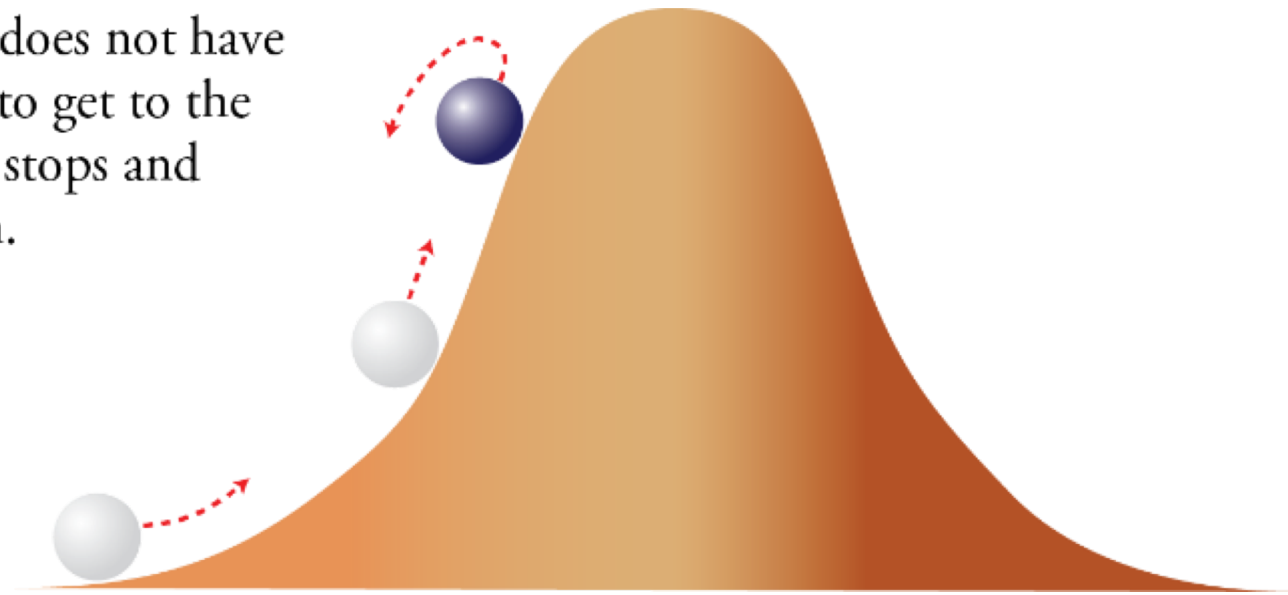
Bond making supplies more energy than is necessary for bond breaking...



so energy is released

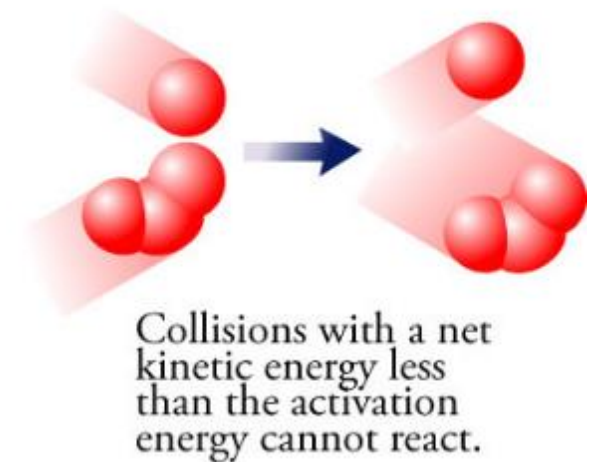
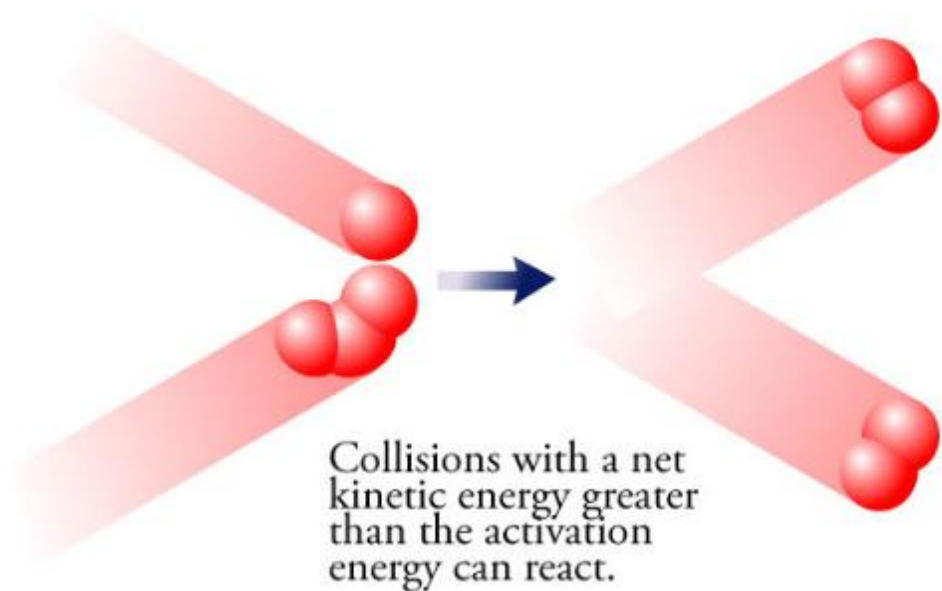
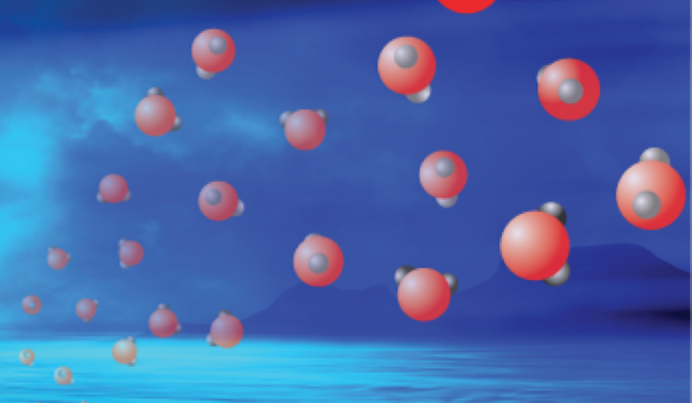
Reactions must have a minimum activation energy...if too little, no change

If a rolling ball does not have enough energy to get to the top of a hill, it stops and rolls back down.



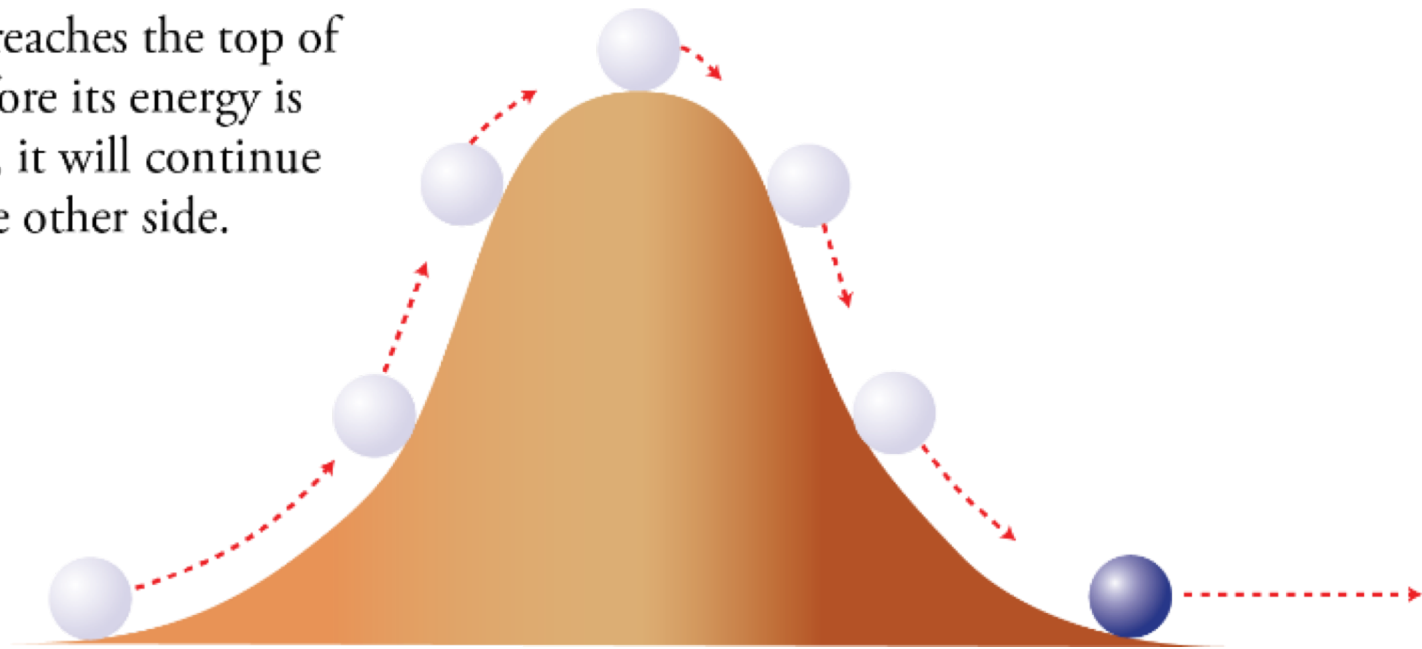


# Collision Energy and Activation Energy

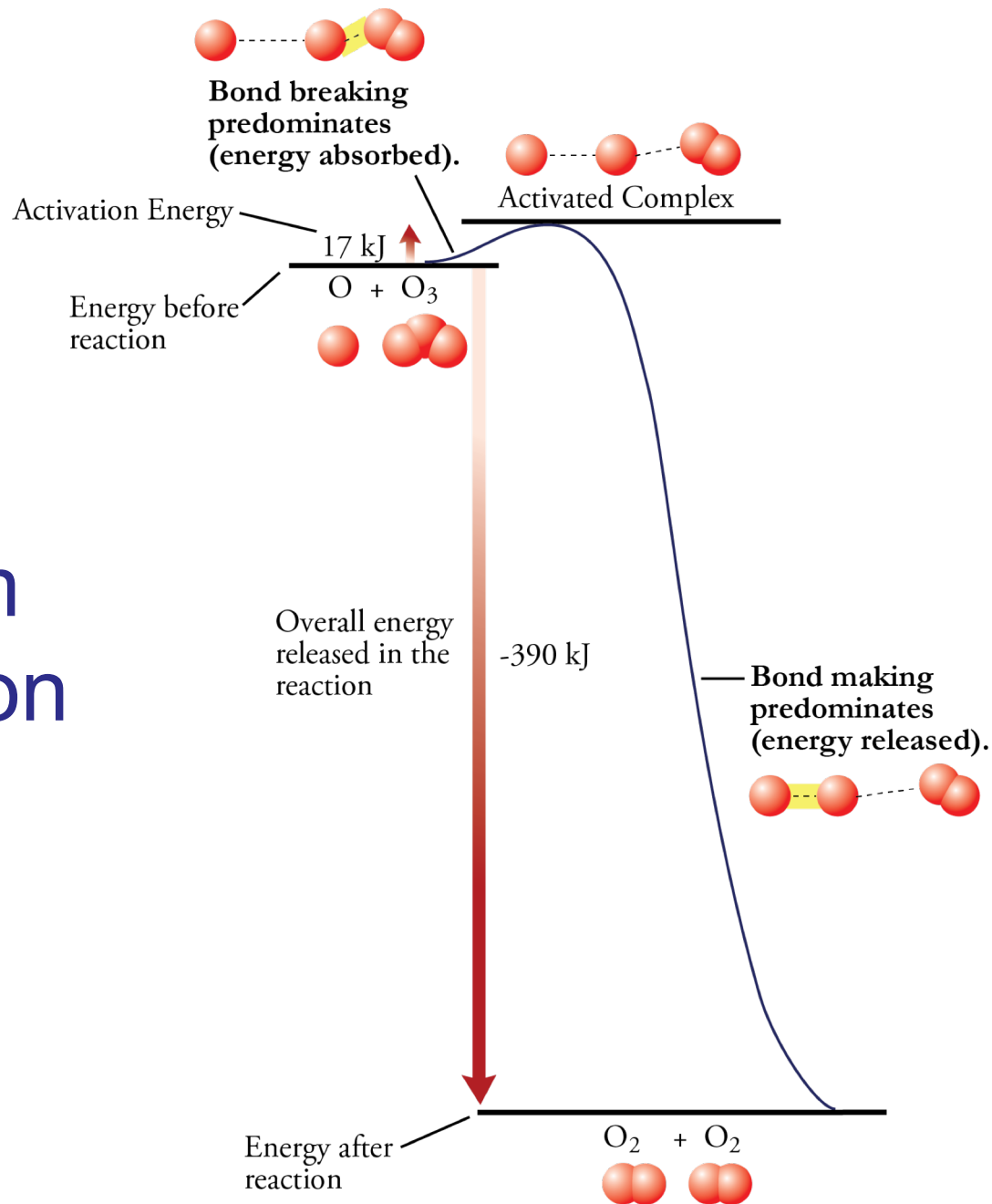


# Reactions must have a minimum activation energy...if enough, change

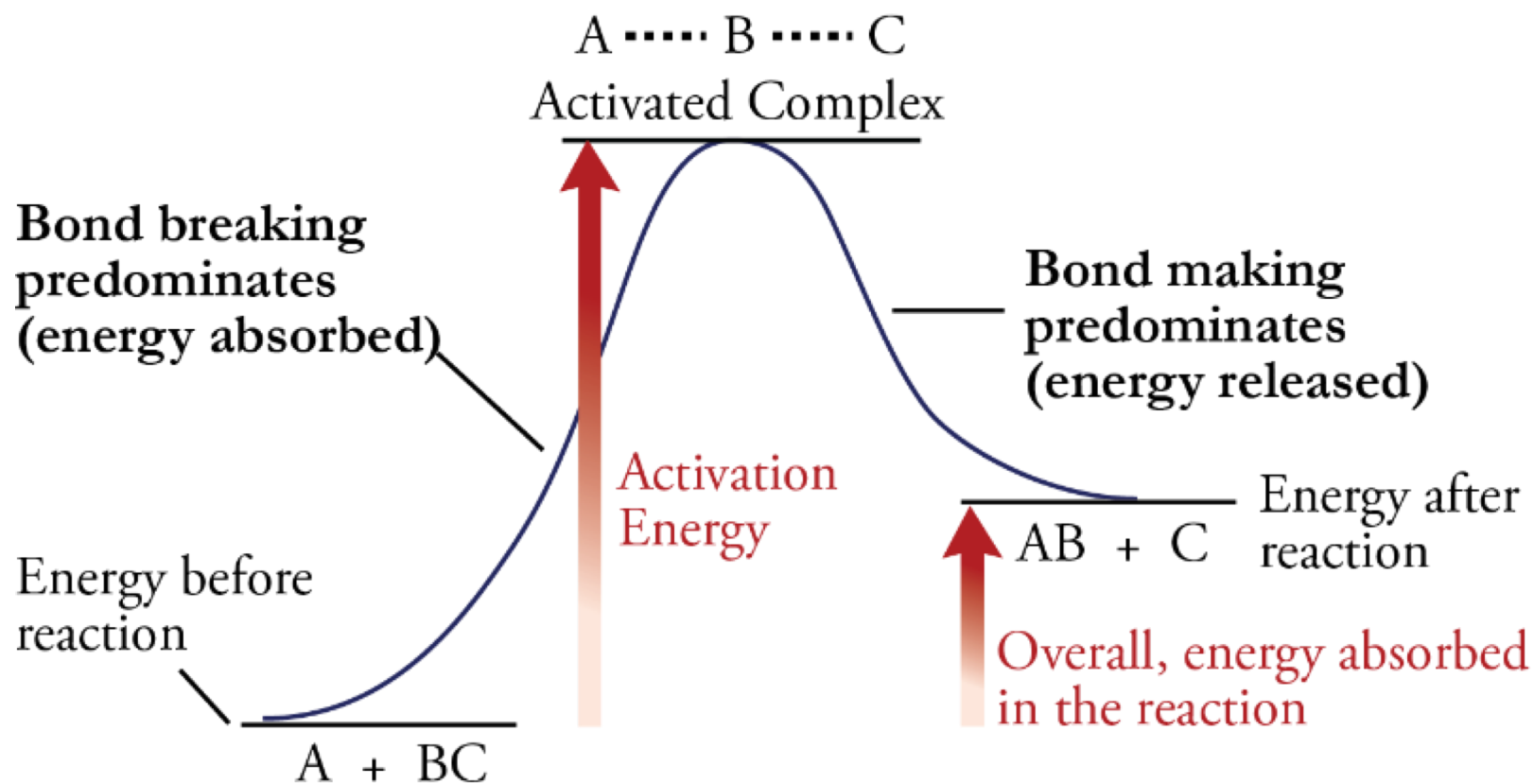
If a ball reaches the top of a hill before its energy is depleted, it will continue down the other side.



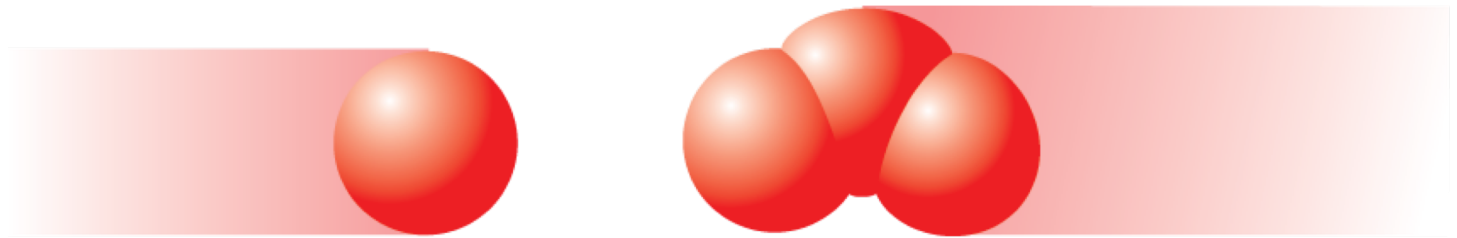
# Energy Diagram for O/O<sub>3</sub> Reaction



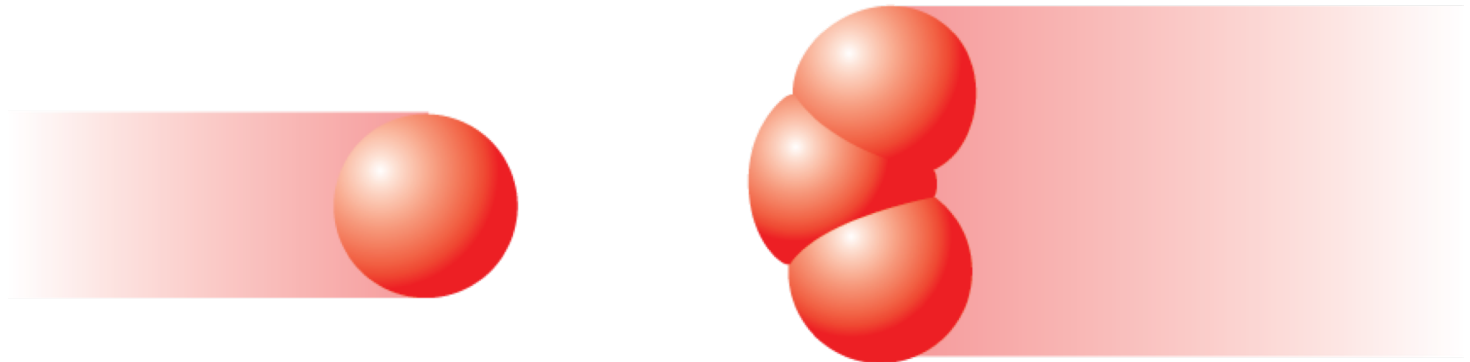
# Endergonic Reactions



# Orientation



One favorable orientation



One unfavorable orientation



# Summary (part 1)

- **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.

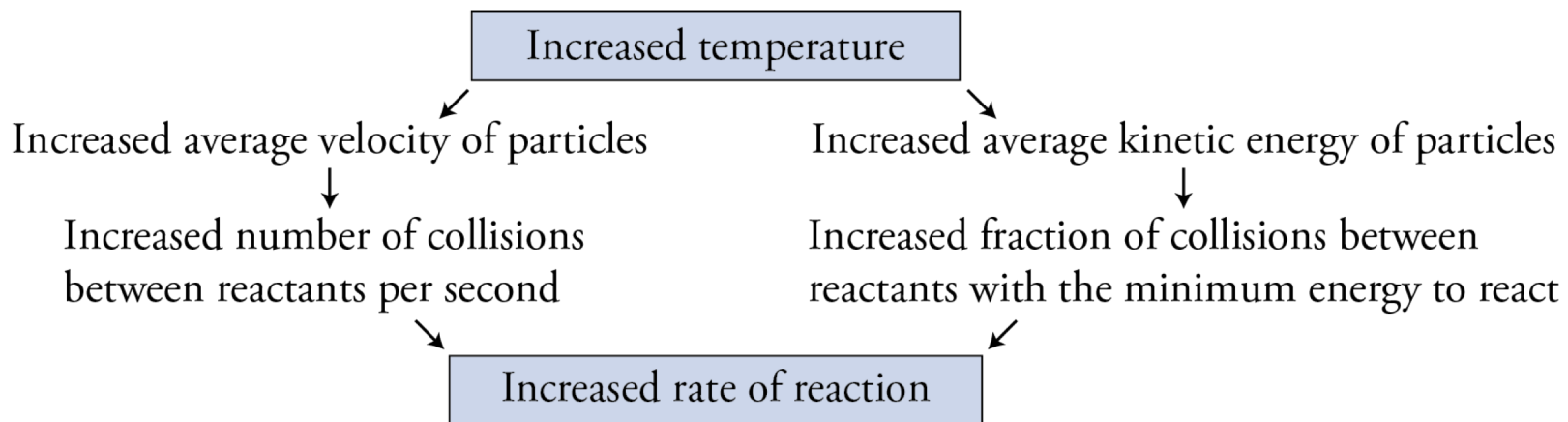
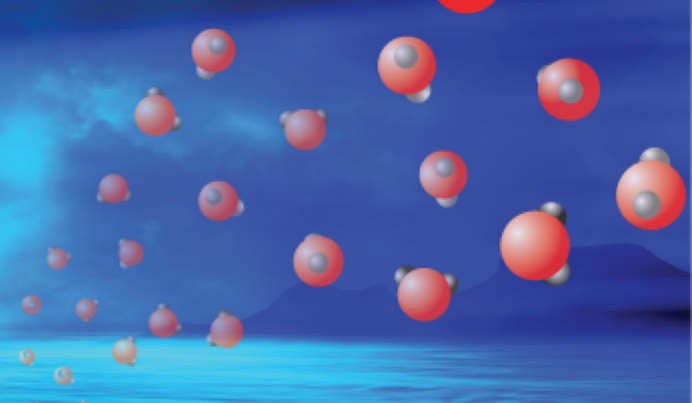
# Summary (part 2)

- **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.

# Summary (part 3)

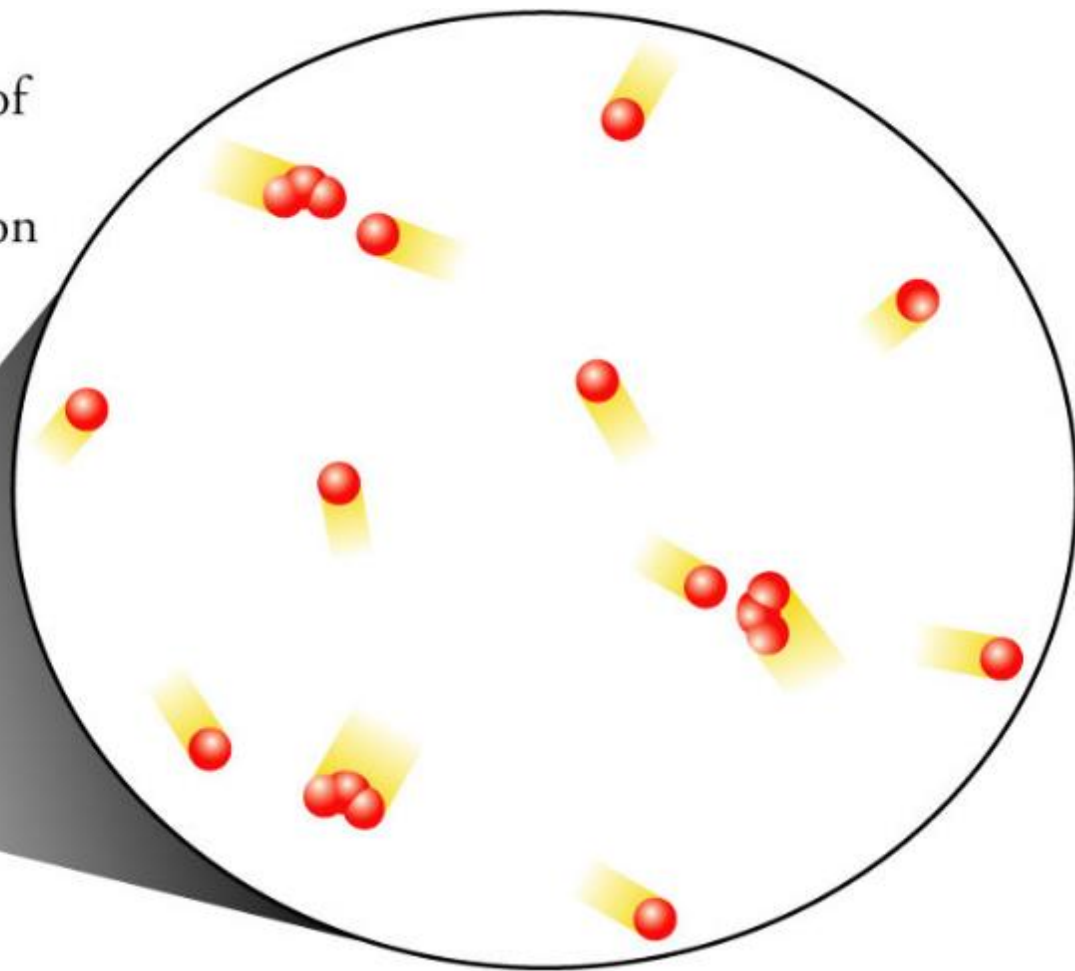
- **The orientation of the colliding particles must favor the formation of the activated complex, in which the new bond or bonds are able to form as the old bond or bonds break .**
  - Because the formation of the new bonds provides some of the energy necessary to break the old bonds, the making and 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



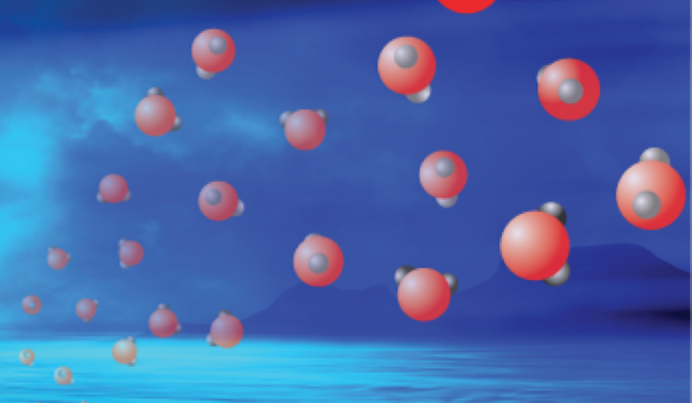
# Increased Concentration of one Reactant

Increased concentration of oxygen atoms leads to increased rate of collision between oxygen atoms and ozone molecules.





# 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

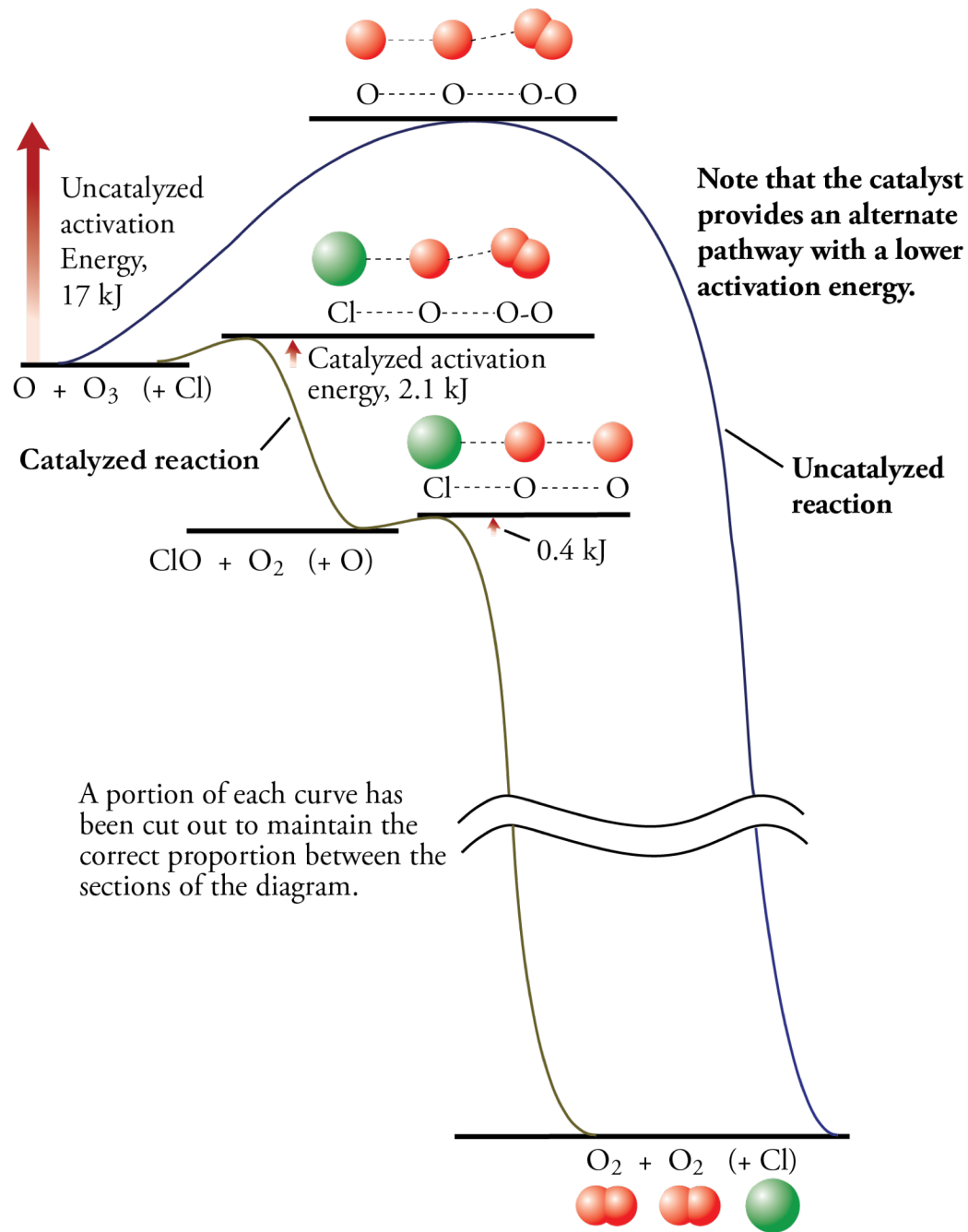


Increased number of particles fulfilling the requirements for reaction

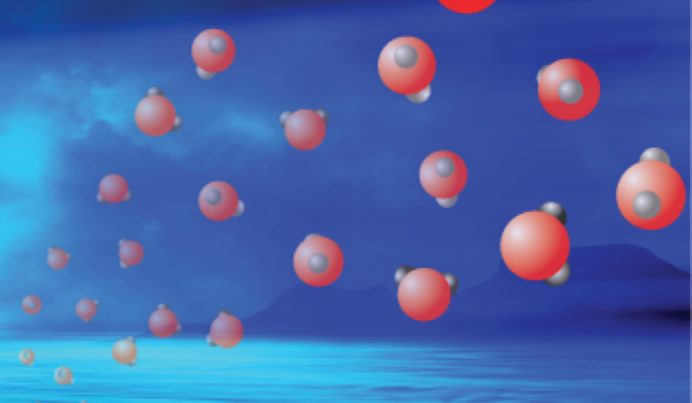


Increased rate of reaction

# Catalyzed $O/O_3$ Reaction



# Catalysts and Rates of Reactions



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



A greater fraction of collisions have the activation energy.

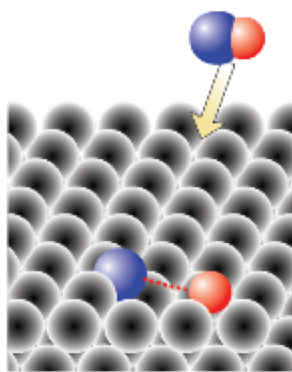


A greater fraction of collisions lead to products.

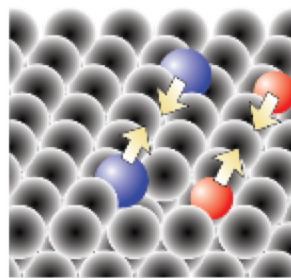


Increased rate of reaction

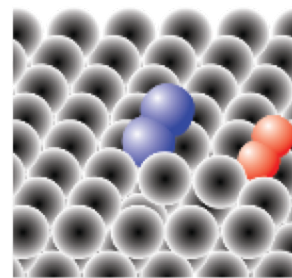
# Heterogeneous Catalysis



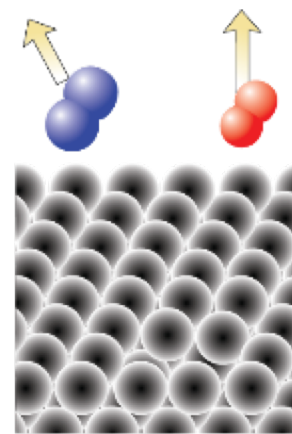
**Step 1** - The reactant molecules are adsorbed, and the bonds are weakened.



**Step 2** - The atoms migrate across the catalyst.



**Step 3** - New bonds form.

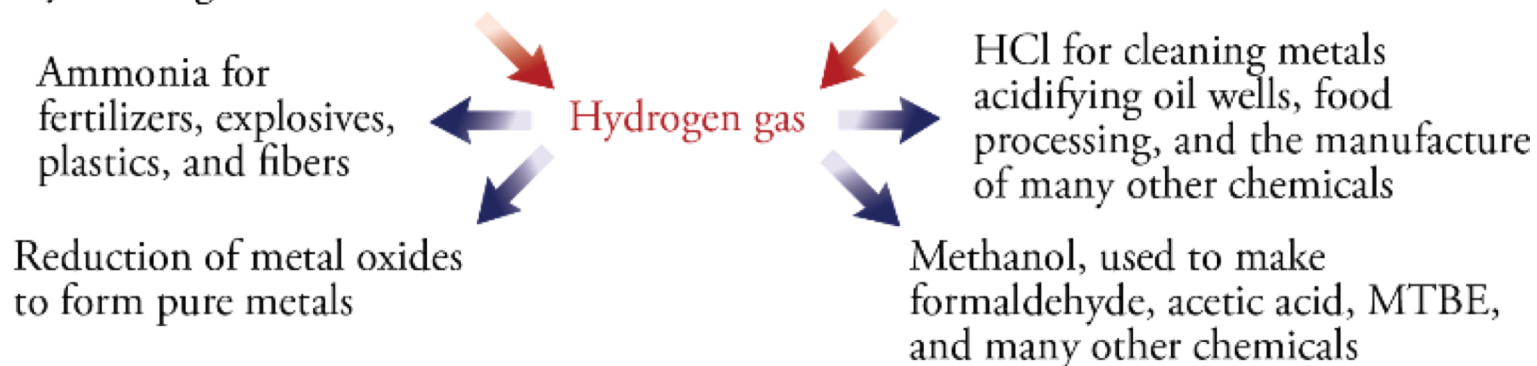


**Step 4** - The products leave the catalyst.

# Production and Uses of Hydrogen Gas

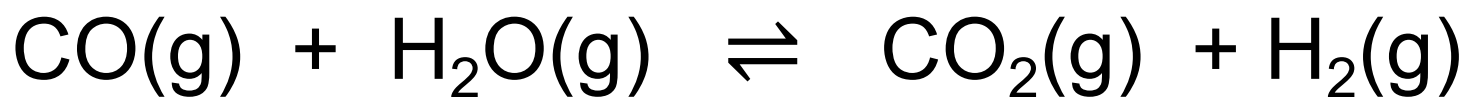
Chemical plants make a mixture of hydrogen gas and carbon monoxide gas called synthesis gas.

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



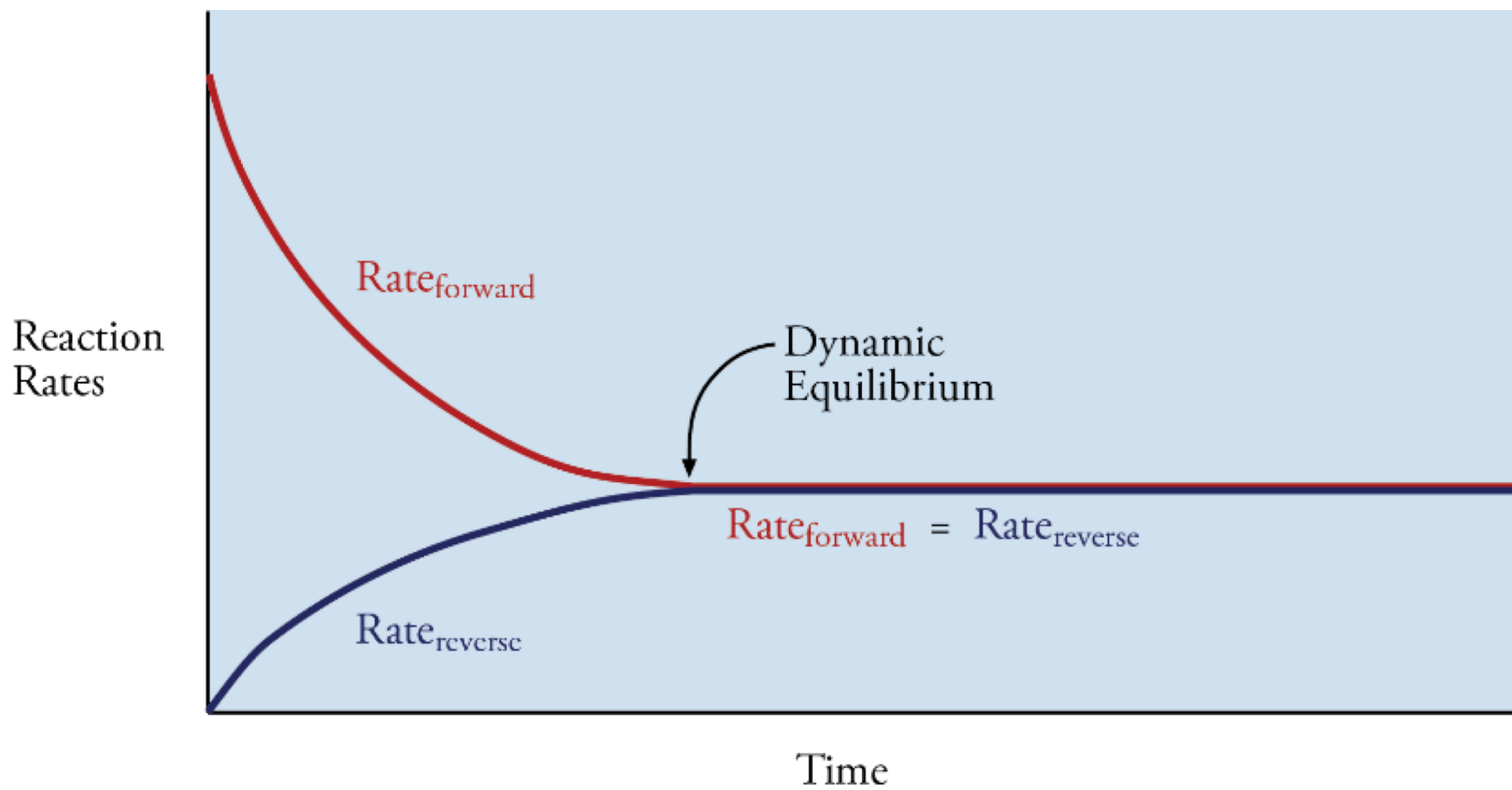


# Dynamic Equilibrium

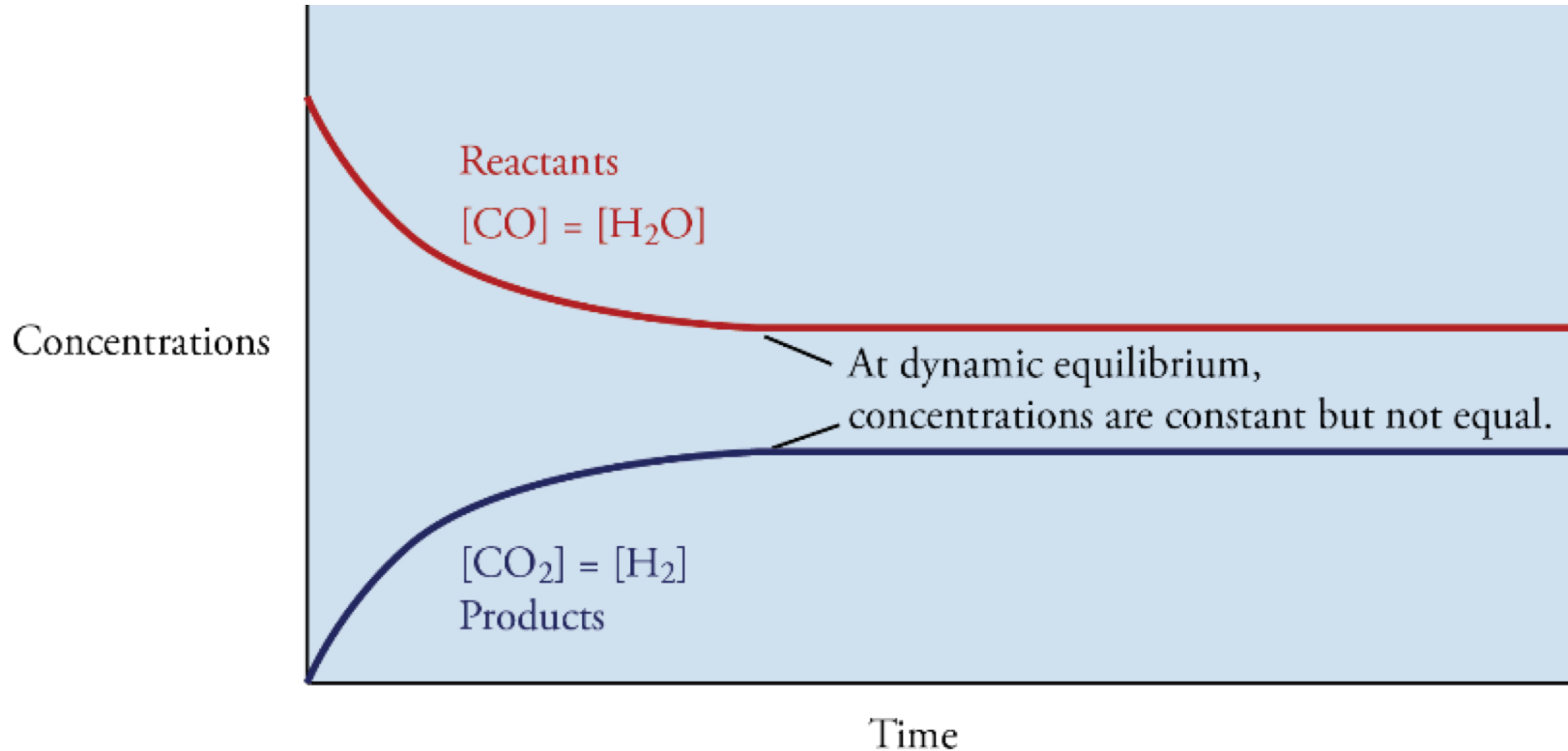
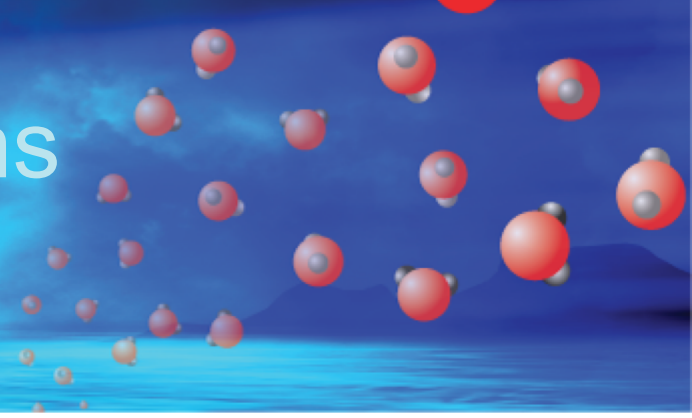


- Initially,  $R_f > R_r$
- Decreased  $[\text{CO}]$  and  $[\text{H}_2\text{O}]$ , so decreased  $R_f$
- Increased  $[\text{CO}_2]$  and  $[\text{H}_2]$ , so increased  $R_r$
- At some point the rates become equal, so although the forward and reverse reactions continue, there is no net change in amounts of reactants and products...dynamic equilibrium

# Rates of Reaction for Reversible Reactions

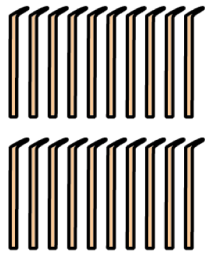


# Changes in Concentrations for a Reversible Reaction



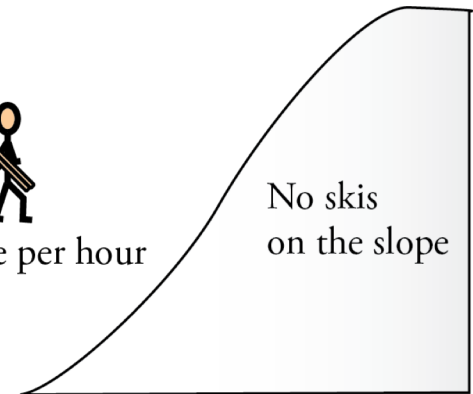
# Ski Shop Analogy for Equilibrium

## Early morning



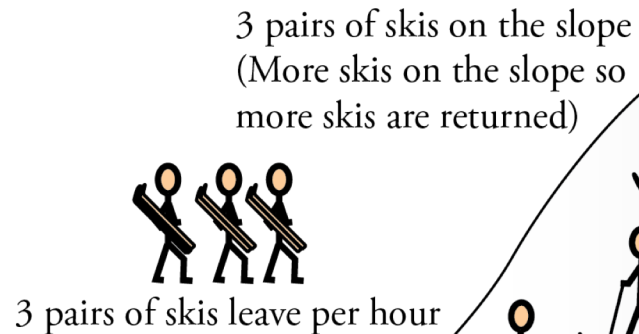
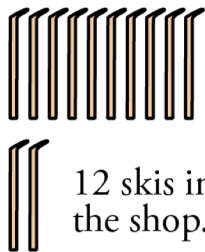
Initially, there are 20 skis in the shop.

0 pairs of skis return per hour



## Later in the day

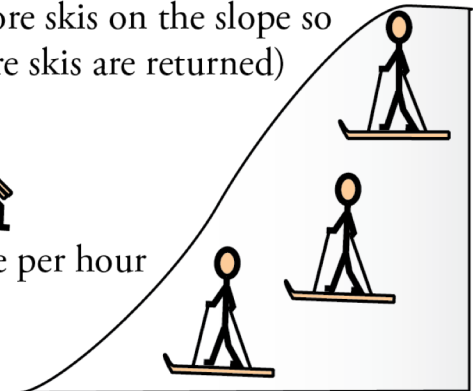
(Fewer skis available so fewer are rented per hour)



12 skis in the shop.

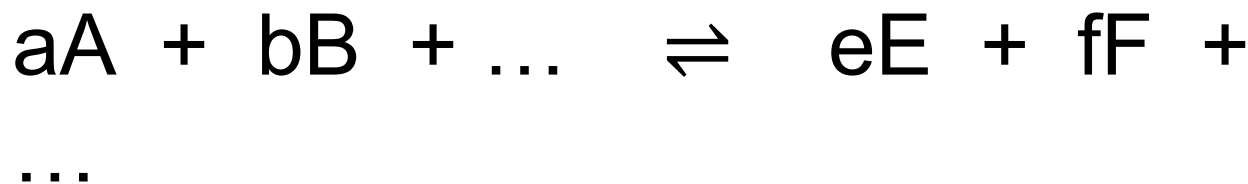
3 pairs of skis return per hour

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



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

# Equilibrium Constant

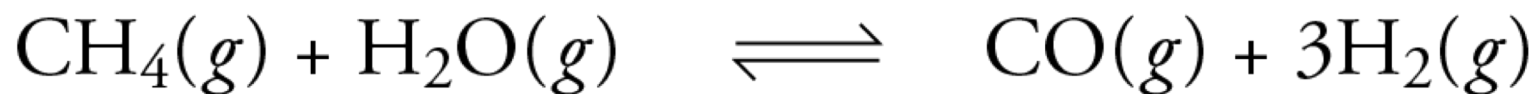


$$\text{Equilibrium constant} = K_C = \frac{[E]^e [F]^f \dots}{[A]^a [B]^b \dots}$$

$$\text{Equilibrium constant} = K_P = \frac{P_E^e P_F^f \dots}{P_A^a P_B^b \dots}$$



# Equilibrium Constant Expression

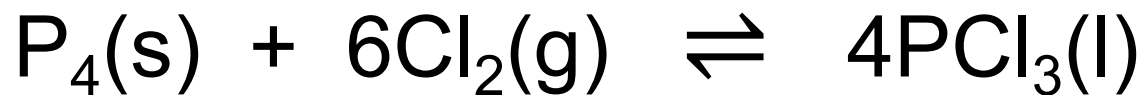


The coefficient before  $\text{H}_2$  is 3, so we raise the concentration or pressure to the third power.

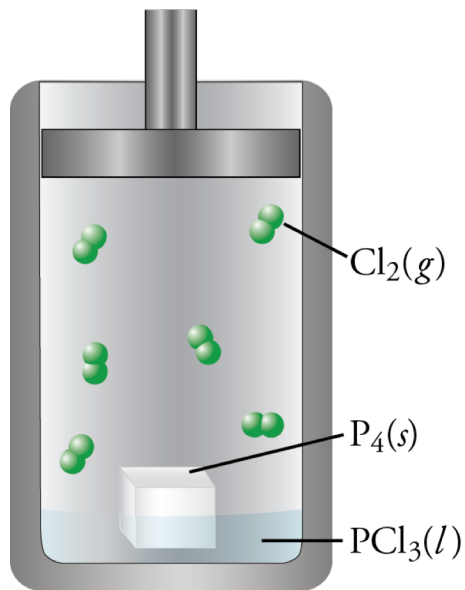
$$K_C = \frac{[\text{CO}] [\text{H}_2]^3}{[\text{CH}_4] [\text{H}_2\text{O}]}$$

$$K_P = \frac{P_{\text{CO}} P_{\text{H}_2}^3}{P_{\text{CH}_4} P_{\text{H}_2\text{O}}}$$

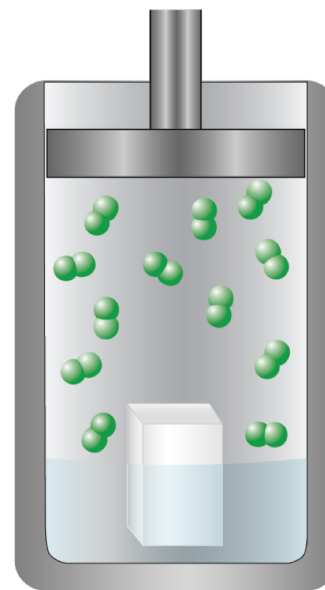
# Heterogeneous Equilibrium



$$K' = \frac{[\text{PCl}_3]^4}{[\text{P}_4] [\text{Cl}_2]^6} \quad \frac{K'[\text{P}_4]}{[\text{PCl}_3]^4} = \frac{1}{[\text{Cl}_2]^6} = K_C$$



Double the moles of  
 $\text{P}_4$ ,  $\text{Cl}_2$ , and  $\text{PCl}_3$   
 Constant volume



Concentration of gas doubles.

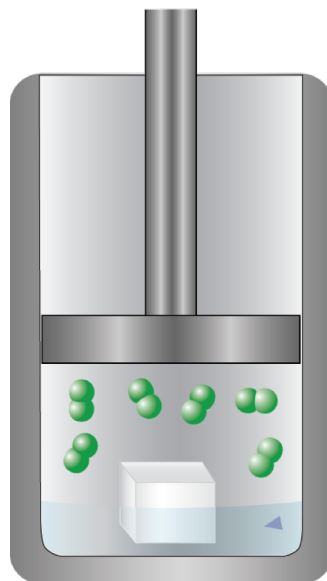
$$\text{Double } \frac{\text{mol Cl}_2}{L}$$

Concentrations of solid and liquid remain constant.

$$\text{Same } \frac{\text{mol P}_4}{L}$$

$$\text{Same } \frac{\text{mol PCl}_3}{L}$$

Half volume,  
 with no change  
 in moles



Concentration of gas doubles.

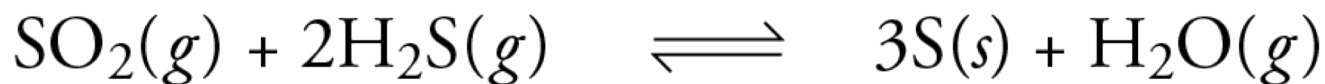
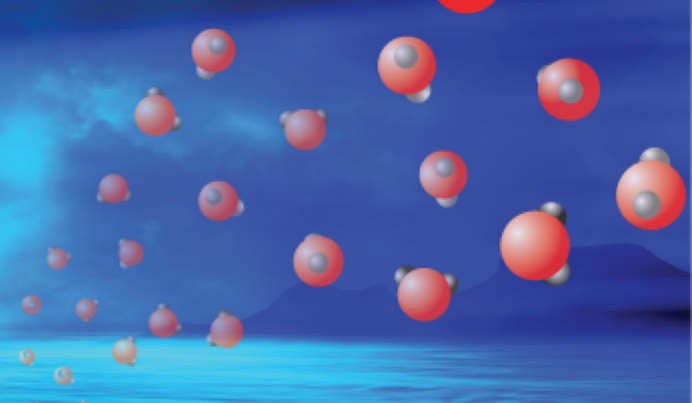
$$\text{Double } \frac{\text{mol Cl}_2}{L}$$

Concentrations of solid and liquid remain constant.

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

# Heterogeneous Equilibrium

# Equilibrium Constant Expressions for Heterogeneous Equilibria



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

$$K_C = \frac{[\text{H}_2\text{O}]}{[\text{SO}_2] [\text{H}_2\text{S}]^2}$$

$$K_P = \frac{P_{\text{H}_2\text{O}}}{P_{\text{SO}_2} P_{\text{H}_2\text{S}}^2}$$

# Extent of Reaction



$$K > 10^2$$

Products favored at equilibrium

$$K < 10^{-2}$$

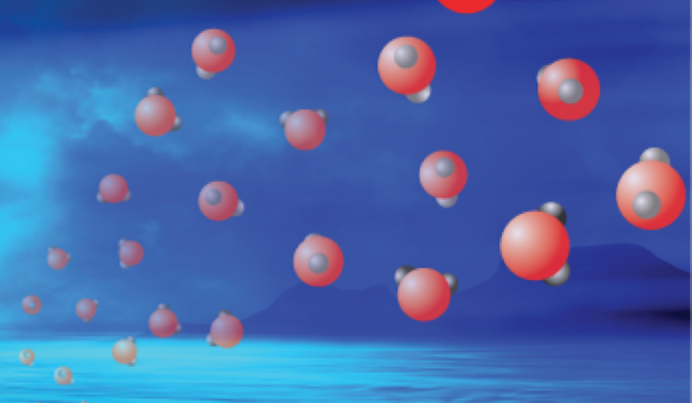
Reactants favored at equilibrium

$$10^{-2} < K < 10^2$$

Neither reactants nor products favored



# Effect of Increased Concentration on Equilibrium

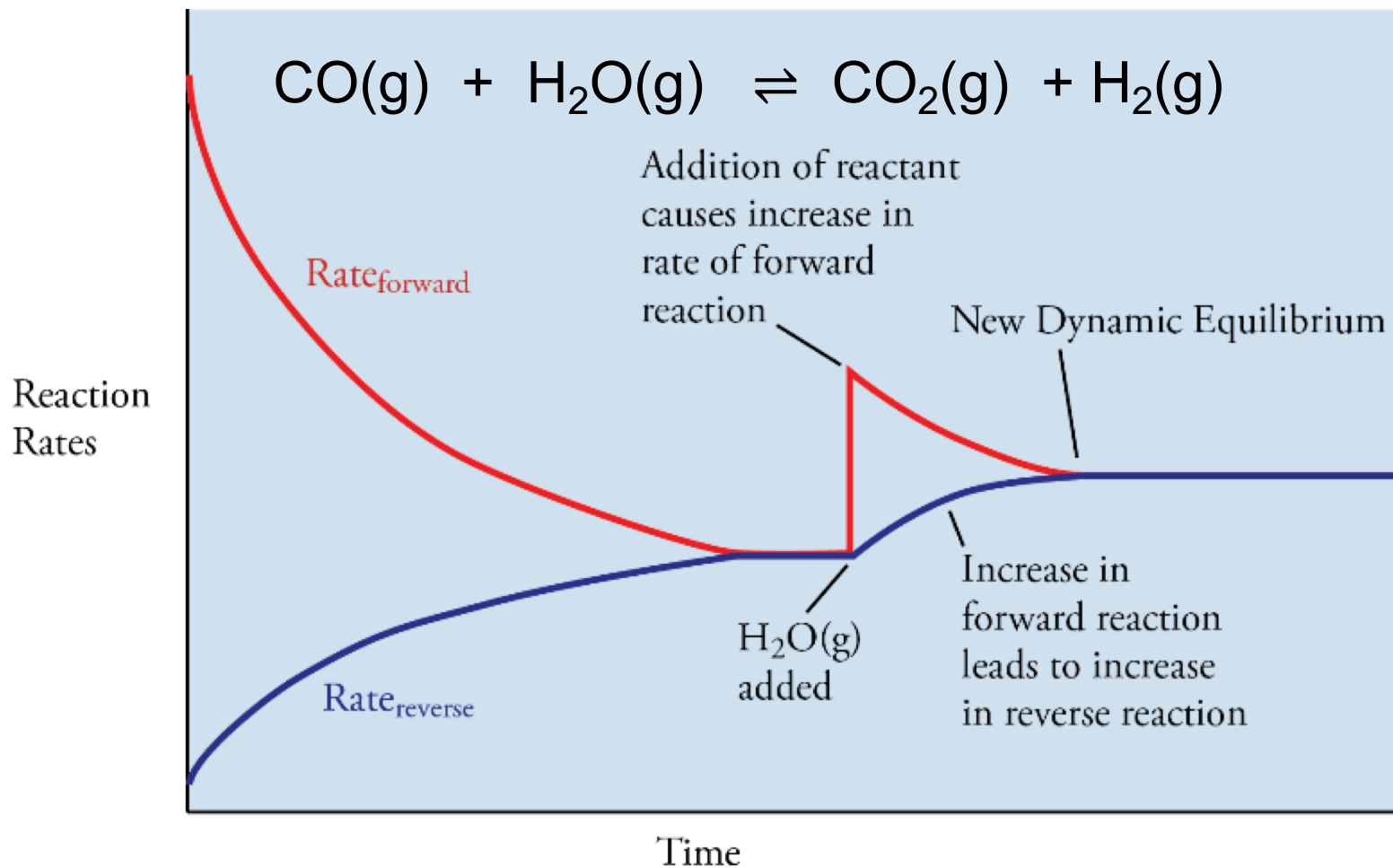
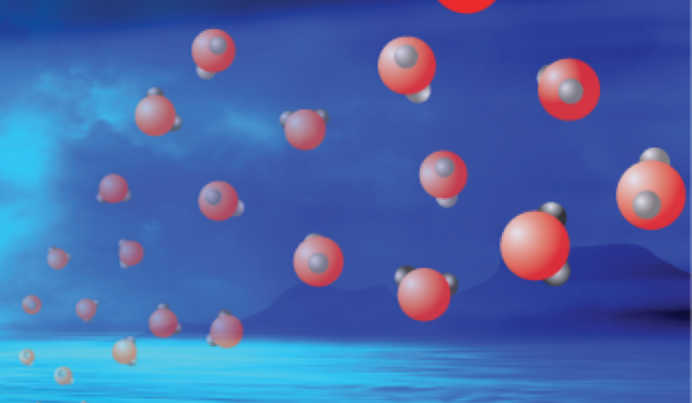


Increased concentration of reactant for a system at equilibrium with  $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

↓  
Increased  $\text{Rate}_{\text{forward}}$   
↓  
 $\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$   
↓

System shifts toward products

# Change in Rates When Reactant Added



# Ski Shop Analogy 2

## Before buying more skis

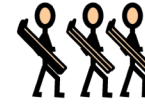
There are 12 skis in the shop.



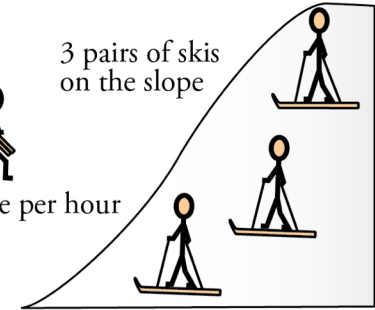
12 skis in the shop.



3 pairs of skis return per hour



3 pairs of skis leave per hour

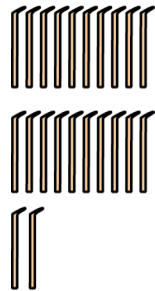


3 pairs of skis on the slope

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

## Immediately after buying more skis

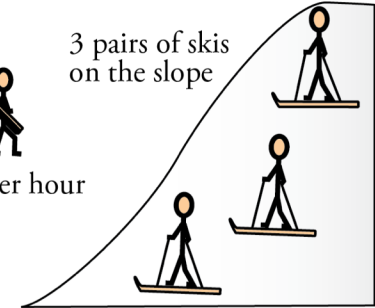
There are 22 skis in the shop. (With more skis in the shop, more are rented per hour.)



3 pairs of skis return per hour



5 pairs of skis leave per hour

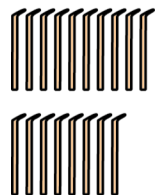


3 pairs of skis on the slope

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

## Later

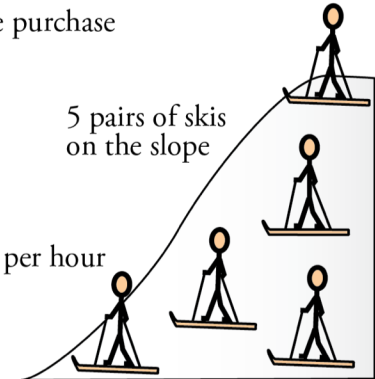
There are 18 skis in the shop. (This is more skis than before the purchase but fewer than immediately after the purchase.)



4 pairs of skis return per hour



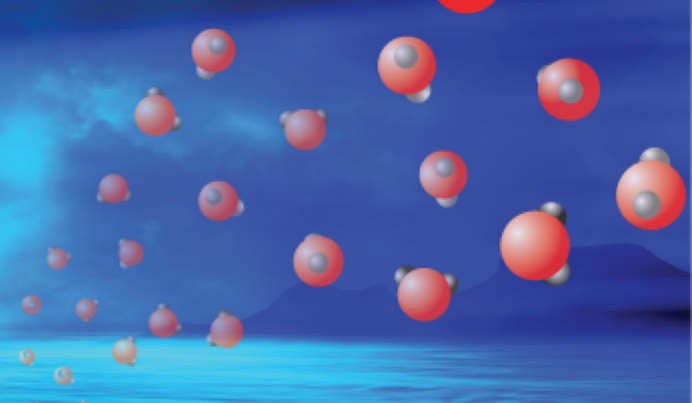
4 pairs of skis leave per hour



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



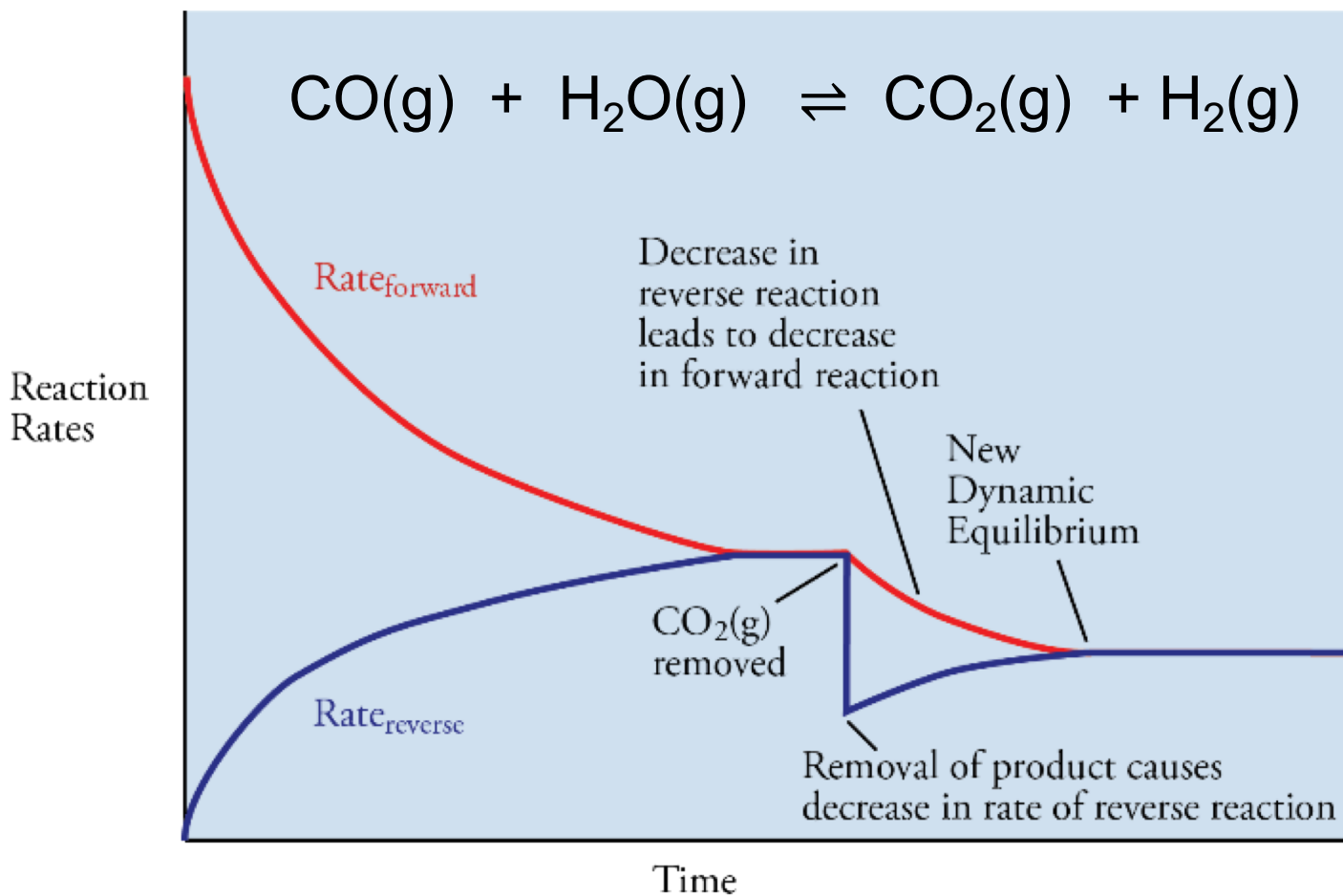
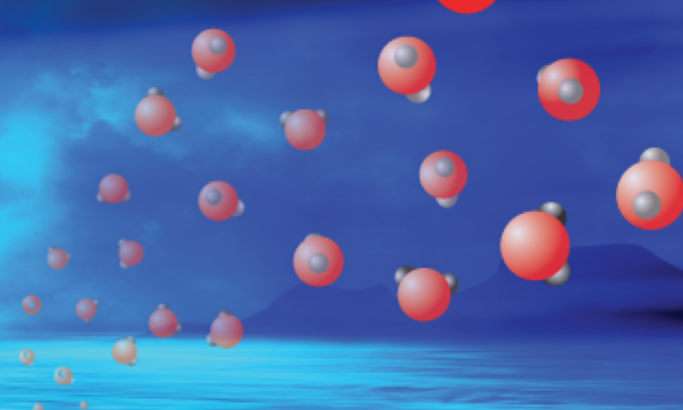
Decreased concentration of one product for a system at equilibrium with  $\text{Rate}_{\text{forward}} = \text{Rate}_{\text{reverse}}$

↓  
Decreased  $\text{Rate}_{\text{reverse}}$

↓  
 $\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$

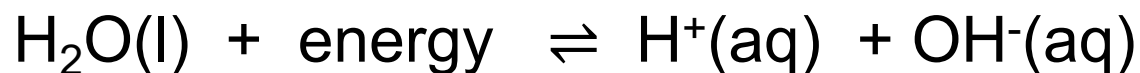
↓  
System shifts toward products

# Change in Rates When Product Removed





# Effect of Increased Temperature on Equilibrium



$$K_w = [\text{H}^+][\text{OH}^-]$$

Temperature	$K_w$
0 °C	$1.14 \times 10^{-15}$
10 °C	$2.92 \times 10^{-15}$
25 °C	$1.01 \times 10^{-14}$
30 °C	$1.47 \times 10^{-14}$
40 °C	$2.92 \times 10^{-14}$
50 °C	$5.47 \times 10^{-14}$
60 °C	$9.61 \times 10^{-14}$

# 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.

# Le Chatelier's Principle

Reaction	Cause of Disruption	To Counteract Change	Direction of Shift
All	Add reactant(s)	Decrease reactant(s)	To products
All	Add product(s)	Decrease product(s)	To reactants
All	Remove reactant(s)	Increase reactant(s)	To reactants
All	Remove product(s)	Increase products(s)	To products
Endothermic forward reaction	Increase temperature	Decrease temperature	To products
Endothermic forward reaction	Decrease temperature	Increase temperature	To reactants
Exothermic forward reaction	Increase temperature	Decrease temperature	To reactants
Exothermic forward reaction	Decrease temperature	Increase temperature	To products