

Organic Chemistry, *Fourth Edition*

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Chapter 6 Understanding Organic Reactions

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Organic Reactions

- 6.1 Writing equations for organic reactions
- 6.2 Kinds of organic reactions
- 6.3 Bond breaking and bond making
- 6.4 Bond dissociation energy
- 6.5 Thermodynamics
- 6.6 Enthalpy and entropy
- 6.7 Energy diagrams
- 6.8 Energy diagram for a two-step reaction mechanism
- 6.9 Kinetics
- 6.10 Catalysts

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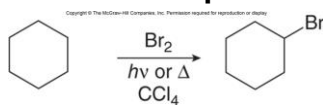
Organic Reactions

- **Reactions** are at the heart of Organic Chemistry.
- Virtually all chemical reactions are woven together by a few basic themes.
 - Begin by looking for **electron-rich** or **deficient** sites at functional groups in the reacting molecules.
 - These are often the location of bonds that might be **easily broken**.
- Learn about how reaction takes place (i.e., does it occur in one step or in a series of steps).

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Writing Equations for Organic Reactions

- Equations for organic reactions are usually drawn with a **single reaction arrow** ($\rightarrow$) between the starting material and product.
- The **reagent** (the chemical substance with which an organic compound reacts) is sometimes drawn on the left side of the equation with the other reactants.
- At other times, the reagent is drawn above the arrow.
- Although the **solvent** is often omitted from the equation, most organic reactions take place in liquid solvent.



CCl₄ is the solvent.

hν—Indicates light is needed.

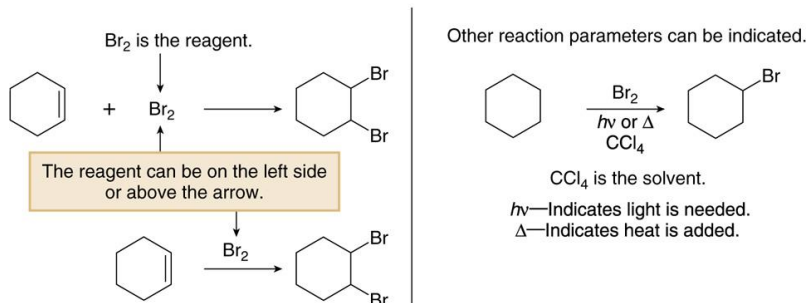
Δ—Indicates heat is added.

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Ways to Write Organic Reactions

Figure 6.1

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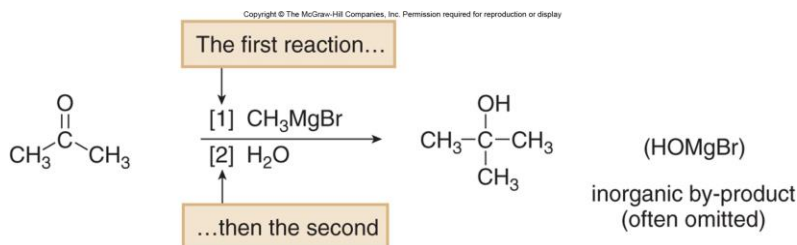


- The **solvent and temperature** of the reaction may be added above or below the arrow.
- The symbols “ $h\nu$ ” and “ Δ ” are used for reactions that require light or heat, respectively.

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Writing Equations for Sequential Reactions

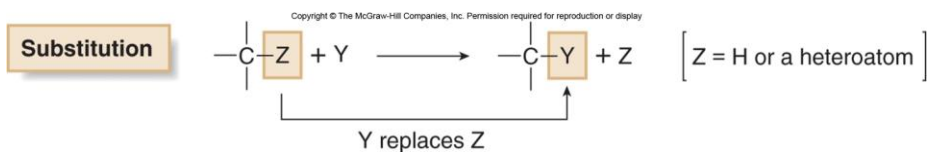
- The steps are numbered **above or below** the reaction arrow.
- This convention signifies that the **first step occurs before** the second step, and the reagents are added in sequence, not at the same time.



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1. Substitution Reactions

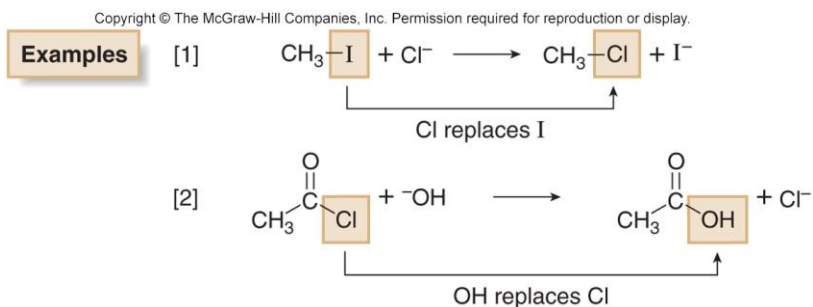
- **Substitution** is a reaction in which an atom or a group of atoms is **replaced** by another atom or group of atoms.
- In a general substitution, Y replaces Z on a carbon atom.



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Substitution Reactions

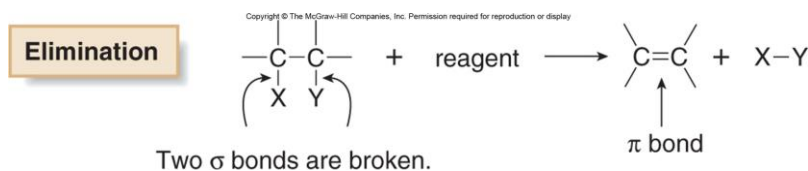
- Substitution reactions involve **σ bonds**: one σ bond breaks and another forms at the same carbon atom.
- While in some cases Z can be a hydrogen atom, the most common examples of substitution occur when **Z** is a heteroatom that is **more electronegative** than carbon.



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2. Elimination Reactions

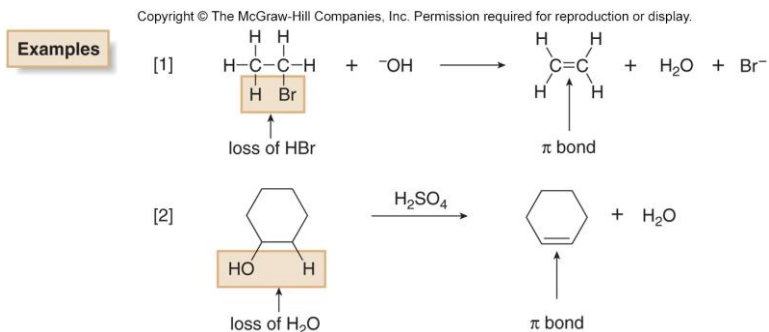
- **Elimination** is a reaction in which elements of the starting material are “lost” and a **π bond is formed**.



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Elimination Reactions

- In an elimination reaction, two groups **X and Y** are removed from a starting material.
- **Two σ bonds** are broken, and a **π bond** is formed between adjacent atoms.
- The most common examples of elimination occur when **X = H** and **Y is a heteroatom** more electronegative than carbon.



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3. Addition Reactions

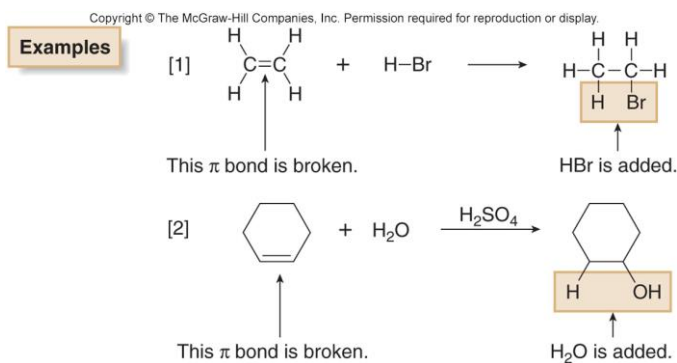
- **Addition** is a reaction in which elements are added to the starting material.



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Addition Reactions

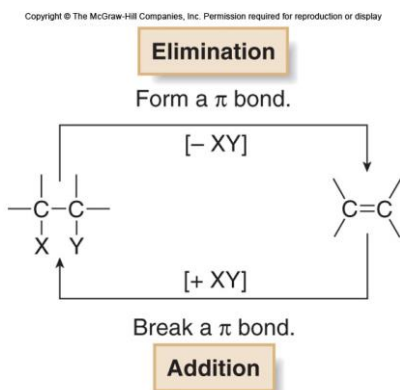
- In an addition reaction, new groups **X and Y** are added to the starting material.
- A **π bond is broken** and two σ bonds are formed.



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Relationship of Addition and Elimination Reactions

- Addition and elimination reactions are **exactly opposite**.
- A π bond is formed in elimination reactions, whereas a π bond is broken in addition reactions.
- Often these reactions are **reversible**.



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Reaction Mechanisms

- A **reaction mechanism** is a detailed **description** of how **bonds are broken and formed** as starting material is converted into product.
- A reaction can occur either in one step or a series of steps.

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- A **one-step reaction** is called a **concerted reaction**. No matter how many bonds are broken or formed, a starting material is converted *directly* to a product.



- A **stepwise reaction** involves more than one step. A starting material is first converted to an unstable intermediate, called a **reactive intermediate**, which then goes on to form the product.



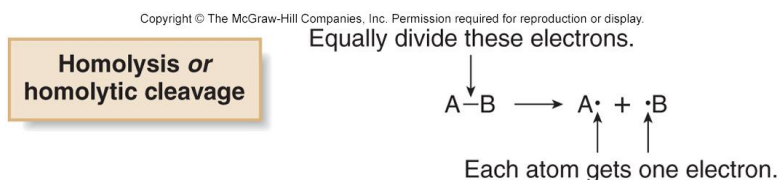
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Bond Breaking

1. Homolytic

Regardless of how many steps there are in a reaction, there are only two ways to break (cleave) a bond:

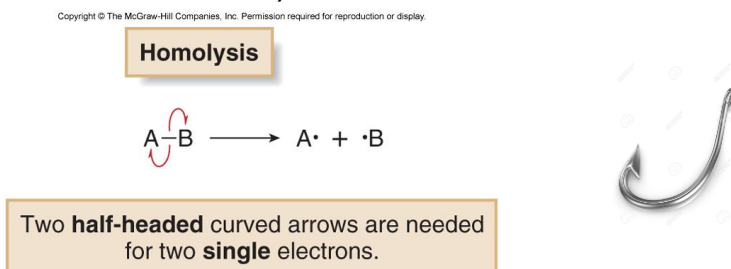
- Breaking a bond by **equally dividing** the electrons between the two atoms in the bond is called homolysis or homolytic cleavage.



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Bond Breaking-Homolytic

- To illustrate the movement of a single electron, use a **half-headed curved arrow**, sometimes called a fishhook.



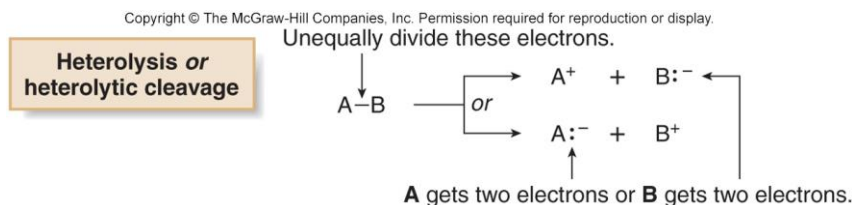
- Homolysis generates two **uncharged species** with unpaired electrons.
- A reactive intermediate with a single unpaired electron is called a **radical**.
- Radicals are **highly unstable** because they contain an atom that does not have an octet of electrons.

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Bond Breaking

2. Heterolytic

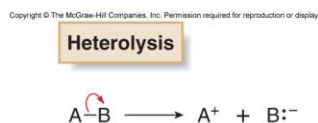
- Breaking a bond by **unequally dividing** the electrons between the two atoms in the bond is called **heterolysis or heterolytic cleavage**.
- When two atoms have different electronegativities, the **electrons end up on the more electronegative atom**.



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Bond Breaking-Heterolytic

- A **full-headed curved** arrow shows the movement of an electron pair.



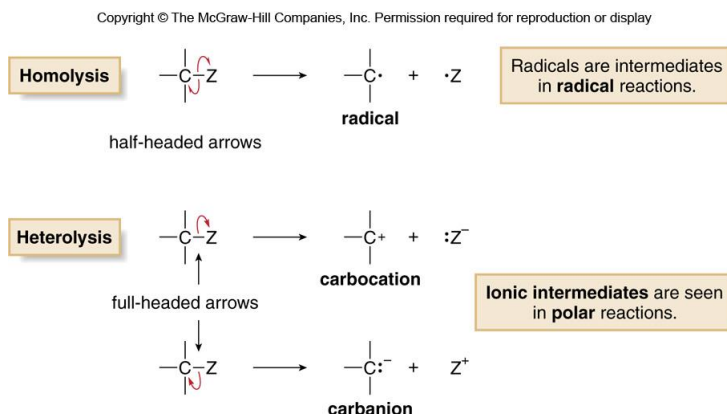
One **full-headed** curved arrow is needed for one electron **pair**.

- Heterolysis of a C—Z bond generates a **carbocation** or a **carbanion**.
- A **carbocation** is an unstable intermediate containing a carbon surrounded by only six electrons.
- A **carbanion** is an unstable intermediate having a negative charge on carbon, which is not a very electronegative atom.

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Reactive Intermediates Resulting from Breaking a C-Z Bond

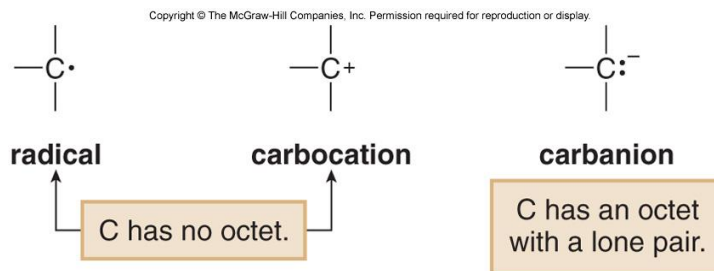
Figure 6.2



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Bond Breaking-Intermediates

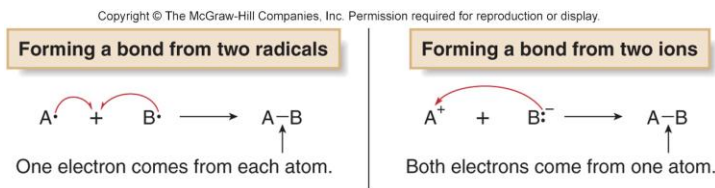
- Radicals and carbocations are **electrophiles** because they contain an electron-deficient carbon.
- Carbanions are **nucleophiles** because they contain a carbon with a lone pair.



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Bond Forming

- Bond formation occurs in two different ways.
 - Two radicals** can each donate one electron to form a two-electron bond.
 - Two ions** with unlike charges can come together, with the negatively charged ion donating both electrons to form the resulting two-electron bond.
- Bond formation always releases energy.**



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Arrows Used in Organic Reactions

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Table 6.1 A Summary of Arrow Types in Chemical Reactions

Arrow	Name	Use
$\longrightarrow$	Reaction arrow	Drawn between the starting materials and products in an equation (6.1)
$\rightleftharpoons$	Double reaction arrows (equilibrium arrows)	Drawn between the starting materials and products in an equilibrium equation (2.2)
$\longleftrightarrow$	Double-headed arrow	Drawn between resonance structures (1.6)
	Full-headed curved arrow	Shows movement of an electron pair (1.6, 2.2)
	Half-headed curved arrow (fishhook)	Shows movement of a single electron (6.3)

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6.8 Energy diagram for a two-step reaction mechanism

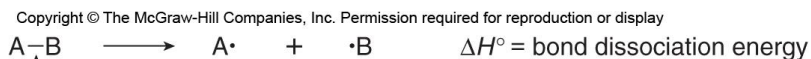
6.9 Kinetics

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Bond Dissociation Energy

- **Bond dissociation energy** is the energy needed to homolytically cleave a covalent bond.



Homolysis requires energy.

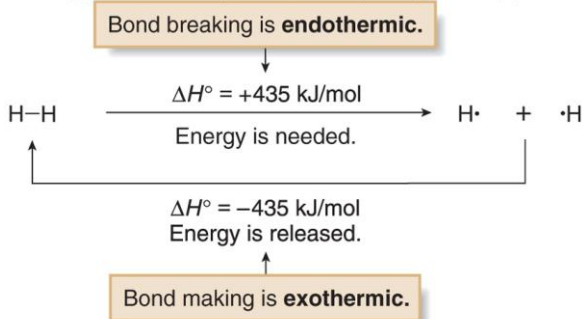
- Because **bond breaking** requires energy, bond dissociation energies are always positive numbers, and homolysis is always **endothermic**.
- Conversely, **bond formation** always releases energy, and thus is always **exothermic**.

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Energy Associated with the H₂ Bond

- Example:** the H-H bond requires +104 kcal/mol to cleave and releases –104 kcal/mol when formed.

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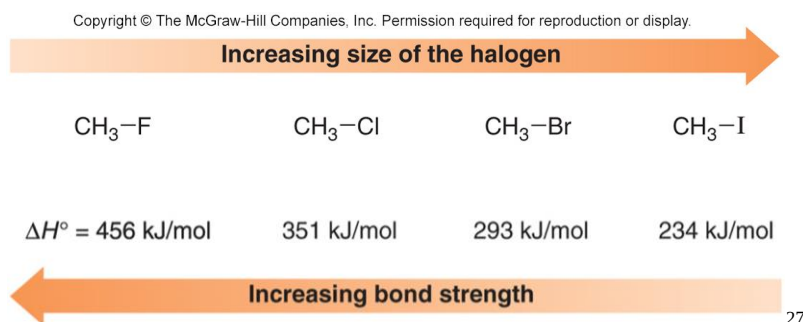
Table 6.2 Bond Dissociation Energies for Some Common Bonds [A–B → A· + ·B]

Bond	ΔH° kJ/mol	(kcal/mol)	Bond	ΔH° kJ/mol	(kcal/mol)
H–Z bonds			R–X bonds		
H–F	569	(136)	CH ₃ –F	456	(109)
H–Cl	431	(103)	CH ₃ –Cl	351	(84)
H–Br	368	(88)	CH ₃ –Br	293	(70)
H–I	297	(71)	CH ₃ –I	234	(56)
H–OH	498	(119)	CH ₃ CH ₂ –F	448	(107)
Z–Z bonds			CH ₃ CH ₂ –Cl	339	(81)
H–H	435	(104)	CH ₃ CH ₂ –Br	285	(68)
F–F	159	(38)	CH ₃ CH ₂ –I	222	(53)
Cl–Cl	242	(58)	(CH ₃) ₂ CH–F	444	(106)
Br–Br	192	(46)	(CH ₃) ₂ CH–Cl	335	(80)
I–I	151	(36)	(CH ₃) ₂ CH–Br	285	(68)
HO–OH	213	(51)	(CH ₃) ₂ CH–I	222	(53)
R–H bonds			(CH ₃) ₂ C–F	444	(106)
CH ₃ –H	435	(104)	(CH ₃) ₂ C–Cl	331	(79)
CH ₃ CH ₂ –H	410	(98)	(CH ₃) ₂ C–Br	272	(65)
CH ₃ CH ₂ CH ₂ –H	410	(98)	(CH ₃) ₂ C–I	209	(50)
(CH ₃) ₂ CH–H	397	(95)	R–OH bonds		
(CH ₃) ₃ C–H	381	(91)	CH ₃ –OH	389	(93)
CH ₂ =CH–H	435	(104)	CH ₃ CH ₂ –OH	393	(94)
HC≡C–H	523	(125)	CH ₃ CH ₂ CH ₂ –OH	385	(92)
CH ₂ =CHCH ₂ –H	364	(87)	(CH ₃) ₂ CH–OH	401	(96)
C ₆ H ₅ –H	460	(110)	(CH ₃) ₃ C–OH	401	(96)
C ₆ H ₅ CH ₂ –H	356	(85)			
R–R bonds					
CH ₃ –CH ₃	368	(88)			
CH ₃ –CH ₂ CH ₃	356	(85)			
CH ₃ –CH=CH ₂	385	(92)			
CH ₃ –C≡CH	489	(117)			

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Bond Dissociation Energy and Bond Strength

- Comparing **bond dissociation energies** is equivalent to comparing **bond strength**.
- The **stronger the bond**, the higher its bond dissociation energy.
- Bond dissociation energies **decrease down a column** of the periodic table.
- Generally, **shorter bonds** are **stronger** bonds.



Enthalpy Change in Reactions

- Bond dissociation energies are used to calculate the enthalpy change (ΔH°) in a reaction in which several bonds are broken and formed.

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- When ΔH° is positive, more energy is needed to break bonds than is released in forming bonds. The bonds broken in the starting material are *stronger* than the bonds formed in the product.
- When ΔH° is negative, more energy is released in forming bonds than is needed to break bonds. The bonds formed in the product are *stronger* than the bonds broken in the starting material.

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$$\Delta H^\circ_{\text{overall enthalpy change}} = \text{sum of } \Delta H^\circ \text{ of bonds broken} + (-) \text{sum of } \Delta H^\circ \text{ of bonds formed}$$

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Determining ΔH° for a Reaction

Sample Problem 6.2

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Use the values in Table 6.2 to determine ΔH° for the following reaction.



Solution

[1] Bonds broken

	ΔH° (kJ/mol)
$(\text{CH}_3)_3\text{C}-\text{Cl}$	+331
$\text{H}-\text{OH}$	+498
Total	+829 kJ/mol

Energy needed to break bonds.

[2] Bonds formed

	ΔH° (kJ/mol)
$(\text{CH}_3)_3\text{C}-\text{OH}$	-401
$\text{H}-\text{Cl}$	-431
Total	-832 kJ/mol

Energy released in forming bonds.

[3] Overall ΔH° =

sum in Step [1]
+
sum in Step [2]

+829 kJ/mol
-832 kJ/mol

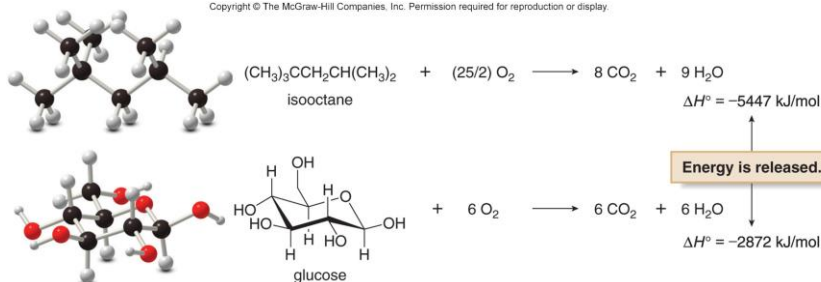
Answer: -3 kJ/mol

Because ΔH° is a negative value, this reaction is **exothermic** and energy is released. **The bonds broken in the starting material are weaker than the bonds formed in the product.**

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Enthalpy Changes in Oxidation Reactions

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- ΔH° is negative for both oxidations, so both reactions are exothermic.
- Both isooctane and glucose release energy on oxidation because the bonds in the products are stronger than the bonds in the reactants.

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Limitations on Bond Dissociation Energies

- Bond dissociation energies present **overall energy changes** only; they reveal nothing about the reaction mechanism or how fast a reaction proceeds.
- Bond dissociation energies are determined for **reactions in the gas phase**, whereas most organic reactions occur in a liquid solvent where solvation energy contributes to the overall enthalpy of a reaction.
 - Though imperfect, using bond dissociation energies to calculate ΔH° gives a **useful approximation** of the energy changes that occur in a reaction.

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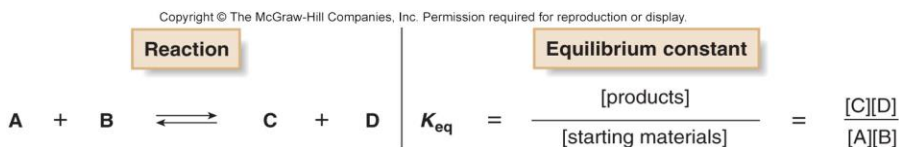
Kinetics and Thermodynamics

- For a reaction to be practical, the equilibrium must favor products and the reaction rate must be fast enough to form them in a reasonable time.
- These two conditions depend on **thermodynamics** and **kinetics** respectively.
 - **Thermodynamics** describes:
 - how the **energies of reactants** and products compare; and
 - what the **relative amounts** of reactants and products are at equilibrium.
 - **Kinetics** describes reaction rates (**how quickly** reactants are converted to products).

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Kinetics and Thermodynamics

- The **equilibrium constant**, K_{eq} , is a mathematical expression that relates the amount of starting material and product at equilibrium.



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The Equilibrium Constant

- The **size of K_{eq}** expresses whether the starting materials or products predominate once equilibrium is reached.
- When **$K_{eq} > 1$** ,
 - equilibrium favors the products.
 - equilibrium lies to the right as the equation is written.
- When **$K_{eq} < 1$** ,
 - equilibrium favors the starting materials.
 - equilibrium lies to the left as the equation is written.
- For a **reaction to be useful**, the equilibrium must favor the products, and $K_{eq} > 1$.
- The position of the equilibrium is determined by the relative energies of the reactants and products.

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The Equilibrium Constant and Free Energy

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Free energy change

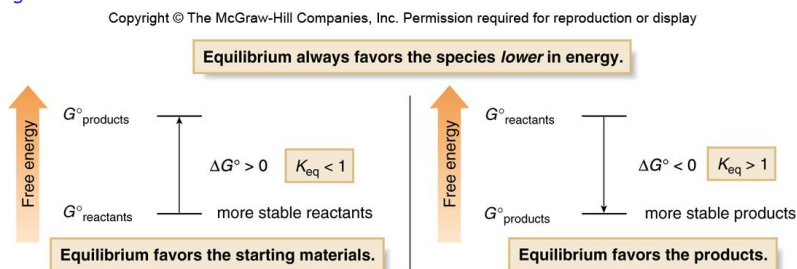
$$\Delta G^\circ = G^\circ_{\text{products}} - G^\circ_{\text{reactants}}$$

$G^\circ_{\text{products}}$
 ↑
 free energy
of the products

$G^\circ_{\text{reactants}}$
 ↑
 free energy
of the reactants

- ΔG° is the overall energy difference between reactants and products.

Figure 6.3



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Relationship Between Equilibrium Constant and Free Energy

- ΔG° is related to the equilibrium constant K_{eq} by the following equation:

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$$\Delta G^\circ = -2.303RT \log K_{eq}$$

$R = 8.314 \text{ J/(K}\cdot\text{mol)}$, the gas constant
 $T = \text{Kelvin temperature (K)}$

K_{eq} depends on the energy difference between reactants and products.

- When $K_{eq} > 1$, $\log K_{eq}$ is positive, making ΔG° **negative**, and energy is released.
 - Equilibrium favors the products.
- When $K_{eq} < 1$, $\log K_{eq}$ is negative, making ΔG° **positive**, and energy is absorbed.
 - Equilibrium favors the reactants.

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Energy Difference and Equilibrium

- Compounds that are lower in energy have **increased stability**.
- Equilibrium **favors** the products when they are more stable than the starting materials.
- Because ΔG° **depends on the logarithm of K_{eq}** , a small change in energy corresponds to a large difference in the relative amount of starting material and product at equilibrium.

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Table 6.3 Representative Values for ΔG° and K_{eq} at 25 °C, for a Reaction $A \rightarrow B$

	ΔG° (kJ/mol)	K_{eq}	Relative amount of A and B at equilibrium
→	+18	10^{-3}	Essentially all A (99.9%)
	+12	10^{-2}	100 times as much A as B
	+6	10^{-1}	10 times as much A as B
	0	1	Equal amounts of A and B
	-6	10^1	10 times as much B as A
	-12	10^2	100 times as much B as A
→	-18	10^3	Essentially all B (99.9%)

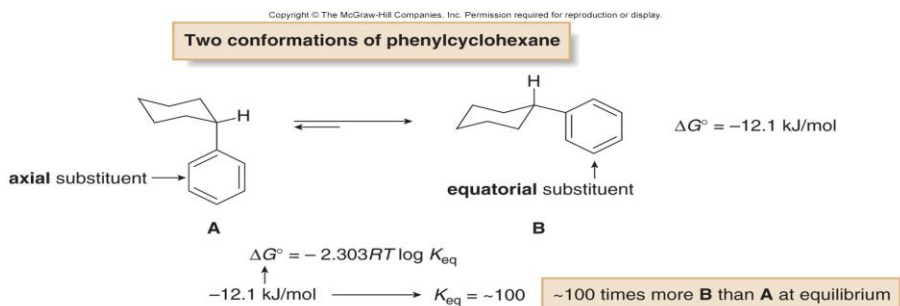
A small difference in free energy means a large difference in the amount of A and B at equilibrium.

↑ increasing [product]

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Conformations and Equilibrium

- **Monosubstituted** cyclohexanes exist as two different chair conformations that rapidly interconvert at room temperature.
- The conformation having the substituent in the roomier **equatorial position is favored**.
- Knowing the energy difference between two conformations permits the calculation of the amount of each at equilibrium.



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Entropy

- **Entropy** is a measure of the **randomness** of a system.
 - The **more freedom** of motion or the more disorder present, the higher the entropy.
 - **Gas molecules** move more freely than liquid molecules and are higher in entropy.
 - **Cyclic molecules** have more restricted bond rotation than similar acyclic molecules and are lower in entropy.

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Role of Entropy in Total Energy Change

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$$\text{Total energy change} \rightarrow \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad [T = \text{Kelvin temperature}]$$

$\uparrow$
 change in
bonding energy

$\uparrow$
 change in
disorder

- The **total energy change** is due to two factors: the change in bonding energy and the change in disorder.
- The change in bonding energy can be calculated from bond dissociation energies.
- In most reactions that are not carried out at high temperature, the entropy term (**$T\Delta S^\circ$**) is **small** compared to the enthalpy term (**ΔH°**), and therefore, it is usually neglected.

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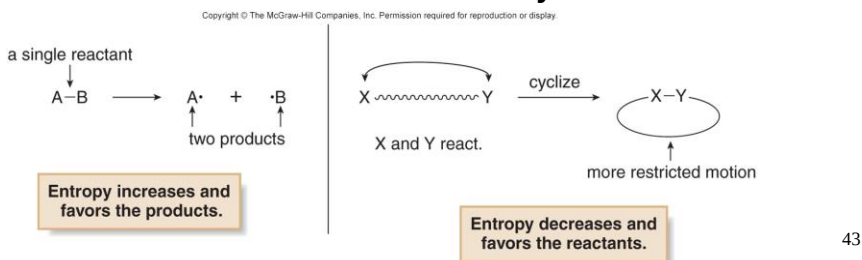
$\Delta G^\circ \approx \Delta H^\circ$

• The total energy change is approximated by the change in bonding energy only.

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Reactions in which ΔS° Plays a Role

- Reactions resulting in increased entropy are favored.
 - ΔS° is (+) when the products are more disordered than the reactants and (-) when the products are more ordered.
- Entropy changes are important when:
 - the **number of molecules** of starting material differs from the number of molecules of product in the balanced chemical equation; and when
 - an **acyclic molecule** is cyclized to a cyclic one, or a cyclic molecule is converted to an acyclic one.



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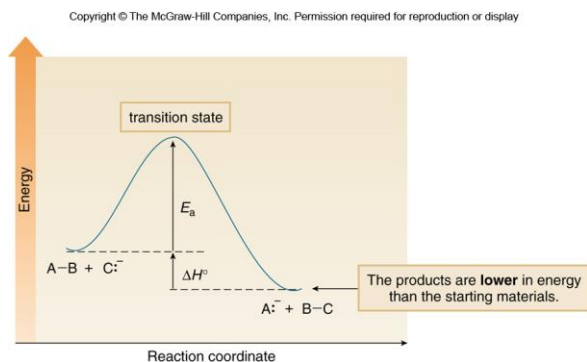
6.9 Kinetics

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Energy Diagrams

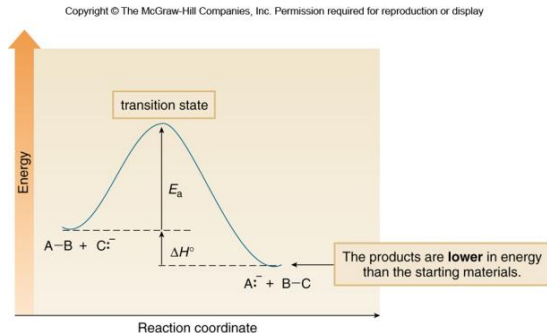
- An **energy diagram** is a schematic representation of the energy changes that take place as reactants are converted to products.
- An energy diagram plots the **energy on the y axis** versus the **progress of reaction**, often labeled as the reaction coordinate, on the x axis.



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Energy Diagrams

- The **energy difference** between reactants and products is ΔH° .
- As a chemical reaction proceeds from reactants to products, it passes through an unstable energy maximum called the **transition state**.
- The energy difference between the transition state and the starting material is called the **energy of activation, E_a** .
- The **larger the E_a** , the greater energy needed to **break bonds**, and the **slower the reaction rate**.



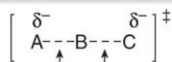
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Transition States

- The structure of the **transition state** is somewhere between the structures of the starting material and product.
 - Any bond that is partially formed or broken is drawn with a **dashed line**.
 - Any atom that gains or loses a charge contains a **partial charge** in the transition state.
 - Transition states are drawn in brackets, with a superscript **double dagger** ($\ddagger$).

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Drawing the structure of a transition state



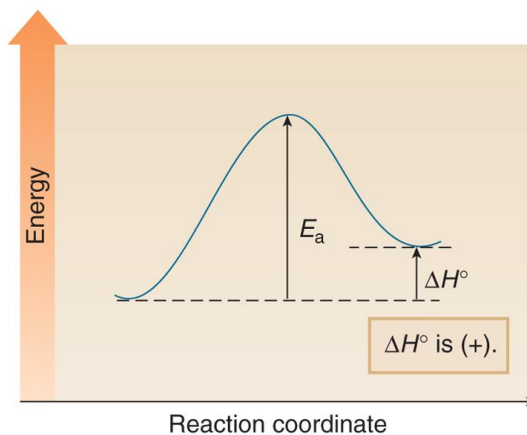
This bond is partially broken. This bond is partially formed.

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Slow, Endothermic Energy Diagram

Figure 6.4

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- Large $E_a \rightarrow$ slow reaction
 - (+) $\Delta H^\circ \rightarrow$ endothermic reaction



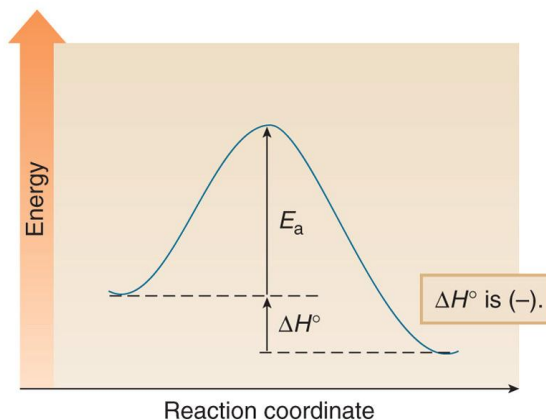
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Slow, Exothermic Energy Diagram

Figure 6.4

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- Large $E_a \rightarrow$ slow reaction
- $(-) \Delta H^\circ \rightarrow$ exothermic reaction



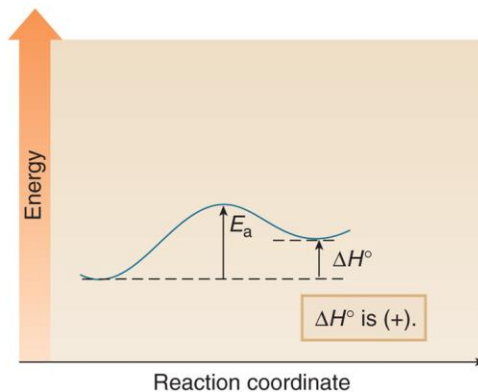
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Fast, Endothermic Energy Diagram

Figure 6.4

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- Low $E_a \rightarrow$ fast reaction
- $(+) \Delta H^\circ \rightarrow$ endothermic reaction



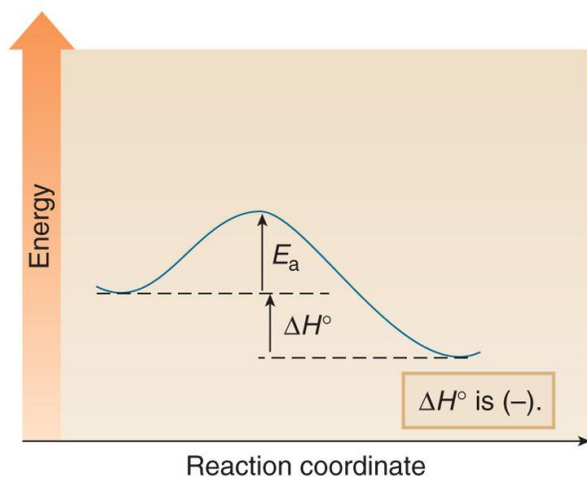
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Fast, Exothermic Energy Diagram

Figure 6.4

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- Low $E_a \rightarrow$ fast reaction
- $(-)\Delta H^\circ \rightarrow$ exothermic reaction

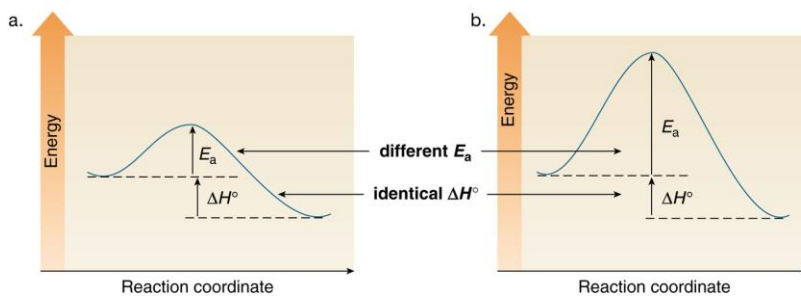


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Comparing ΔH° and E_a in Energy Diagrams

Figure 6.5

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- Energy diagrams in (a) and (b) both depict exothermic reactions with the same negative value of ΔH° .
- E_a in (a) is lower than E_a in (b), so reaction (a) is faster than reaction (b).

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Organic Reactions

6.1 Writing equations for organic reactions

6.2 Kinds of organic reactions

6.3 Bond breaking and bond making

6.4 Bond dissociation energy

6.5 Thermodynamics

6.6 Enthalpy and entropy

6.7 Energy diagrams

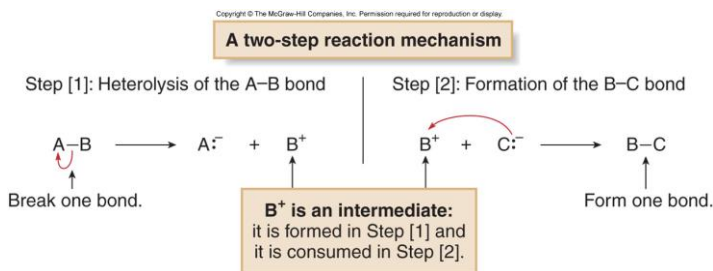
6.8 Energy diagram for a two-step reaction mechanism

6.9 Kinetics

6.10 Catalysts

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Energy Diagrams and Two-Step Reactions

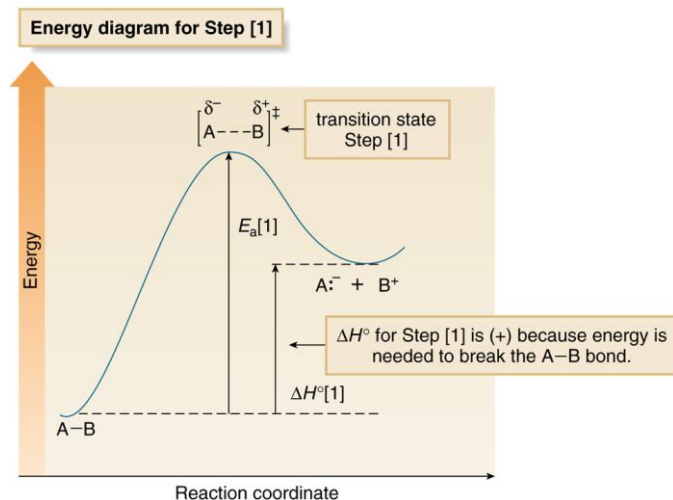


- An energy diagram must be drawn **for each step**.
- The two energy diagrams must then be **combined** to form an energy diagram for the overall two-step reaction.
- Each step has its own **energy barrier**, with a transition state at the energy maximum.

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Stepwise Reaction Energy Diagram–Step 1

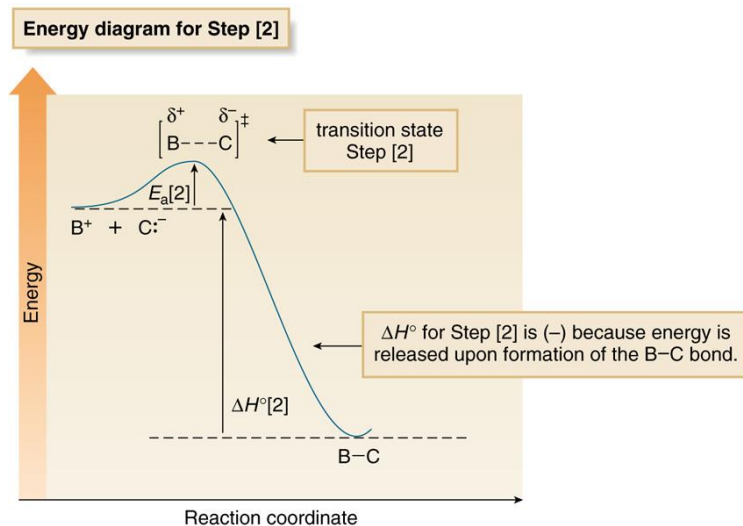
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Stepwise Reaction Energy Diagram–Step 2

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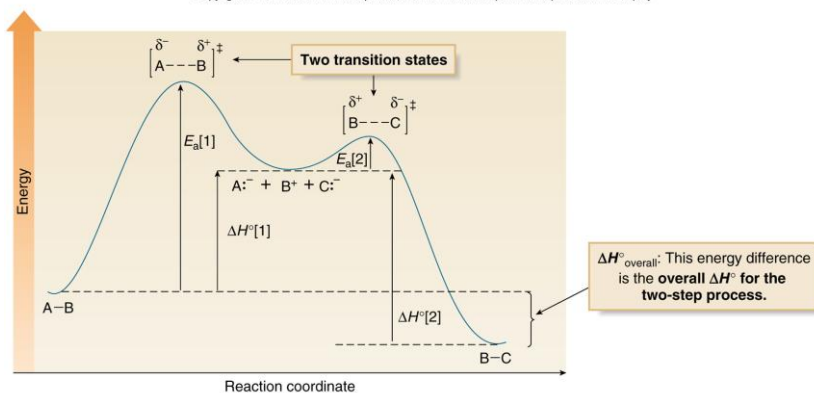


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Stepwise Reaction Overall Energy Diagram

Figure 6.6

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- The transition states are located at energy maxima, while the reactive intermediate $B^{\delta+}$ is located at an energy minimum.
- Each step is characterized by its own value of ΔH° and E_a .
- The overall energy difference between starting material and products is called $\Delta H^\circ_{\text{overall}}$. In this example, the products of the two-step sequence are at lower energy than the starting materials.
- Since Step [1] has the higher energy transition state, it is the **rate-determining step**.

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6.8 Energy diagram for a two-step reaction mechanism

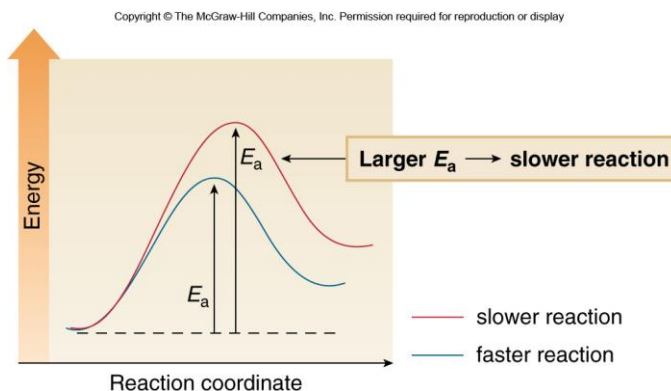
6.9 Kinetics

6.10 Catalysts

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Kinetics and Energy Diagrams

- **Kinetics** is the study of **reaction rates**.
- E_a is the **energy barrier** that must be exceeded for reactants to be converted to products.



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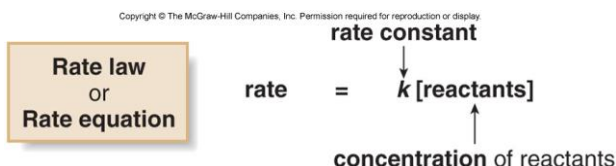
Factors Affecting Reaction Rates

1. The higher the **concentration**, the faster the rate.
 2. The higher the **temperature**, the faster the rate.
- ΔG° , ΔH° , and K_{eq} **do not** determine the rate of a reaction.
 - These quantities indicate the **direction** of the equilibrium and the relative energy of reactants and products.

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Rate Law

- A **rate law** or **rate equation** shows the relationship between the reaction rate and the concentration of the reactants.
- It is **experimentally determined** by measuring the decrease in concentrations of reactants or the appearance of products over time.

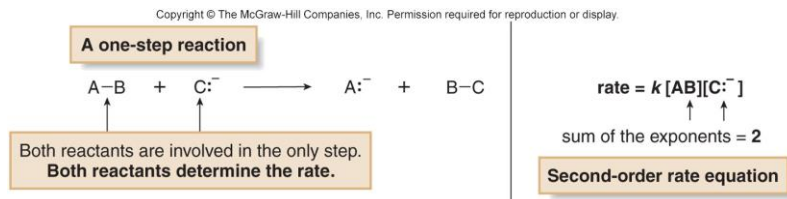


- Fast reactions have **large rate** constants.
- Slow reactions have **small rate** constants.

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Rate equations

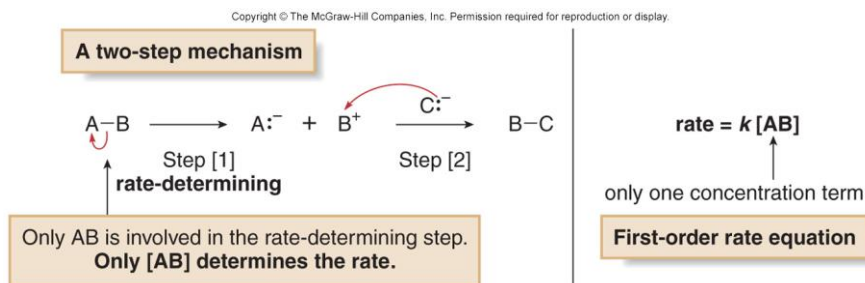
- The **rate constant** k and the energy of activation E_a are **inversely** related; a high E_a corresponds to a small k .
- A rate equation contains concentration terms for **all reactants in a one-step mechanism**.
- A rate equation contains concentration terms for only the reactants involved in the **rate-determining step** in a **multistep** reaction.
- The **order** of a rate equation equals the sum of the exponents of the concentration terms in the rate equation.



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Rate equations for Two-Step Reactions

- A **two-step reaction** has a **slow** rate-determining step, and a **fast** step.
- In a **multistep** mechanism, the reaction can occur no faster than its **rate-determining** step.
- Only the concentration of the reactants in the rate-determining step appears in the rate equation.



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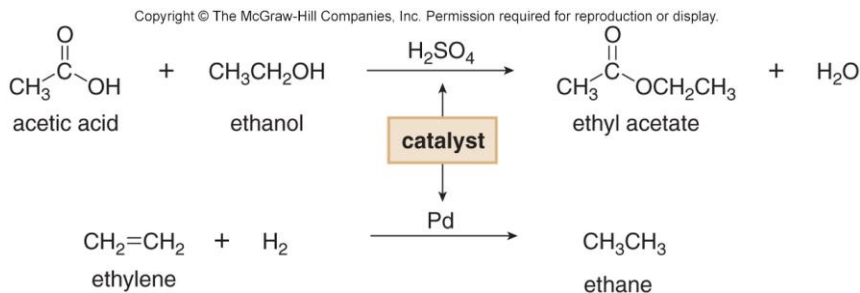
6.9 Kinetics

6.10 Catalysts

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Catalysts

- Some reactions do not proceed at a reasonable rate unless a catalyst is added.

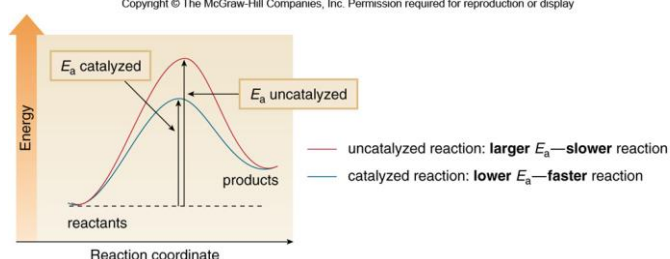


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Role of the Catalyst

- A **catalyst** is a substance that **speeds up** the rate of a reaction.
 - It is **recovered unchanged** in a reaction, and it does not appear in the product.
 - A catalyst **lowers the activation energy**, thus increasing the rate of the catalyzed reaction.
 - The **energy** of the reactants and products **is the same** in both the catalyzed and uncatalyzed reactions, the position of equilibrium is unaffected.

Figure 6.7



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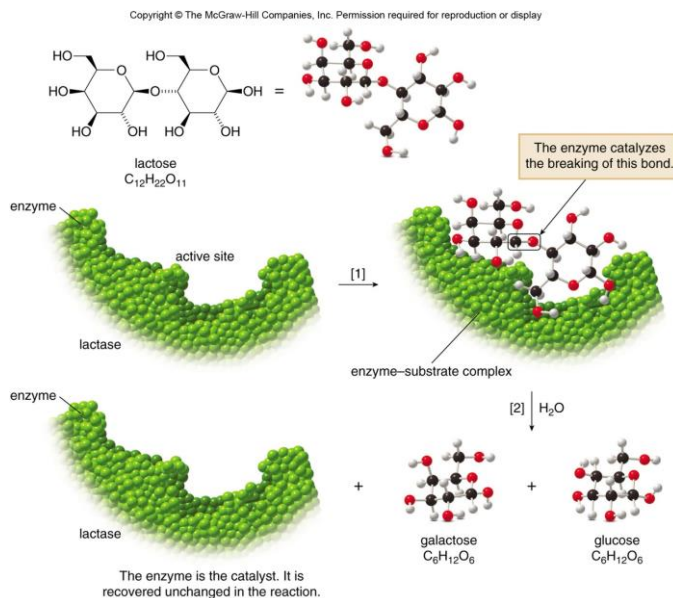
Enzymes

- **Enzymes** are **biochemical catalysts** composed of amino acids held together in a very specific three-dimensional shape.
- An enzyme contains a region called its **active site** which binds an organic reactant, called a **substrate**.
- The resulting unit is called the **enzyme-substrate complex**.
- Once bound, the organic substrate undergoes a **very specific reaction** at an enhanced rate.
- The products are then released.

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Lactase—a Biological Catalyst

Figure 6.7



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