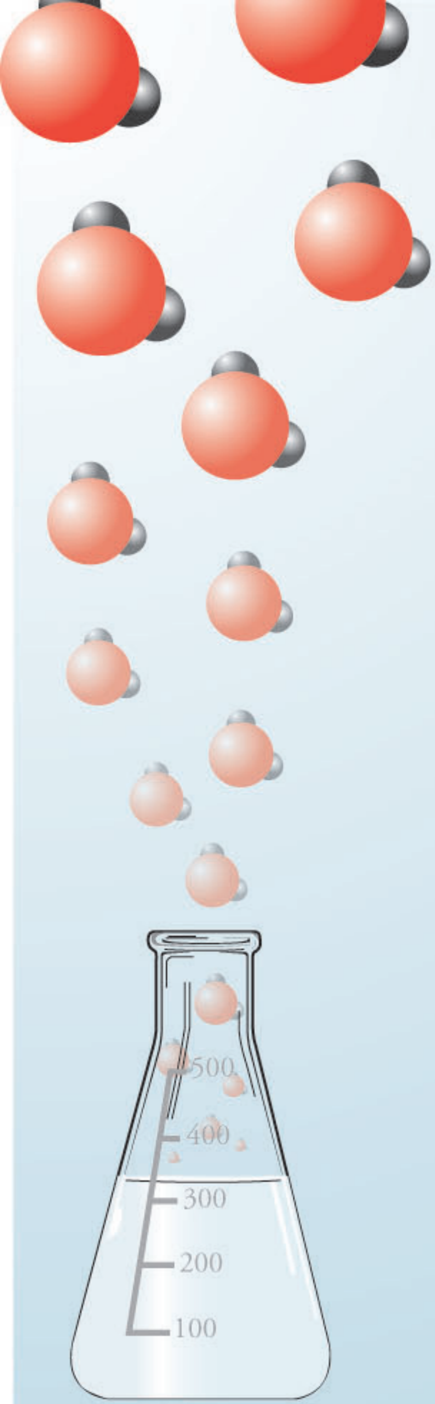


The Process of Chemical Reactions, Equilibrium, Proteins, and Enzymes

http://preparatorychemistry.com/Bishop_Book_atoms_14.pdf

http://preparatorychemistry.com/Bishop_Book_atoms_15.pdf

Collision Theory

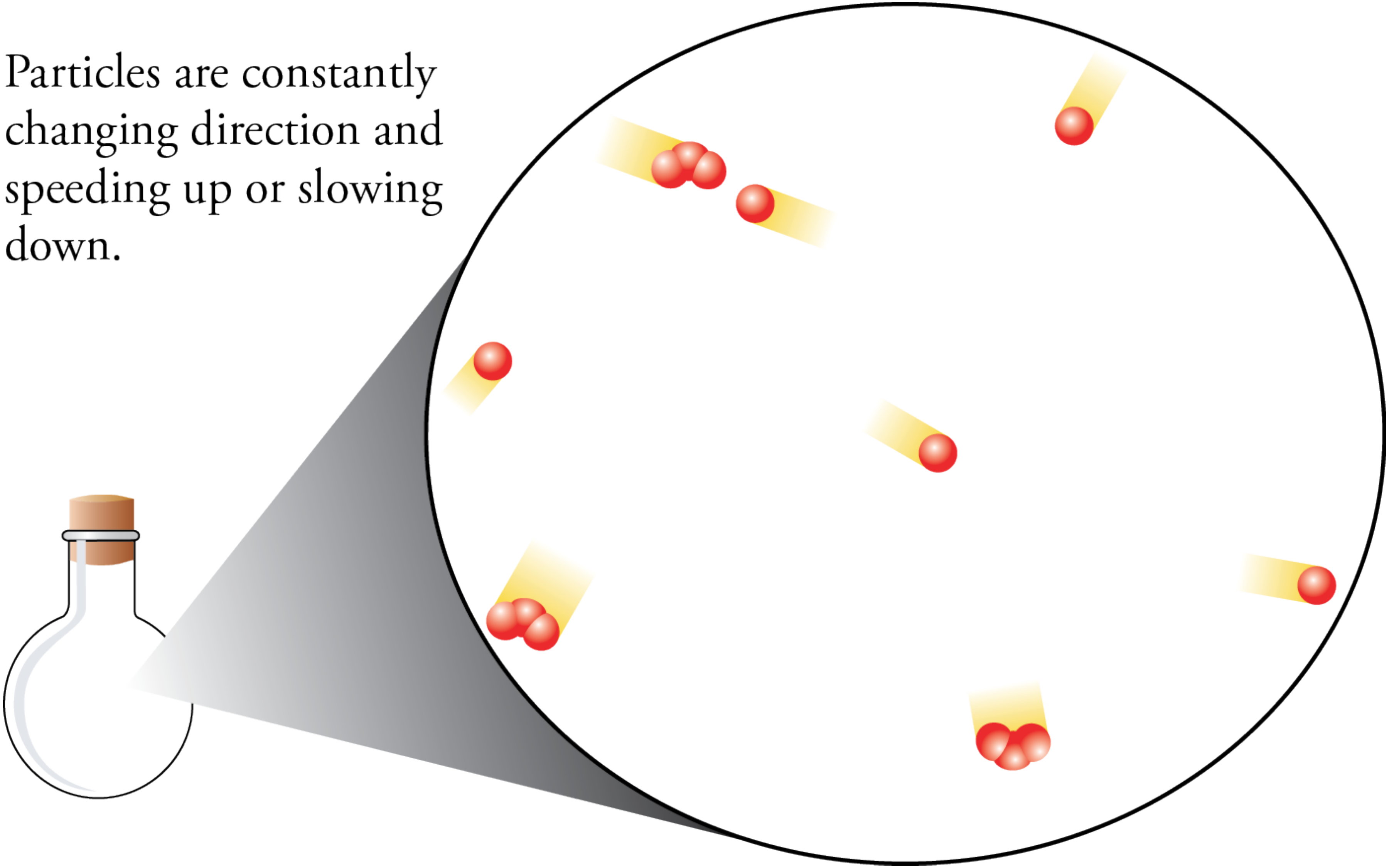
- Reactants must collide

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

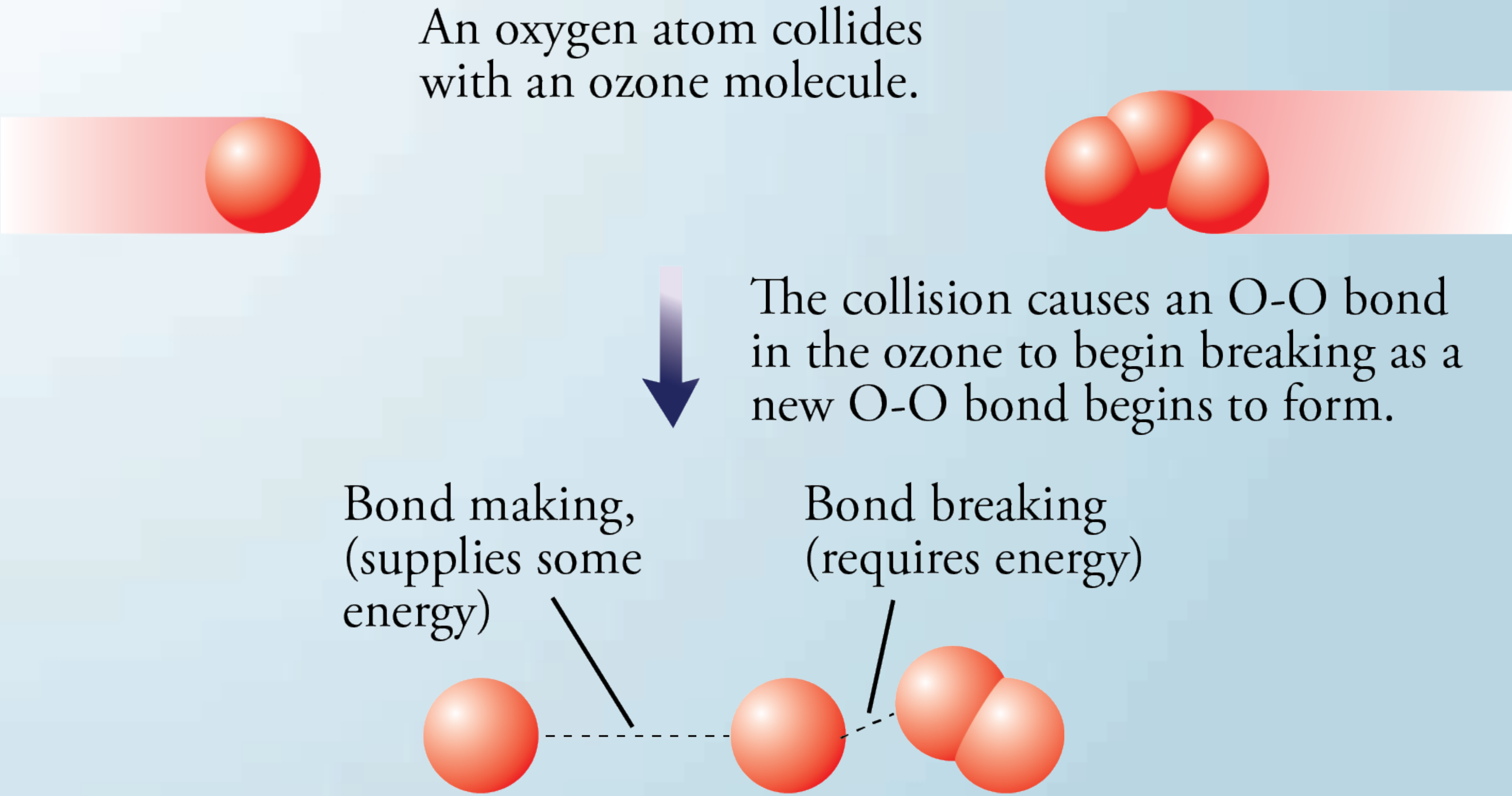
  - – collision brings contact between reactants
  - – collision provides energy to break bonds

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

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

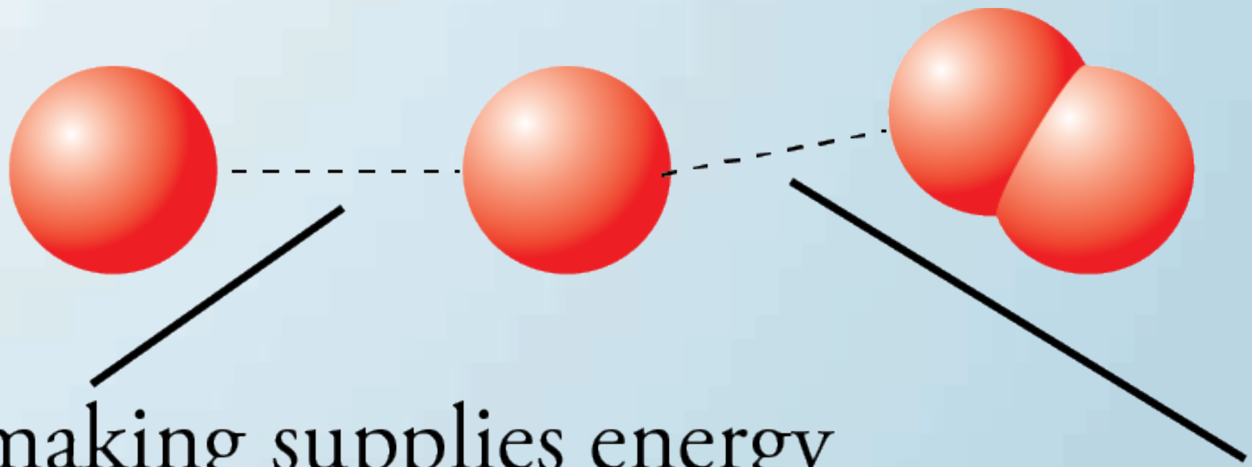


Bond Breaking and Making



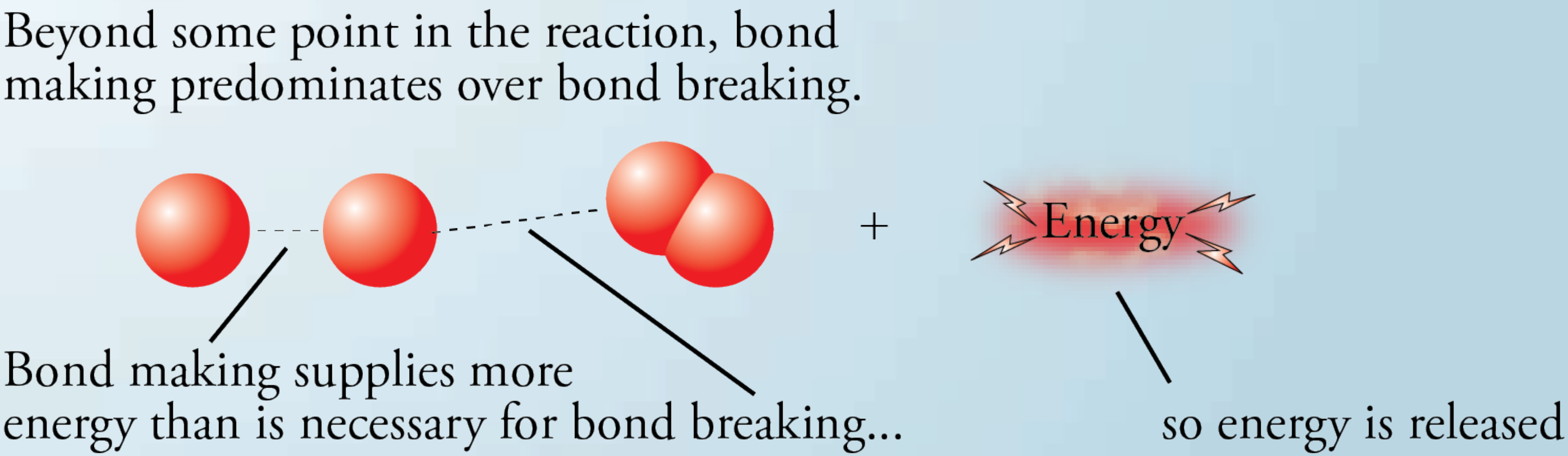
Initially, the energy required for bond breaking is greater than the energy supplied from bond making. The extra energy necessary for the reaction comes from the kinetic energy of the colliding particles.

Formation of Activated Complex



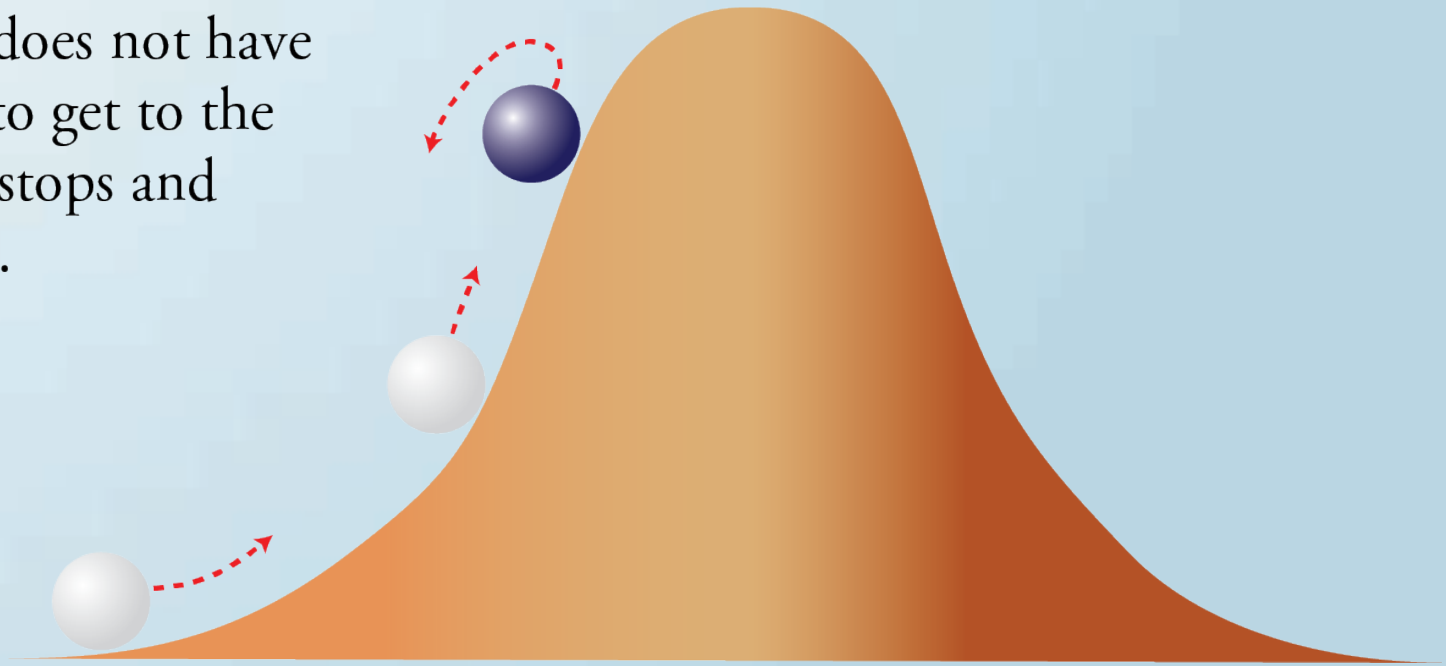
Bond making supplies energy equal to the energy required for bond breaking.

Formation of Product

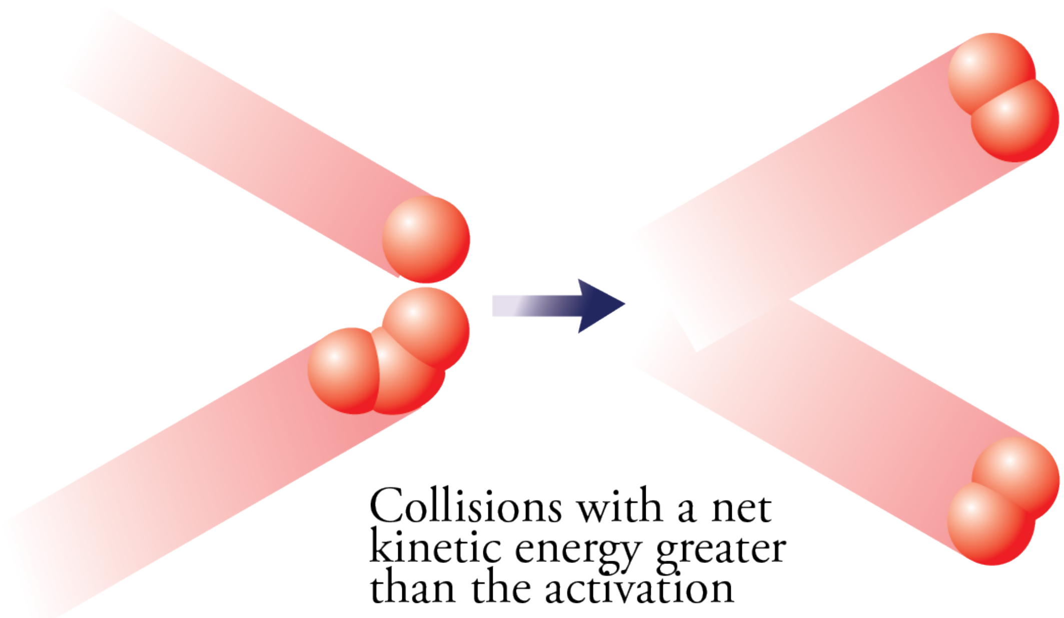


Reactions must have a minimum activation energy…if too little, no change

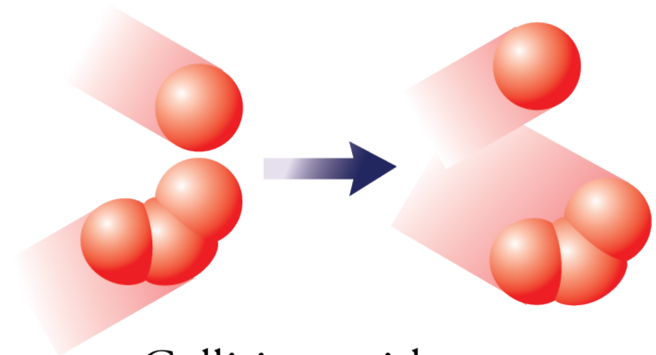
If a rolling ball does not have enough energy to get to the top of a hill, it stops and rolls back down.



Collision Energy and Activation Energy



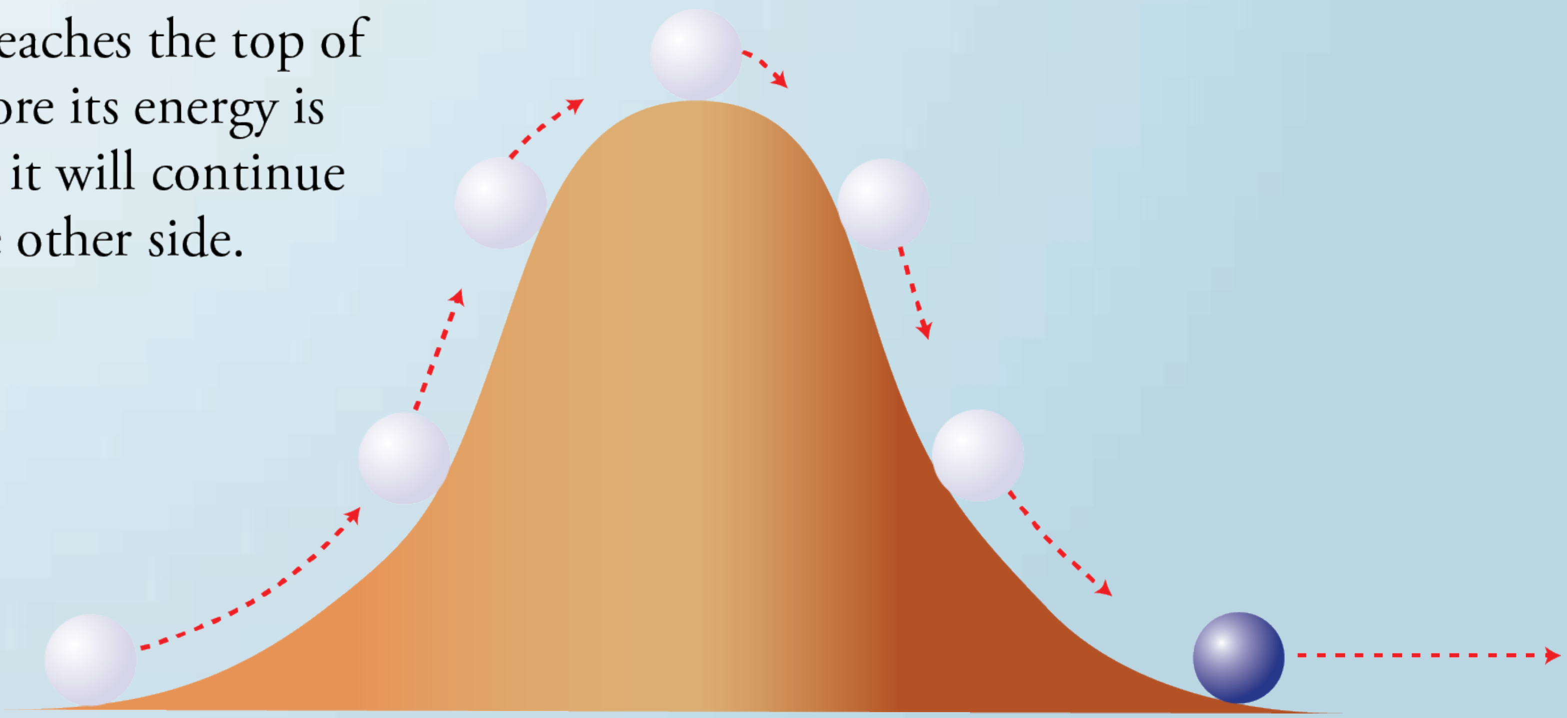
Collisions with a net kinetic energy greater than the activation energy can react.



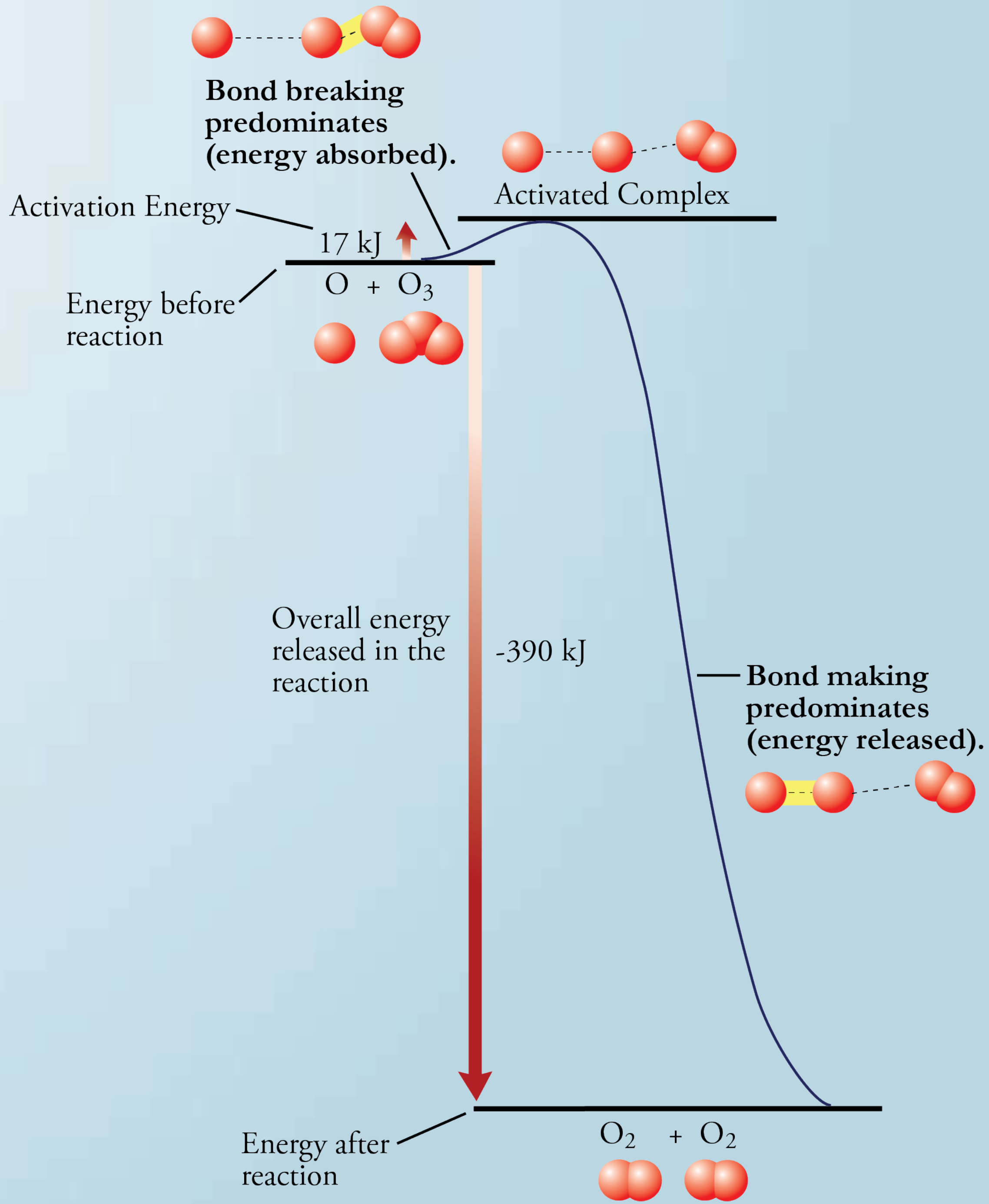
Collisions with a net kinetic energy less than the activation energy cannot react.

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

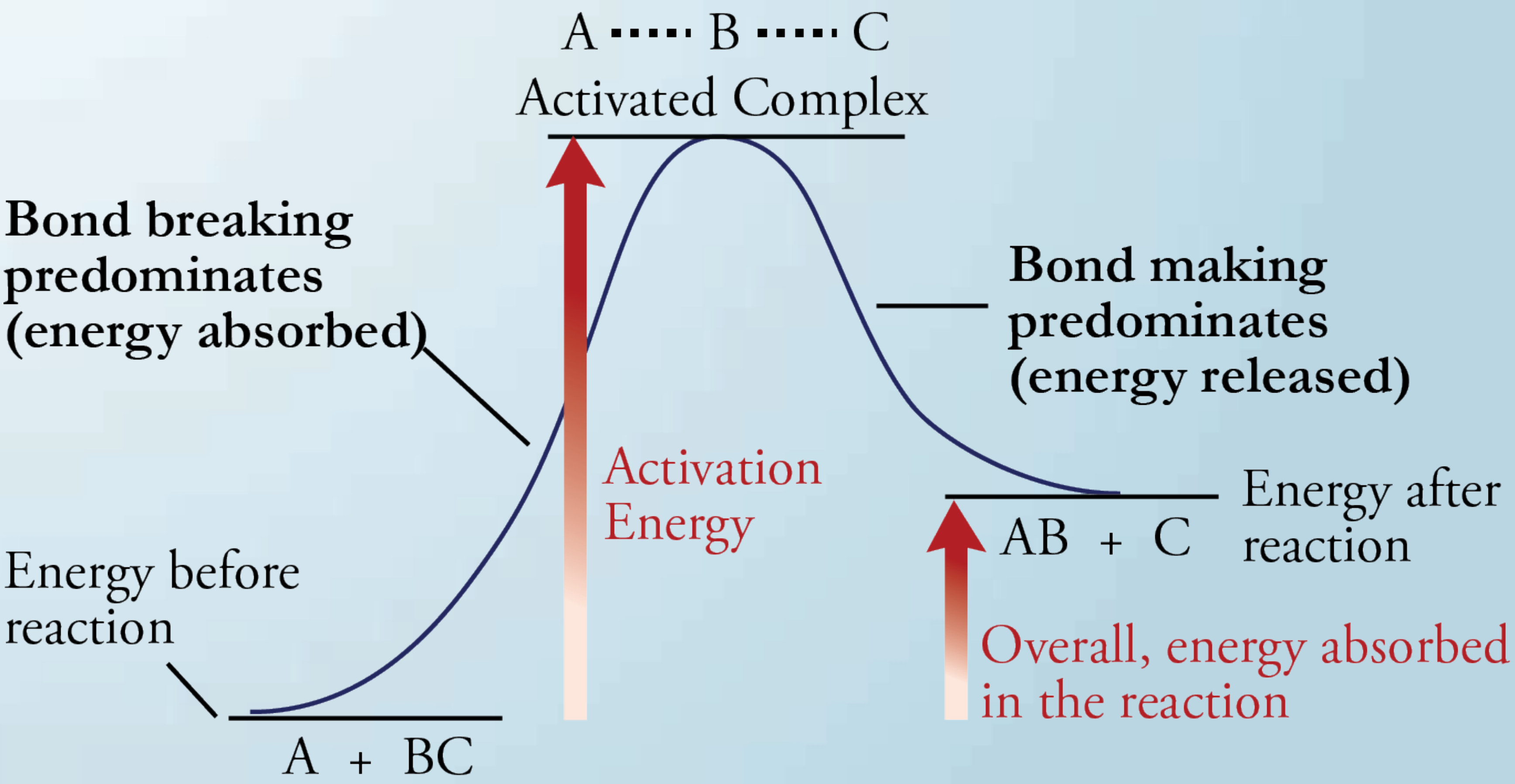
If a ball reaches the top of a hill before its energy is depleted, it will continue down the other side.



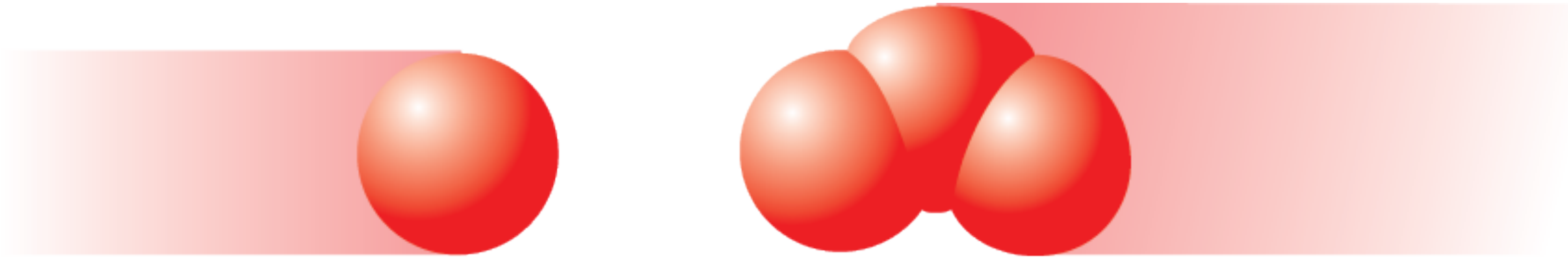
Energy Diagram for O/O_3 Reaction



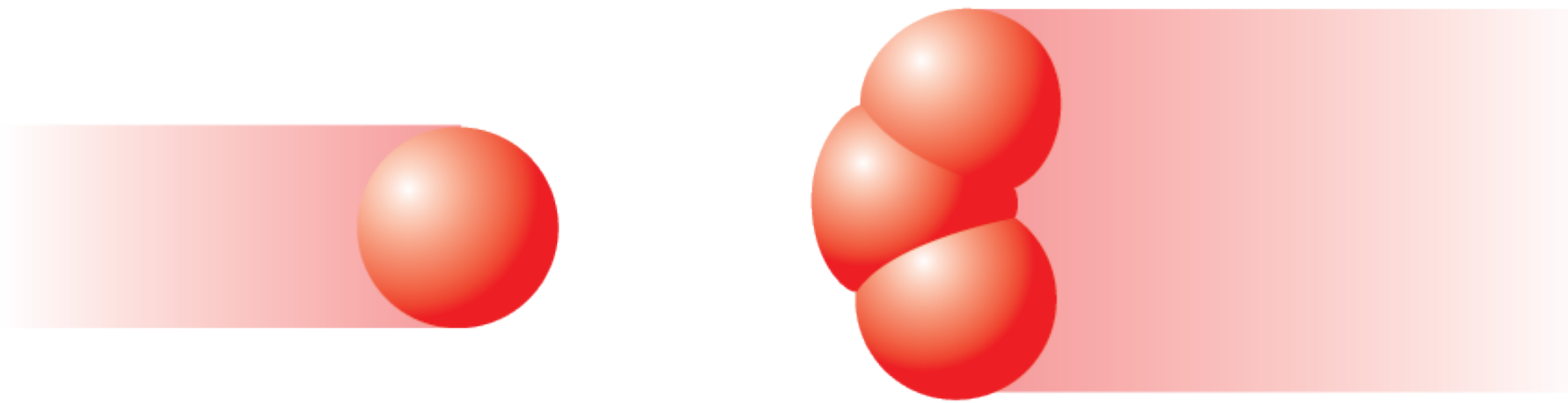
Endogonic Reactions



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

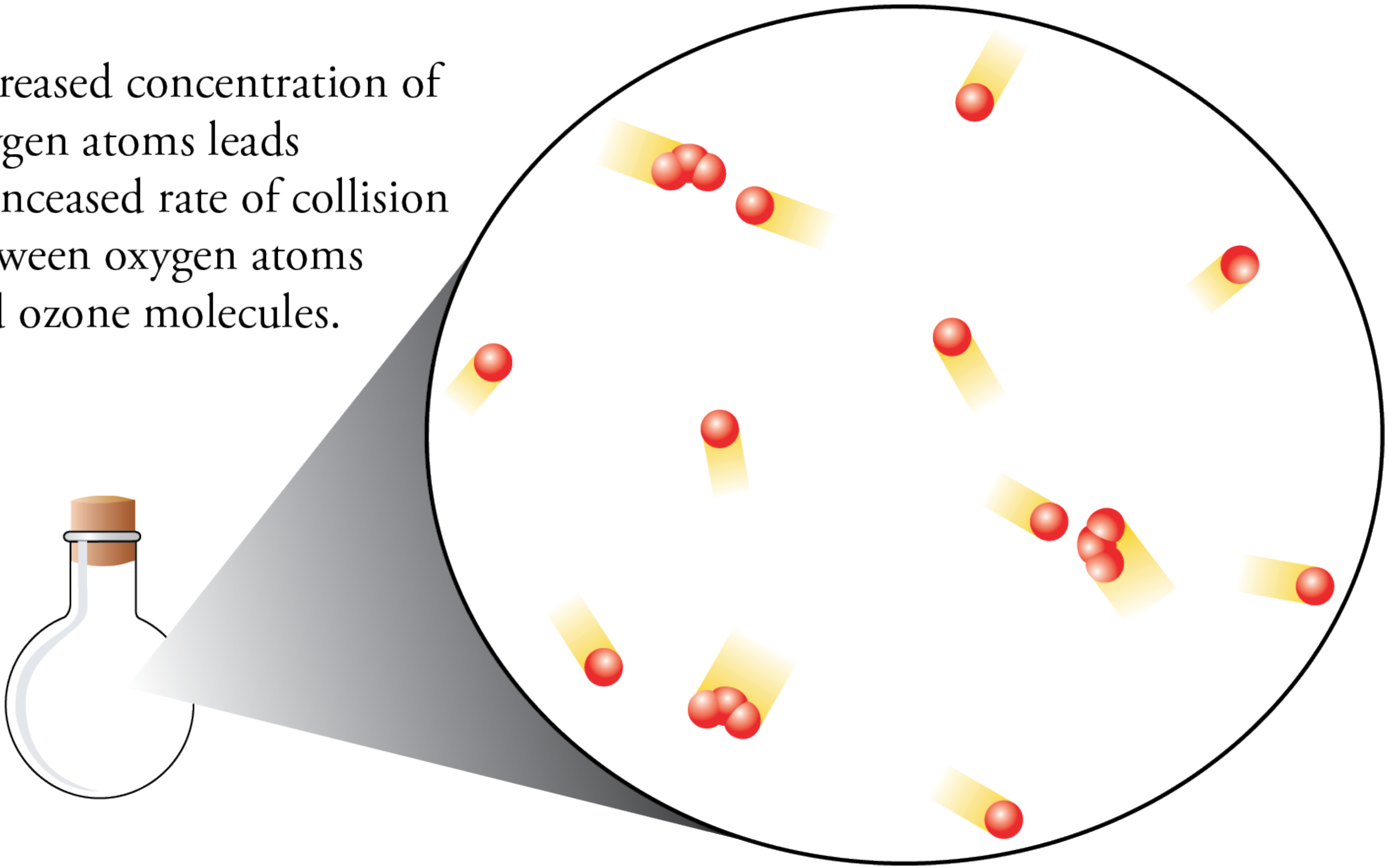
Increased average kinetic energy of particles

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

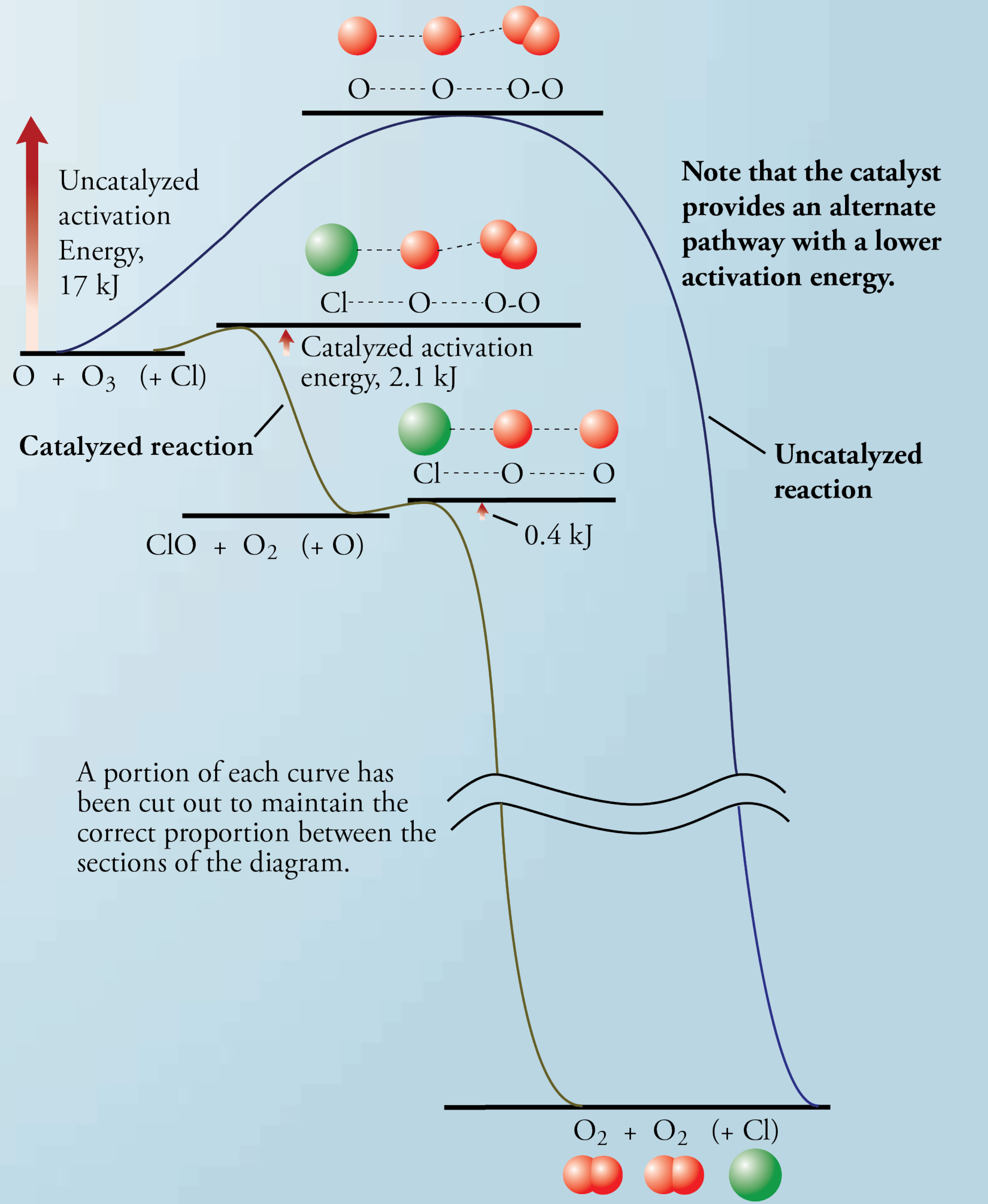
↓

Increased number of particles fulfilling the requirements for reaction

↓

Increased rate of reaction

Catalyzed O/O_3 Reaction



Catalysts and Rate of Reactions

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

↓

A greater fraction of collisions have the activation energy.

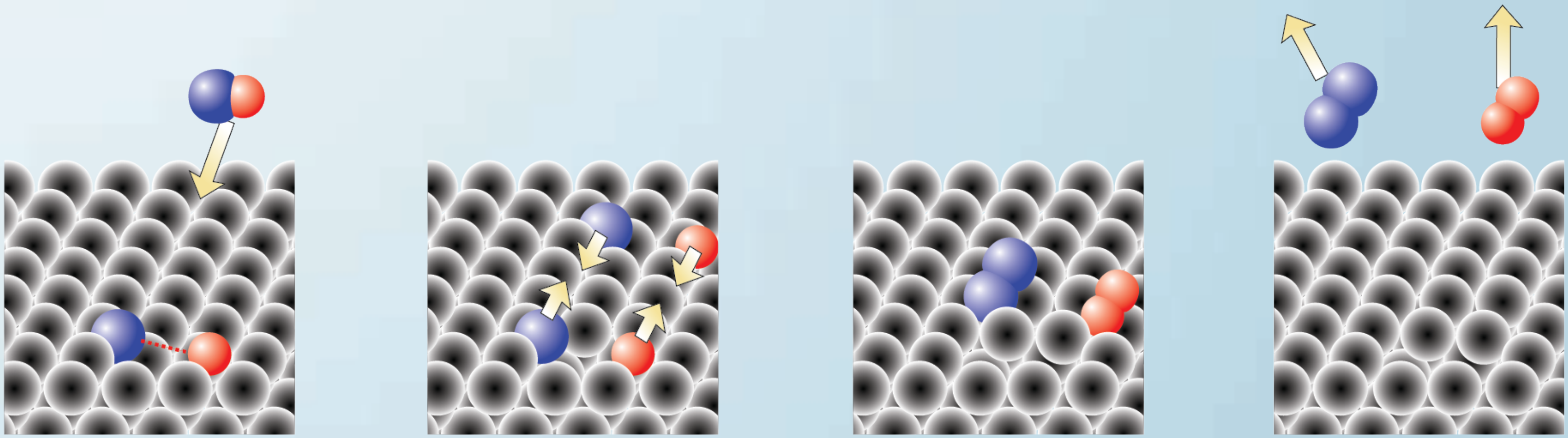
↓

A greater fraction of collisions lead to products.

↓

Increased rate of reaction

Heterogeneous Catalysis



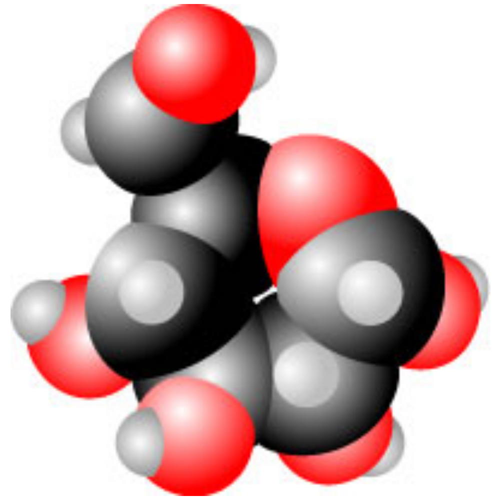
Step 1 - The reactant molecules are adsorbed, and the bonds are weakened.

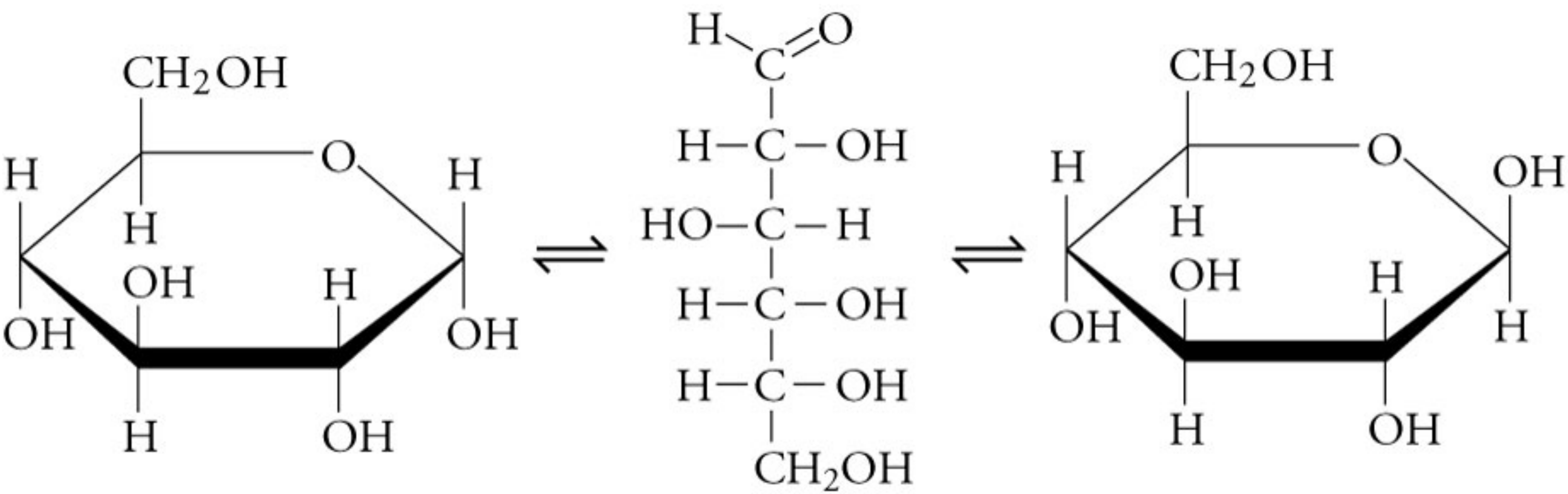
Step 2 - The atoms migrate across the catalyst.

Step 3 - New bonds form.

Step 4 - The products leave the catalyst.

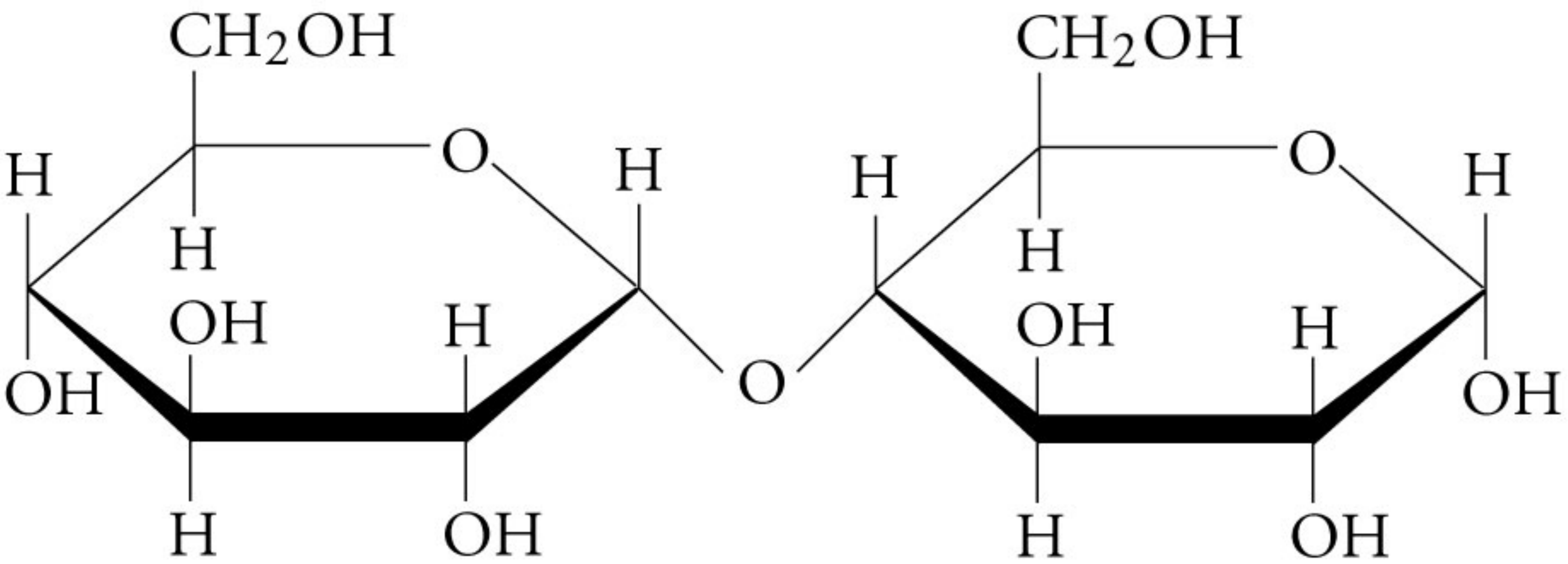
Glucose





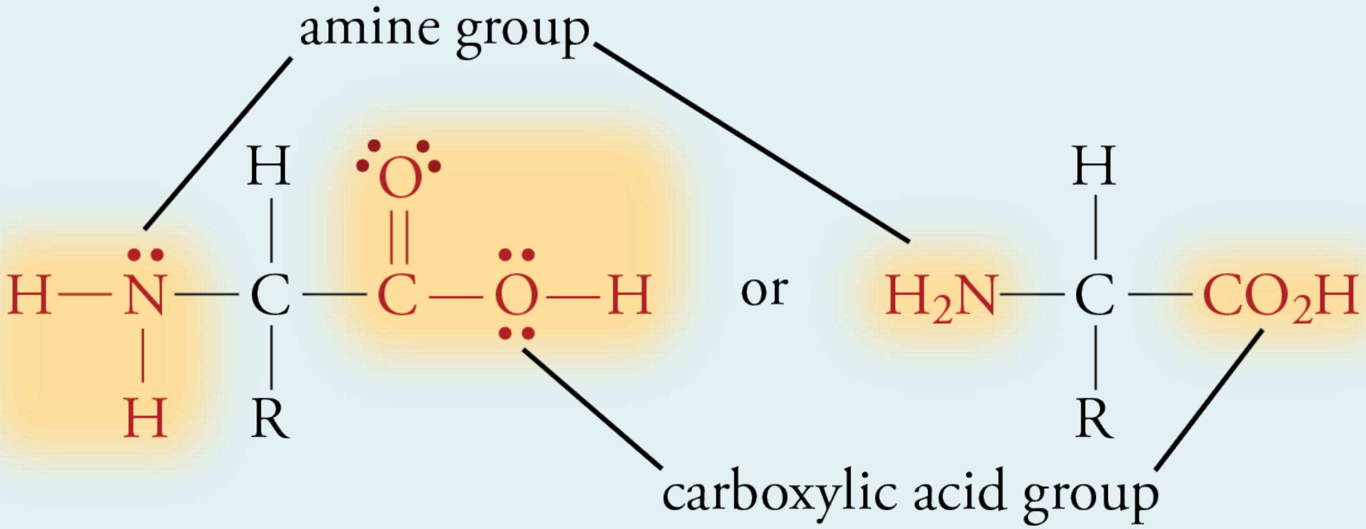
glucose

Maltose

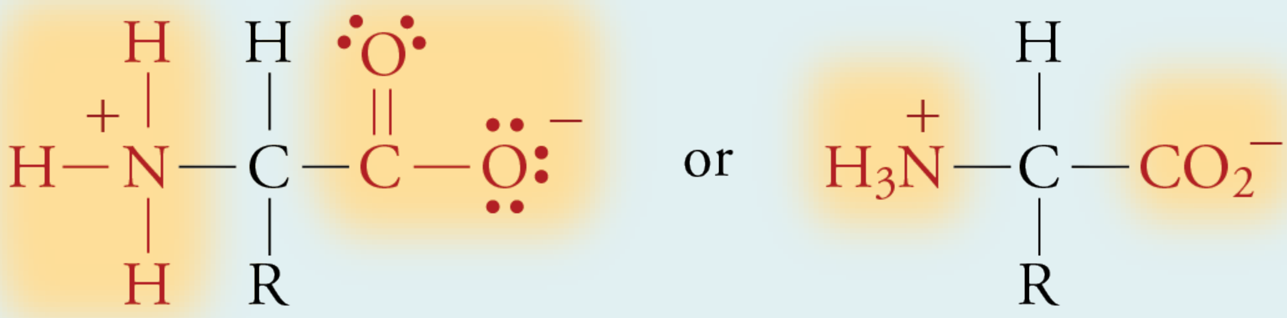


Maltose (glucose and glucose)

Amino Acids

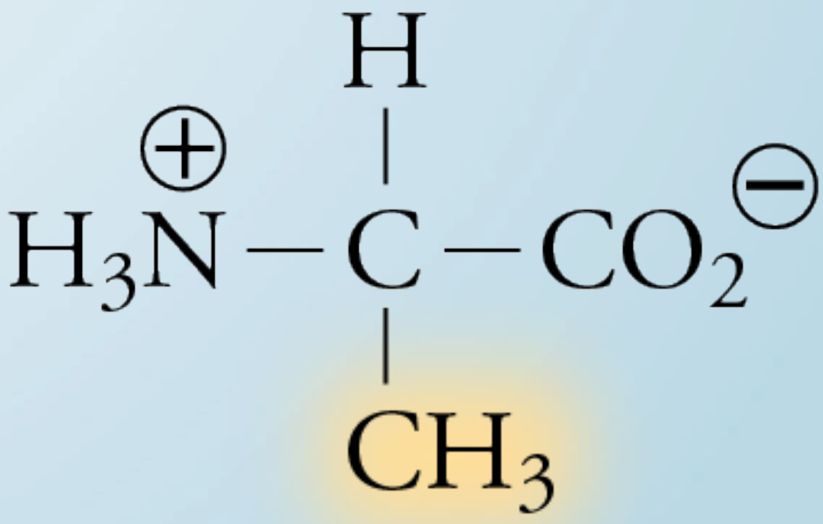


amine group
H
O
H—N—C—C—O—H
H R
or
H
H_2N—C—CO_2H
R
carboxylic acid group

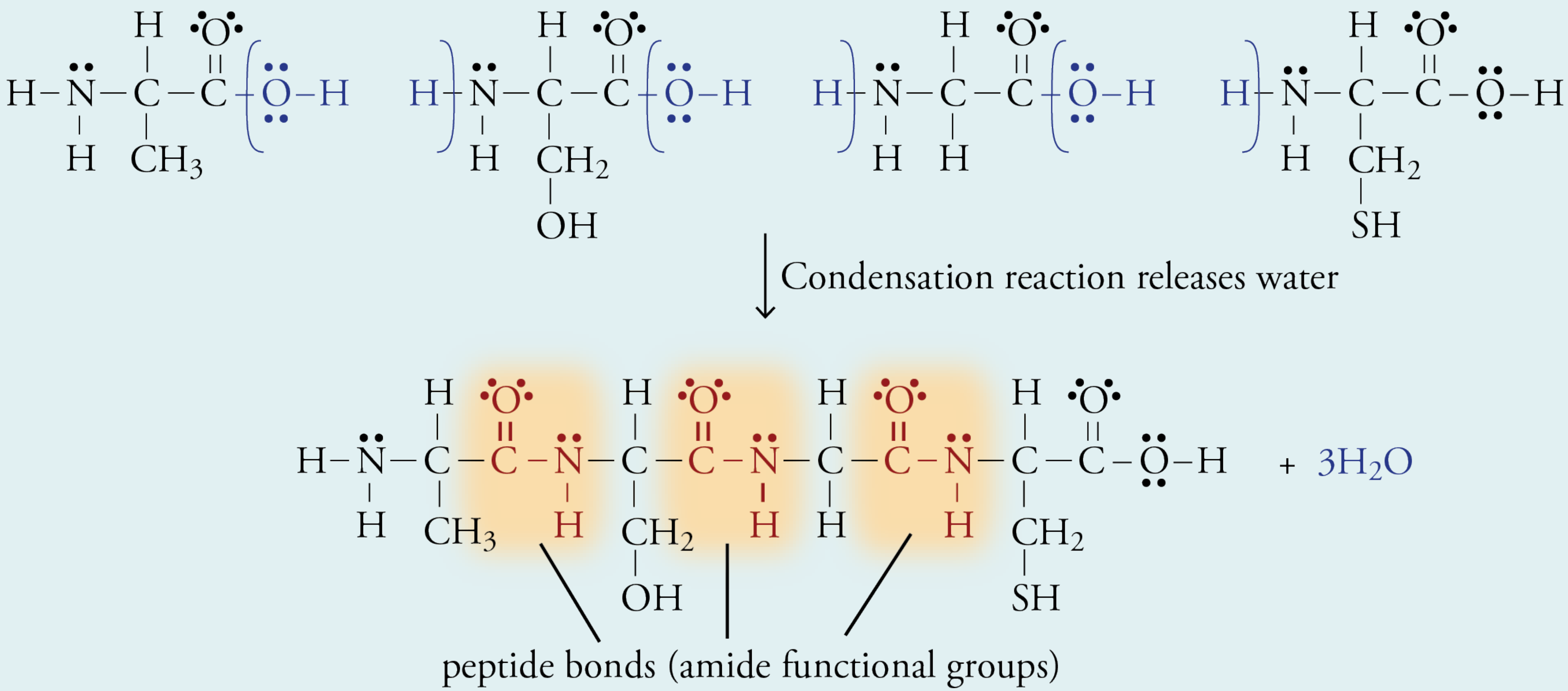


H H O
+ −
H—N—C—C—O
H R
or
H
+
H_3N—C—CO_2^-
R

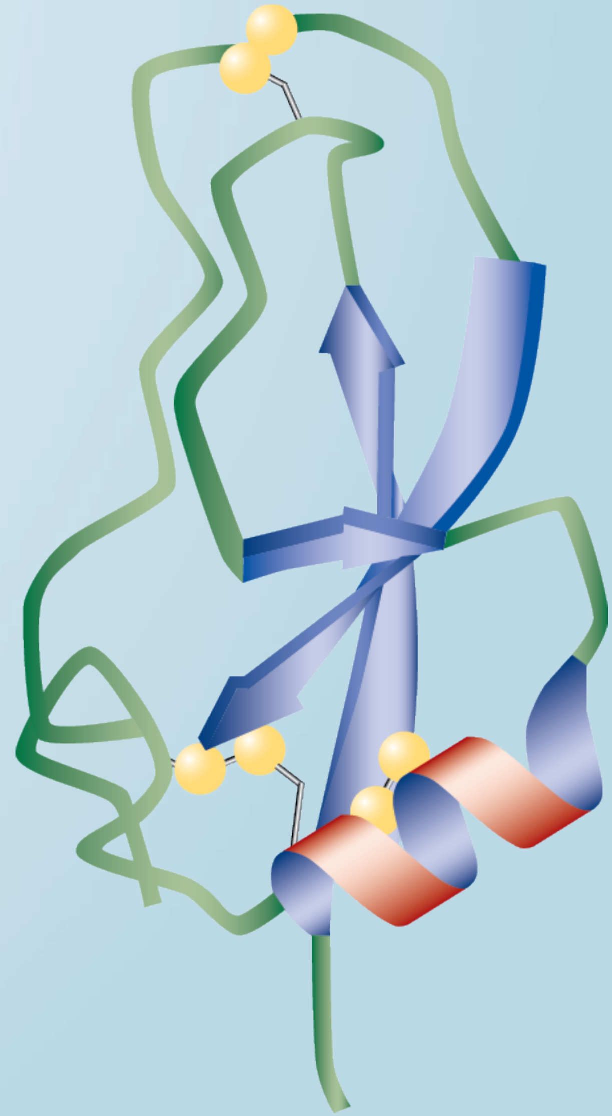
Alanine



Formation of Ala-Ser-Gly-Cys



Protein - Bovine Pancreatic Trypsin Inhibitor (BPTI)

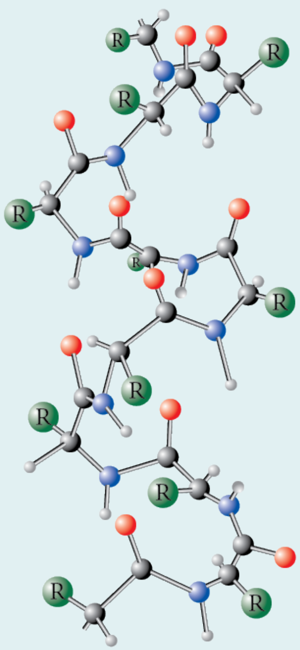


Primary and Secondary Protein Structures

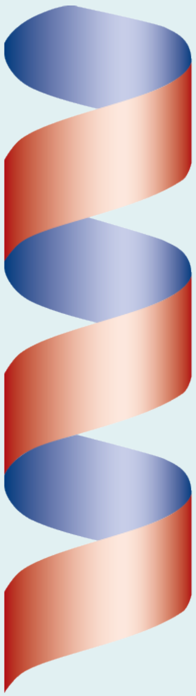
- ***Primary Structure*** = the sequence of amino acids in the protein
- The arrangement of atoms that are close to each other in the polypeptide chain is called the ***secondary structure*** of protein.
  - Three types
    - α-helix
    - β-sheet
    - irregular

α-helix - Secondary Structure

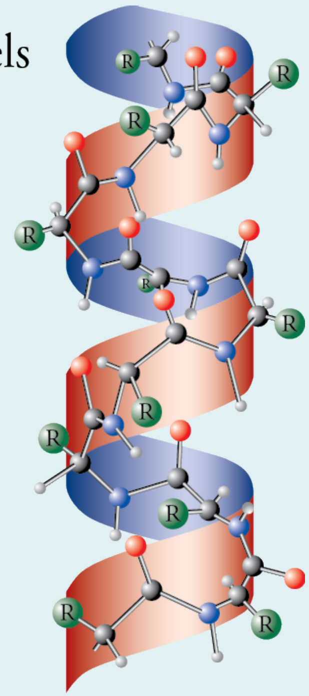
Ball-and-stick model of a portion of the α-helical secondary structure of a protein molecule



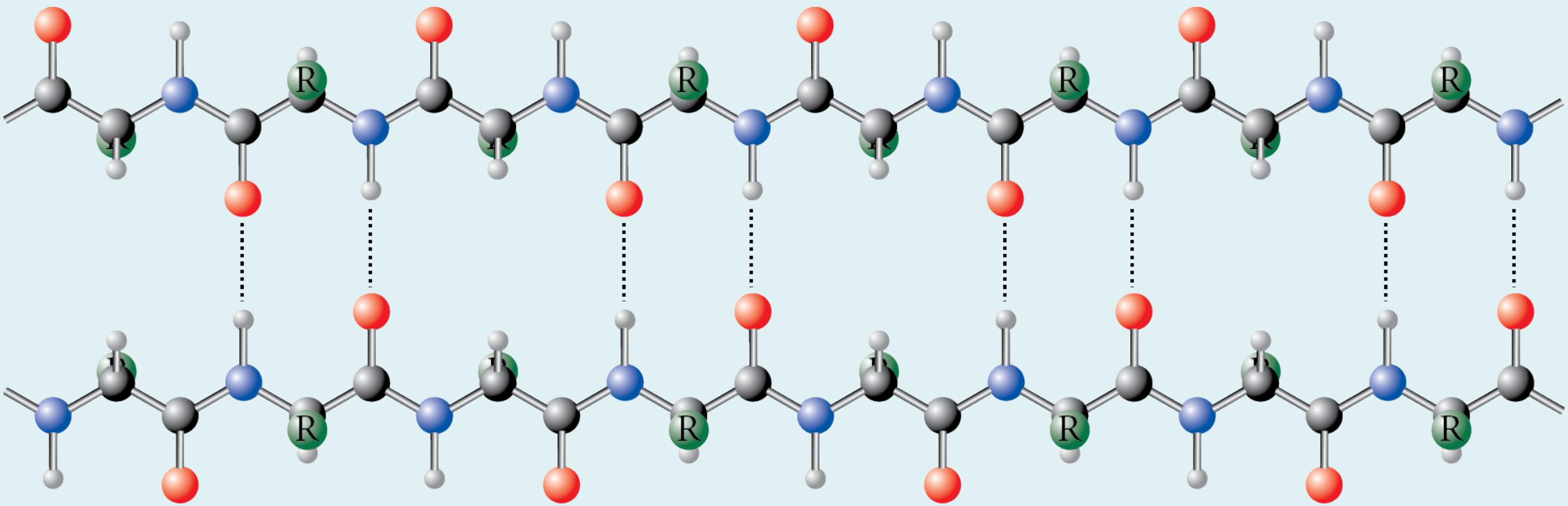
This ribbon model shows the general arrangement of atoms in a portion of the α-helical secondary structure of a protein molecule.



The two models superimposed



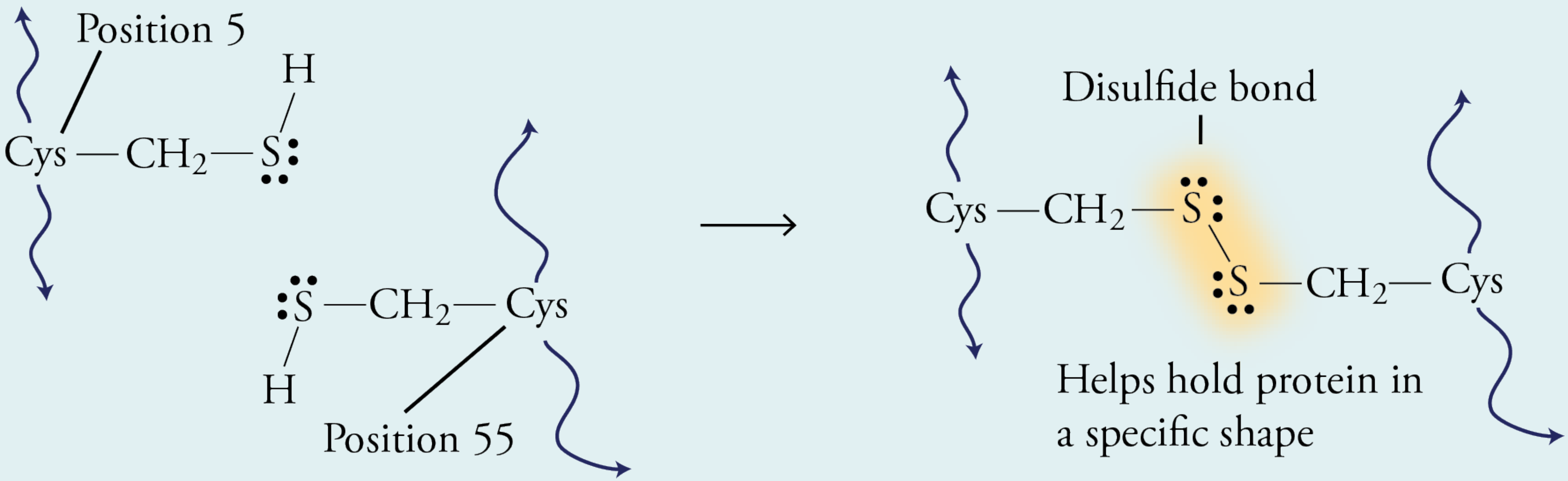
β-Sheet Secondary Structure



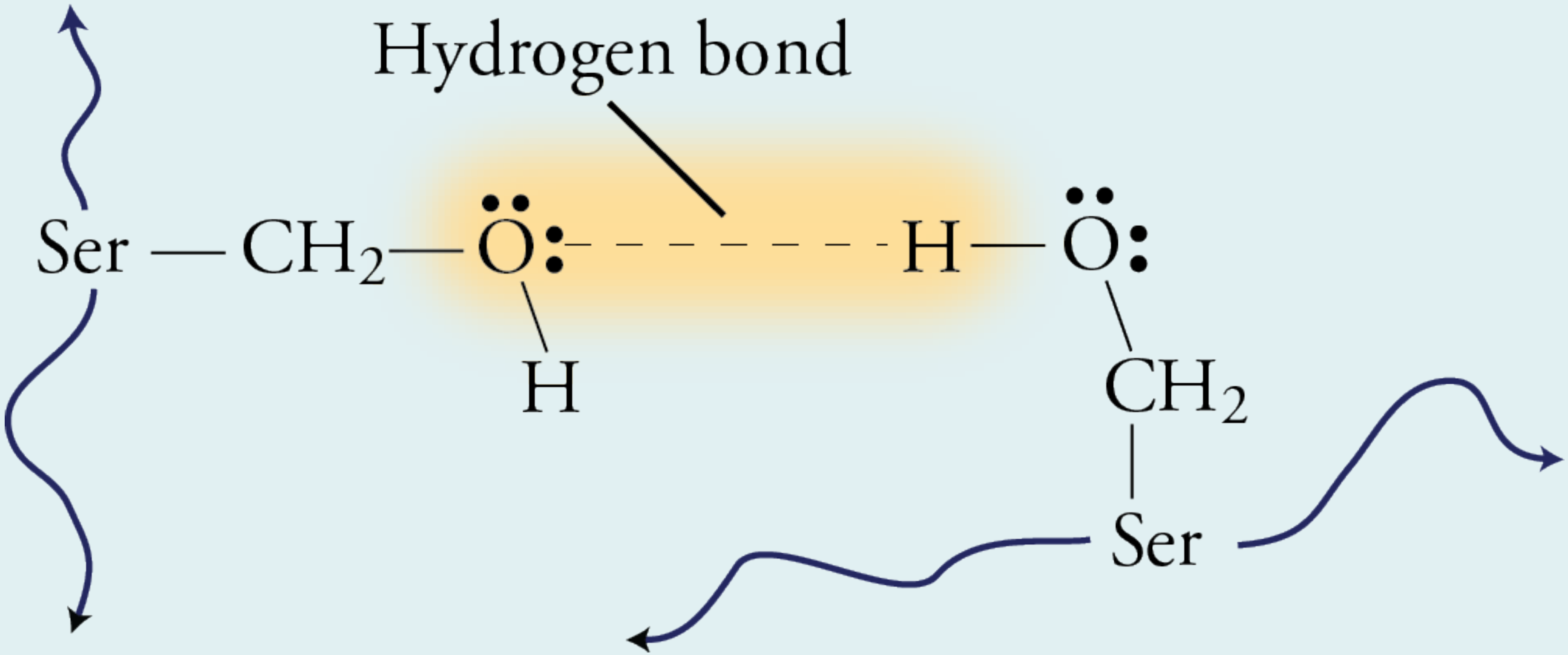
Tertiary Protein Structure

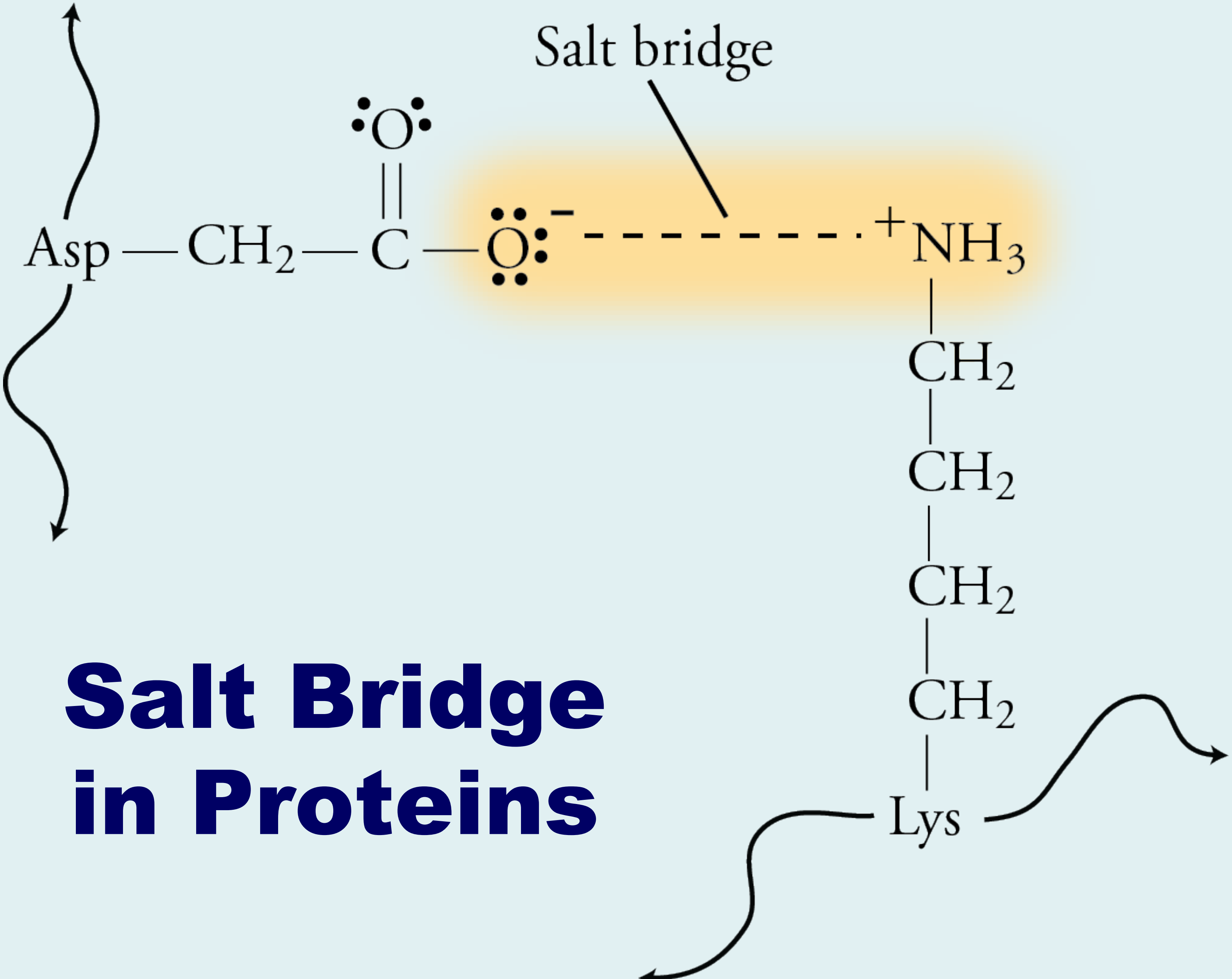
- The very specific overall shape of the protein called its ***tertiary structure***.
- The protein chain is held in its tertiary structure by interactions between the side chains of its amino acids.
  - Disulfide bonds
  - Hydrogen bonds
  - Salt bridges

Disulfide Bonds in Proteins



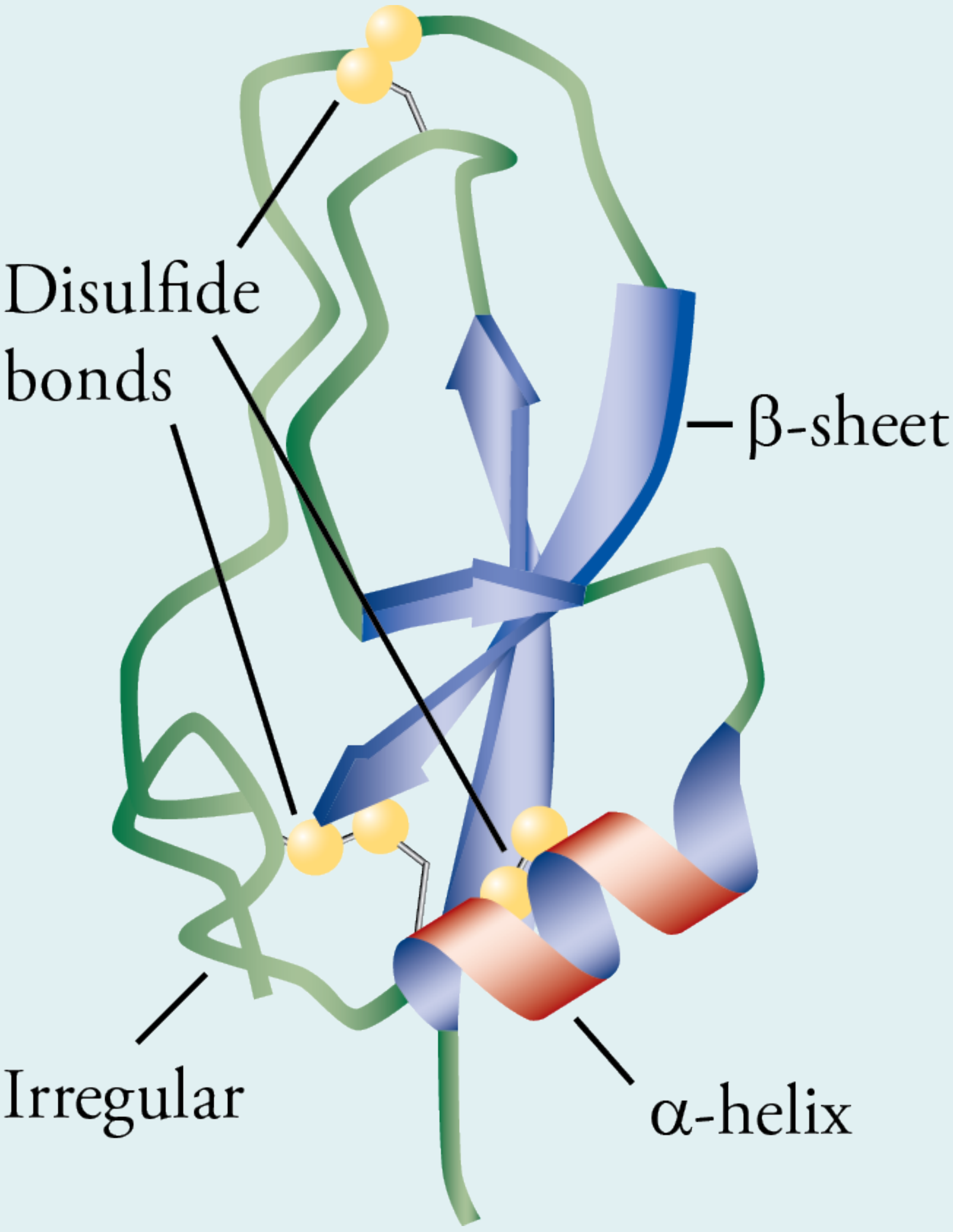
Hydrogen Bonding in Proteins



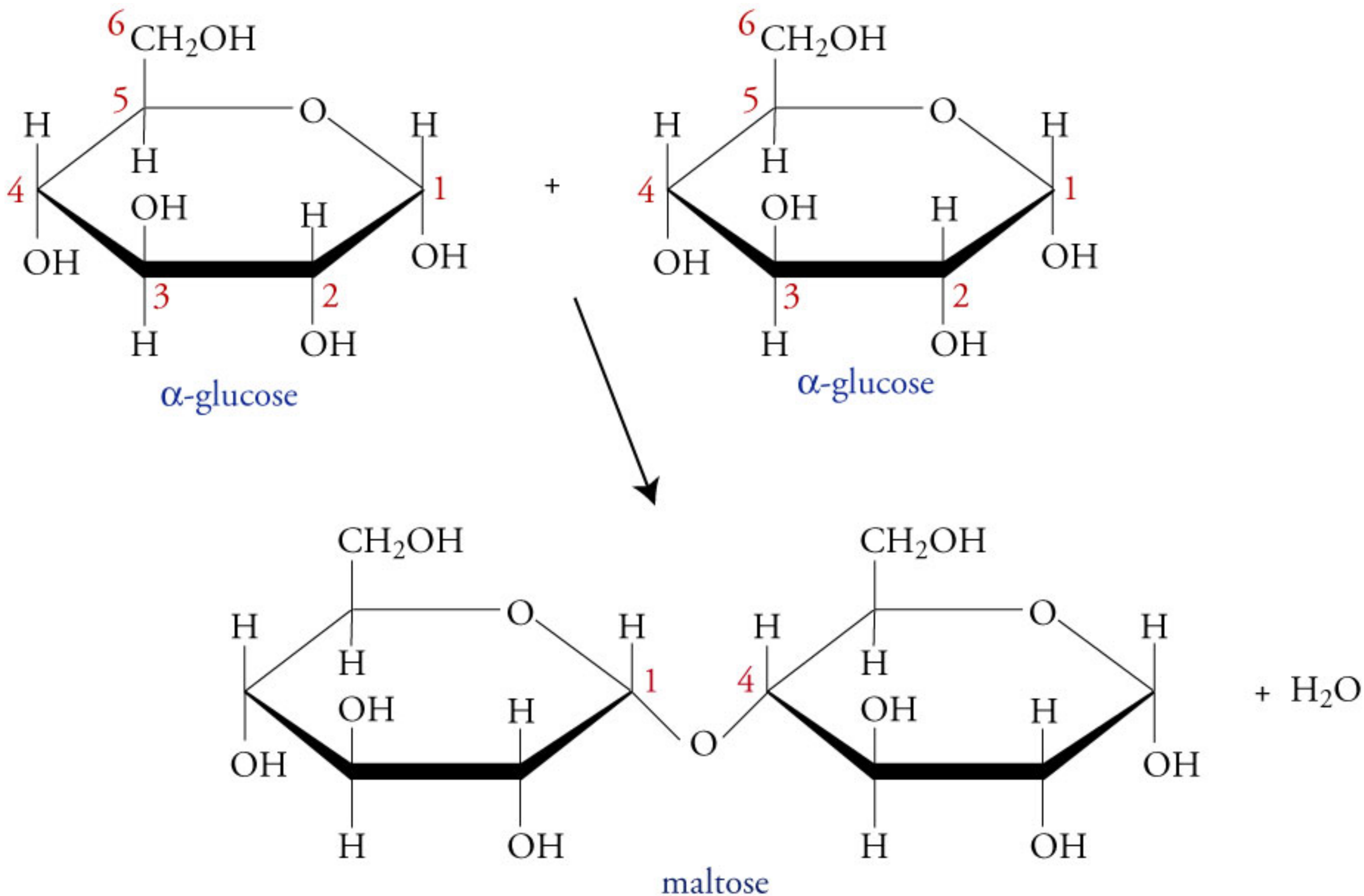


Salt Bridge in Proteins

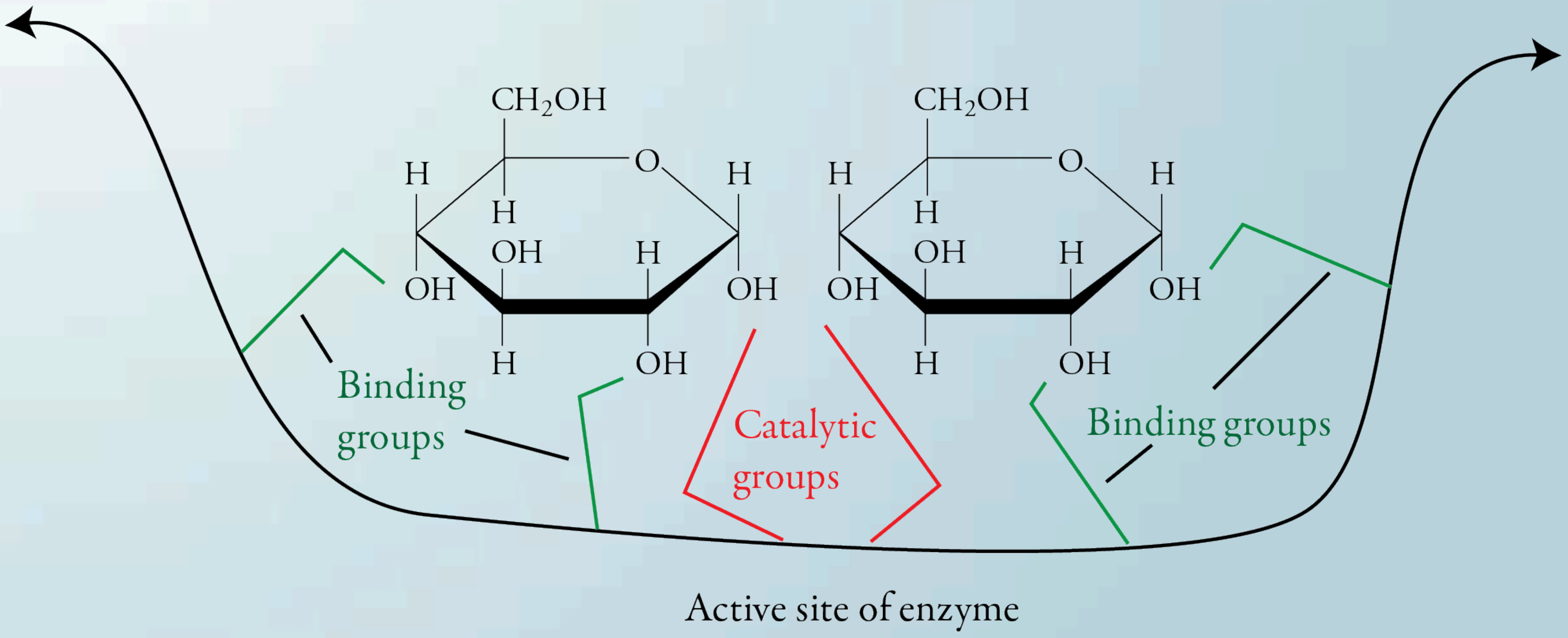
The Ribbon Structure of the Protein BPTI



The Formation of Maltose

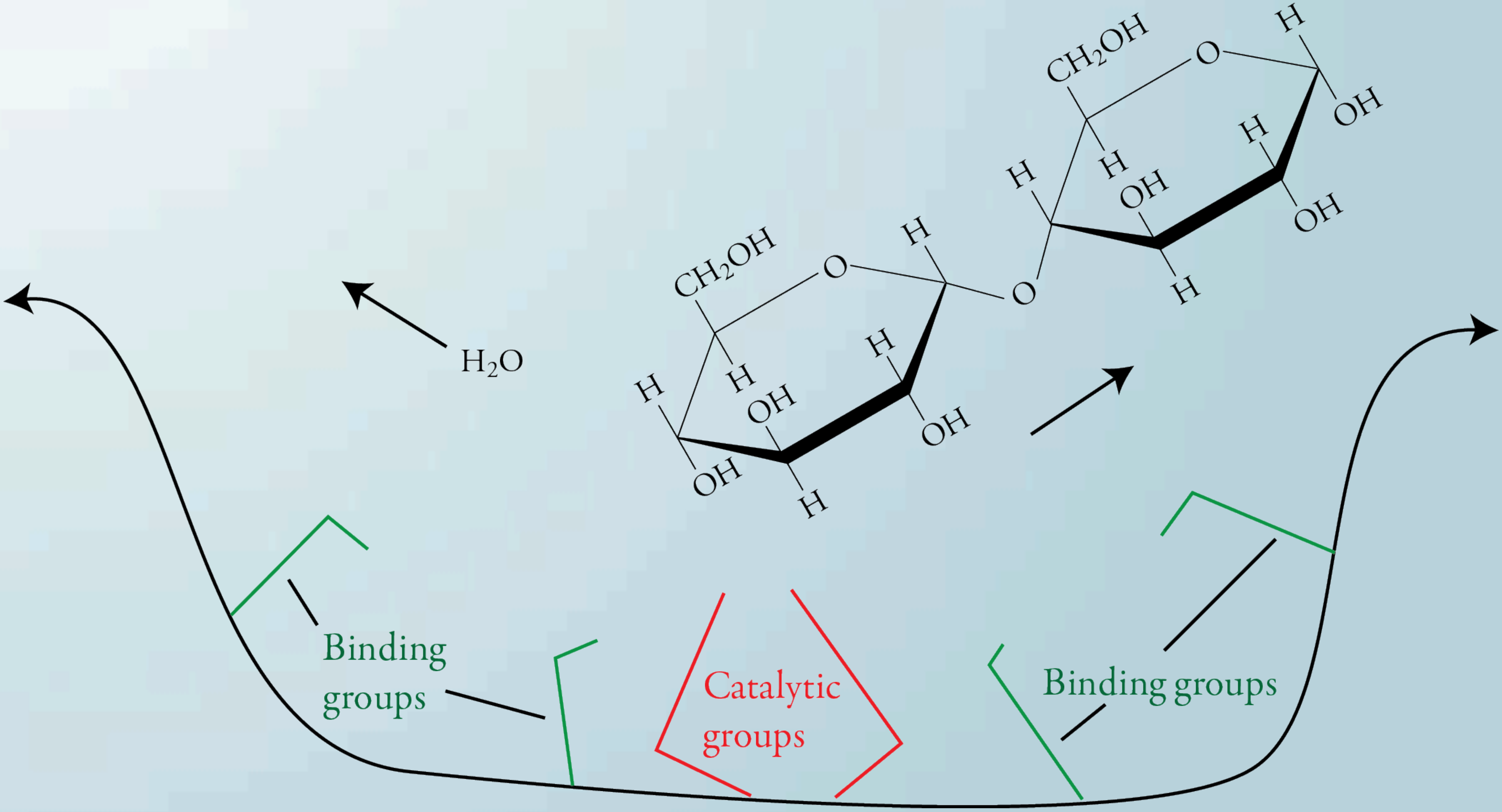


Maltose



CH2OH
O
H
H
OH
H
OH
OH
H
OH
CH2OH
O
H
H
OH
H
OH
OH
H
OH
Binding groups
Catalytic groups
Binding groups
Active site of enzyme

Maltose



CH_2OH
O
H
OH
H
H
OH
H
OH
H
O
CH_2OH
O
H
H
H
OH
H
OH
OH
H
H_2O
Binding groups
Catalytic groups
Binding groups

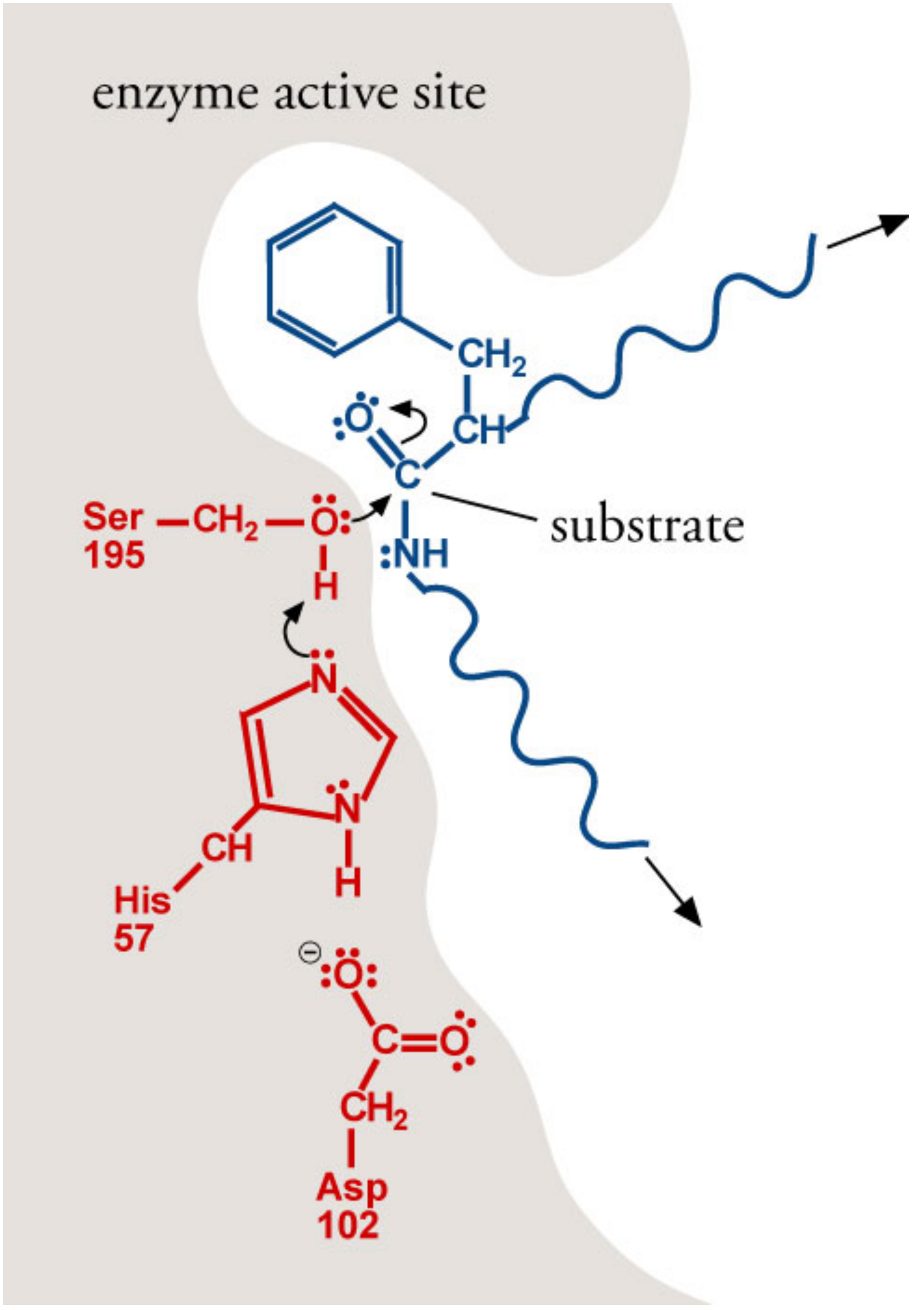
Enzymes

- Enzymes are naturally occurring catalysts. ***Catalysts*** speed chemical changes without being permanently altered themselves.
- The chemicals that they act on are called ***substrates***.
- Very specific due to
  - Shape – “Lock and Key”
  - Positions of binding groups, which attract substrates to the active site, the portion of the enzyme where the reaction occurs.
  - Positions of the catalytic groups that speed the reaction.

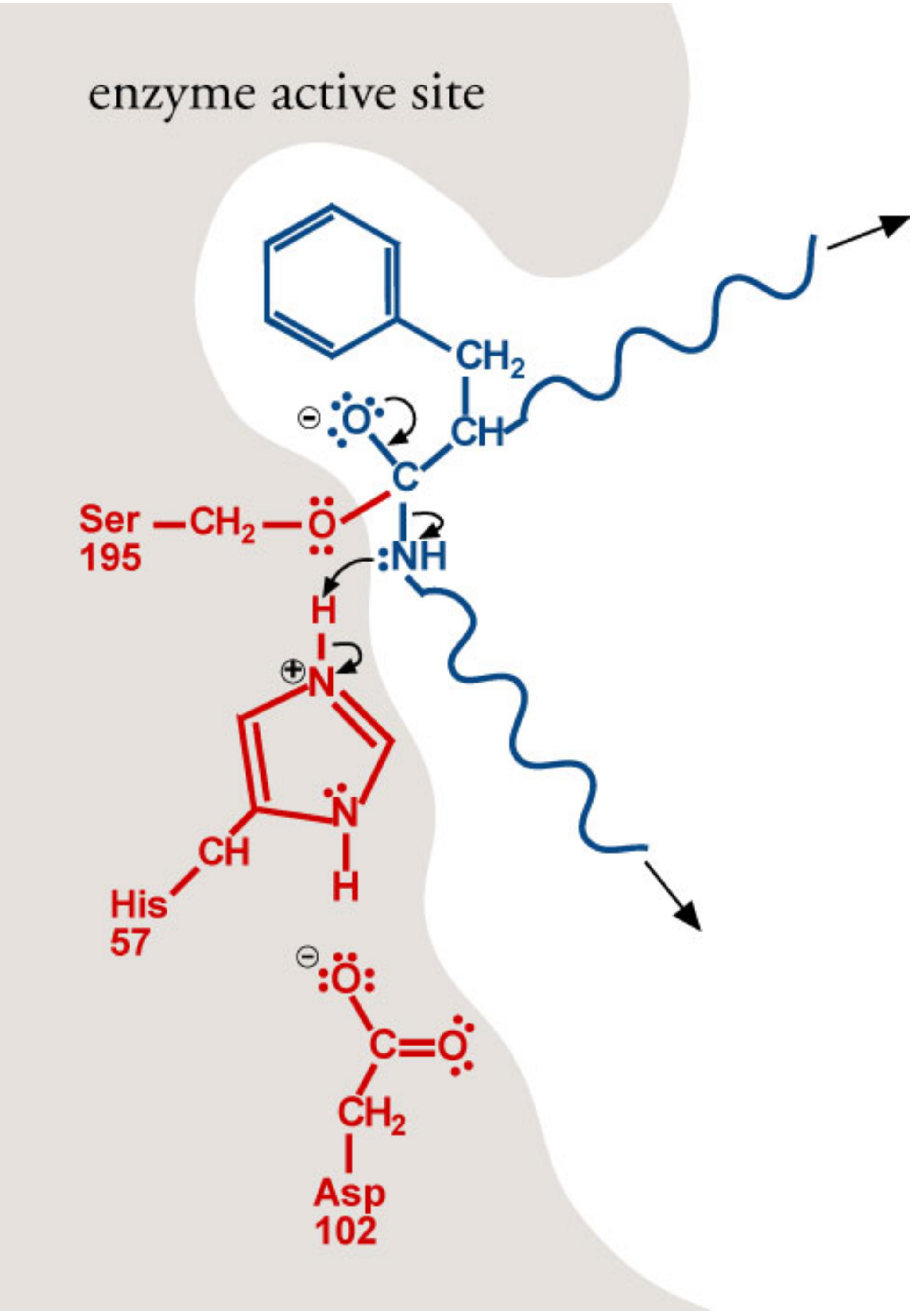
Enzymes Speed Chemical Reactions

- Provide a different path to products that has more stable intermediates and therefore requires less energy.
- Give the correct orientation every time.

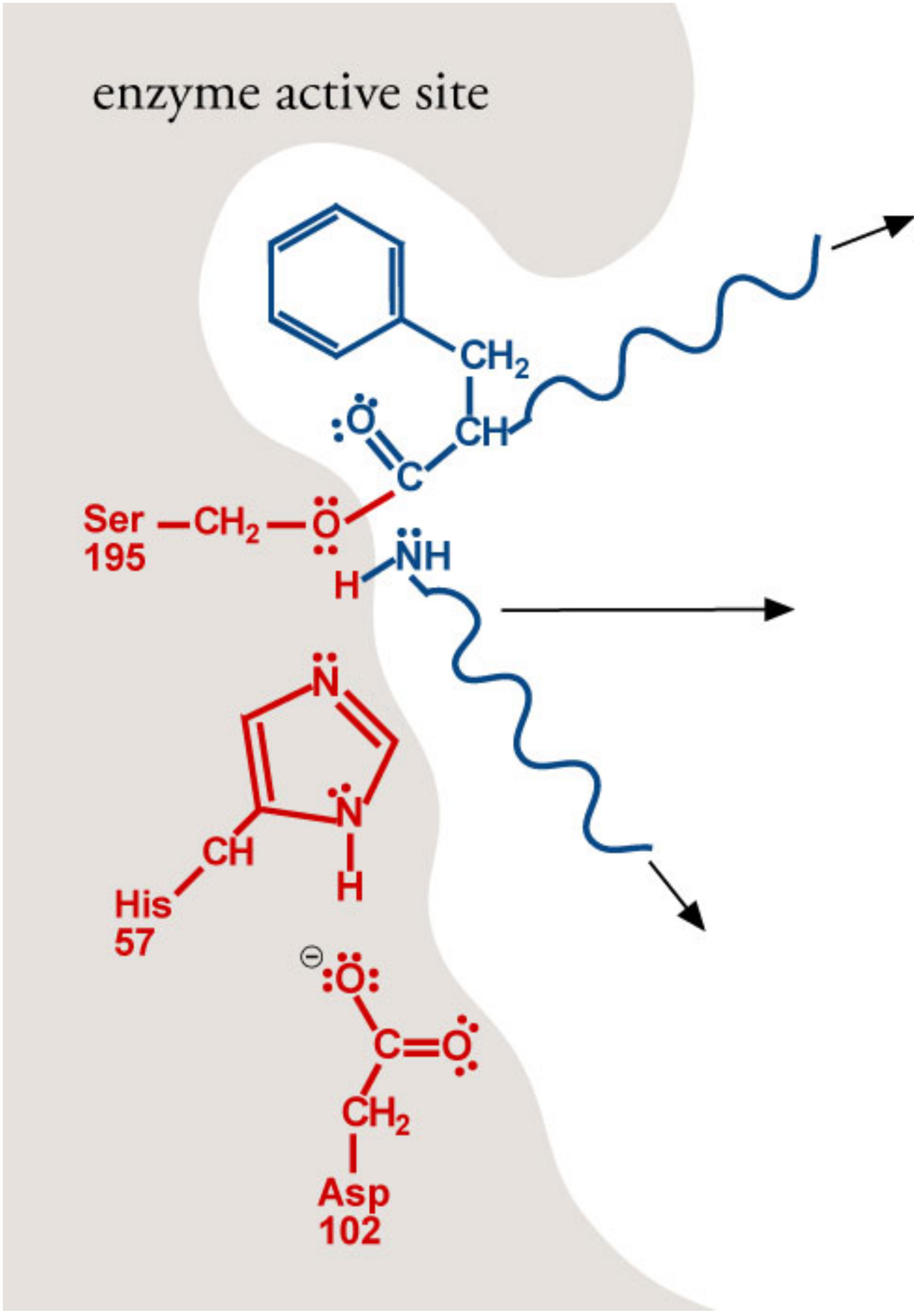
Chymotrypsin - Step 1



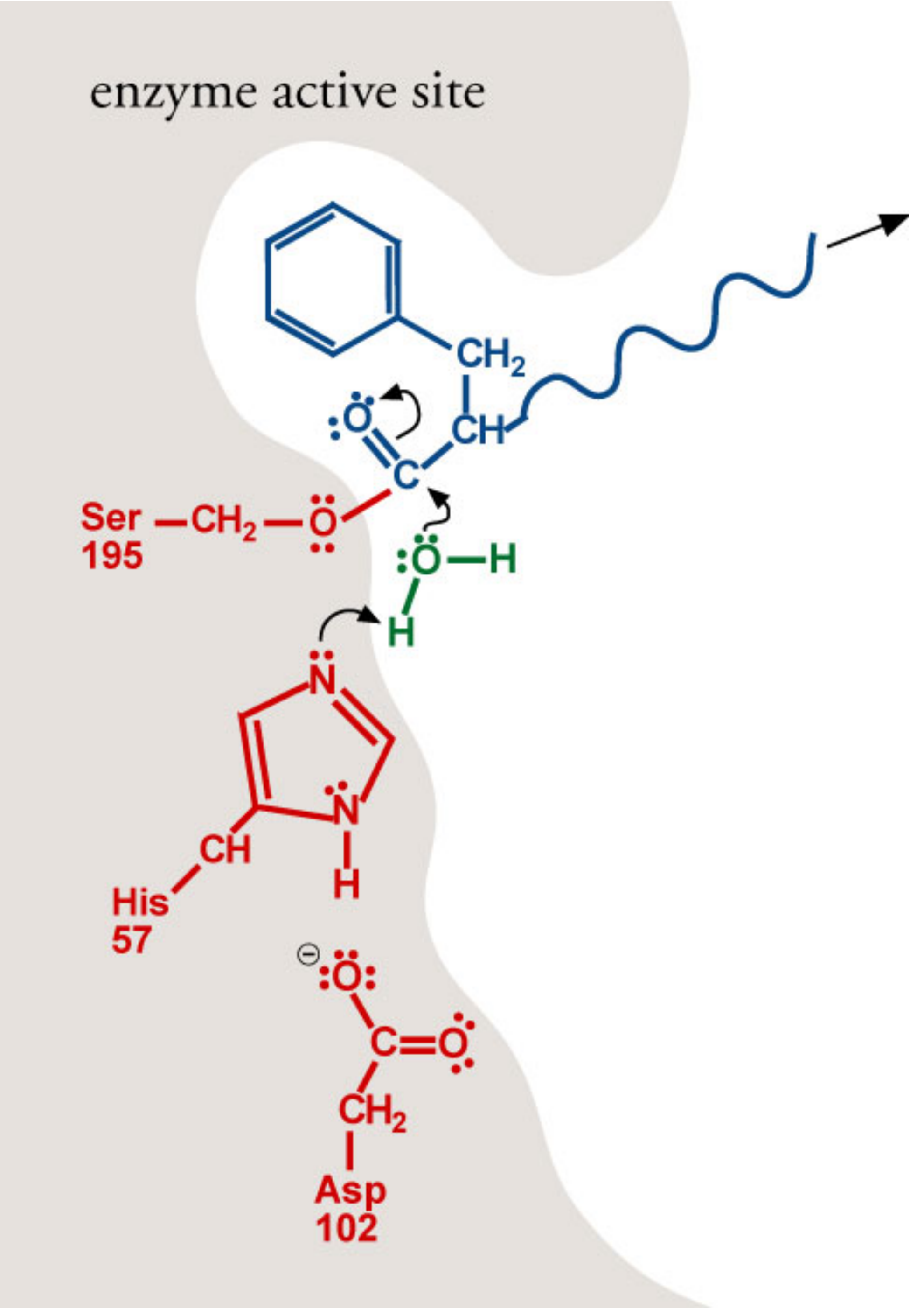
Chymotrypsin - Step 2



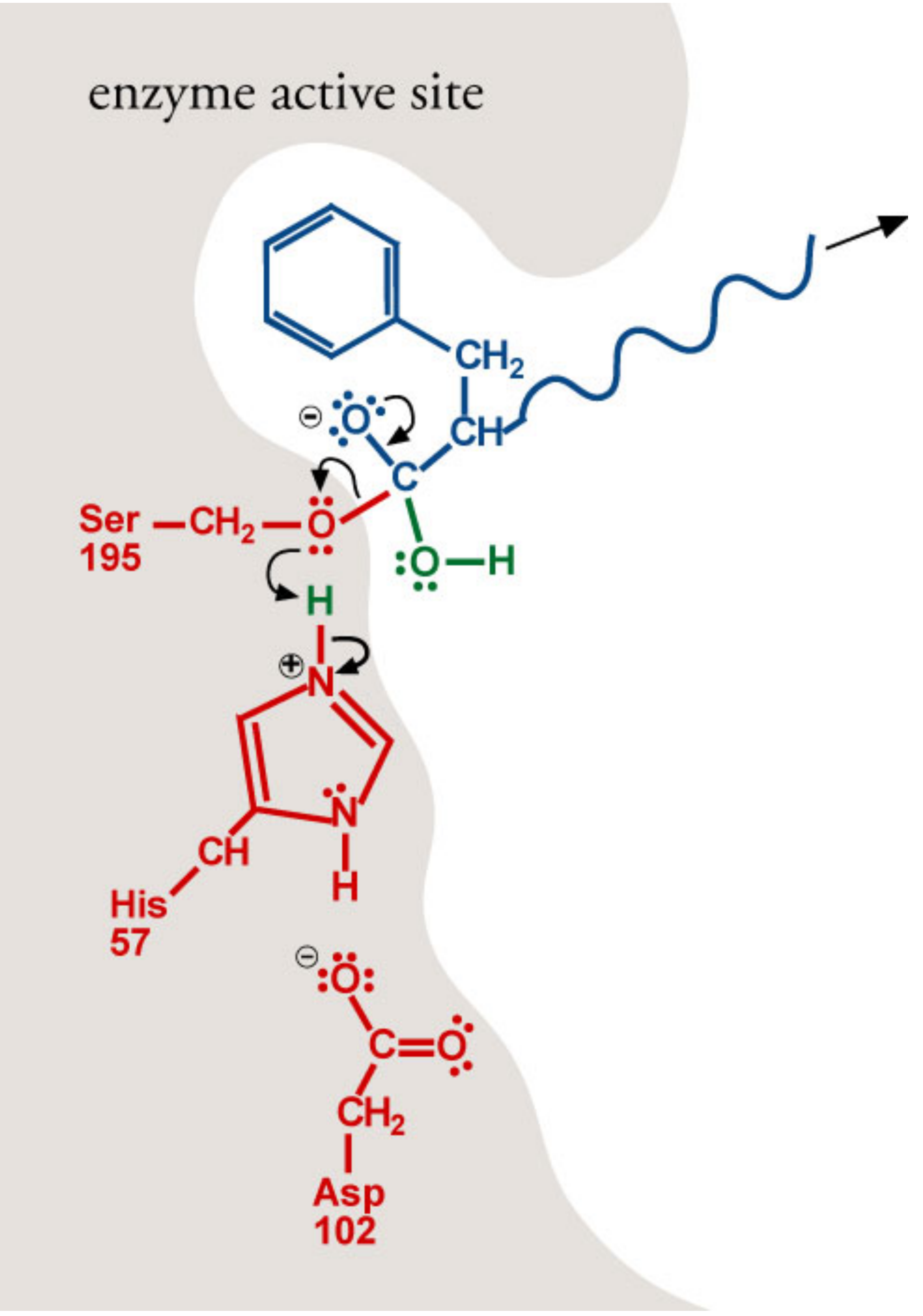
Chymotrypsin - Step 3



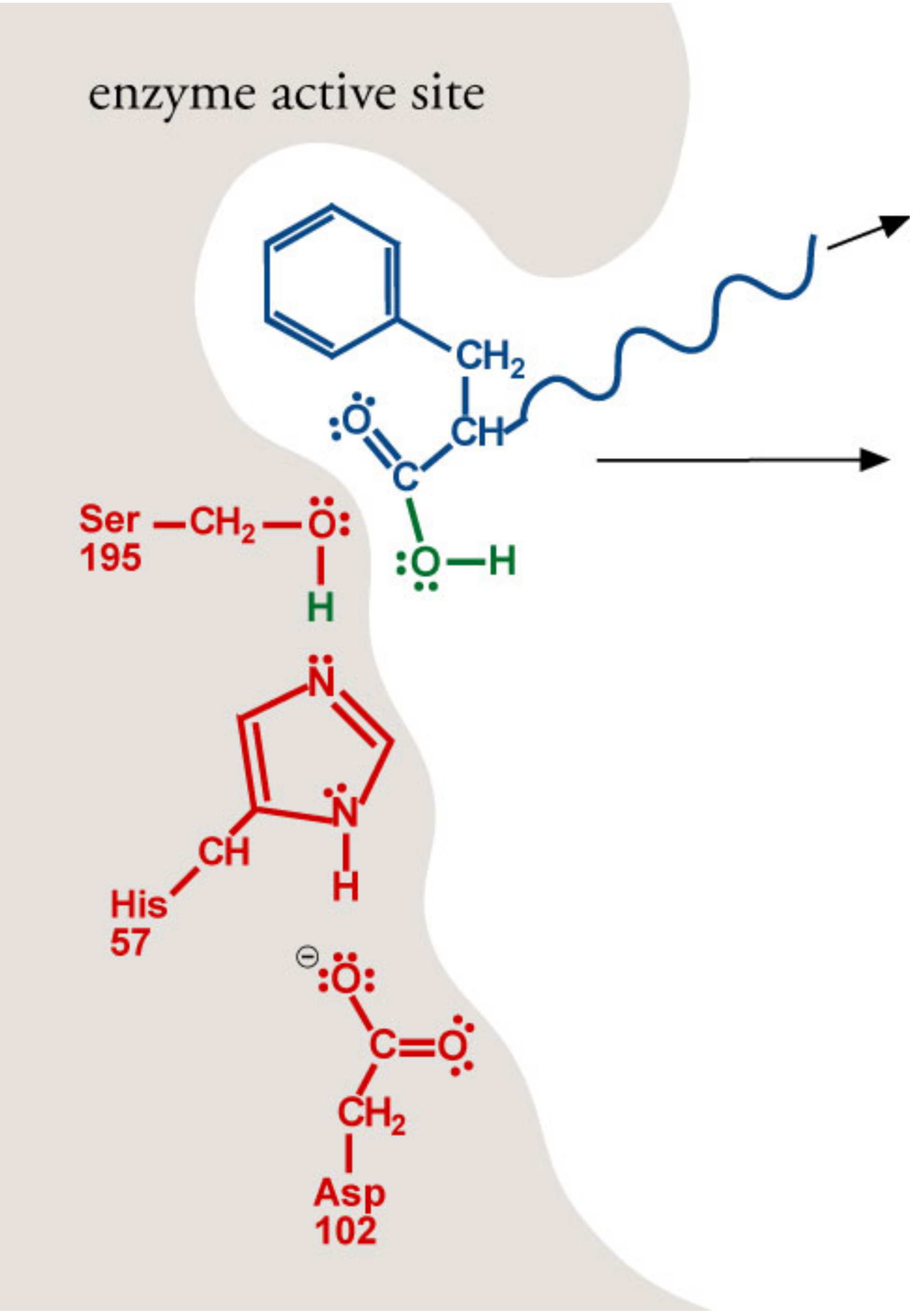
Chymotrypsin - Step 4



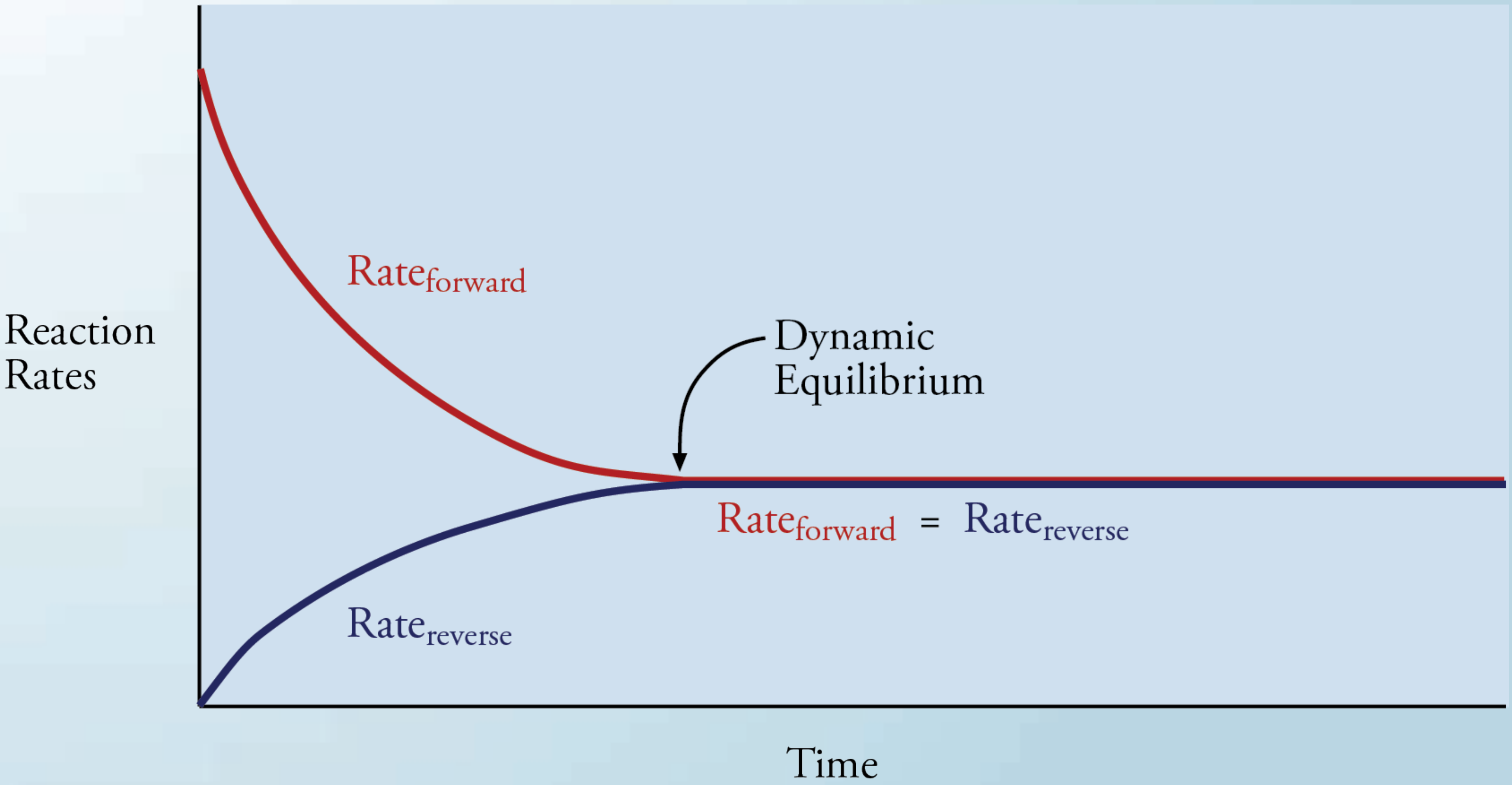
Chymotrypsin - Step 5



Chymotrypsin - Step 6

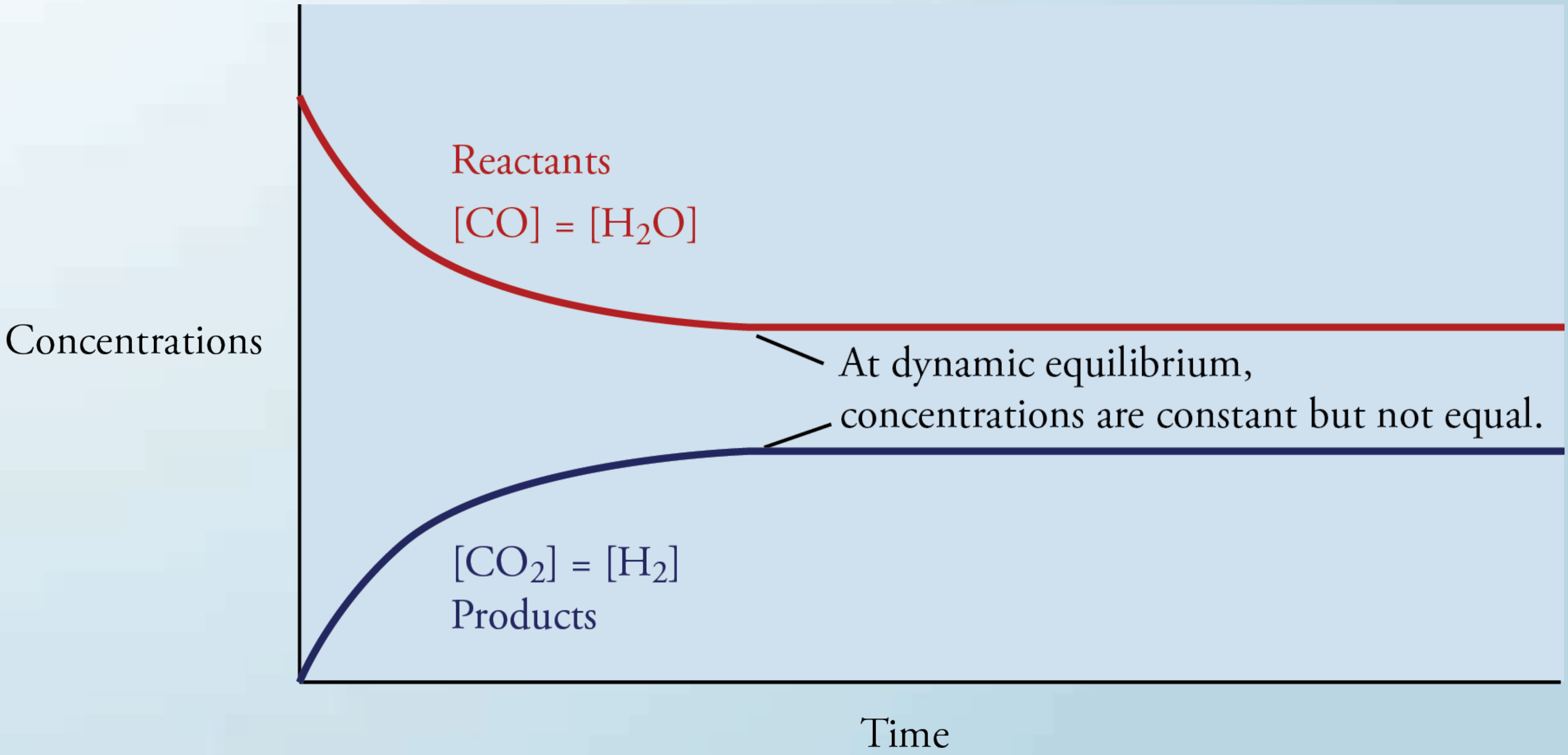


Rates of Reaction for Reversible Reactions



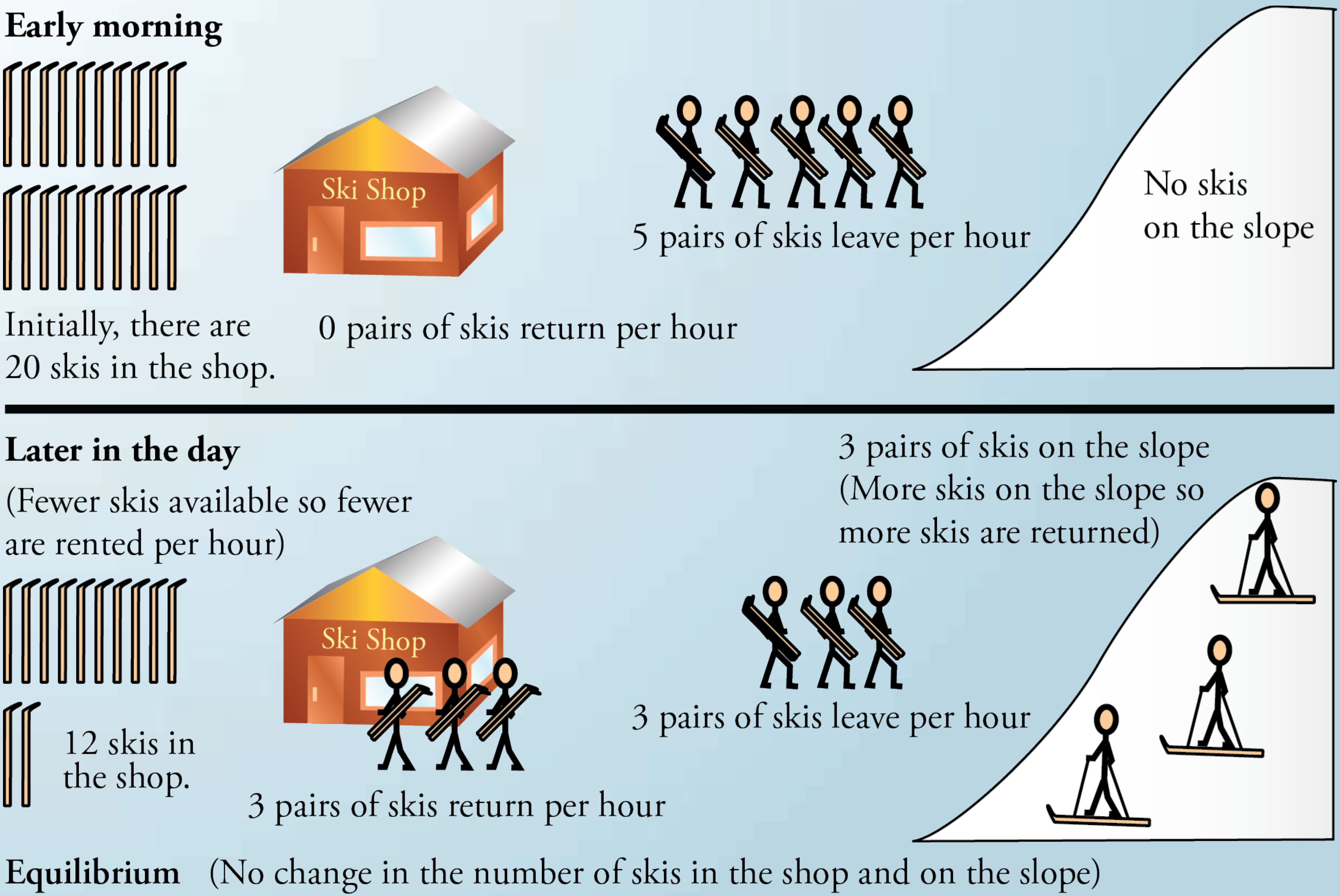
$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Changes in Concentrations for a Reversible Reaction



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

Ski Shop Analogy for Equilibrium



Equilibrium Constant

$$aA + bB + \ldots \rightleftharpoons eE + fF + \ldots$$

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

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

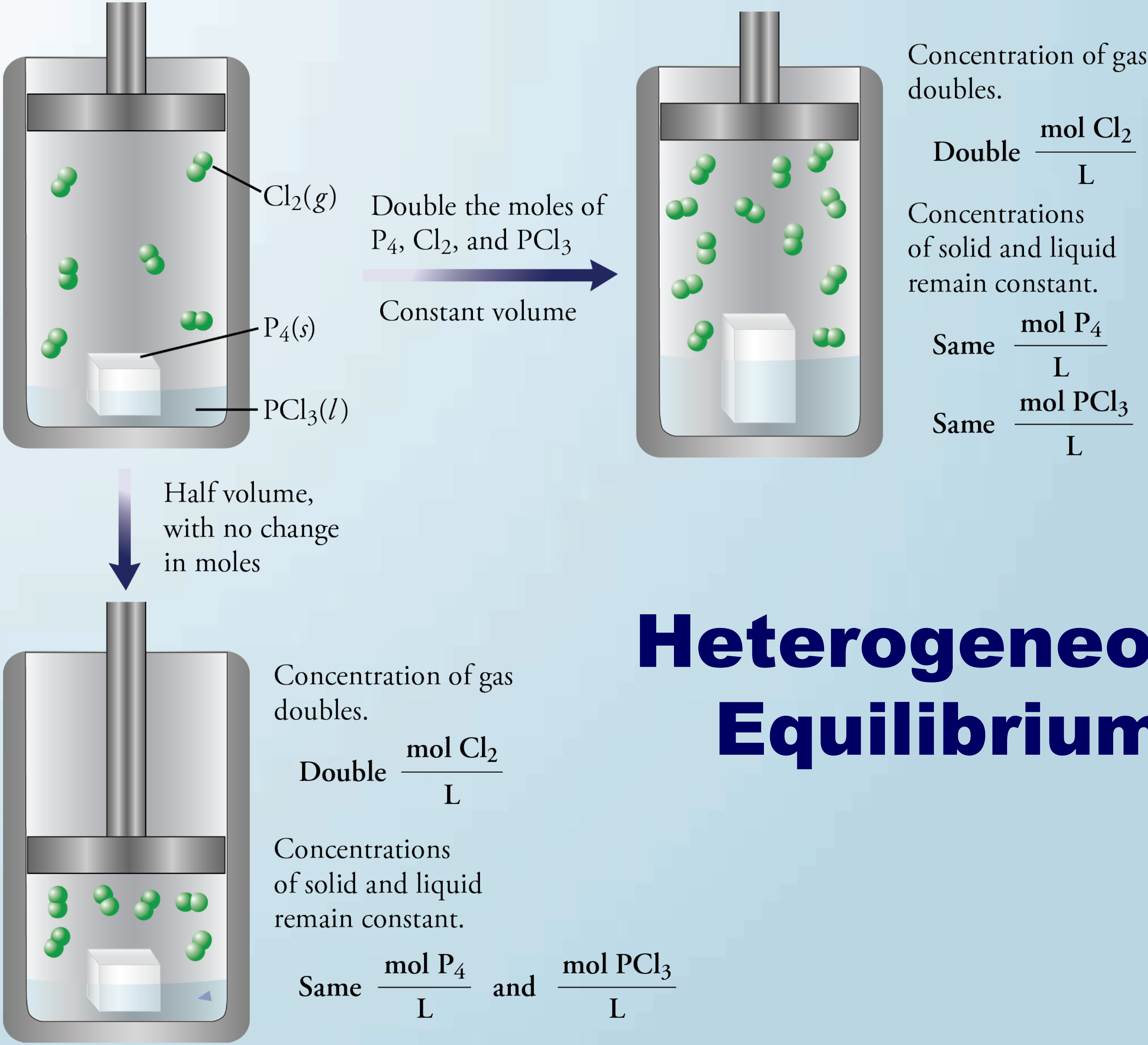
Equilibrium Constant Expression

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

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



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

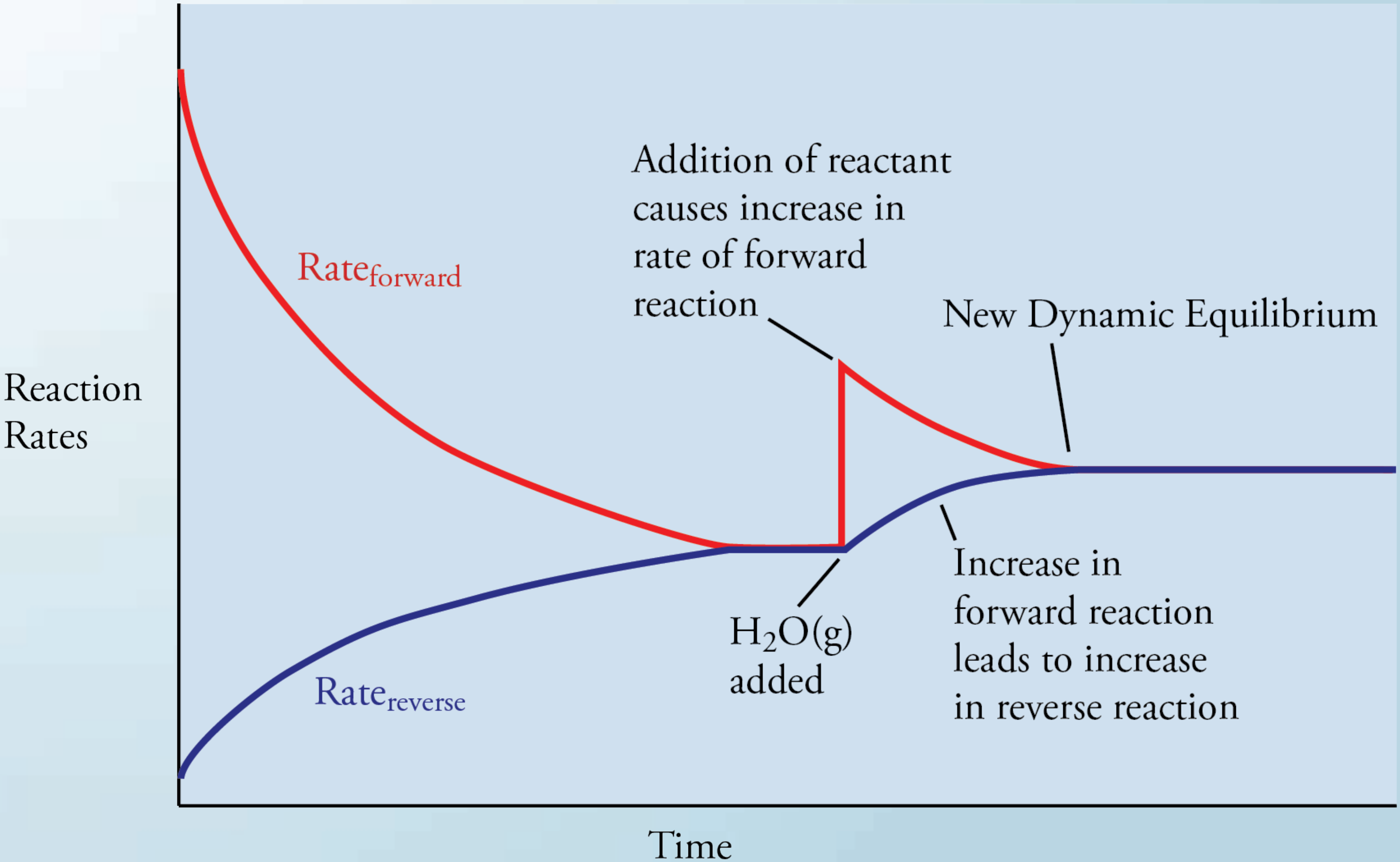
$K > 10^2$	Products favored at equilibrium
$K < 10^{-2}$	Reactants favored at equilibrium
$10^{-2} < K < 10^2$	Neither reactants nor products favored

Effect of Increased Concentration on Equilibrium

$$\boxed{\text{Increased concentration of reactant for a system at equilibrium with } Rate_{forward} = Rate_{reverse}}$$
$$\downarrow$$
$$\text{Increased } Rate_{forward}$$
$$\downarrow$$
$$Rate_{forward} > Rate_{reverse}$$
$$\downarrow$$
$$\boxed{\text{System shifts toward products}}$$

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

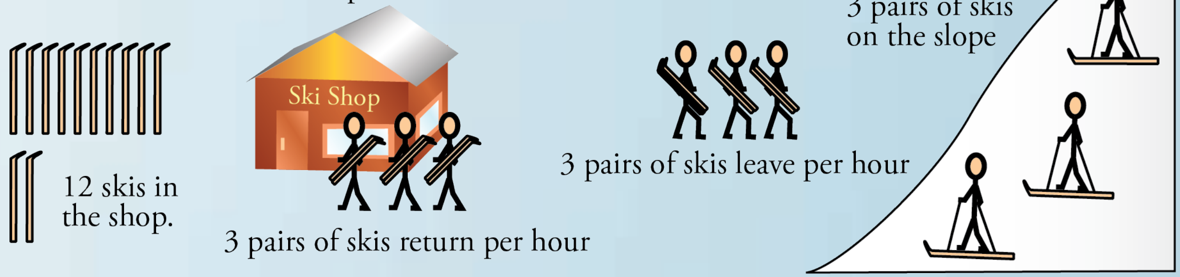
Change in Rates When Reactant Added



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

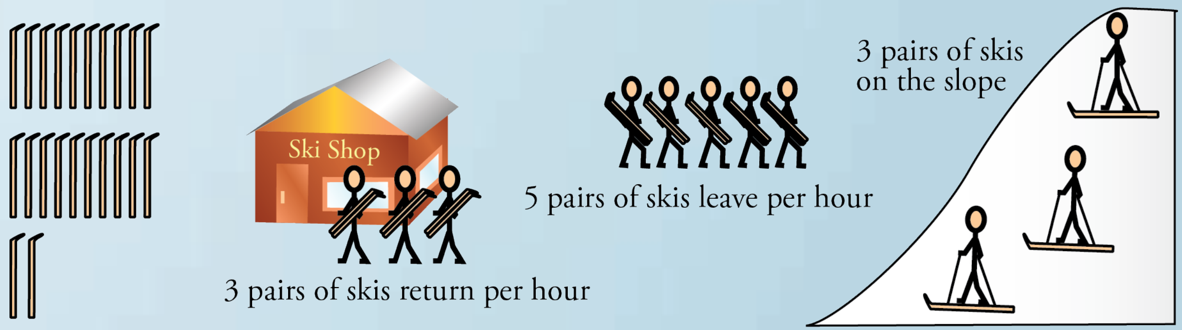
Ski Shop Analogy 2

Before buying more skis
There are 12 skis in the shop.



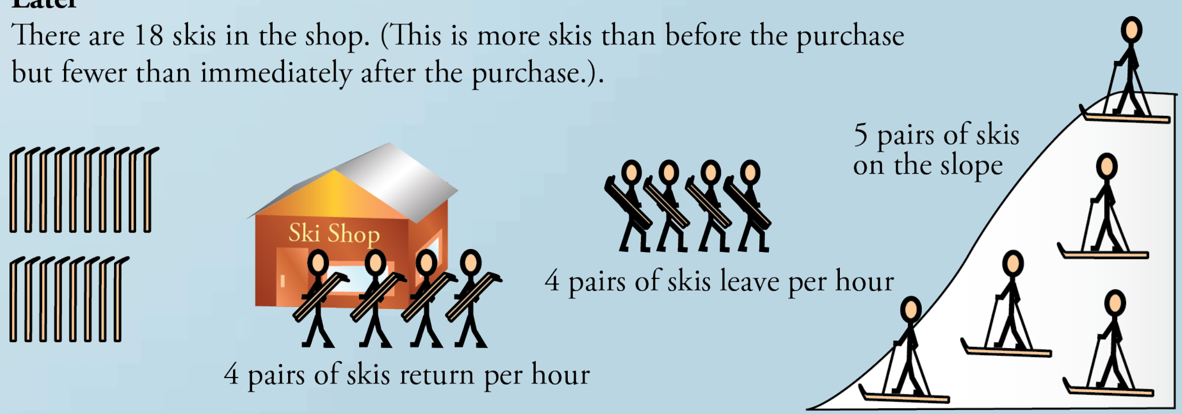
Equilibrium (No change in the number of skis in the shop and on the slope)

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



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.).



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

$\downarrow$

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

$\downarrow$

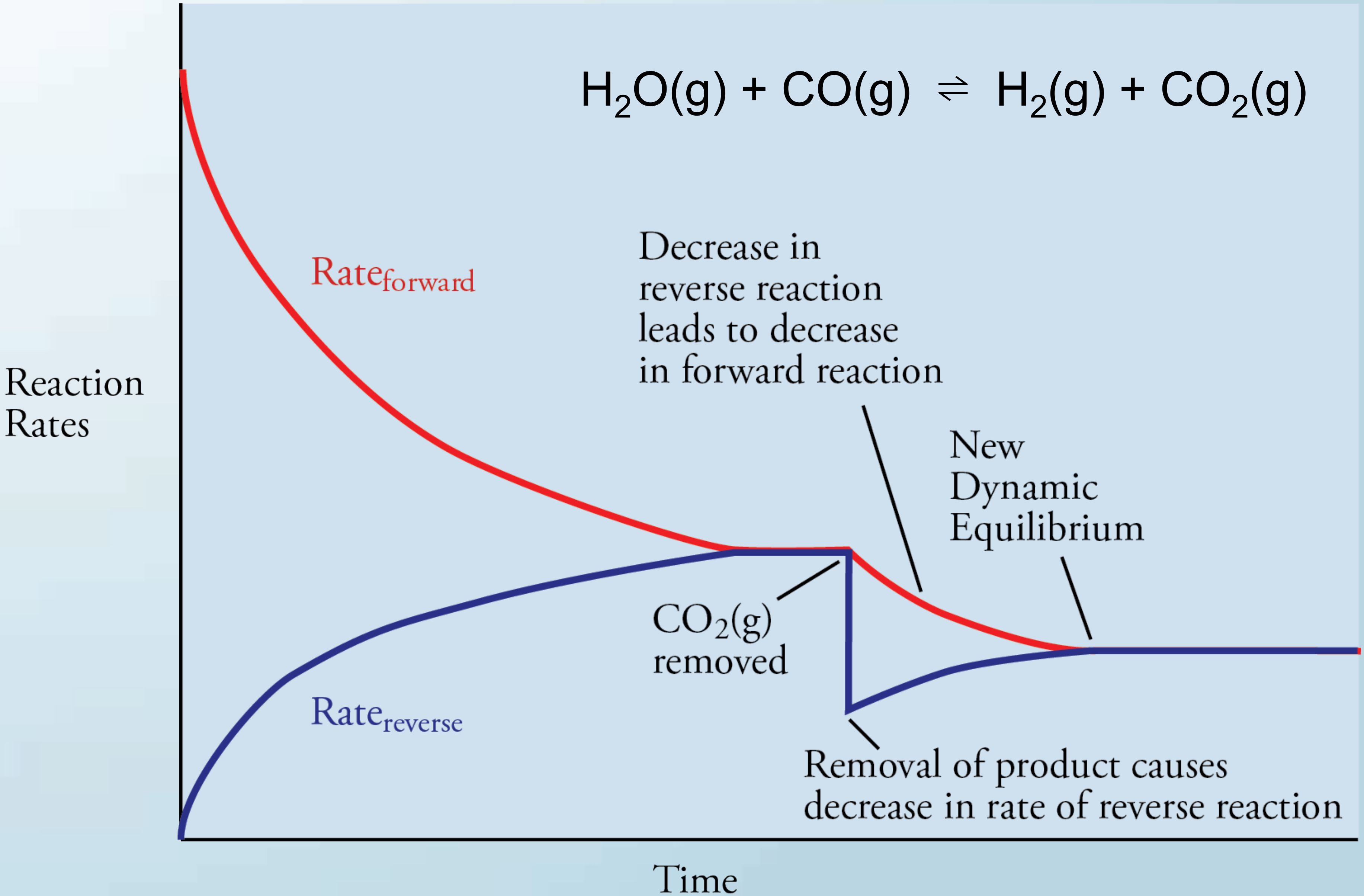
$\text{Rate}_{\text{forward}} > \text{Rate}_{\text{reverse}}$

$\downarrow$

System shifts toward products

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

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.