Organic Chemistry, *Fourth Edition*

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Chapter 6

Understanding Organic Reactions

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Organic Reactions

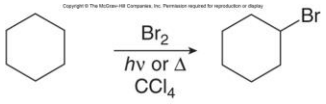
- **6.1 Writing equations for organic reactions**
- **6.2 Kinds of organic reactions**
- **6.3 Bond breaking and bond making**
- **6.4 Bond dissociation energy**
- **6.5 Thermodynamics**
- **6.6 Enthalpy and entropy**
- **6.7 Energy diagrams**
- **6.8 Energy diagram for a two-step reaction mechanism**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

Organic Reactions

- **Reactions are at the heart of Organic Chemistry.**
- **Virtually all <u>chemical reactions</u> 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).**

Writing Equations for Organic Reactions

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

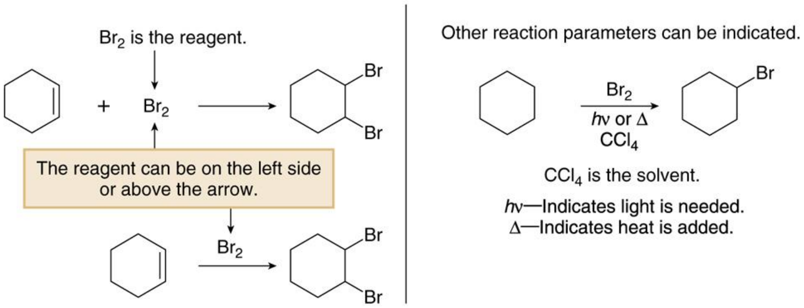


CCl_4 is the solvent.

hν—Indicates light is needed.
Δ—Indicates heat is added.

Ways to Write Organic Reactions

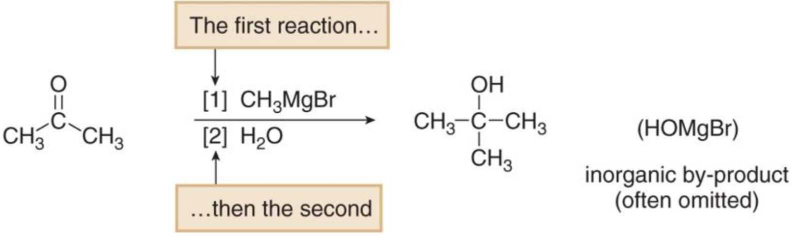
Figure 6.1



- The **solvent and temperature** of the reaction may be added above or below the arrow.
- The symbols "**hν**" and "**Δ**" are used for reactions that require light or heat, respectively.

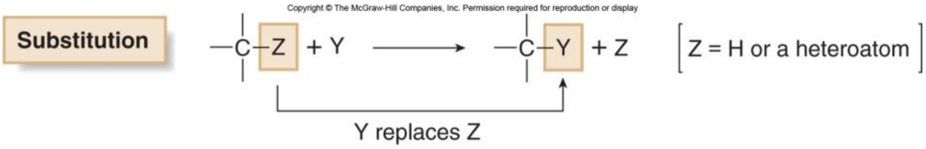
Writing Equations for Sequential Reactions

- 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.



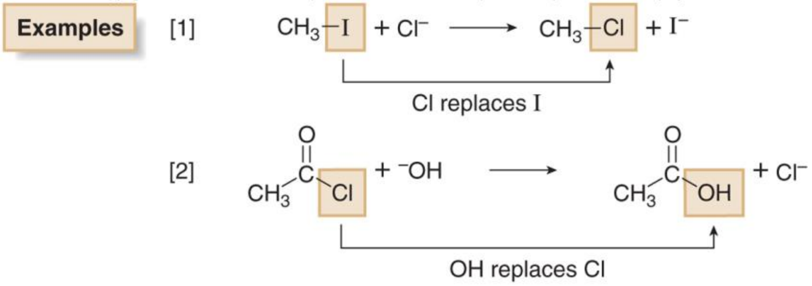
1. Substitution Reactions

- **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.



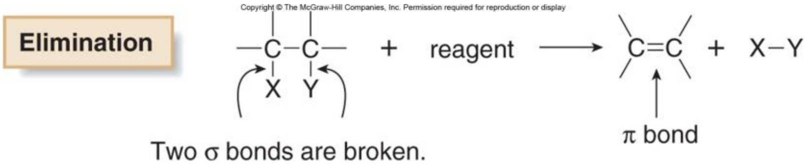
Substitution Reactions

- 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.



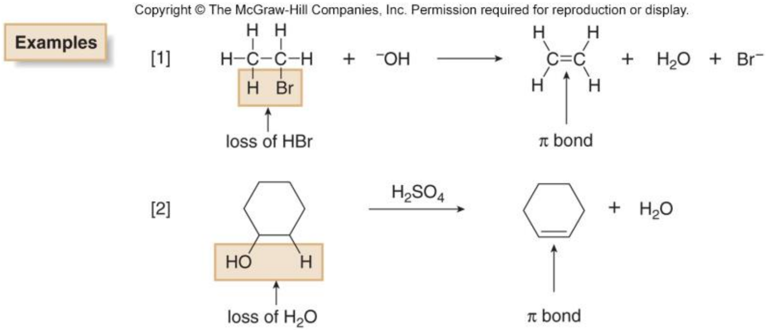
2. Elimination Reactions

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



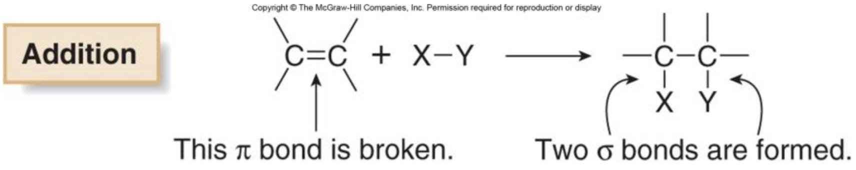
Elimination Reactions

- **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.**



3. Addition Reactions

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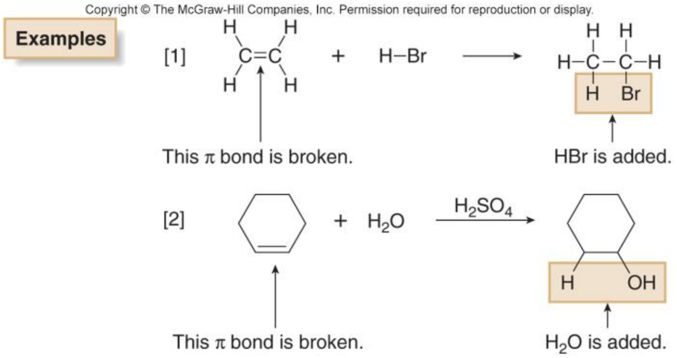
Addition Reactions

- 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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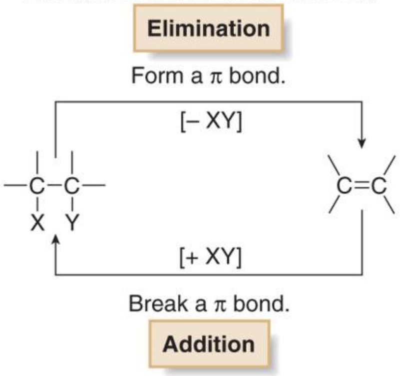
Relationship of Addition and Elimination Reactions

- 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.



Elimination

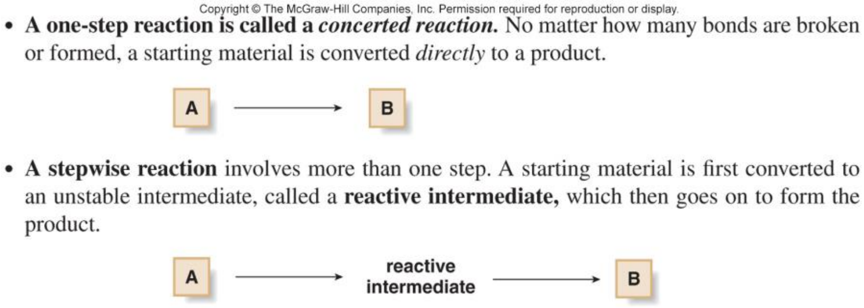
Form a π bond.

Break a π bond.

Addition

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.



- **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 → B

- **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.

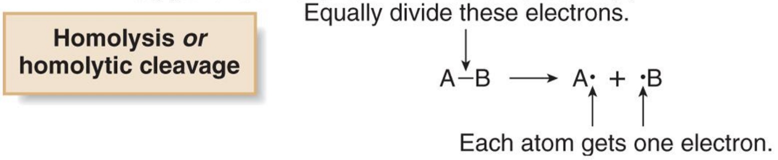
A → reactive intermediate → B

Bond Breaking

1. Homolytic

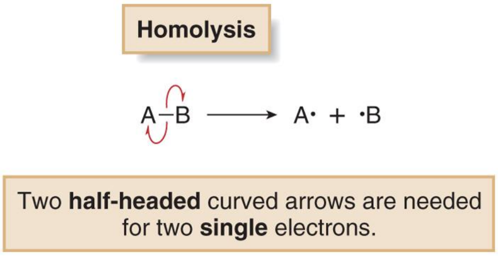
Regardless of how many steps there are in a reaction, there are only two ways to break (cleave) a bond:

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



Bond Breaking–Homolytic

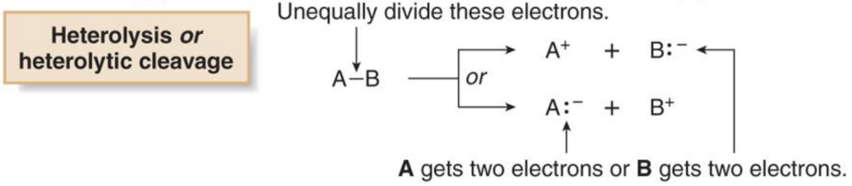
- **To illustrate the movement of a single electron, use a half-headed curved arrow, sometimes called a fishhook.**



- **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.**

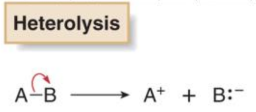
Bond Breaking
2. Heterolytic

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



Bond Breaking–Heterolytic

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

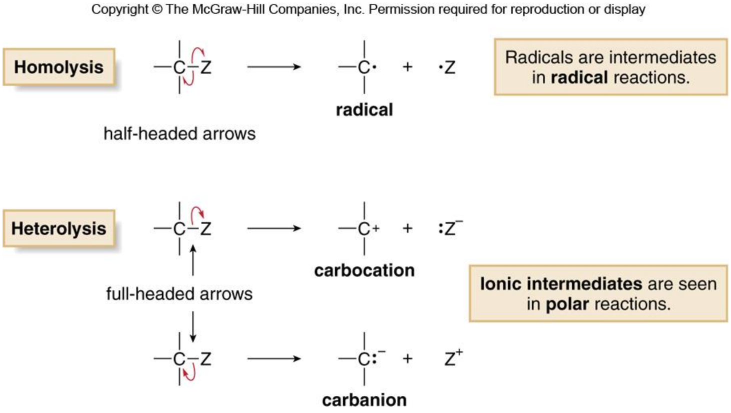


One **full-headed** curved arrow is needed for one electron **pair.**

- **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.**

Reactive Intermediates Resulting from Breaking a C-Z Bond

Figure 6.2

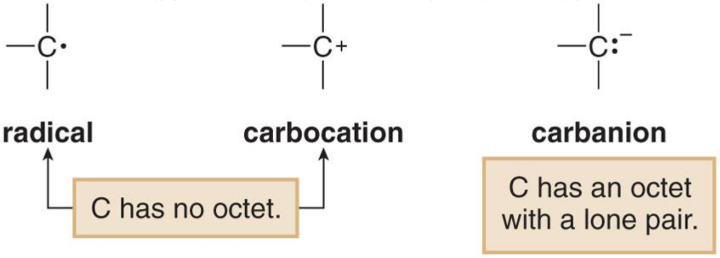


Radicals are intermediates in **radical** reactions.

Ionic intermediates are seen in **polar** reactions.

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.

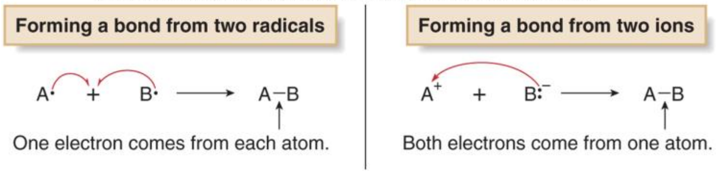


C has no octet.

C has an octet with a lone pair.

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**.



Arrows Used in Organic Reactions

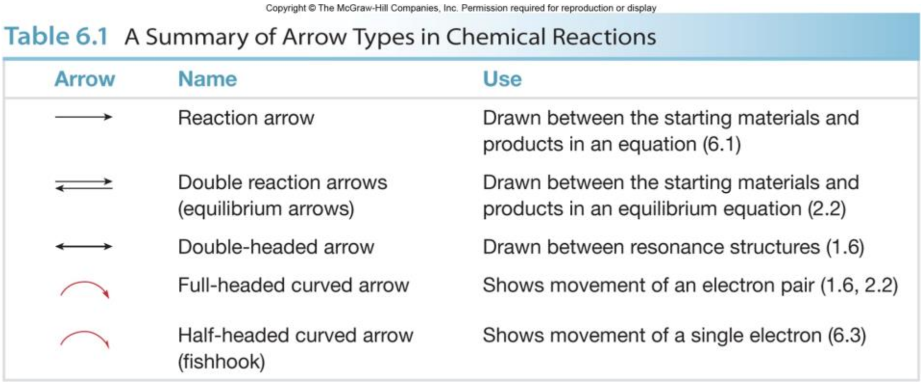


Table 6.1 A Summary of Arrow Types in Chemical Reactions

Arrow	Name	Use
⟶	Reaction arrow	Drawn between the starting materials and products in an equation (6.1)
⇄	Double reaction arrows (equilibrium arrows)	Drawn between the starting materials and products in an equilibrium equation (2.2)
⟷	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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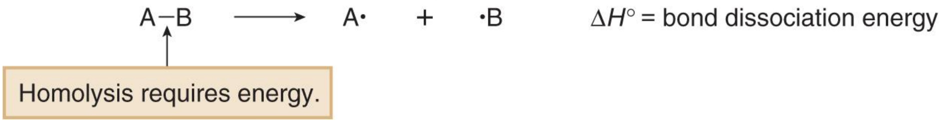
Bond Dissociation Energy

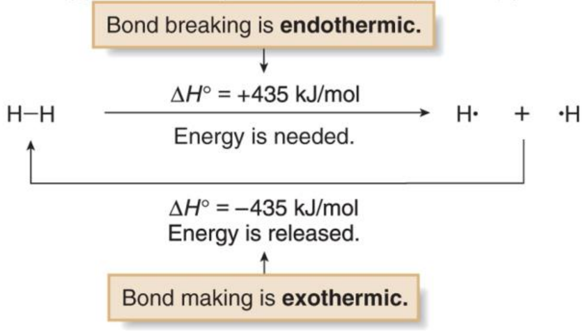
- **Bond dissociation energy is the energy needed to homolytically cleave a covalent bond.**



- **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.**

Energy Associated with the H_2 Bond

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



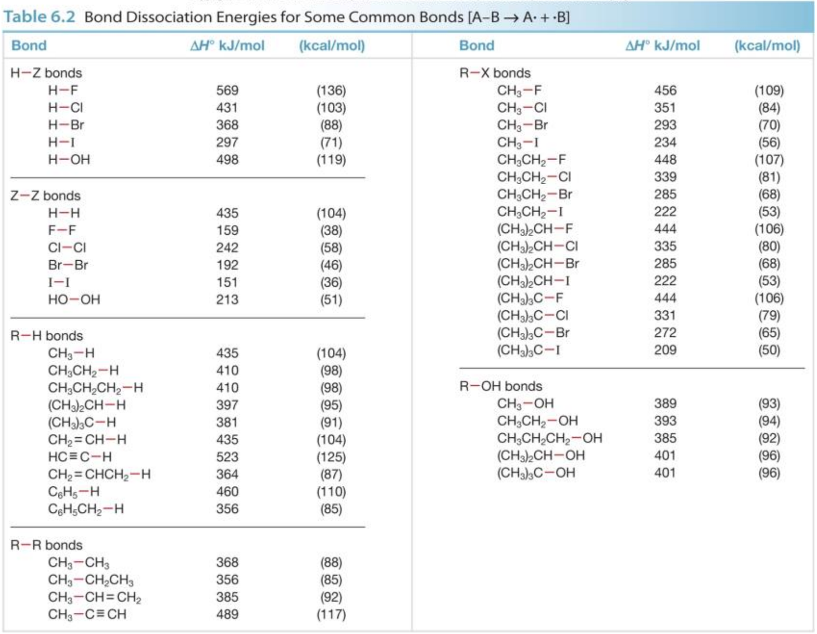
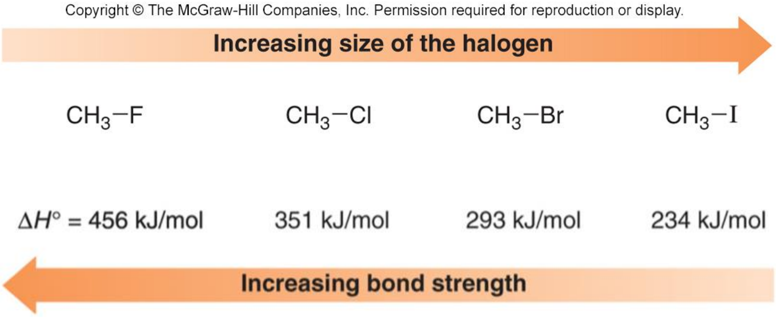


Table 6.2 Bond Dissociation Energies for Some Common Bonds [$A–B \rightarrow A\cdot + \cdot B$]

Bond	$\Delta H°$ kJ/mol	(kcal/mol)
H−Z bonds		
H−F	569	(136)
H−Cl	431	(103)
H−Br	368	(88)
H−I	297	(71)
H−OH	498	(119)
Z−Z bonds		
H−H	435	(104)
F−F	159	(38)
Cl−Cl	242	(58)
Br−Br	192	(46)
I−I	151	(36)
HO−OH	213	(51)
R−H bonds		
CH_3−H	435	(104)
CH_3CH_2−H	410	(98)
$CH_3CH_2CH_2$−H	410	(98)
$(CH_3)_2CH$−H	397	(95)
$(CH_3)_3C$−H	381	(91)
$CH_2=CH$−H	435	(104)
$HC\equiv C$−H	523	(125)
$CH_2=CHCH_2$−H	364	(87)
C_6H_5−H	460	(110)
$C_6H_5CH_2$−H	356	(85)
R−R bonds		
CH_3−CH_3	368	(88)
CH_3−CH_2CH_3	356	(85)
CH_3−$CH=CH_2$	385	(92)
CH_3−$C\equiv CH$	489	(117)
R−X bonds		
CH_3−F	456	(109)
CH_3−Cl	351	(84)
CH_3−Br	293	(70)
CH_3−I	234	(56)
CH_3CH_2−F	448	(107)
CH_3CH_2−Cl	339	(81)
CH_3CH_2−Br	285	(68)
CH_3CH_2−I	222	(53)
$(CH_3)_2CH$−F	444	(106)
$(CH_3)_2CH$−Cl	335	(80)
$(CH_3)_2CH$−Br	285	(68)
$(CH_3)_2CH$−I	222	(53)
$(CH_3)_3C$−F	444	(106)
$(CH_3)_3C$−Cl	331	(79)
$(CH_3)_3C$−Br	272	(65)
$(CH_3)_3C$−I	209	(50)
R−OH bonds		
CH_3−OH	389	(93)
CH_3CH_2−OH	393	(94)
$CH_3CH_2CH_2$−OH	385	(92)
$(CH_3)_2CH$−OH	401	(96)
$(CH_3)_3C$−OH	401	(96)

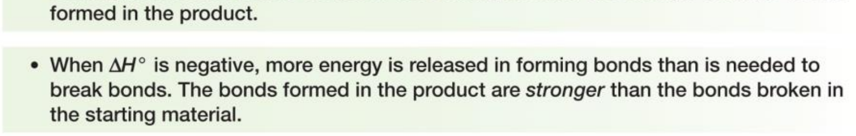
Bond Dissociation Energy and Bond Strength

- 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.

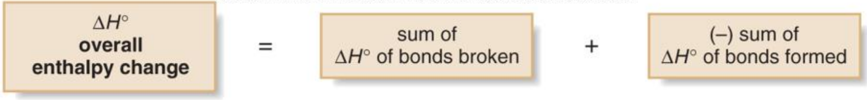


Enthalpy Change in Reactions

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

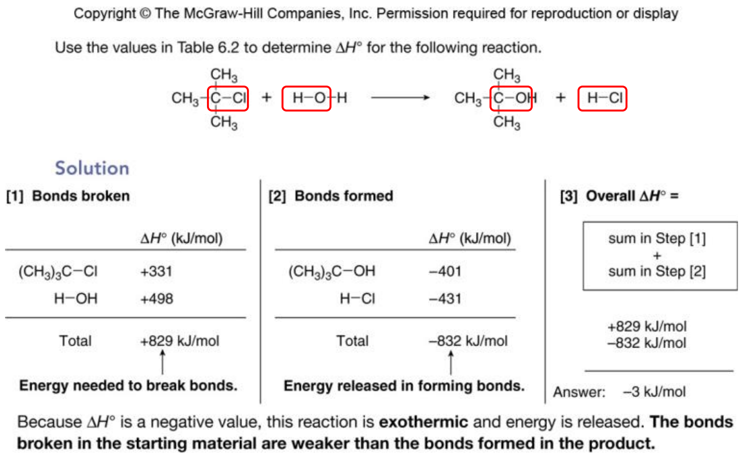


- When ΔH° is positive, more energy is needed to break bonds than is released in forming bonds. The bonds broken in the starting material are *stronger* than the bonds formed in the product.
- When ΔH° is negative, more energy is released in forming bonds than is needed to break bonds. The bonds formed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



Determining ΔH° for a Reaction

Sample Problem 6.2



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

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + H-O-H \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH + H-Cl$$

Solution

[1] Bonds broken

	ΔH° (kJ/mol)
$(CH_3)_3C-Cl$	+331
H–OH	+498
Total	+829 kJ/mol

Energy needed to break bonds.

[2] Bonds formed

	ΔH° (kJ/mol)
$(CH_3)_3C-OH$	−401
H–Cl	−431
Total	−832 kJ/mol

Energy released in forming bonds.

[3] Overall ΔH° =

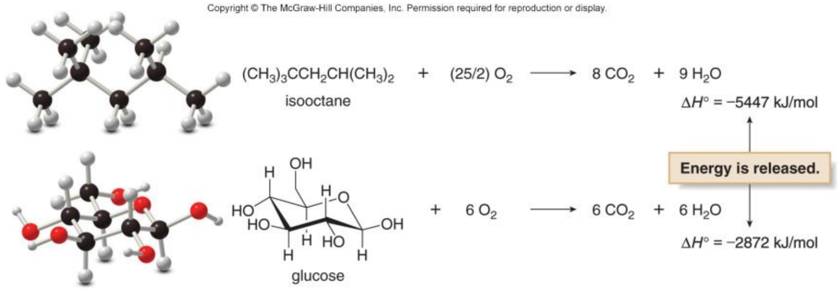
sum in Step [1]
+
sum in Step [2]

+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.**

Enthalpy Changes in Oxidation Reactions



- 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.**

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 $\Delta H°$ gives a useful approximation of the energy changes that occur in a reaction.

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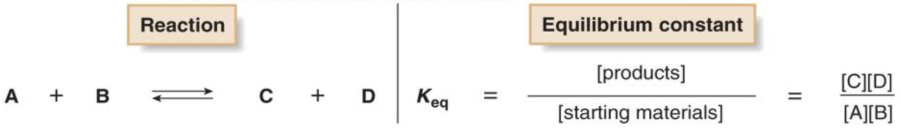
Kinetics and Thermodynamics

- **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).**

Kinetics and Thermodynamics

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



Reaction

$$A + B \rightleftharpoons C + D$$

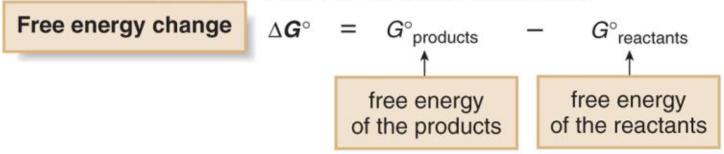
Equilibrium constant

$$K_{eq} = \frac{[\text{products}]}{[\text{starting materials}]} = \frac{[C][D]}{[A][B]}$$

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.**

The Equilibrium Constant and Free Energy



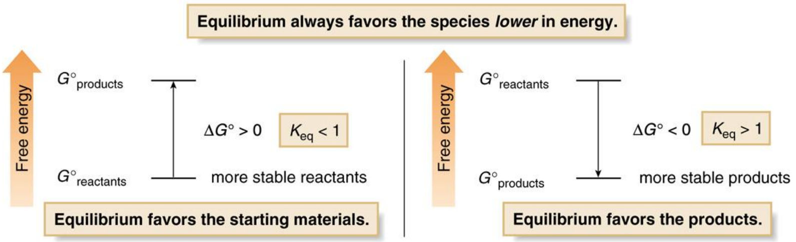
Free energy change $\Delta G^\circ = G^\circ_{products} - G^\circ_{reactants}$

free energy of the products

free energy of the reactants

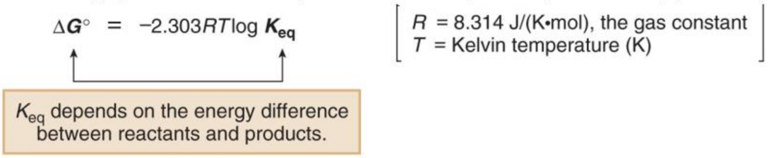
- **ΔG° is the overall energy difference between reactants and products.**

Figure 6.3



Relationship Between Equilibrium Constant and Free Energy

- **$\Delta G°$ is related to the equilibrium constant K_{eq} by the following equation:**



$$\Delta G° = -2.303RT\log K_{eq}$$

R = 8.314 J/(K•mol), the gas constant
T = Kelvin temperature (K)

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

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

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 $\Delta G°$ 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.**

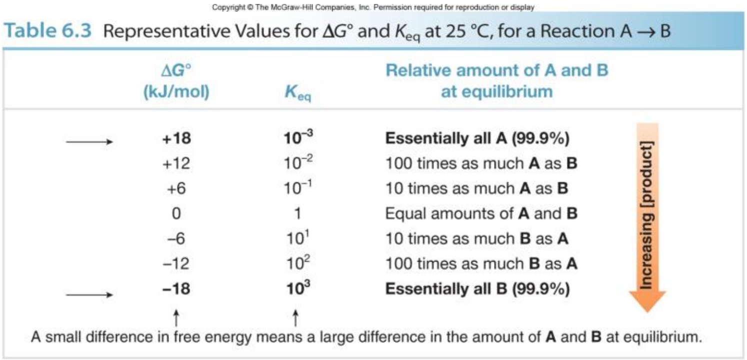


Table 6.3 Representative Values for $\Delta G°$ and K_{eq} at 25 °C, for a Reaction A → B

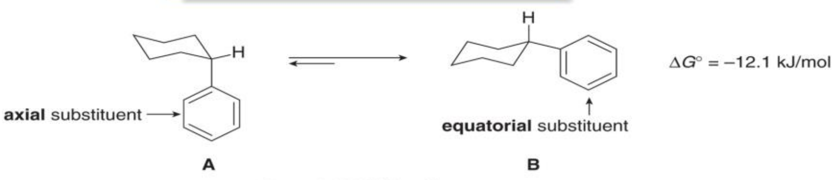
$\Delta G°$ (kJ/mol)	K_{eq}	Relative amount of A and B at equilibrium
+18	**10^{-3}**	**Essentially all A (99.9%)**
+12	10^{-2}	100 times as much **A** as **B**
+6	10^{-1}	10 times as much **A** as **B**
0	1	Equal amounts of **A** and **B**
–6	10^{1}	10 times as much **B** as **A**
–12	10^{2}	100 times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

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.**

Two conformations of phenylcyclohexane



$\Delta G^\circ = -12.1$ kJ/mol

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

-12.1 kJ/mol $\longrightarrow K_{eq} = \sim 100$

~100 times more **B** than **A** at equilibrium

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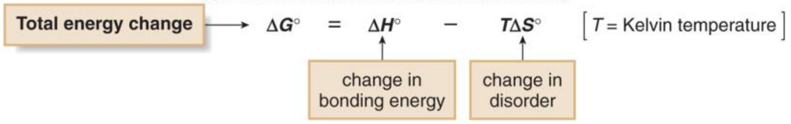
Entropy

- **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.**

Role of Entropy in Total Energy Change

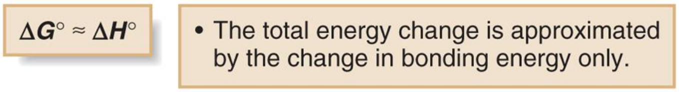


Total energy change $\longrightarrow$ $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ [T = Kelvin temperature]

ΔH°: change in bonding energy

$T\Delta S^\circ$: 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.**

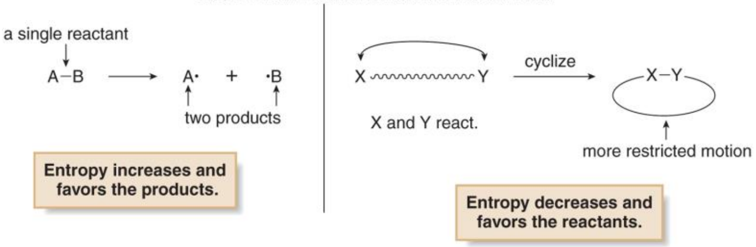


$\Delta G^\circ \approx \Delta H^\circ$

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

Reactions in which $\Delta S°$ Plays a Role

- **Reactions resulting in increased entropy are favored.**
  - **$\Delta S°$ 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.**



Entropy increases and favors the products.

Entropy decreases and favors the reactants.

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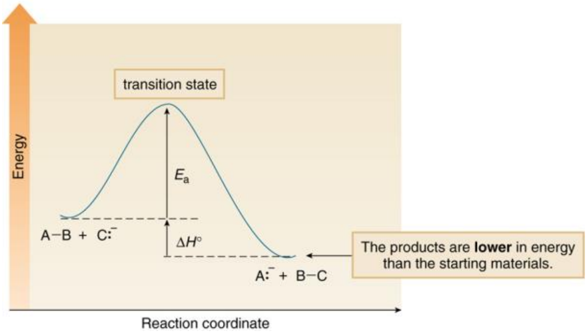
Energy Diagrams

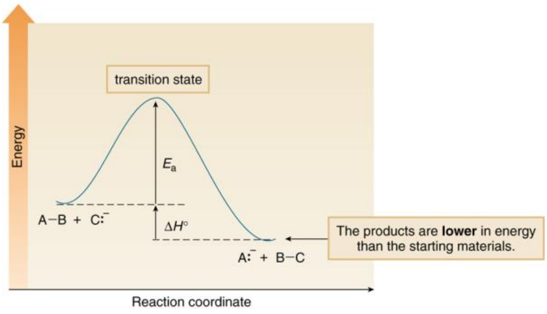
- An **energy diagram** is a schematic representation of the energy changes that take place as reactants are converted to products.
- An energy diagram plots the **energy on the *y* axis** versus the **progress of reaction**, often labeled as the reaction coordinate, on the *x* axis.



The products are **lower** in energy than the starting materials.

Energy Diagrams

- The **energy difference** between reactants and products is $\Delta H°$.
- 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.

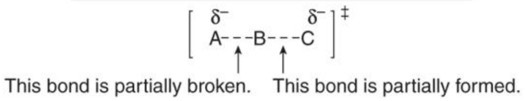


The products are **lower** in energy than the starting materials.

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 (‡).**

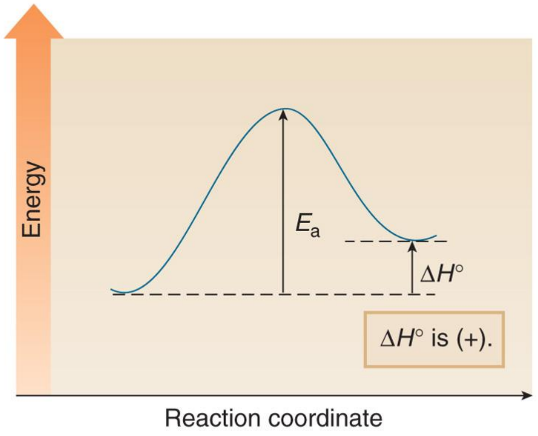
Drawing the structure of a transition state



Slow, Endothermic Energy Diagram

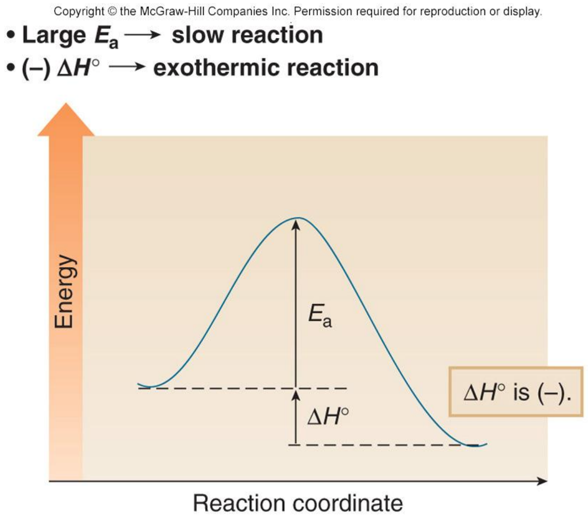
Figure 6.4

- **Large E_a ⟶ slow reaction**
- **(+) $\Delta H°$ ⟶ endothermic reaction**



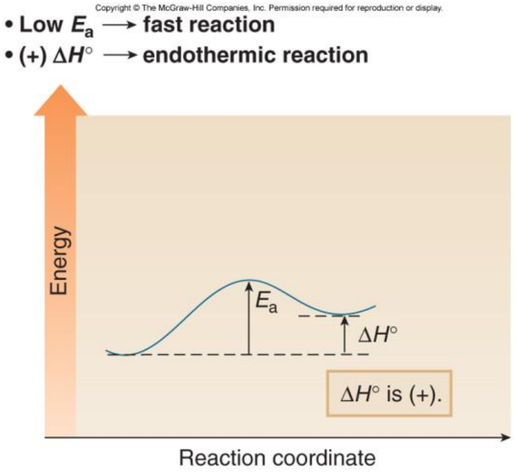
Slow, Exothermic Energy Diagram

Figure 6.4



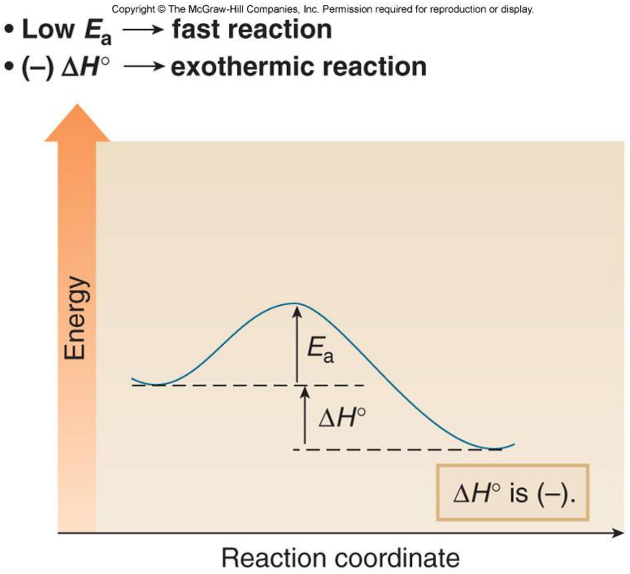
Fast, Endothermic Energy Diagram

Figure 6.4



Fast, Exothermic Energy Diagram

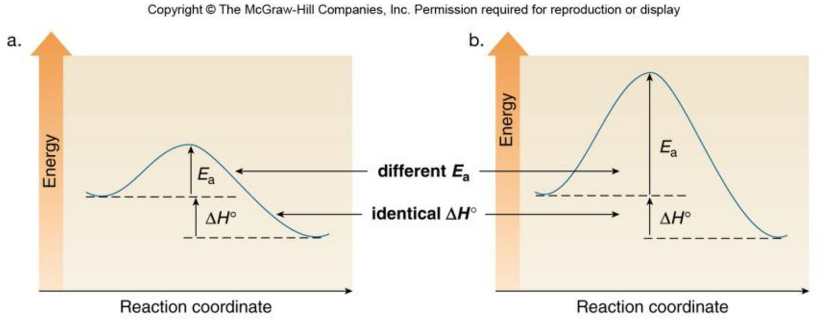
Figure 6.4



- Low E_a → fast reaction
- (–) $\Delta H°$ → exothermic reaction

Comparing $\Delta H°$ and E_a in Energy Diagrams

Figure 6.5



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

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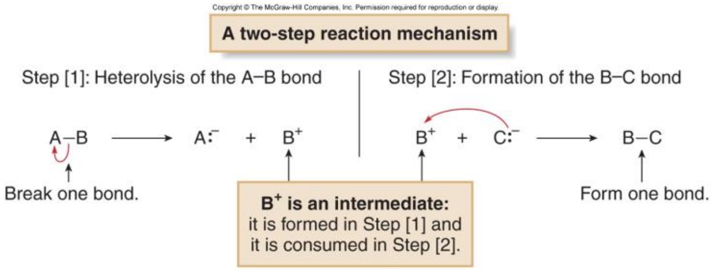
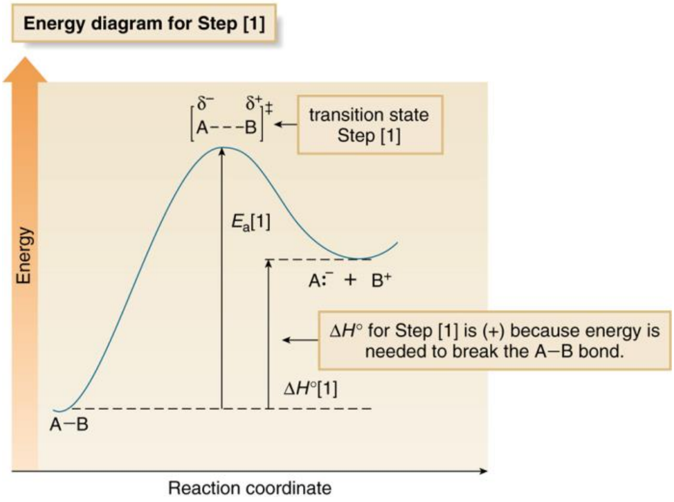
Energy Diagrams and Two-Step Reactions



- **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.**

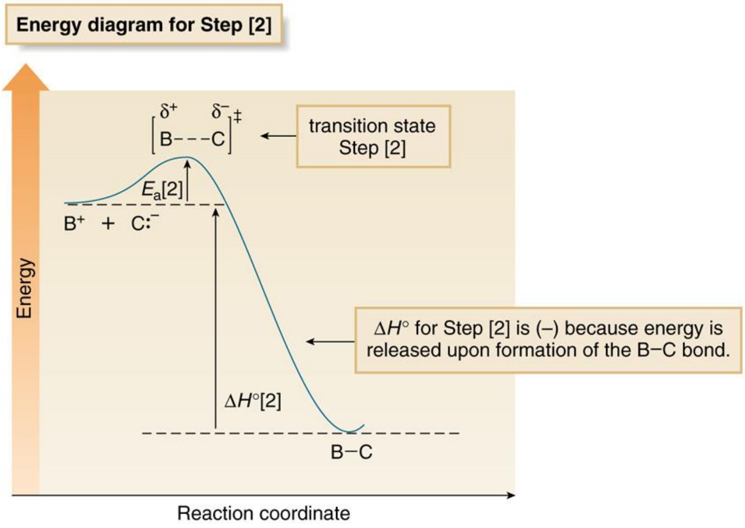
Stepwise Reaction Energy Diagram–Step 1



Energy diagram for Step [1]

ΔH° for Step [1] is (+) because energy is needed to break the A–B bond.

Stepwise Reaction Energy Diagram–Step 2

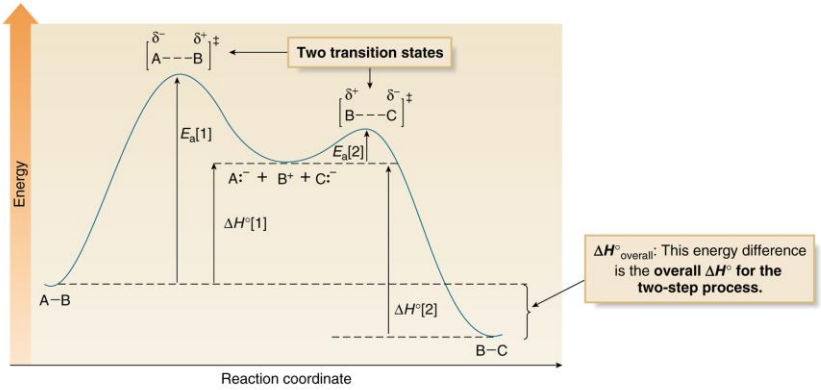


Energy diagram for Step [2]

ΔH° for Step [2] is (–) because energy is released upon formation of the B–C bond.

Stepwise Reaction Overall Energy Diagram

Figure 6.6



- **The transition states are located at energy maxima, while the reactive intermediate B^+ is located at an energy minimum.**
- Each step is characterized by its own value of $\Delta H°$ and E_a.
- The overall energy difference between starting material and products is called $\Delta H°_{overall}$. 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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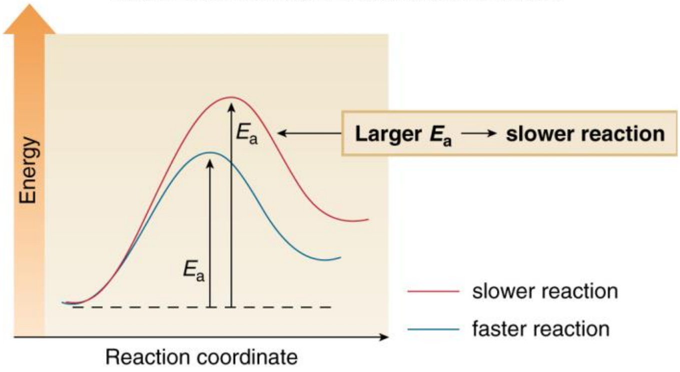
Kinetics and Energy Diagrams

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



Factors Affecting Reaction Rates

1. The higher the concentration, the faster the rate.

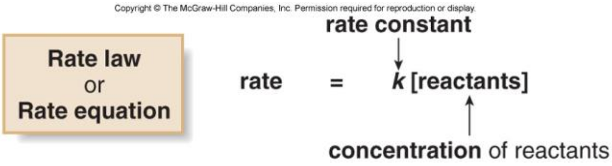
2. The higher the temperature, the faster the rate.

- **– $\Delta G°$, $\Delta H°$, 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.**

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.



Rate law
or
Rate equation

rate constant

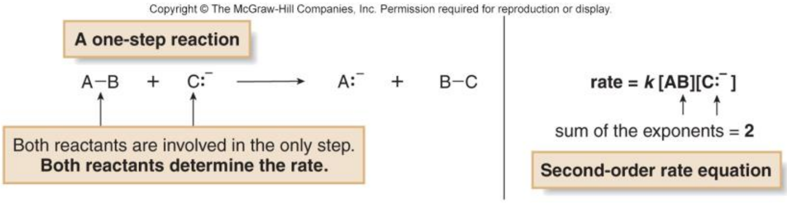
$$\text{rate} = k\,[\text{reactants}]$$

concentration of reactants

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

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.



A one-step reaction

$$A{-}B \;+\; C{:}^- \longrightarrow A{:}^- \;+\; B{-}C$$

Both reactants are involved in the only step.
Both reactants determine the rate.

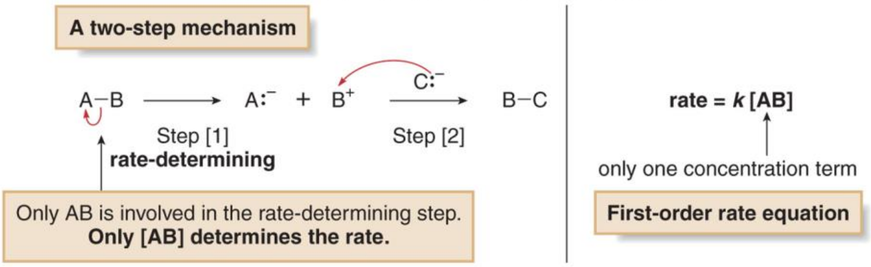
$$\text{rate} = k\,[AB][C{:}^-]$$

sum of the exponents = **2**

Second-order rate equation

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.



A two-step mechanism

$$A{-}B \xrightarrow{} A\!:^- + B^+ \xrightarrow{C:^-} B{-}C$$

Step [1]
rate-determining

Step [2]

Only AB is involved in the rate-determining step.
Only [AB] determines the rate.

rate = *k* [AB]

only one concentration term

First-order rate equation

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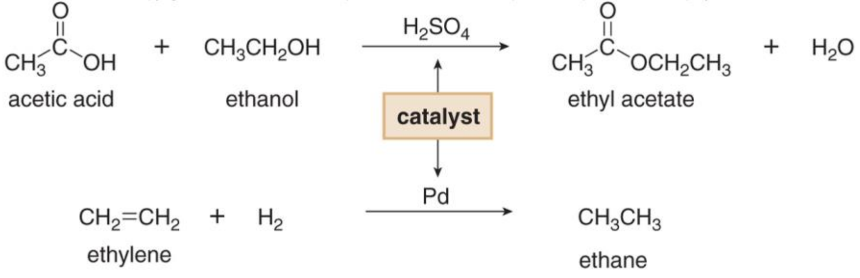
Catalysts

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



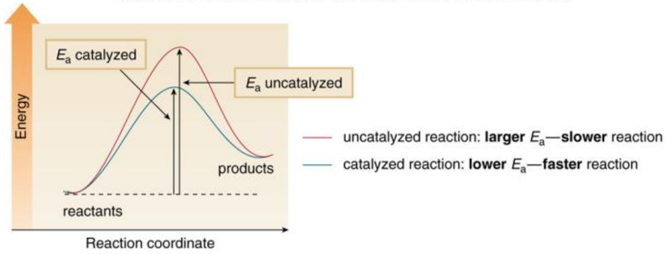
$CH_3COOH + CH_3CH_2OH \xrightarrow{H_2SO_4} CH_3COOCH_2CH_3 + H_2O$

$CH_2{=}CH_2 + H_2 \xrightarrow{Pd} CH_3CH_3$

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 equilibium is unaffected.**

Figure 6.7

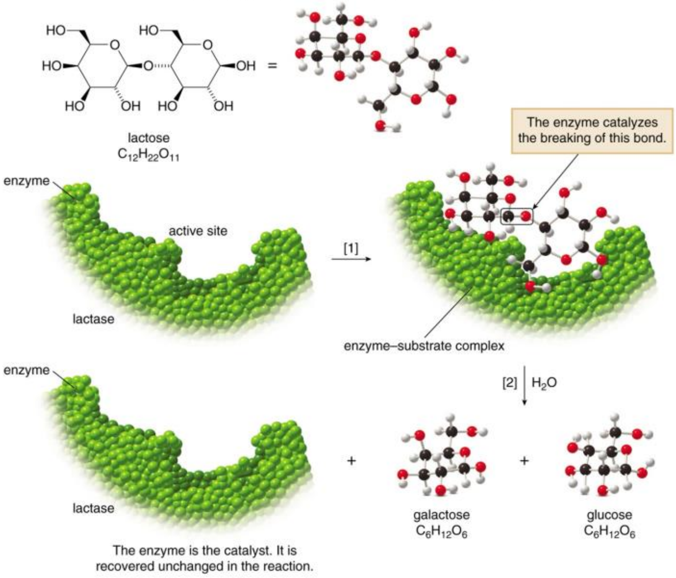


Enzymes

- **<u>Enzymes</u> 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.**

Lactase–a Biological Catalyst

Figure 6.7



The enzyme catalyzes the breaking of this bond.

The enzyme is the catalyst. It is recovered unchanged in the reaction.