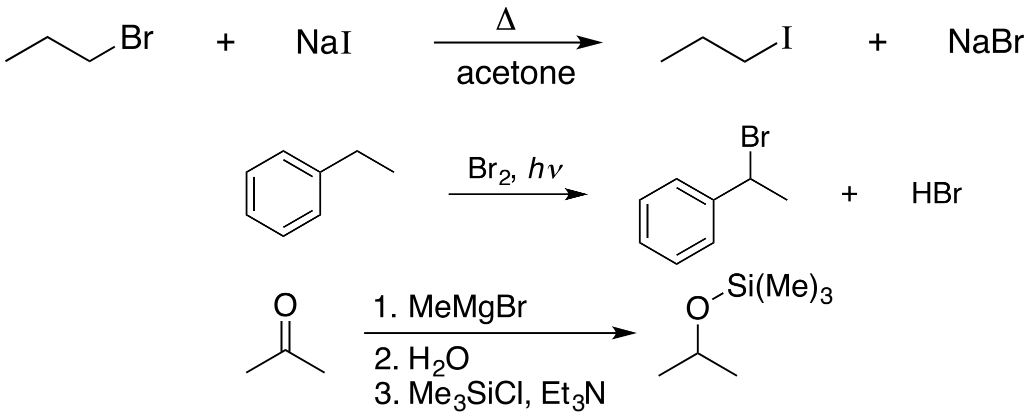
Chapter 6: Chemical Reactivity and Mechanisms

Learning Objectives:

- Discover the details of writing reactions in organic chemistry
- Understand the arrows used in organic chemistry
- Explore the energy concepts (energy profile diagrams & calculate ΔH) for organic reactions
- Examine the kinetics (rates) of some organic reactions
- Survey important concepts related to drawing mechanisms and carbocation rearrangements 6.7–6.12 (full coverage later)

Writing Equations for Organic Reactions



- The reagents can be added above the arrow, most important one is usually first.
- The solvent is often omitted from the equation; however, most organic reactions take place in a liquid solvent.
- The symbols "Δ" and "*hν*" are used for reactions that require heat and light, respectively.

The Arrows Used by Organic Chemists

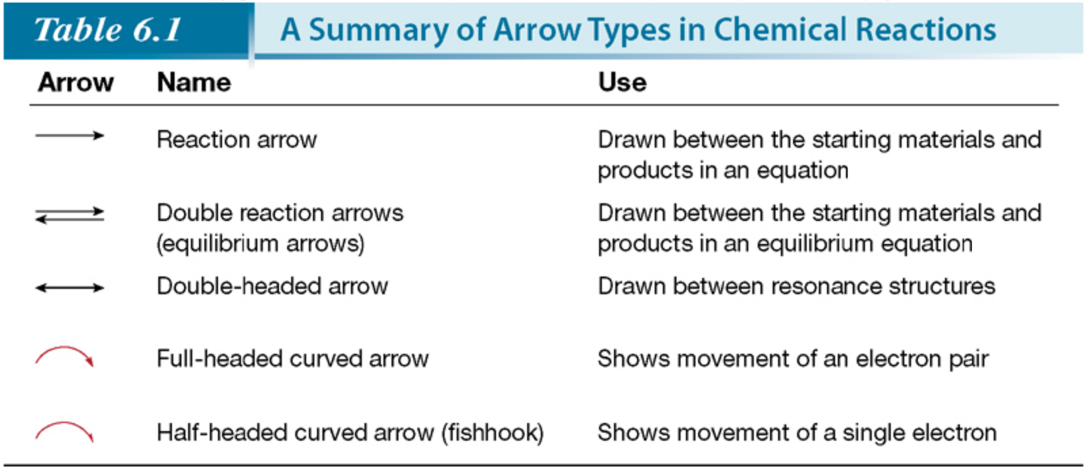


Table 6.1 A Summary of Arrow Types in Chemical Reactions

Arrow	Name	Use
→	Reaction arrow	Drawn between the starting materials and products in an equation
⇄	Double reaction arrows (equilibrium arrows)	Drawn between the starting materials and products in an equilibrium equation
↔	Double-headed arrow	Drawn between resonance structures
↷	Full-headed curved arrow	Shows movement of an electron pair
↷	Half-headed curved arrow (fishhook)	Shows movement of a single electron

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Reaction Mechanisms

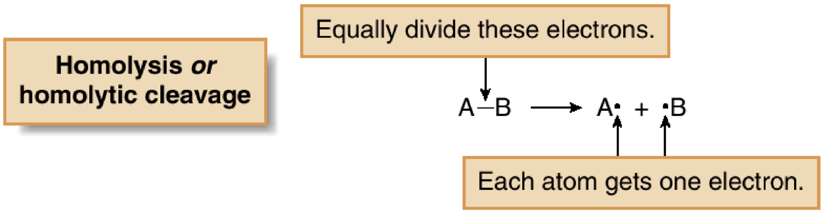
- A reaction mechanism is a detailed description of how bonds are broken and formed as starting material is converted into product.
- Mechanisms can never be proved only disproved.
- A reaction can occur either in one step or a series of steps.
  - **A one-step reaction is called a *concerted reaction.*** 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 Making and Bond Breaking

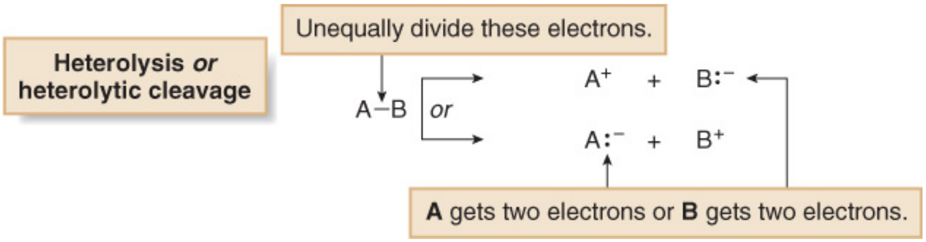


Homolysis *or* homolytic cleavage

Equally divide these electrons.

$A{-}B \longrightarrow A\cdot + \cdot B$

Each atom gets one electron.



Heterolysis *or* heterolytic cleavage

Unequally divide these electrons.

$A{-}B \longrightarrow A^+ + B{:}^-$ *or* $A{:}^- + B^+$

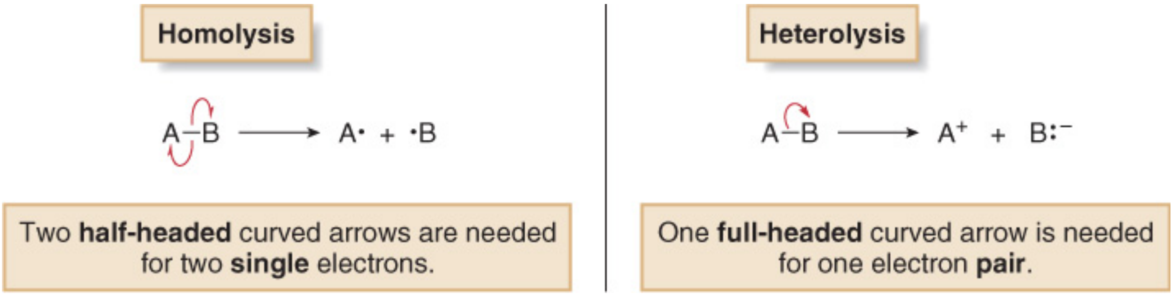
A gets two electrons or **B** gets two electrons.

In heterolysis, the more electronegative atom always gets the electrons!!

- **Homolysis** and **heterolysis** require energy.
- **Homolysis generates uncharged reactive intermediates with unpaired electrons.**
- **Heterolysis generates charged intermediates.**

Drawing Arrows and Bond Breaking

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



Homolysis

$A{-}B \longrightarrow A\cdot + \cdot B$

Two **half-headed** curved arrows are needed for two **single** electrons.

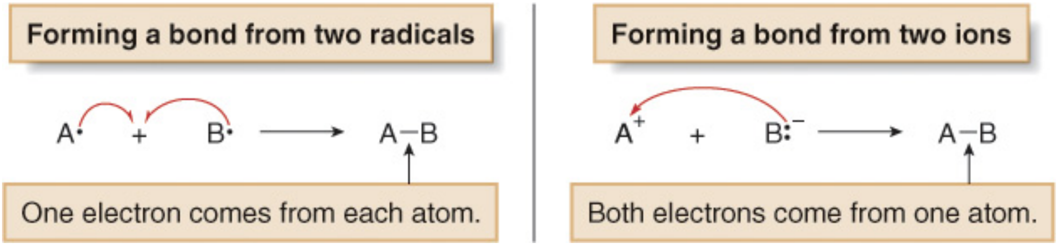
Heterolysis

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

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

Drawing Arrows and Bond Making

- **Bond formation occurs in two different ways.**
- **Two radicals can each donate one electron to form a two-electron bond.**
- **Alternatively, 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.**



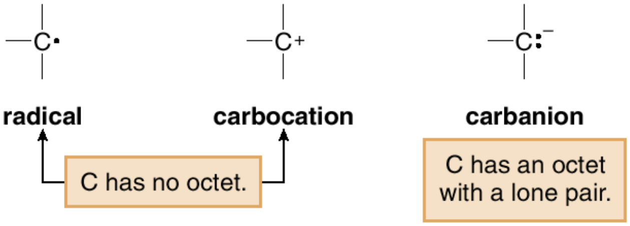
Forming a bond from two radicals

One electron comes from each atom.

Forming a bond from two ions

Both electrons come from one atom.

Radicals, Cations, and Carbanions



radical

carbocation

carbanion

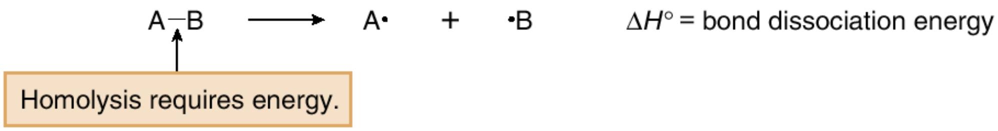
C has no octet.

C has an octet with a lone pair.

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

Bond Dissociation Energy

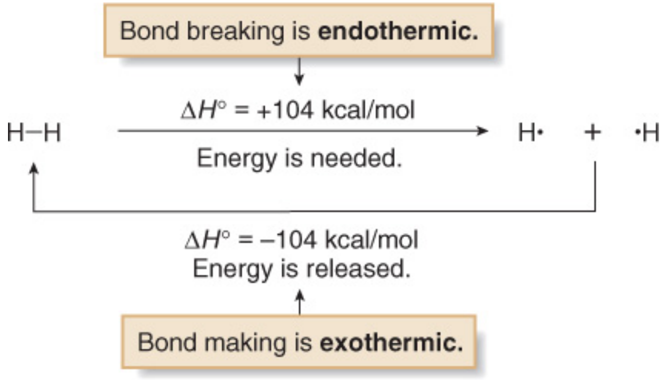
- The *bond dissociation energy* is the energy needed to homolytically cleave a covalent bond.



$$\text{A–B} \longrightarrow \text{A}\cdot + \cdot\text{B} \qquad \Delta H^\circ = \text{bond dissociation energy}$$

Homolysis requires energy.

- When ΔH° is positive (+), energy is absorbed and the reaction is *endothermic.*
- When ΔH° is negative (–), energy is released and the reaction is *exothermic.*



Bond breaking is **endothermic.**

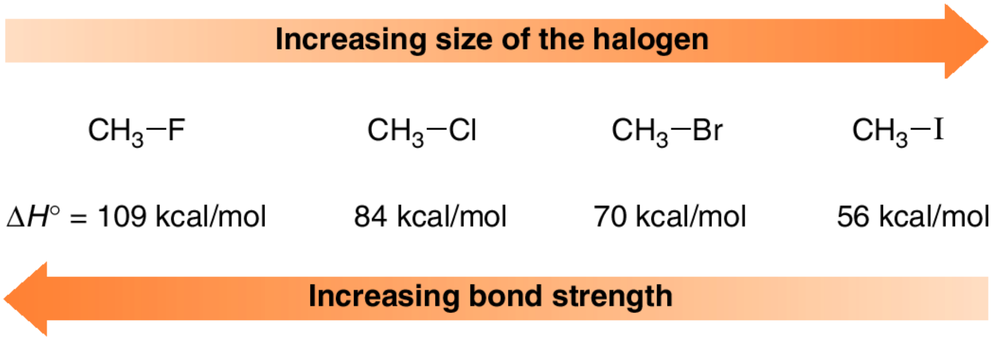
$$\text{H–H} \xrightarrow[\text{Energy is needed.}]{\Delta H^\circ = +104\ \text{kcal/mol}} \text{H}\cdot + \cdot\text{H}$$

$\Delta H^\circ = –104$ kcal/mol
Energy is released.

Bond making is **exothermic.**

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.

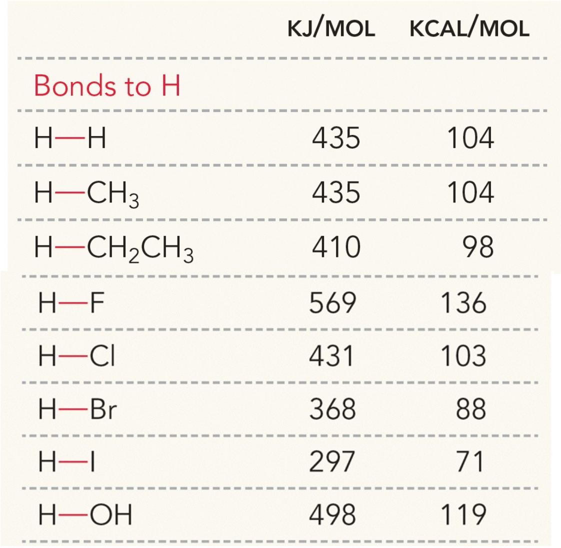


Increasing size of the halogen

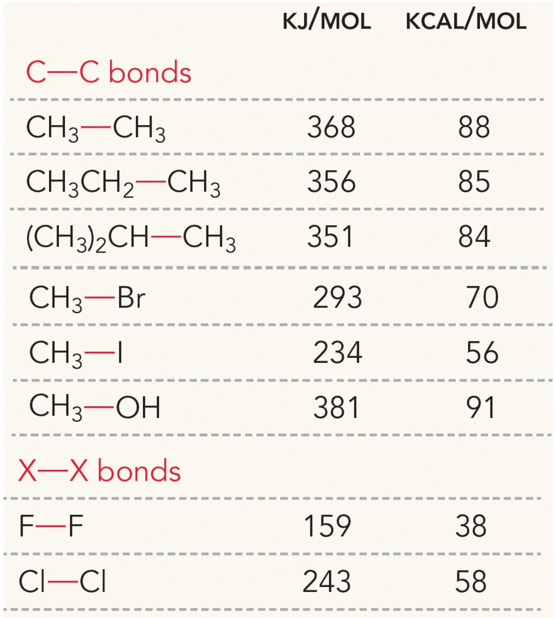
CH_3–F	CH_3–Cl	CH_3–Br	CH_3–I
ΔH° = 109 kcal/mol	84 kcal/mol	70 kcal/mol	56 kcal/mol

Increasing bond strength

6.1 Bond Dissociation Energies



	KJ/MOL	KCAL/MOL
Bonds to H		
H—H	435	104
H—CH_3	435	104
H—CH_2CH_3	410	98
H—F	569	136
H—Cl	431	103
H—Br	368	88
H—I	297	71
H—OH	498	119

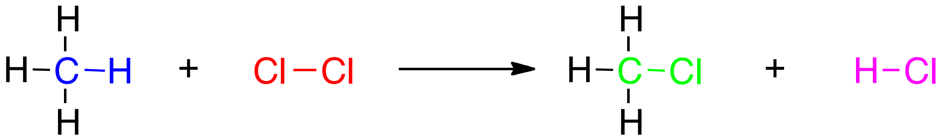


	KJ/MOL	KCAL/MOL
C—C bonds		
CH_3—CH_3	368	88
CH_3CH_2—CH_3	356	85
$(CH_3)_2CH$—CH_3	351	84
CH_3—Br	293	70
CH_3—I	234	56
CH_3—OH	381	91
X—X bonds		
F—F	159	38
Cl—Cl	243	58

More BDEs in table 6.1

Calculating Reaction Enthalpies

$\Delta H°$ overall enthalpy change = sum of $\Delta H°$ of bonds broken + (–) sum of $\Delta H°$ of bonds formed



$$CH_4 + Cl{-}Cl \longrightarrow CH_3{-}Cl + H{-}Cl$$

Reactant Bonds Broken

C-H	ΔH° =	104 kcal/mol
Cl-Cl	ΔH° =	58 kcal/mol
Total		162 kcal/mol

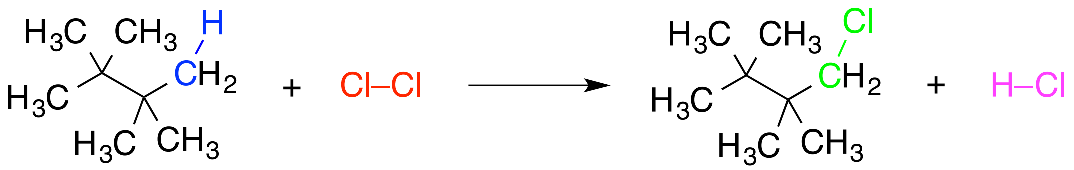
Product Bonds Formed

C-Cl	ΔH° =	84 kcal/mol
H-Cl	ΔH° =	103 kcal/mol
Total		187 kcal/mol

ΔH° = 162 kcal/mol – 187 kcal/mol = –25 kcal/mol

Calculating Reaction Enthalpies

$\Delta H°$ overall enthalpy change = sum of $\Delta H°$ of bonds broken + (–) sum of $\Delta H°$ of bonds formed



Reactant Bonds Broken

C–H	ΔH° = 98 kcal/mol
Cl–Cl	ΔH° = 58 kcal/mol
Total	156 kcal/mol

Product Bonds Formed

C–Cl	ΔH° = 81 kcal/mol
H–Cl	ΔH° = 103 kcal/mol
Total	184 kcal/mol

ΔH° = 156 kcal/mol – 187 kcal/mol = –31 kcal/mol

Limitations of 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.**
- **Bond dissociation energies are imperfect indicators of energy changes in a reaction; however, useful approximations of the energy changes in a reaction can be made.**

Thermodynamics: Equilibrium

- **Thermodynamics describes how the energies of reactants and products compare, and what the relative amounts of reactants and products are at equilibrium.**
- **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

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

- **When $K_{eq} > 1$, the equilibrium lies to the right.**
- **When $K_{eq} < 1$, the equilibrium lies to the left.**
- **The position of the equilibrium (magnitude of K_{eq}) is determined by the relative energies (ΔG°) of the reactants and products.**

Thermodynamics

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

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

R = 1.987 cal/(K•mol), the gas constant
T = Kelvin temperature (K)

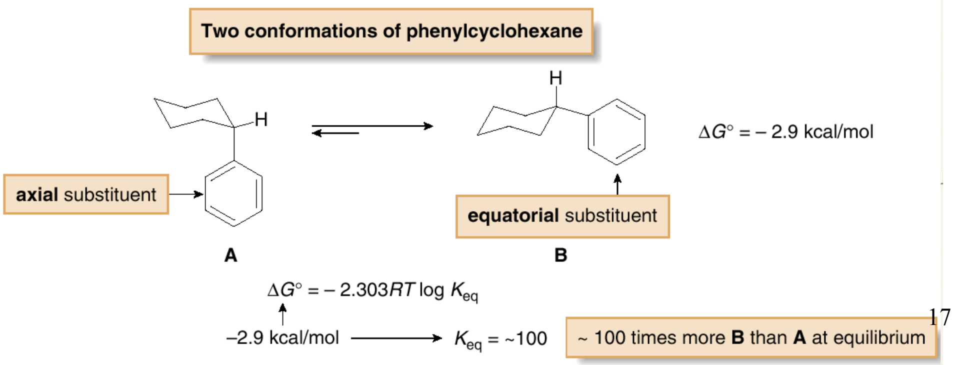
K_{eq} depends on the energy difference between reactants and products.

TABLE 6.2 SAMPLE VALUES OF ΔG AND CORRESPONDING K_{eq}

ΔG° (KJ/MOL)	K_{eq}	% PRODUCTS AT EQUILIBRIUM
-17	10^{3}	99.9%
-11	10^{2}	99%
-6	10^{1}	90%
0	1	50%
$+6$	10^{-1}	10%
$+11$	10^{-2}	1%
$+17$	10^{-3}	0.1%

Thermodynamics

- Compounds that are lower in energy have increased stability.
- The equilibrium favors the products when they are more stable (lower in energy) than the starting materials of a reaction.
- 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.
- For example, knowing the energy difference between two conformations permits the calculation of the amount of each at equilibrium.



Two conformations of phenylcyclohexane

$\Delta G^\circ = -2.9$ kcal/mol

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

$$-2.9 \text{ kcal/mol} \longrightarrow K_{eq} = \sim 100$$

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

Enthalpy and Entropy

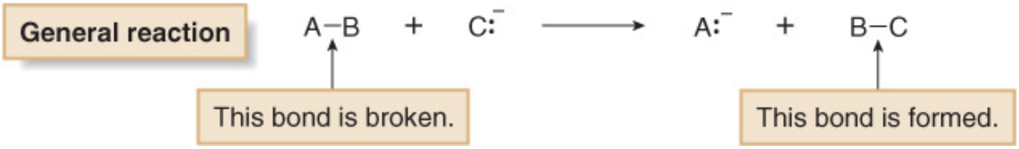
Total energy change → $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ [T = Kelvin temperature]

ΔH°: change in bonding energy

$T\Delta S^\circ$: change in disorder

- This equation indicates that the total energy change is due to two factors: the change in bonding energy and the change in disorder (ΔS°, entropy).
- ΔS° is (+) when the products are more disordered than the reactants. ΔS° is (–) when the products are less disordered than the reactants.
- Reactions resulting in increased entropy are favored.
- Entropy changes are important when
  - The number of molecules of starting material differ from the number of molecules of product in the balanced chemical equation.
  - An acyclic molecule is cyclized to a cyclic one, or a cyclic molecule is converted to an acyclic one.

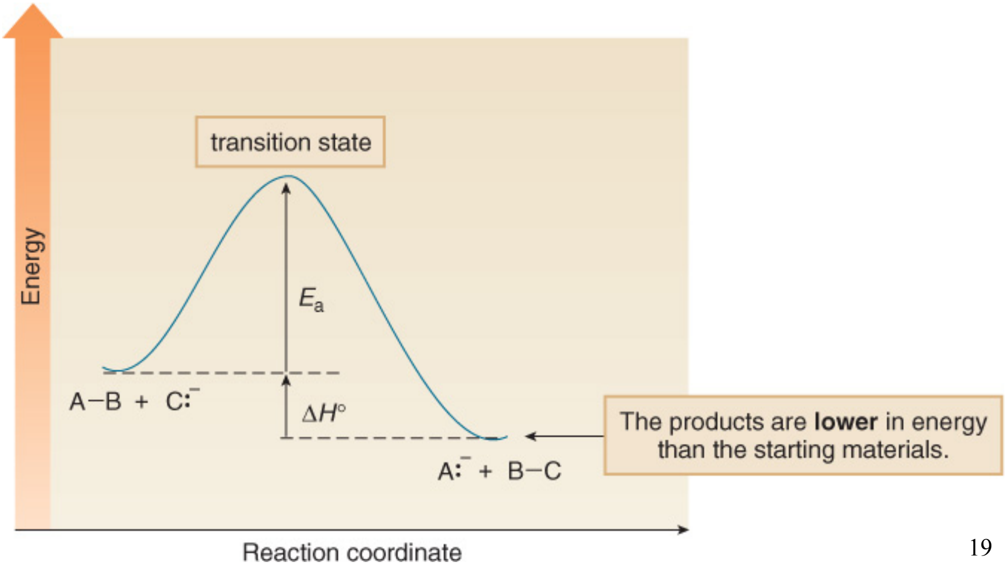
Energy Diagrams



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

This bond is broken.

This bond is formed.

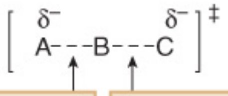


The products are **lower** in energy than the starting materials.

E_a and the Transition State

- **The energy of activation is the minimum amount of energy needed to break the bonds in the reactants.**
- **The larger the E_a, the greater the amount of energy that is needed to break bonds, and the slower the reaction rate.**
- **The structure of the transition state is somewhere between the structures of the starting material and product. Bonds that are forming or breaking are drawn with a dashed line, and 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

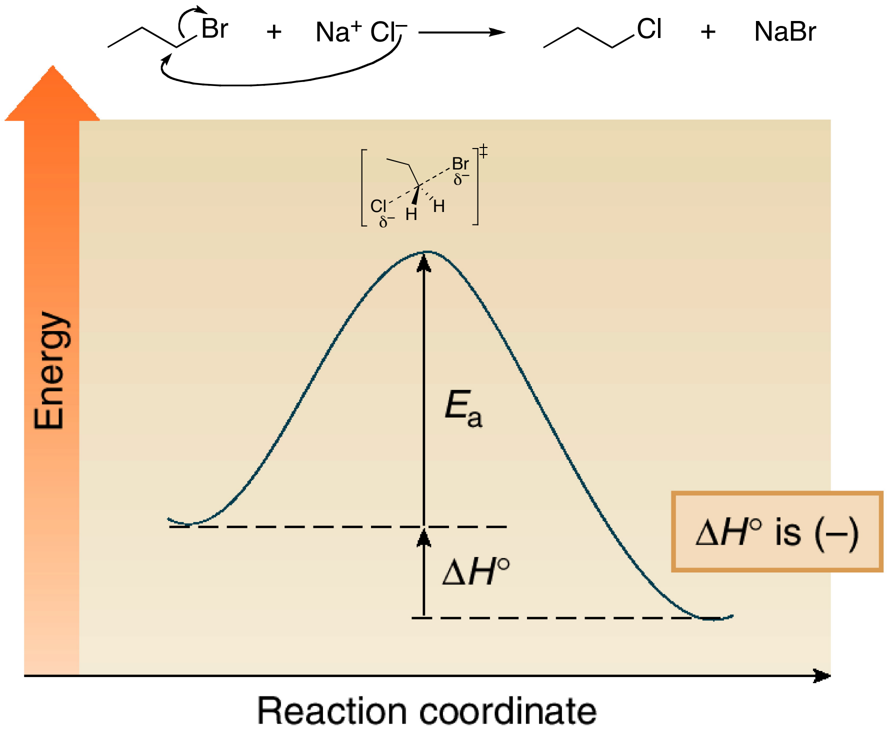


$$\left[\overset{\delta^-}{A}\text{- - -}B\text{- - -}\overset{\delta^-}{C}\right]^\ddagger$$

This bond is partially broken.

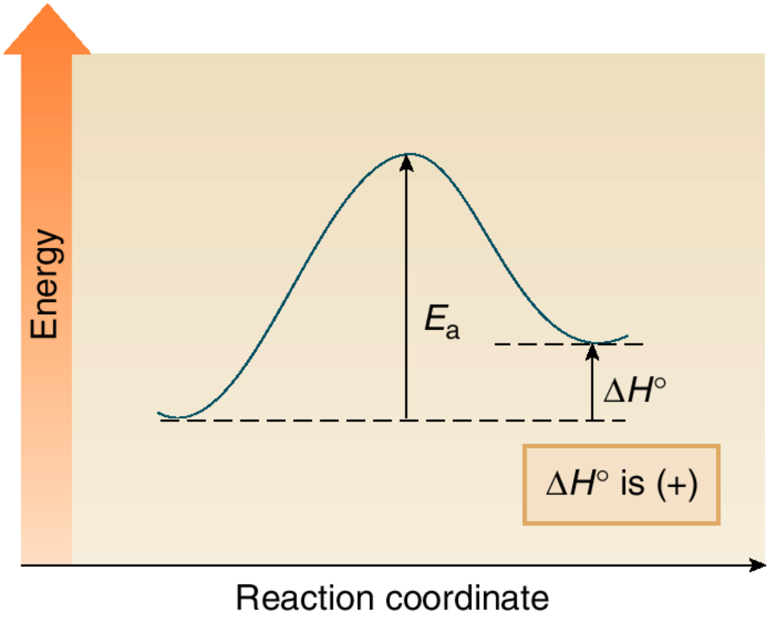
This bond is partially formed.

Energy Diagrams: An Example of a Substitution Reaction



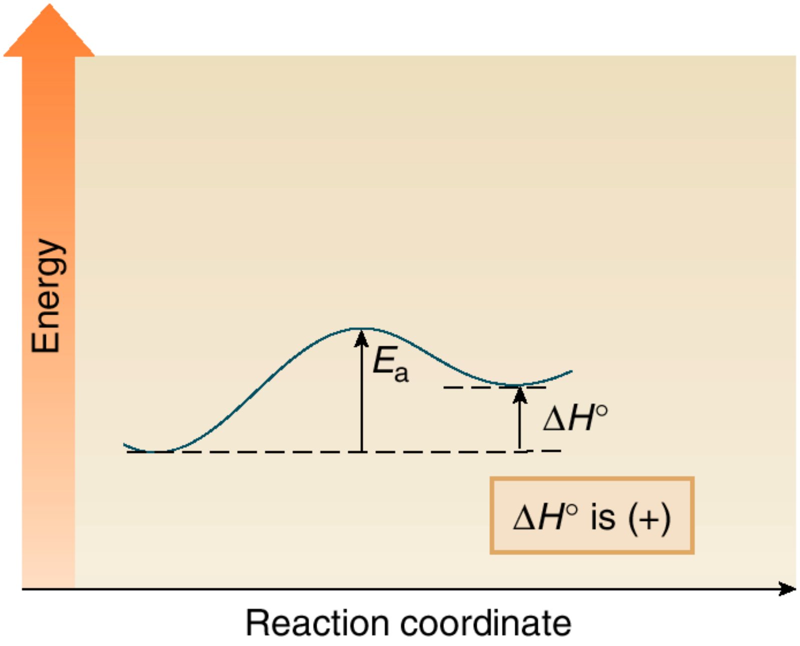
A Slow Endothermic Reaction

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



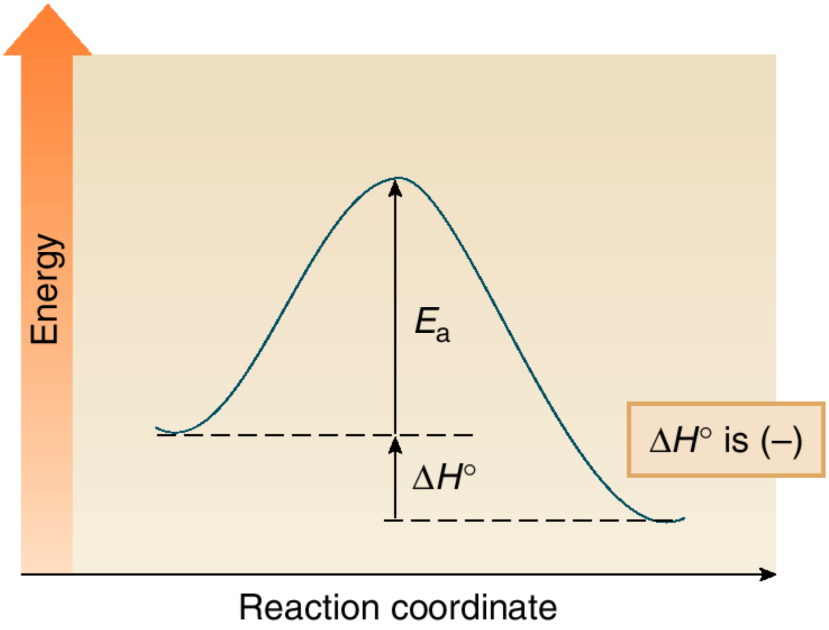
A Fast Endothermic Reaction

- Low **E_a** ⟶ **fast reaction**
- **(+) $\Delta H°$** ⟶ **endothermic reaction**



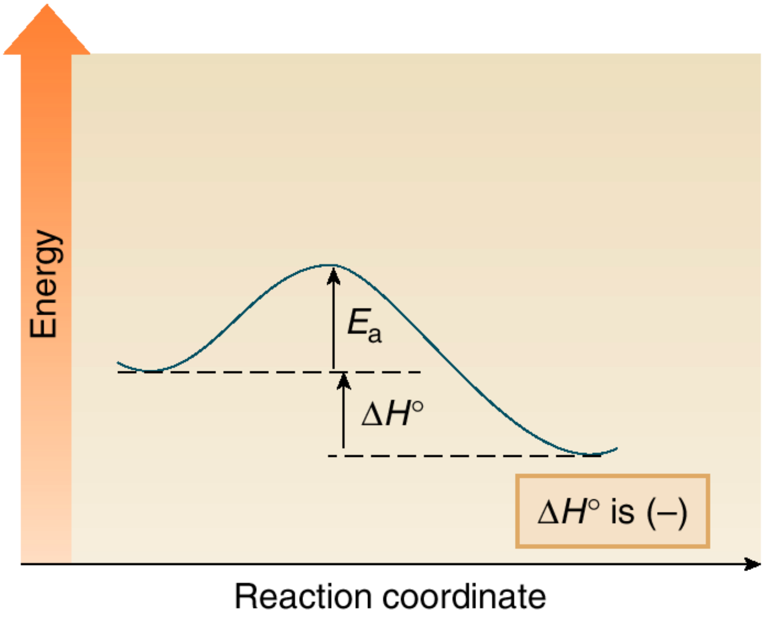
A Slow Exothermic Reaction

- **Large E_a** ⟶ **slow reaction**
- **(–) $\Delta H°$** ⟶ **exothermic reaction**

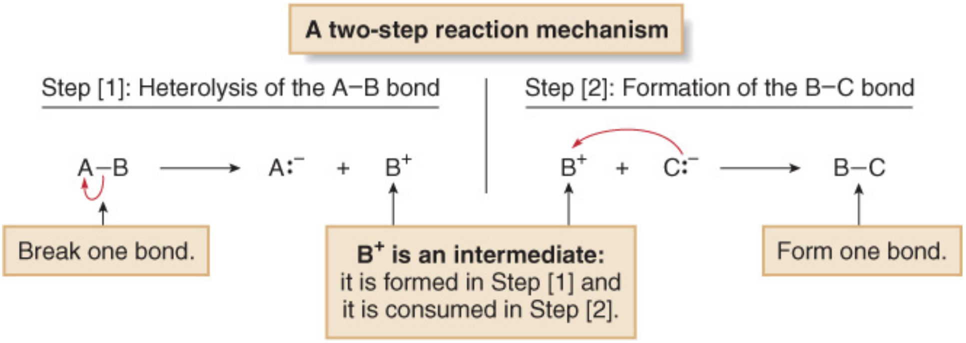


A Fast Exothermic Reaction

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



An Energy Profile Diagram for a 2-Step Reaction



A two-step reaction mechanism

Step [1]: Heterolysis of the A–B bond

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

Break one bond.

Step [2]: Formation of the B–C bond

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

Form one bond.

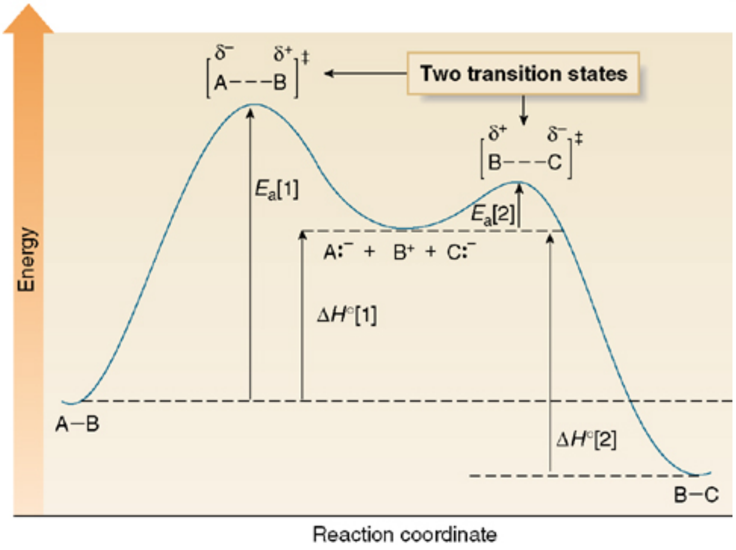
B^+ is an intermediate: it is formed in Step [1] and it is consumed in Step [2].

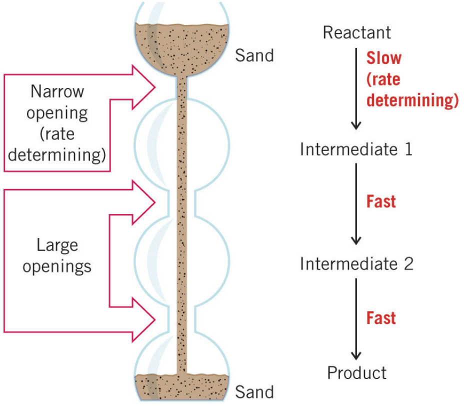
- **An energy diagram must be drawn for each step.**
- **The two energy diagrams must then be combined to form an energy diagram for the overall two-step reaction.**
- **Each step has its own energy barrier, with a transition state at each energy maximum.**

An Energy Profile Diagram for a 2-Step Reaction

$$\text{Reactant} \xrightarrow[\text{(slow)}]{k_1} \text{intermediate 1} \xrightarrow[\text{(fast)}]{k_2} \text{intermediate 2} \xrightarrow[\text{(fast)}]{k_3} \text{product}$$

Step 1 *Step 2* *Step 3*

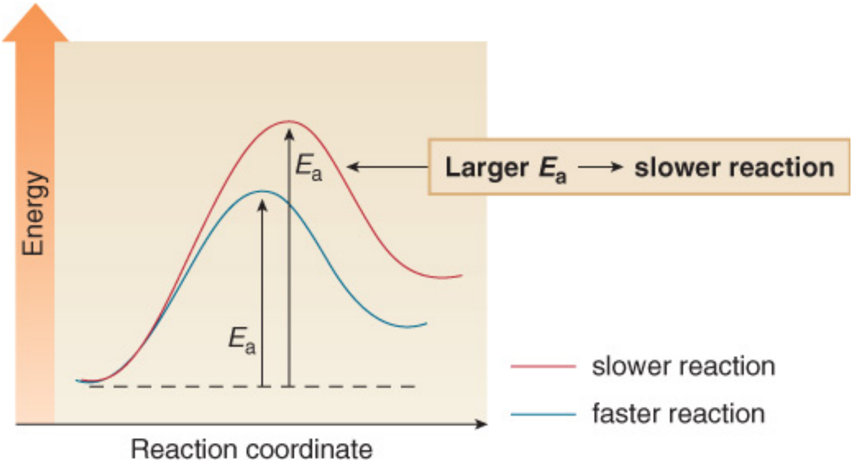




- The overall rate of a multi-step reaction will be determined by the rate of the step with the highest E_a.

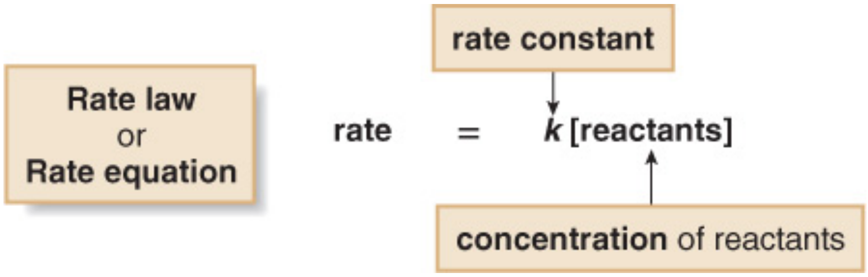
Kinetics (Reaction Rates)

- **Recall that E_a is the energy barrier that must be exceeded for reactants to be converted to products.**



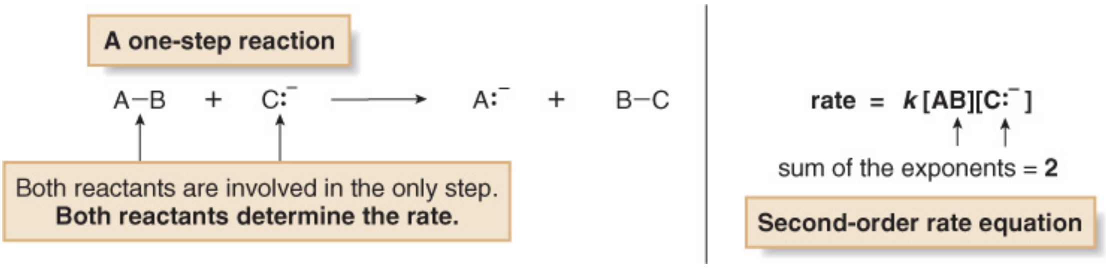
Controlling the Kinetics of a Reaction

- **The higher the concentration, the faster the rate.**
- **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.**
- **The rate law or rate equation shows the relationship between the reaction rate and the concentration of the reactants. It is experimentally determined.**



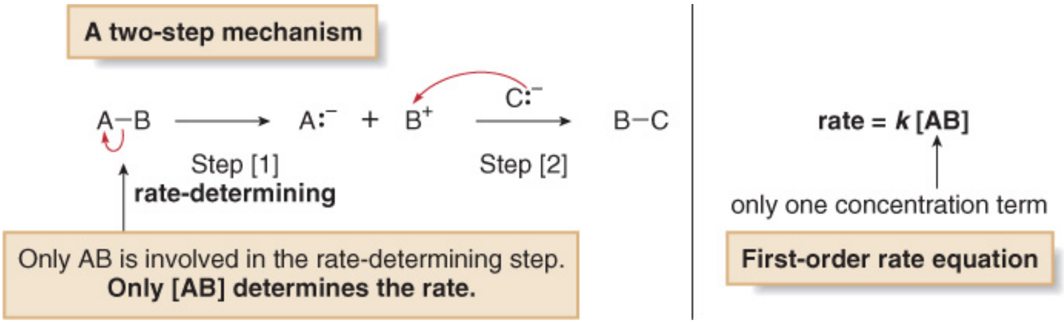
The Rate Equation

- **Fast reactions have large rate constants.**
- **Slow reactions have small rate constants.**
- **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 the slowest step of the reaction.**
- **The order of a rate equation equals the sum of the exponents of the concentration terms in the rate equation.**



The Rate-Determining Step (RDS) of a Reaction

- **Reactions have a rate-determining step in their mechanism. This is always the slowest step of the reaction.**
- **In a multi-step mechanism, the reaction can occur no faster than its rate-determining step.**
- **Only the concentration of the reactants in the rate-determining step are included in the rate equation.**



Catalysts

- **A catalyst increases the rate of reaction, but it is not consumed.**
- **A catalyst lowers the E_a by creating a multiple step reaction. This increases the rate of the reaction.**
- **The energy of the reactants and products is the same in both the catalyzed and uncatalyzed reactions. Thus, K_{eq} does not change.**