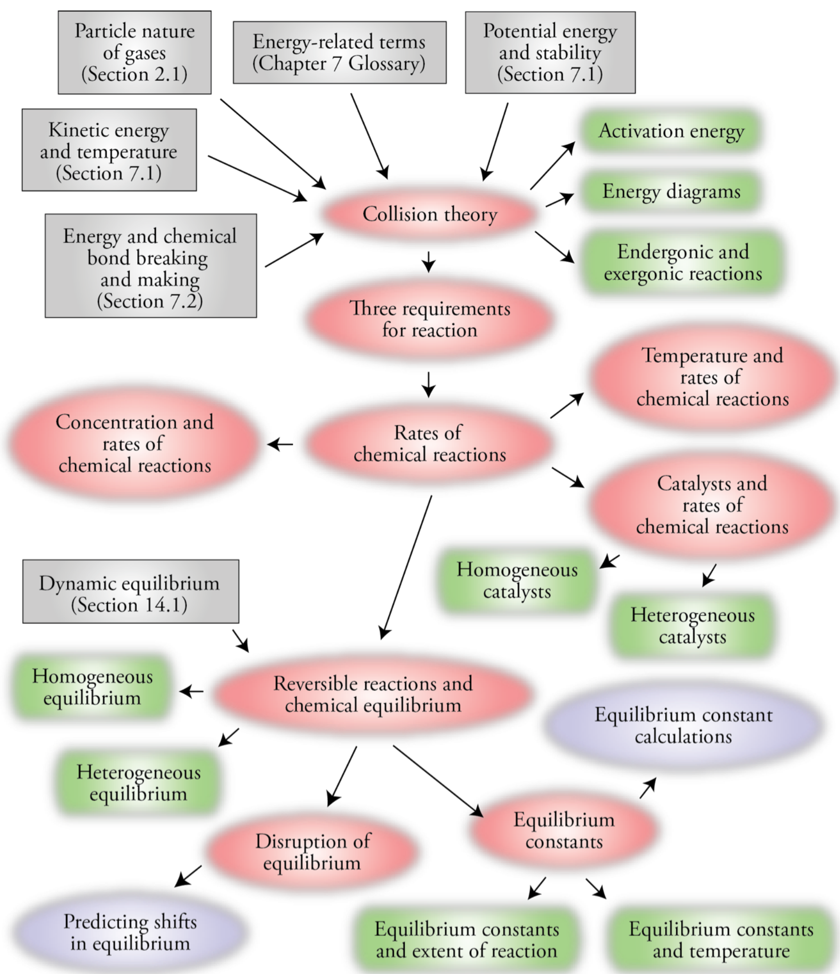
Chapter 16
The Process of Chemical Reactions

An Introduction to Chemistry

by Mark Bishop

Chapter Map



Particle nature of gases (Section 2.1)
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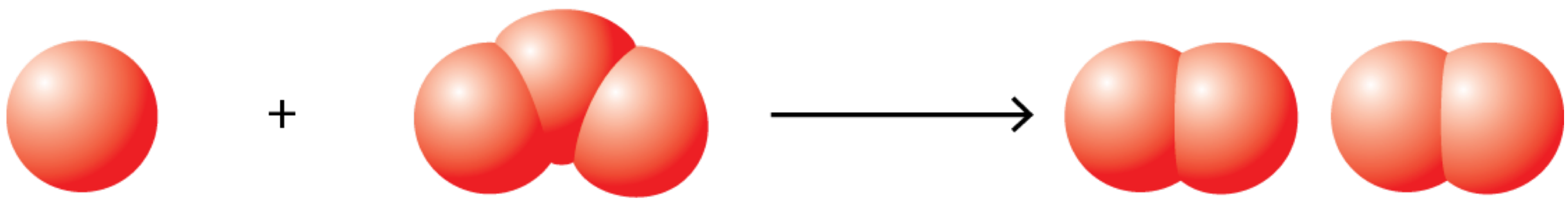
Collision Theory

- Reactants must collide

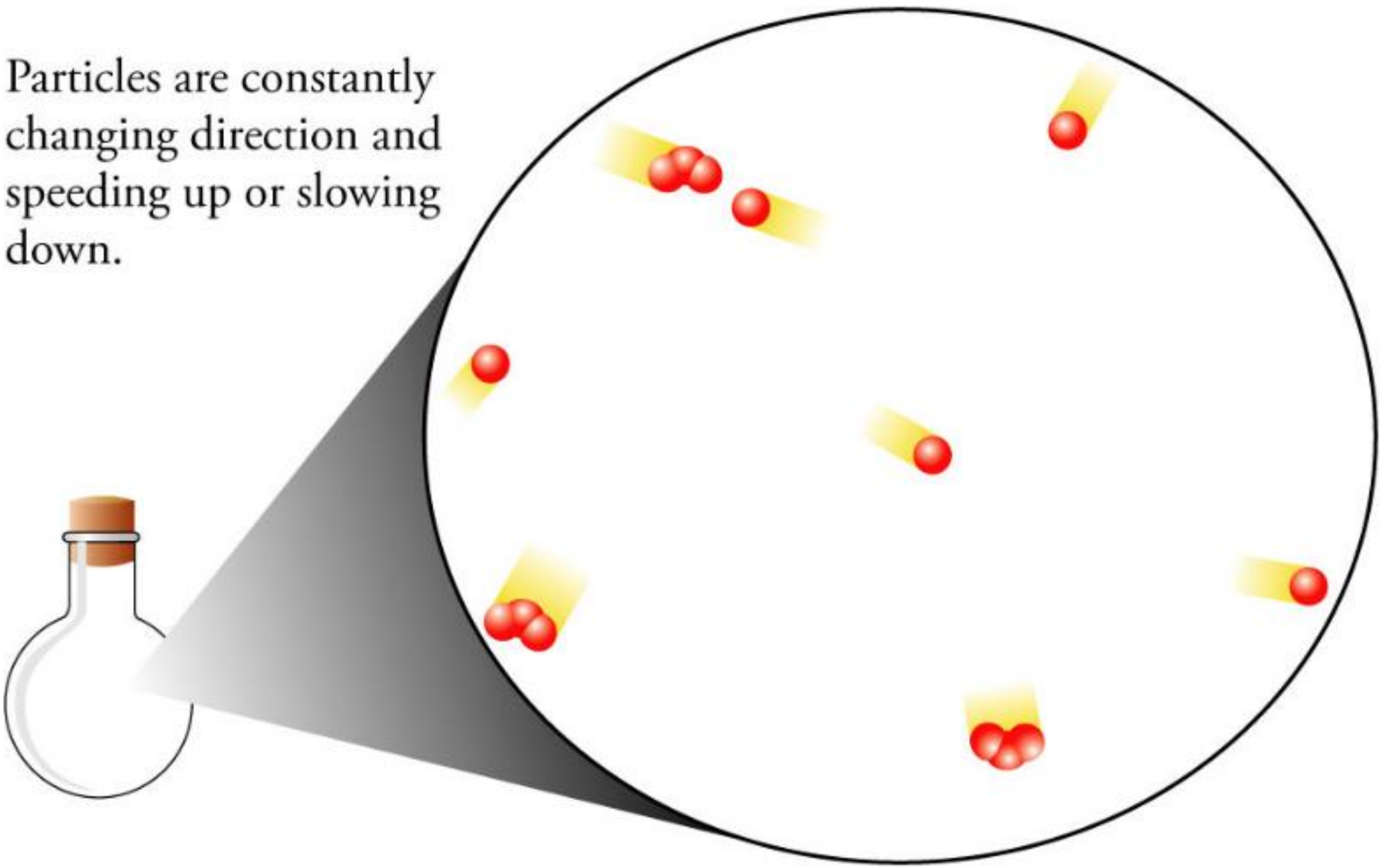
$$O(g) + O_3(g) \longrightarrow 2O_2(g)$$



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

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

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

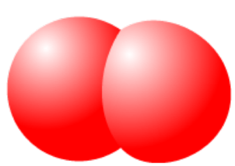
Bond Breaking and Potential Energy

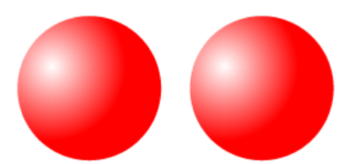
atoms in bond + Energy → separate atoms

more stable + Energy → less stable

lower PE + Energy → higher PE

$$O_2(g) + \text{energy} \longrightarrow 2O(g)$$





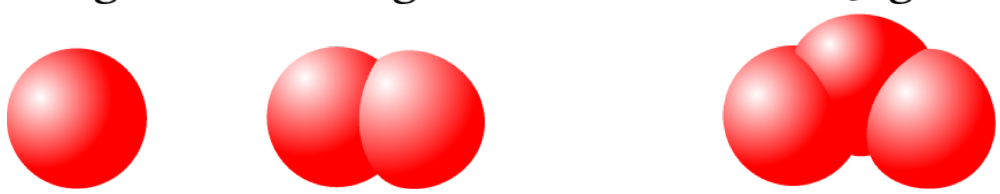
Bond Making and Potential Energy

separate atoms → atoms in bond + Energy

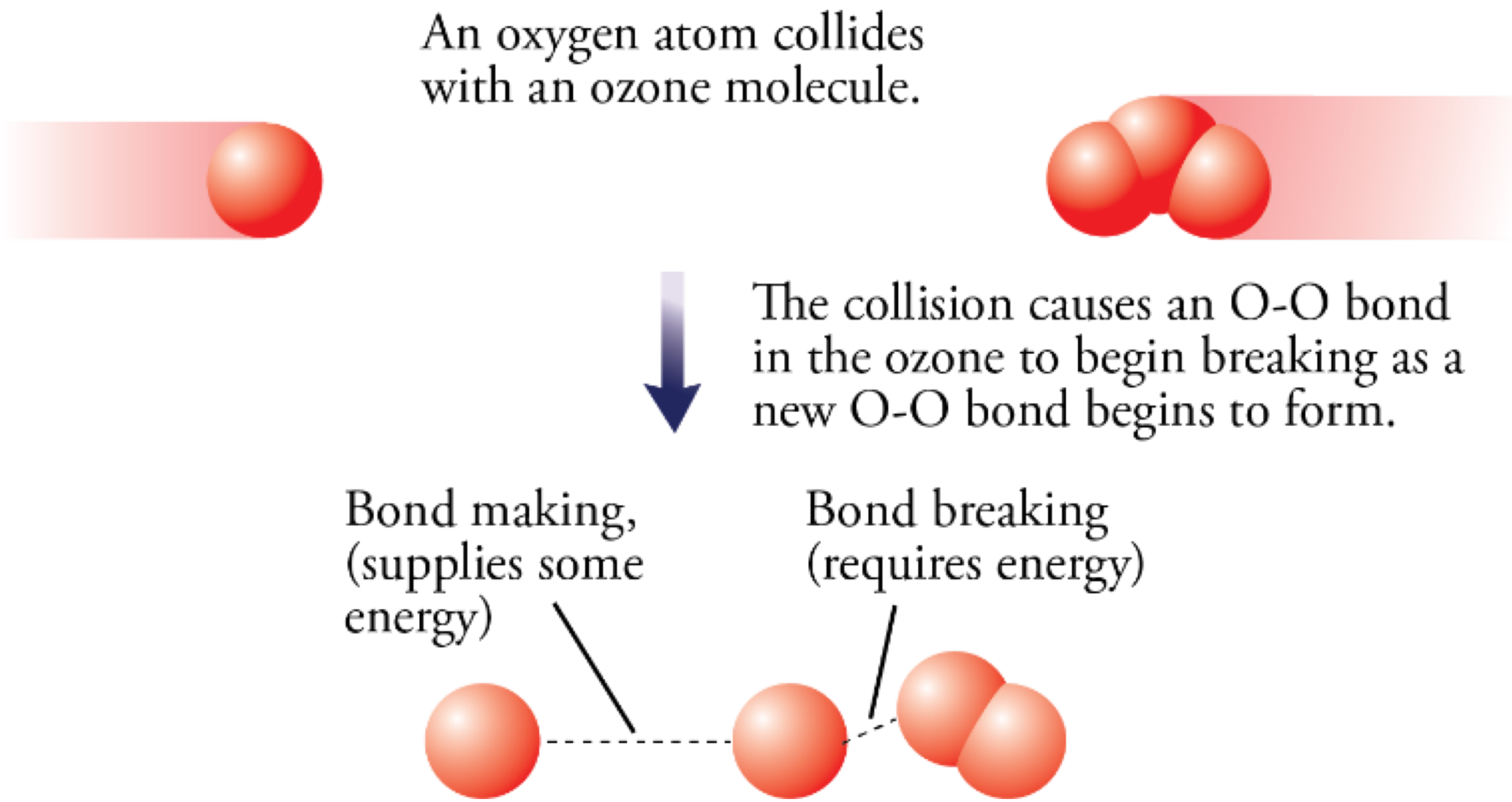
less stable → more stable + Energy

higher PE → lower PE + Energy

$O(g) + O_2(g) \longrightarrow O_3(g) + \text{energy}$

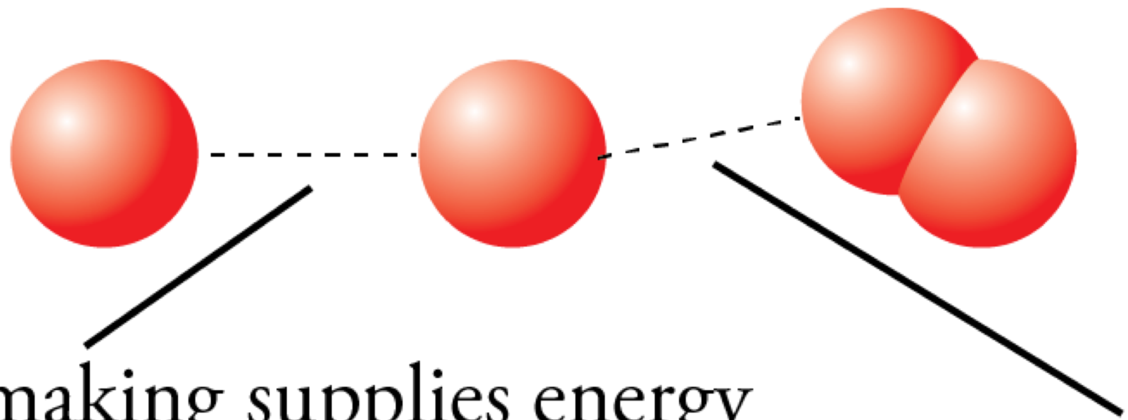


Bond Breaking and Making



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.

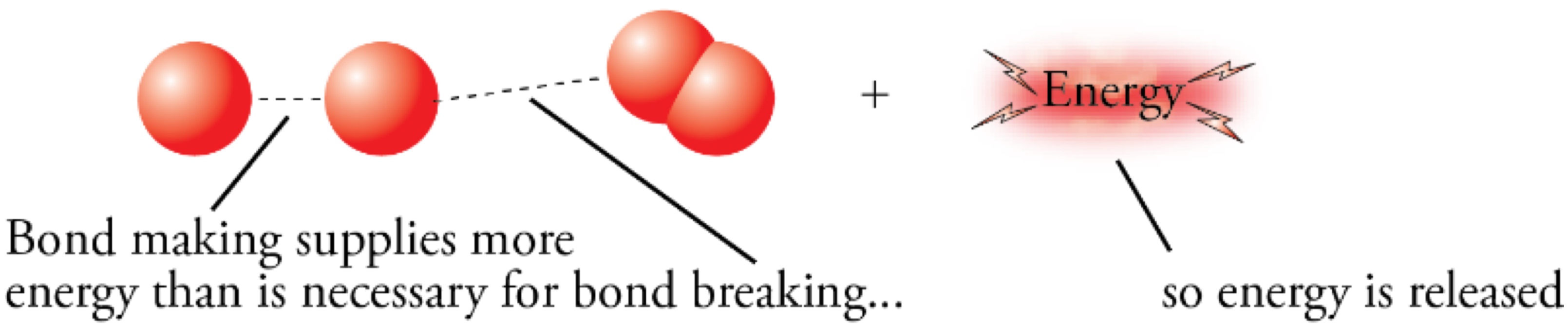
Formation of Activated Complex



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

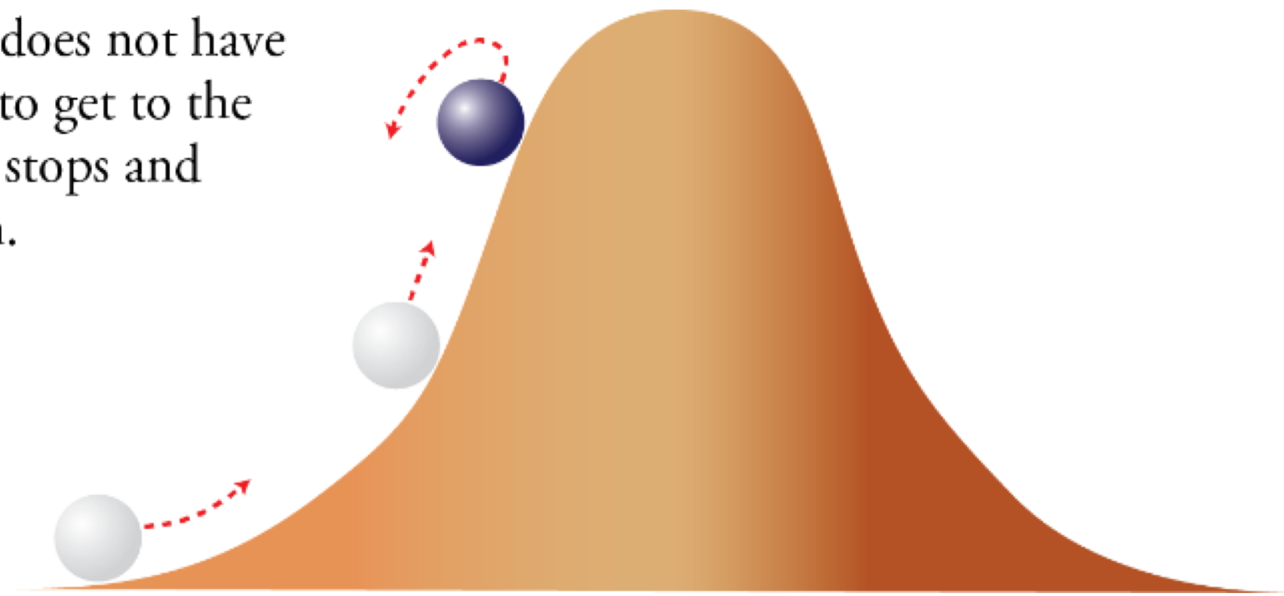
Formation of Product

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

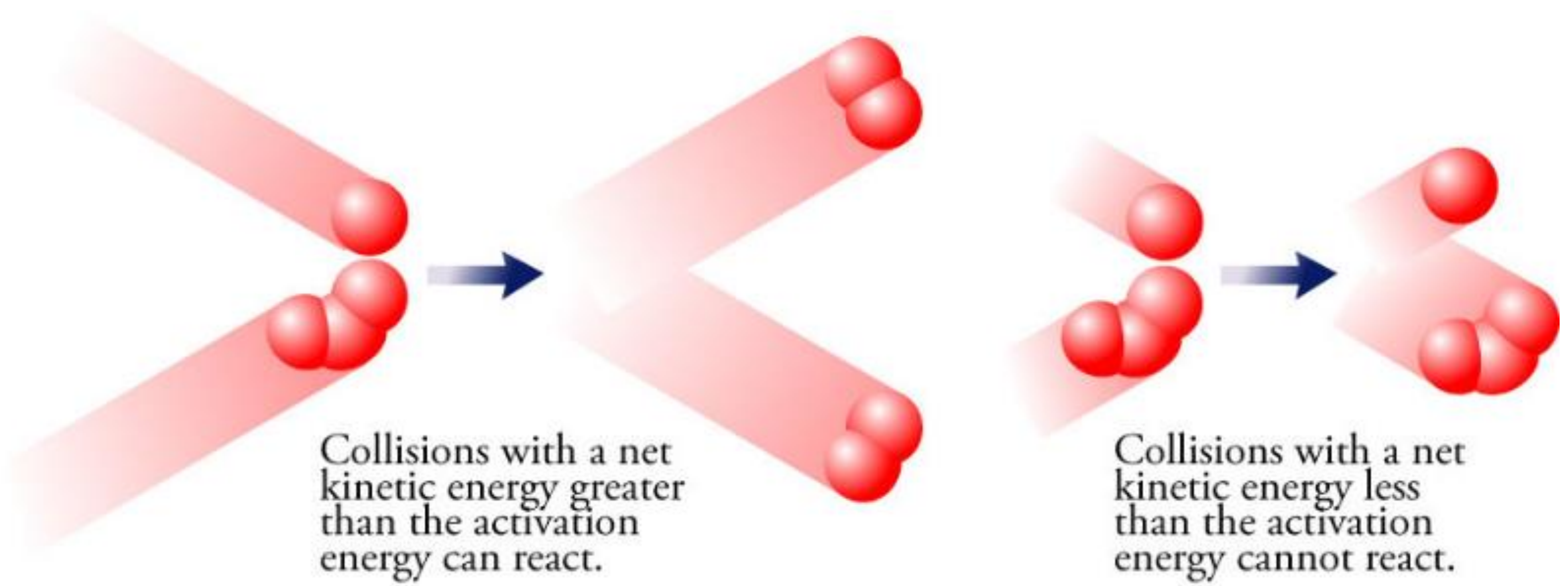


Reactions must have a minimum activation energy…if too little, no change

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

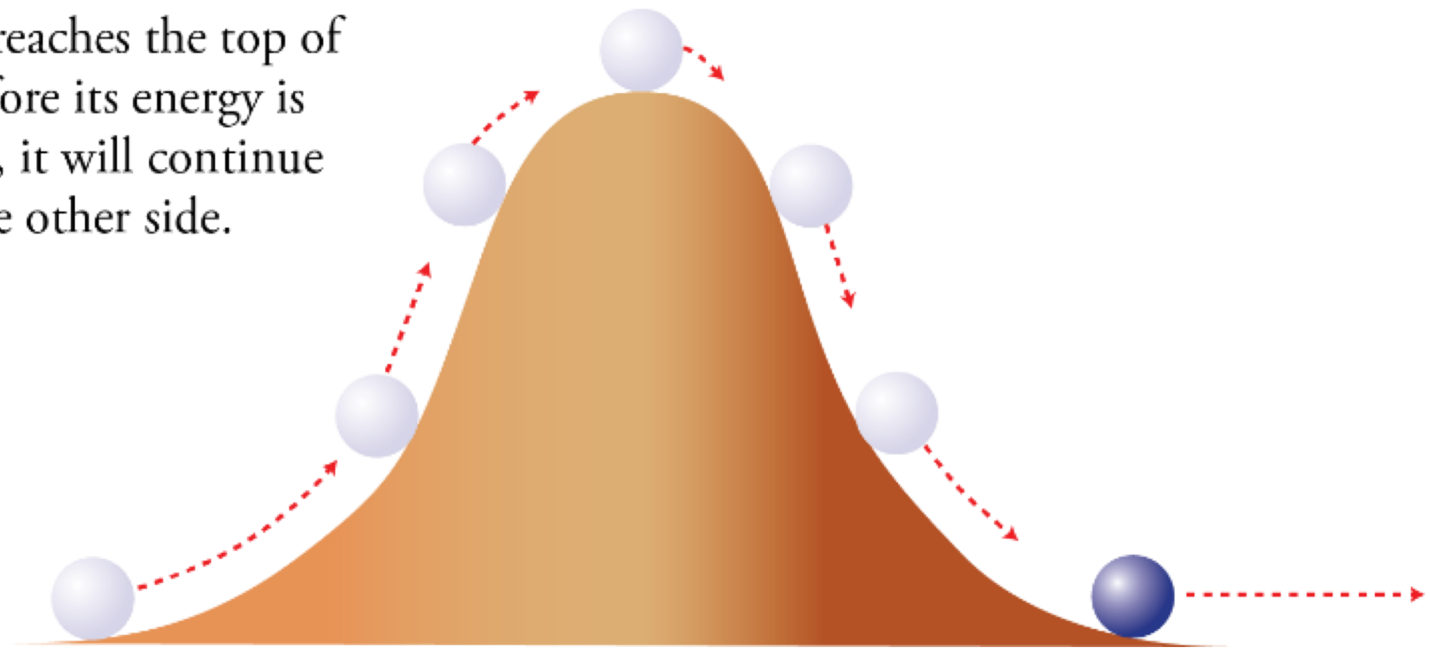


Collision Energy and Activation Energy

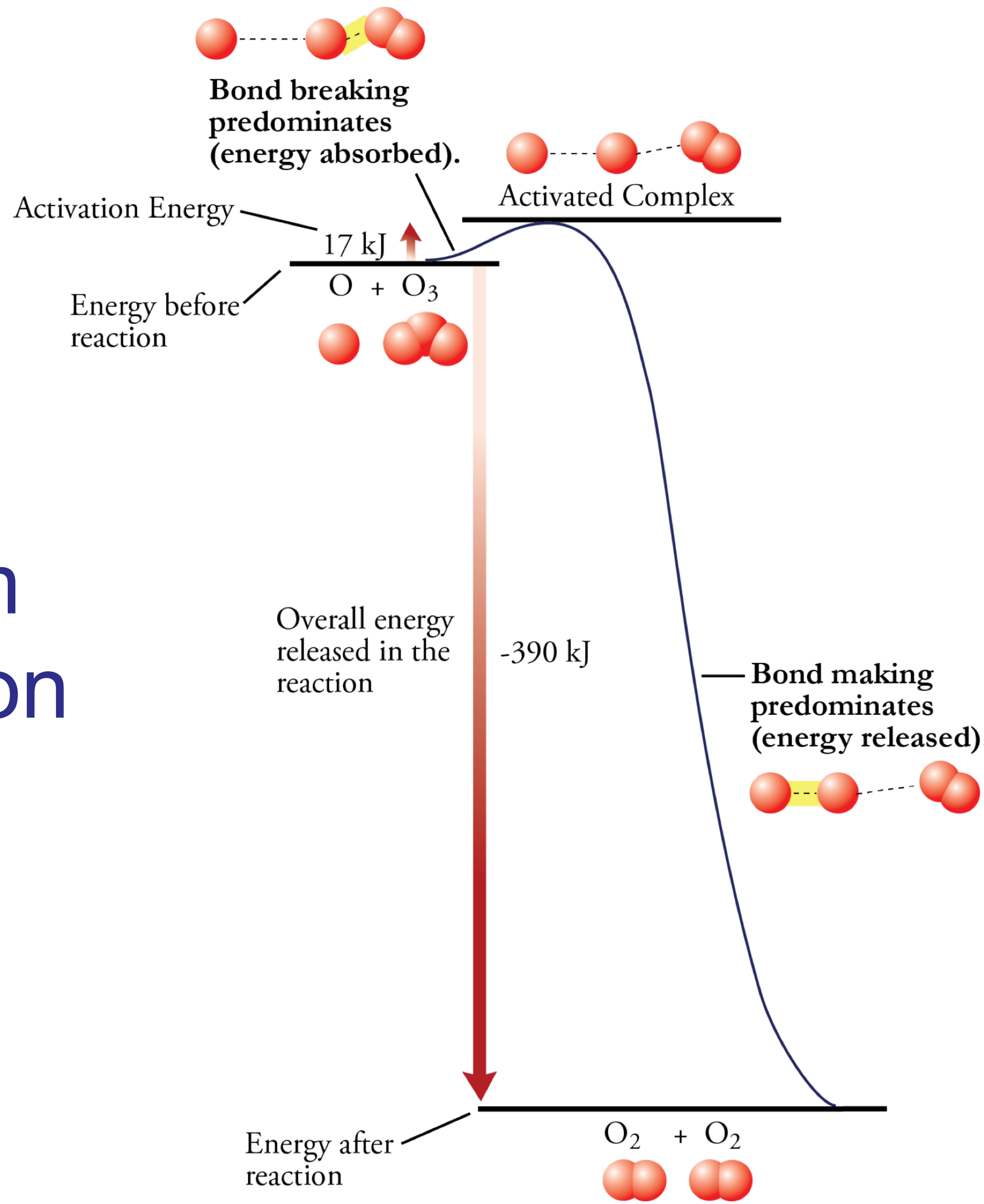


Reactions must have a minimum activation energy…if enough, change

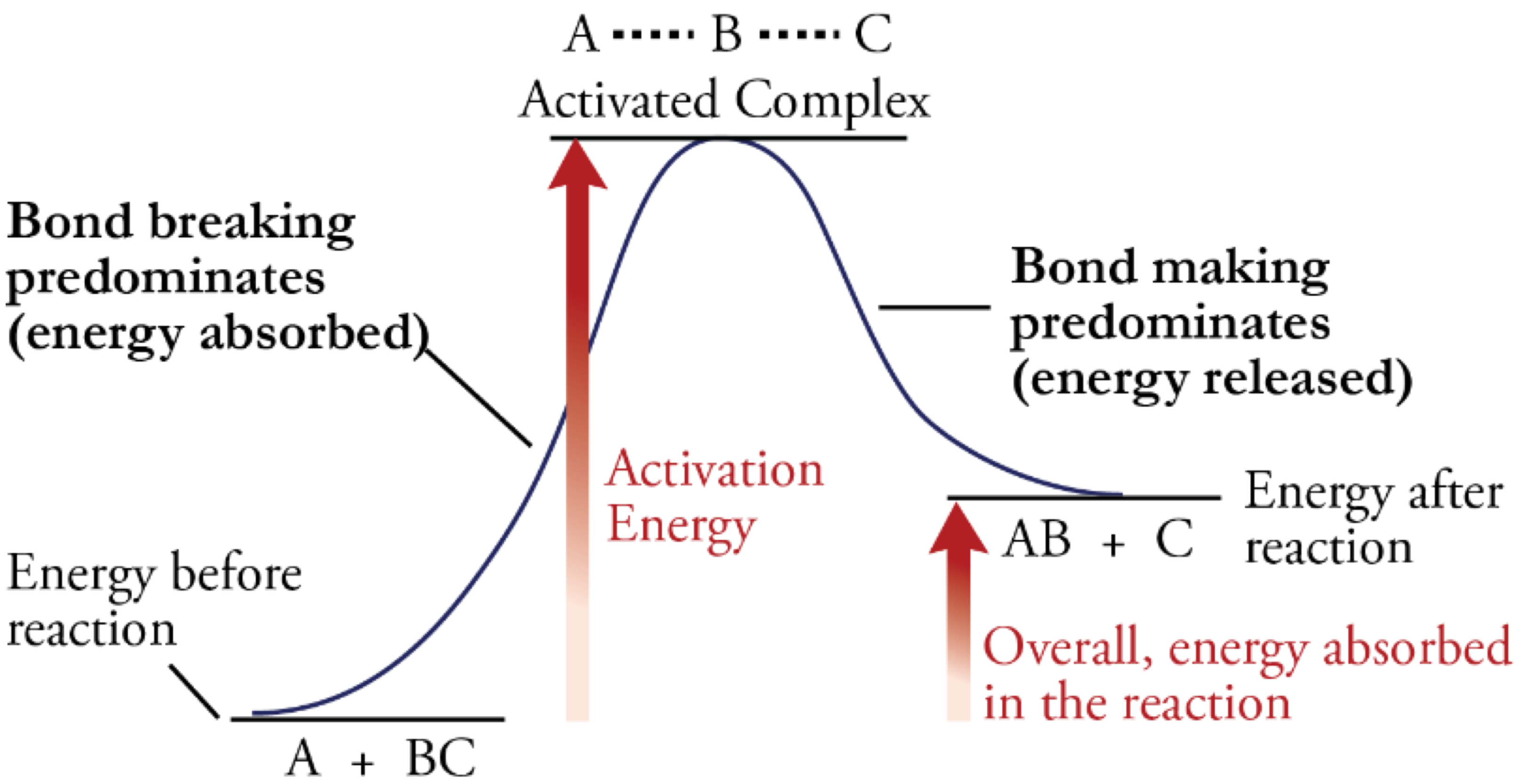
If a ball reaches the top of a hill before its energy is depleted, it will continue down the other side.



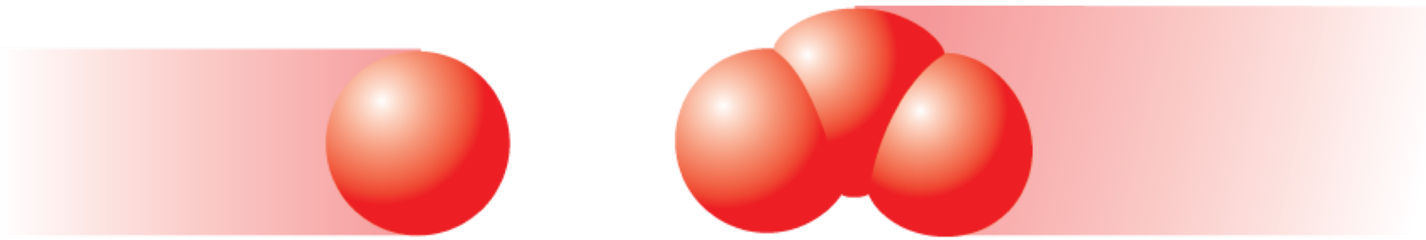
Energy Diagram for O/O_3 Reaction



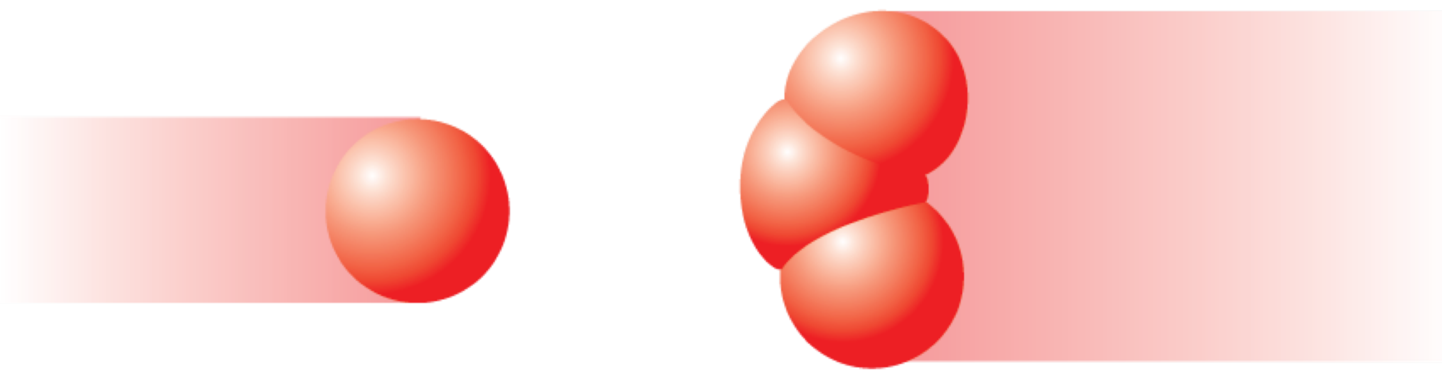
Endergonic Reactions



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 temperature

↙ ↘

Increased average velocity of particles → Increased number of collisions between reactants per second

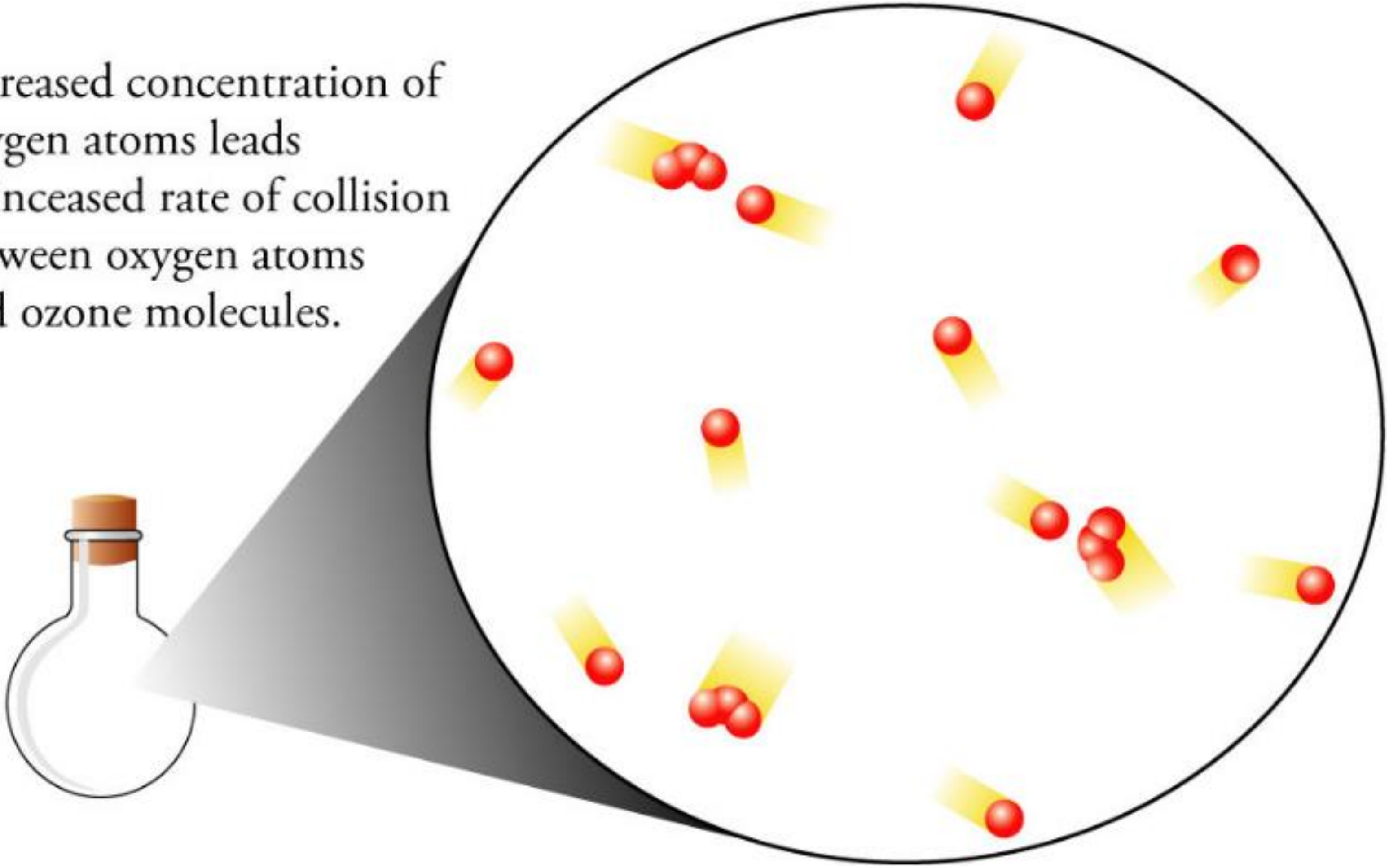
Increased average kinetic energy of particles → Increased fraction of collisions between reactants with the minimum energy to react

↘ ↙

Increased rate of reaction

Increased Concentration of one Reactant

Increased concentration of oxygen atoms leads to inceased 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

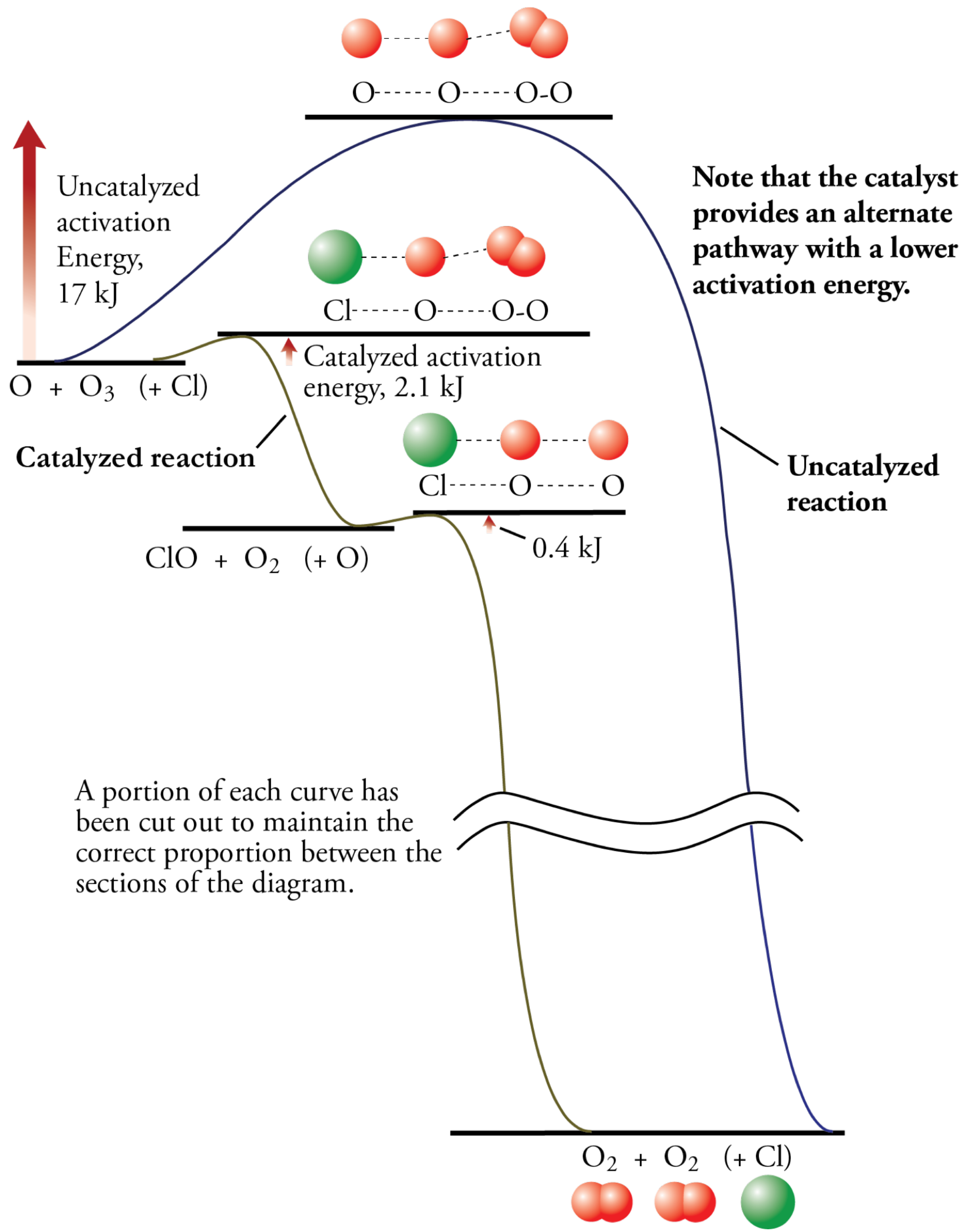
↓

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.

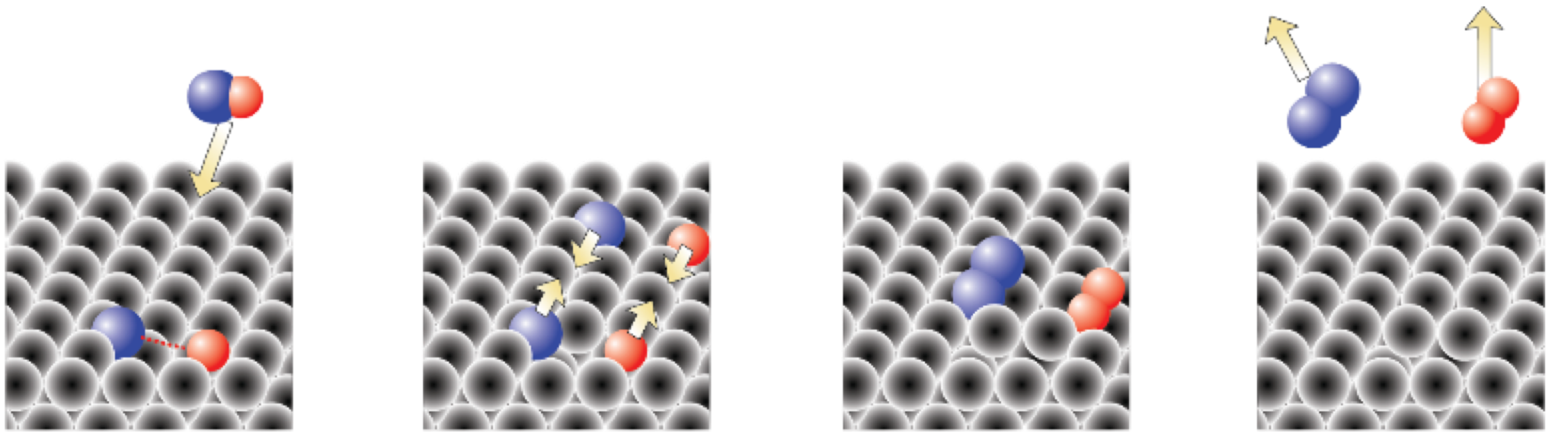
↓

A greater fraction of collisions lead to products.

↓

Increased rate of reaction

Heterogeneous Catalysis



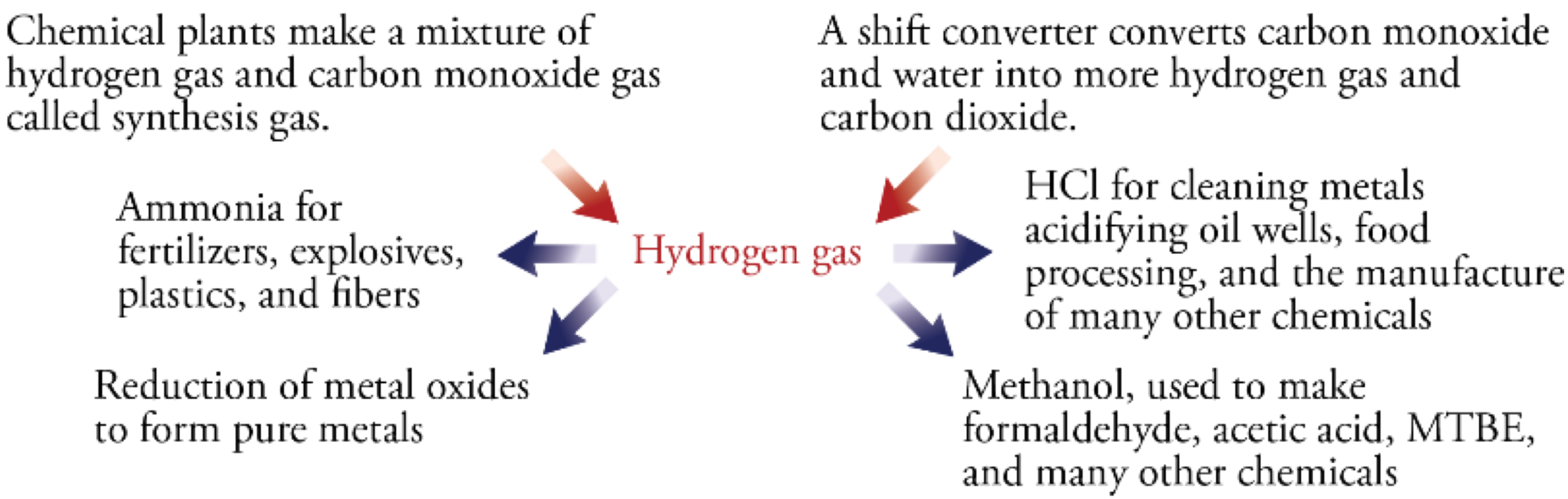
Step 1 - The reactant molecules are adsorbed, and the bonds are weakened.

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

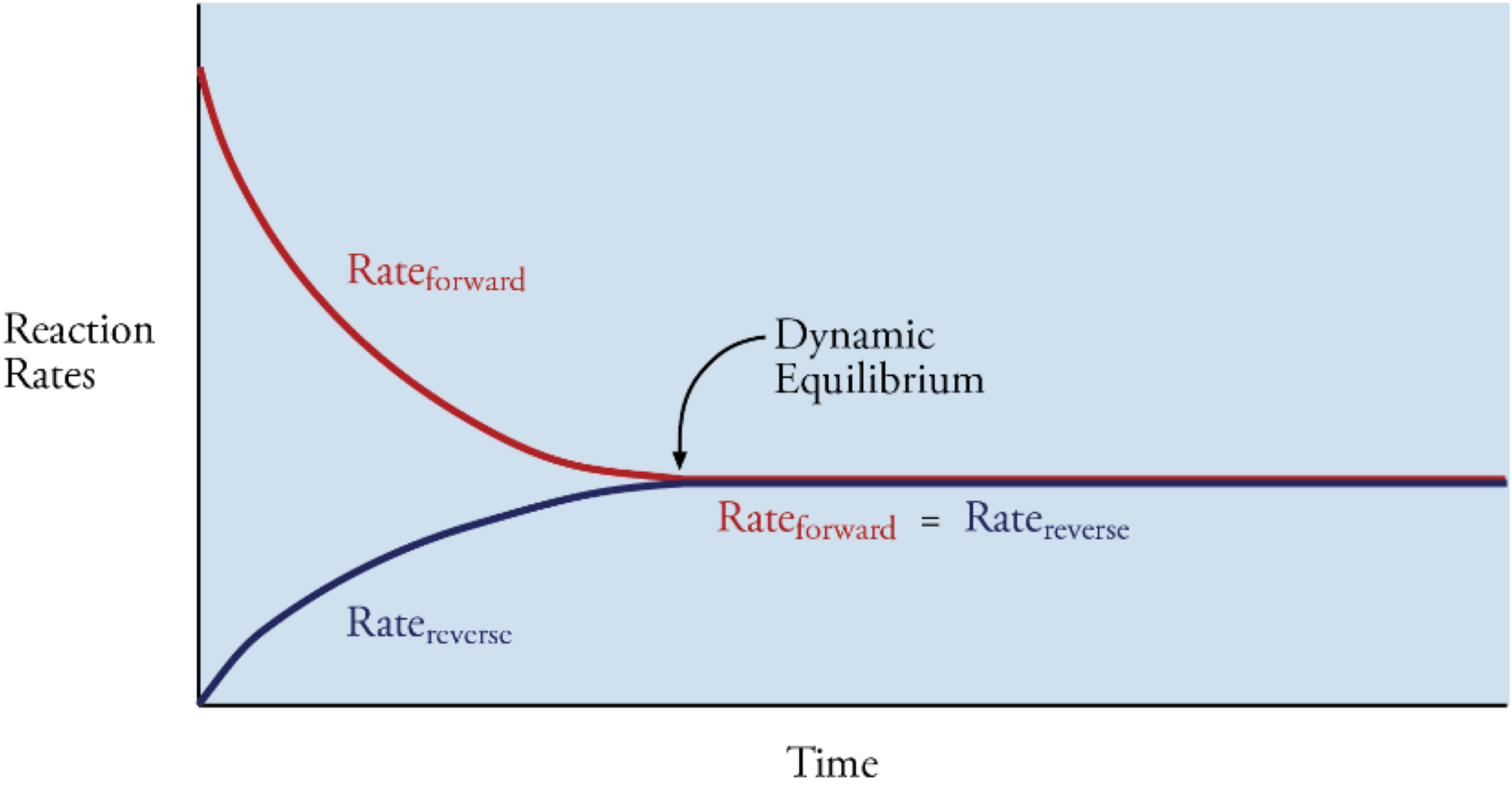


Dynamic Equilibrium

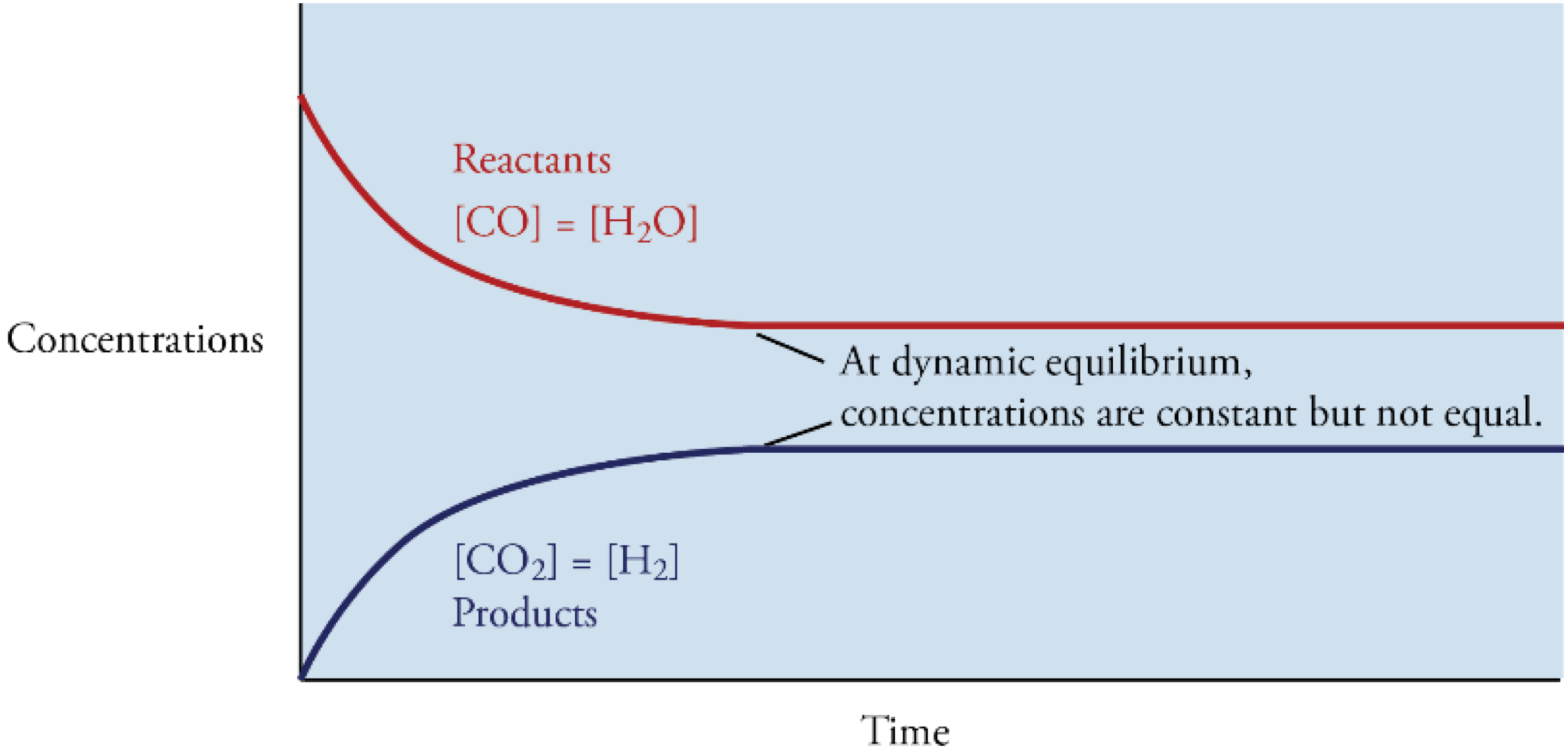
$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

- Initially, $R_f > R_r$
- Decreased [CO] and [H_2O], so decreased R_f
- Increased [CO_2] and [H_2], so increased R_f
- 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

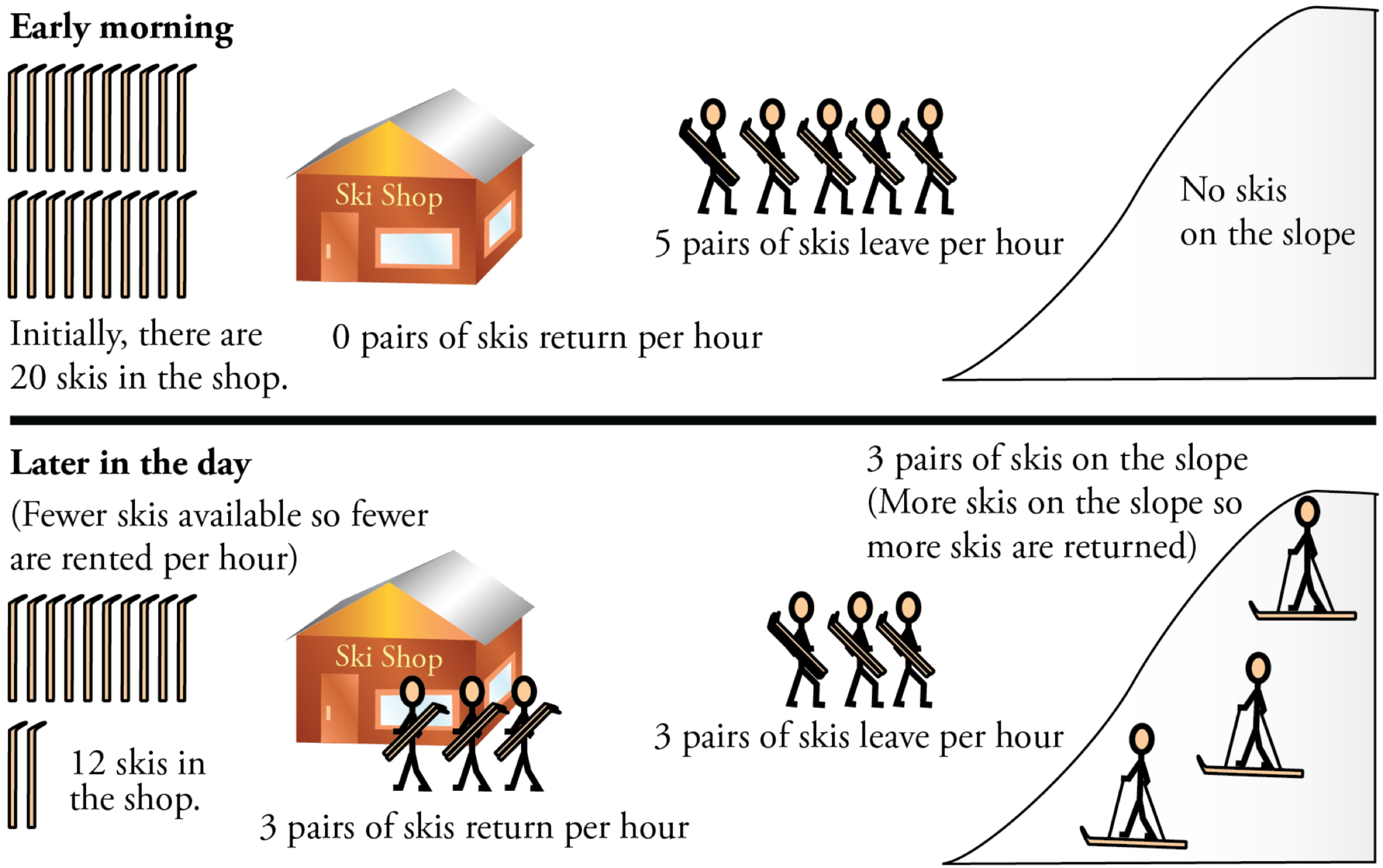
Rates of Reaction for Reversible Reactions



Changes in Concentrations for a Reversible Reaction



Ski Shop Analogy for Equilibrium



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

Equilibrium Constant

aA + bB + … ⇌ eE + fF + …

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

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

Equilibrium Constant Expression

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

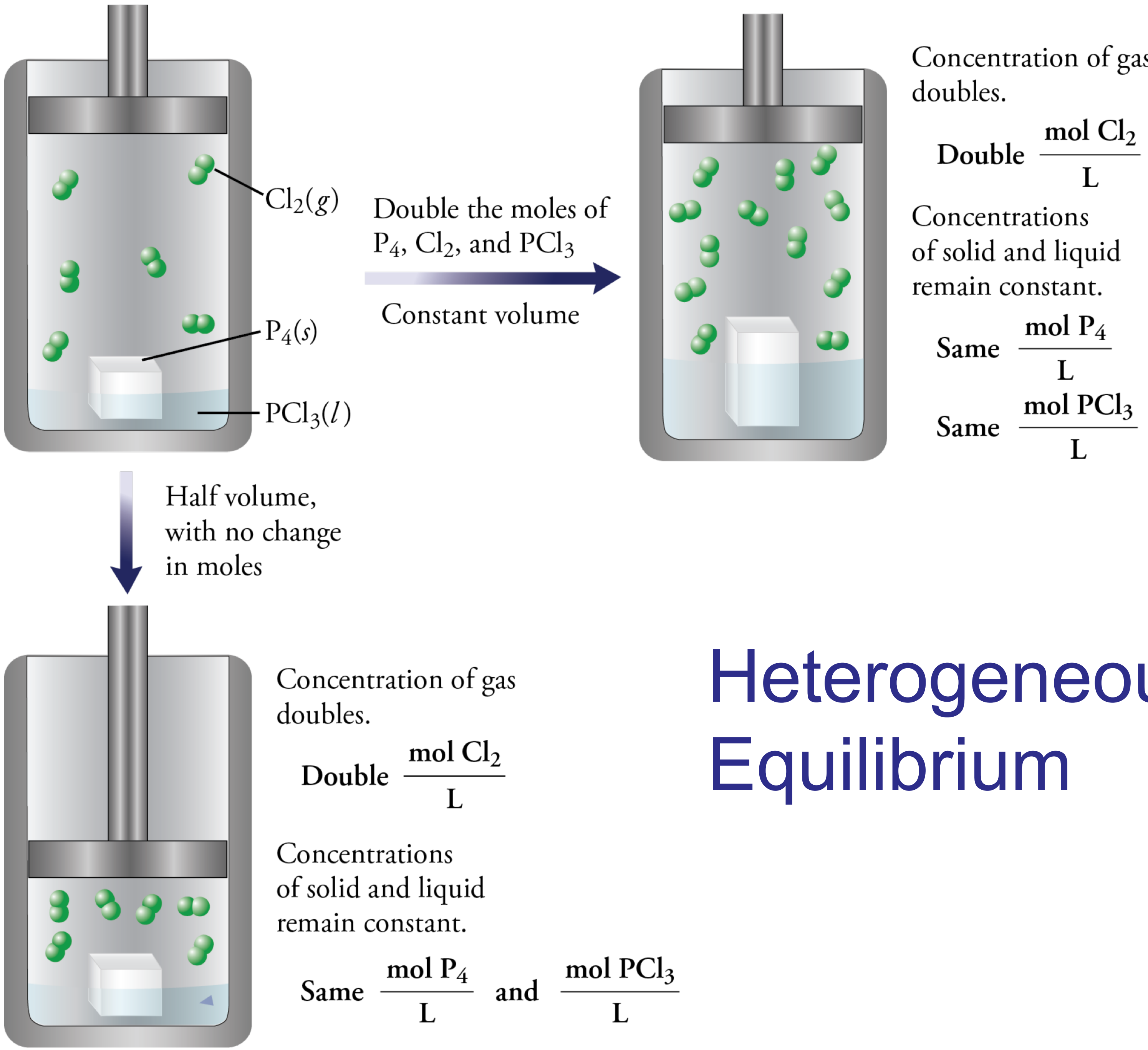
The coefficient before H_2 is 3, so we raise the concentration or pressure to the third power.

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

Heterogeneous Equilibrium

$$P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$$

$$K' = \frac{[PCl_3]^4}{[P_4]\,[Cl_2]^6} \qquad \frac{K'[P_4]}{[PCl_3]^4} = \frac{1}{[Cl_2]^6} = K_C$$



Heterogeneous Equilibrium

Equilibrium Constant Expressions for Heterogeneous Equilibria

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

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

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

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 $\text{Rate}_{\text{forward}}$

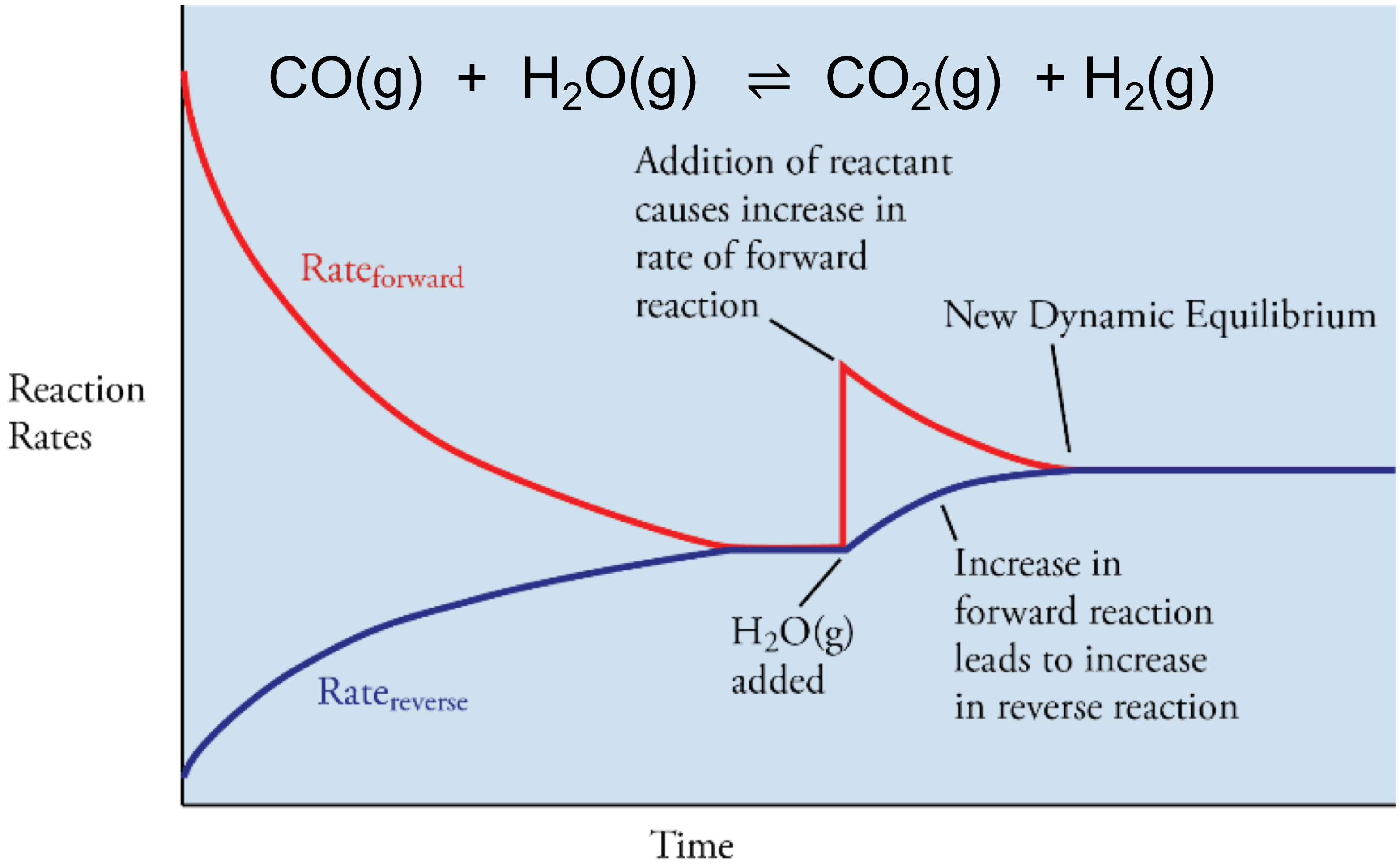
↓

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

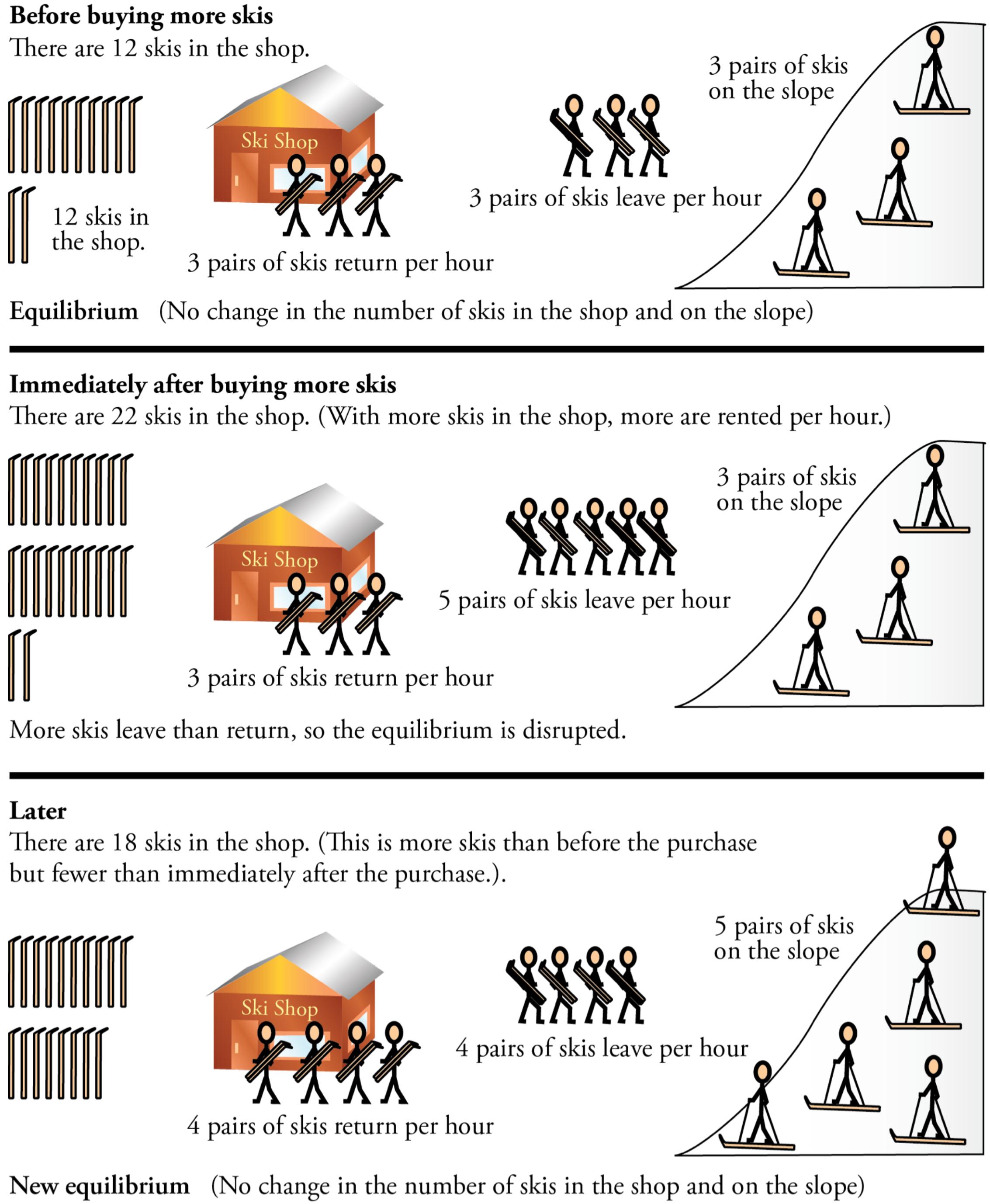
↓

System shifts toward products

Change in Rates When Reactant Added



Ski Shop Analogy 2



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

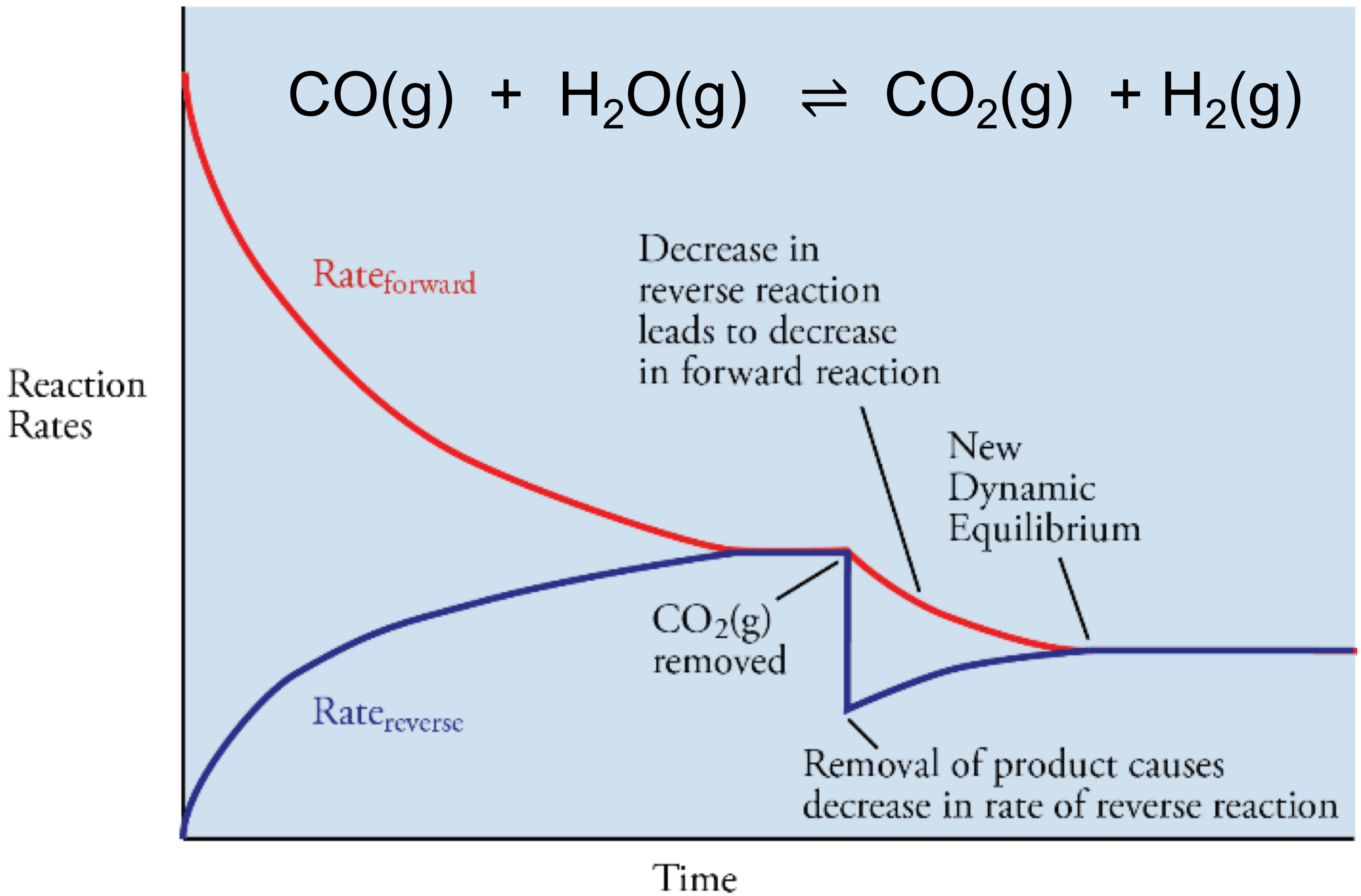
↓

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

↓

System shifts toward products

Change in Rates When Product Removed



Effect of Increased Temperature on Equilibrium

$H_2O(l) + \text{energy} \rightleftharpoons H^+(aq) + OH^-(aq)$

$K_w = [H^+][OH^-]$

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