

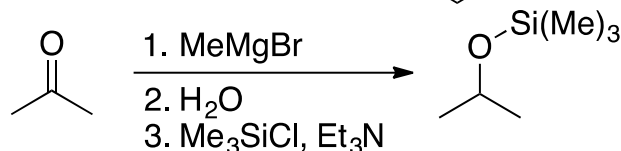
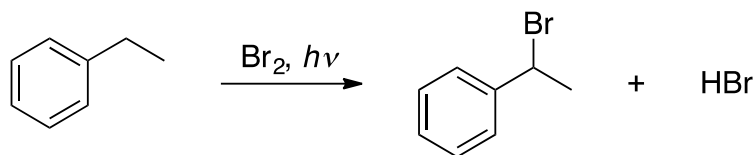
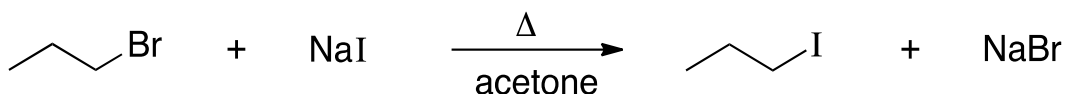
Chapter 6: Chemical Reactivity and Mechanisms

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/**READ!!!** important concepts related to drawing mechanisms and carbocation rearrangements 6.7–6.12 (full coverage later)

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Writing Equations for Organic Reactions



- Reagents often added above the arrow, most important is usually first.
- Solvent is often omitted; however, most organic reactions take place in a liquid solvent.
- Symbols “ Δ ” and “ $h\nu$ ” are used for reactions that require heat and light, respectively.






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The Arrows Used by Organic Chemists

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Table 6.1

A Summary of Arrow Types in Chemical Reactions

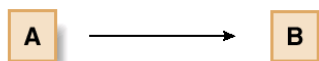
Arrow	Name	Use
	Reaction arrow	Drawn between the starting materials and products in an equation
	Double reaction arrows (equilibrium arrows)	Drawn between the starting materials and products in an equilibrium equation
	Double-headed arrow	Drawn between resonance structures
	Full-headed curved arrow	Shows 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.
- Mechanisms can never be proved only disproved.
- Reactions 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 **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.

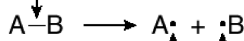


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Bond Making and Bond Breaking

Homolysis or
homolytic cleavage

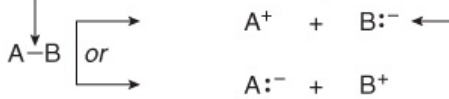
Equally divide these electrons.



Each atom gets one electron.

Heterolysis or
heterolytic cleavage

Unequally divide these electrons.



A gets two electrons or B gets two electrons.

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

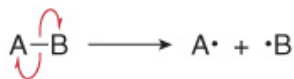
- **Bond Breaking requires energy.**
 - ★ **Homolysis generates uncharged reactive intermediates with unpaired electrons called radicals.**
 - ★ **Heterolysis generates charged intermediates.**

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Drawing Arrows and Bond Breaking

- **Movement of a single electron uses a half-headed curved arrow, sometimes called a fishhook.**
- **Movement of an electron pair uses a full headed curved arrow.**

Homolysis



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

Heterolysis



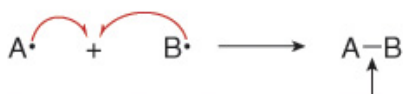
One **full-headed** curved arrow is needed for one electron **pair**.

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Drawing Arrows and Bond Making

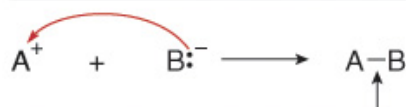
- Bond formation occurs in two different ways:
 1. Two radicals can each donate one electron to form a two-electron bond.
 2. Two ions with different charges can come together to form the resulting two-electron bond. Note: arrow starts with (-).
- Bond formation always releases energy.

Forming a bond from two radicals



One electron comes from each atom.

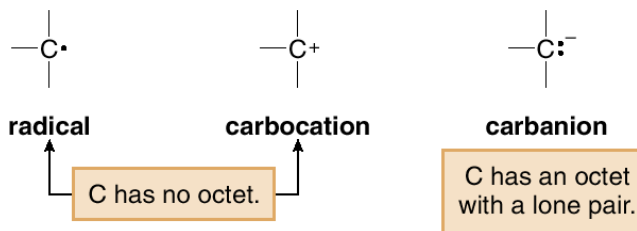
Forming a bond from two ions



Both electrons come from one atom.

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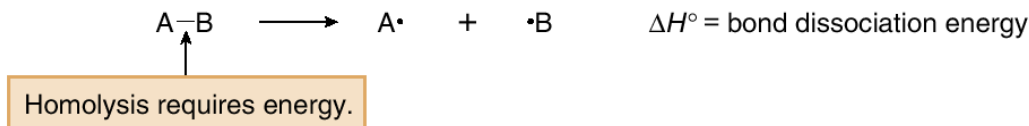
Radicals, Cations, and Carbanions



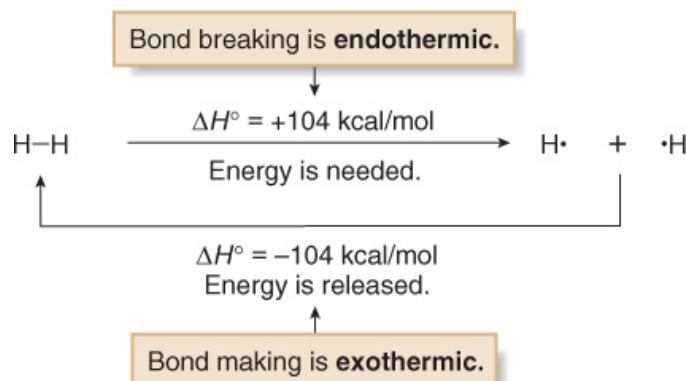
- Radicals and carbocations are electrophiles because they contain an electron-deficient carbon.
- Carbanions are nucleophiles because they contain a carbon with a lone pair.

Bond Dissociation Energy

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



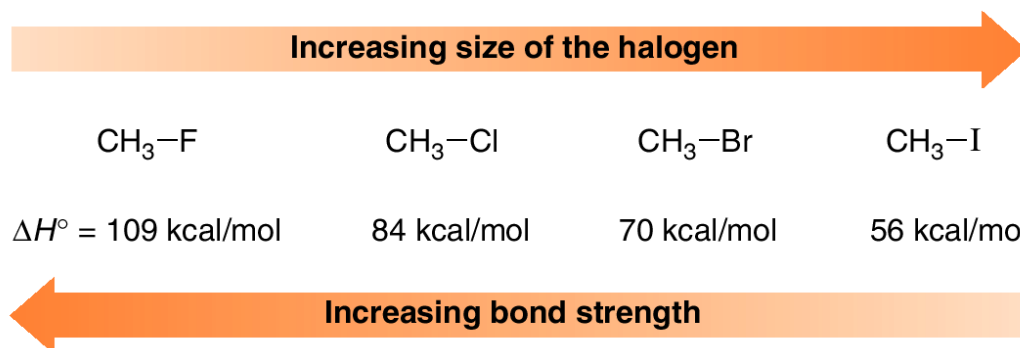
- When ΔH° is positive (+), energy is absorbed and the reaction is *endothermic*.
- When ΔH° is negative (-), energy is released and the reaction is *exothermic*.



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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.



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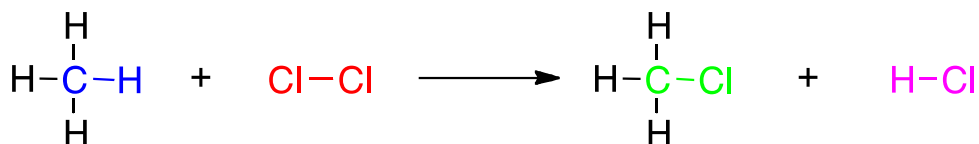
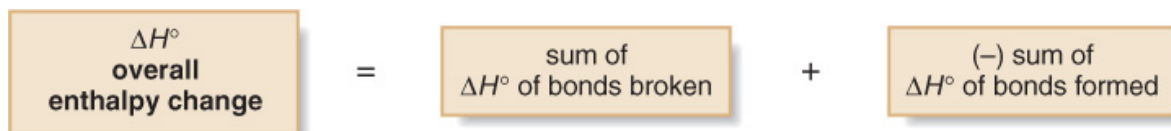
Bond Dissociation Energies

	KJ/MOL	KCAL/MOL		KJ/MOL	KCAL/MOL
Bonds to H			C—C bonds		
H—H	435	104	CH ₃ —CH ₃	368	88
H—CH ₃	435	104	CH ₃ CH ₂ —CH ₃	356	85
H—CH ₂ CH ₃	410	98	(CH ₃) ₂ CH—CH ₃	351	84
H—F	569	136	CH ₃ —Br	293	70
H—Cl	431	103	CH ₃ —I	234	56
H—Br	368	88	CH ₃ —OH	381	91
H—I	297	71	X—X bonds		
H—OH	498	119	F—F	159	38
			Cl—Cl	243	58

More BDEs in table 6.1

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Calculating Reaction Enthalpies



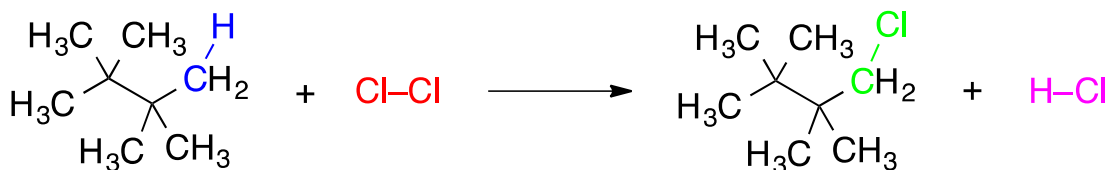
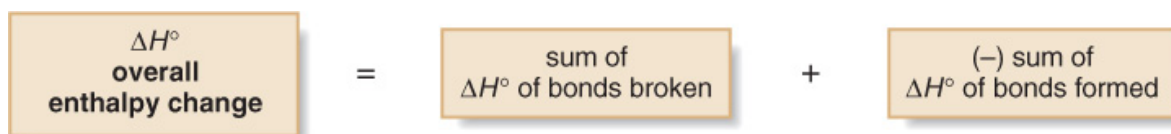
Reactant Bonds Broken	
C-H	$\Delta H^\circ = 104 \text{ kcal/mol}$
Cl-Cl	$\Delta H^\circ = 58 \text{ kcal/mol}$
Total	162 kcal/mol

Product Bonds Formed	
C-Cl	$\Delta H^\circ = 84 \text{ kcal/mol}$
H-Cl	$\Delta H^\circ = 103 \text{ kcal/mol}$
Total	187 kcal/mol

$$\Delta H^\circ = 162 \text{ kcal/mol} - 187 \text{ kcal/mol} = -25 \text{ kcal/mol}$$

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Calculating Reaction Enthalpies



Reactant Bonds Broken	
C-H	$\Delta H^\circ = 98 \text{ kcal/mol}$
Cl-Cl	$\Delta H^\circ = 58 \text{ kcal/mol}$
Total	156 kcal/mol

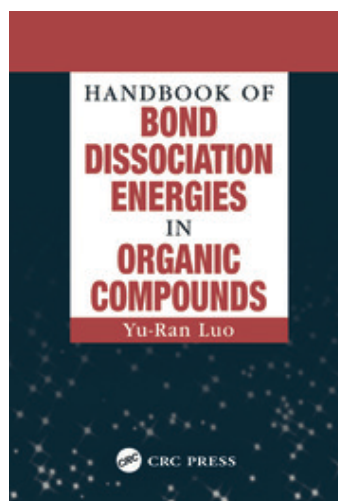
Product Bonds Formed	
C-Cl	$\Delta H^\circ = 81 \text{ kcal/mol}$
H-Cl	$\Delta H^\circ = 103 \text{ kcal/mol}$
Total	184 kcal/mol

$$\Delta H^\circ = 156 \text{ kcal/mol} - 187 \text{ kcal/mol} = -31 \text{ kcal/mol}$$

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Limitations of Bond Dissociation Energies

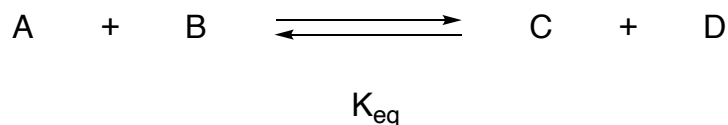
1. They present overall energy changes, but nothing about the mechanism or reaction rate.
2. They are determined for reactions in the gas phase, but most organic reactions occur in a liquid solvent where solvation energy contributes to the overall enthalpy of a reaction.



While these are imperfect indicators of energy changes in a reaction, they are useful approximations of the energy changes in a reaction.

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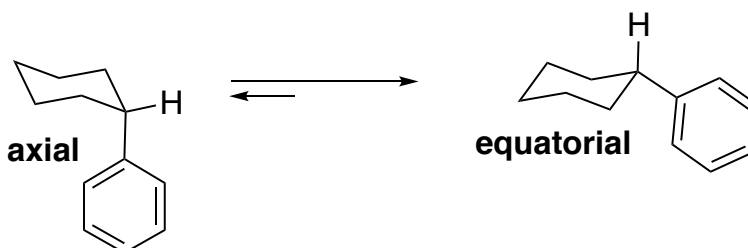
Thermodynamics: Equilibrium



- Thermodynamics describes how the energies of reactants and products compare, and what the relative amounts of reactants and products are at equilibrium.
- Mathematically this is described as K_{eq}
- When $K_{eq} > 1$, the equilibrium lies to the right.
- When $K_{eq} < 1$, the equilibrium lies to the left.
- The magnitude of K_{eq} is determined by the relative energies (ΔG°) of the reactants and products.

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Thermodynamics



- Compounds that are lower in energy have increased stability.
- 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.

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Thermodynamics K_{eq}

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

$$\Delta G^\circ = -2.303RT \log K_{eq} \quad \left[\begin{array}{l} R = 1.987 \text{ cal}/(\text{K}\cdot\text{mol}), \text{ the gas constant} \\ T = \text{Kelvin temperature (K)} \end{array} \right]$$

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%

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Enthalpy and Entropy

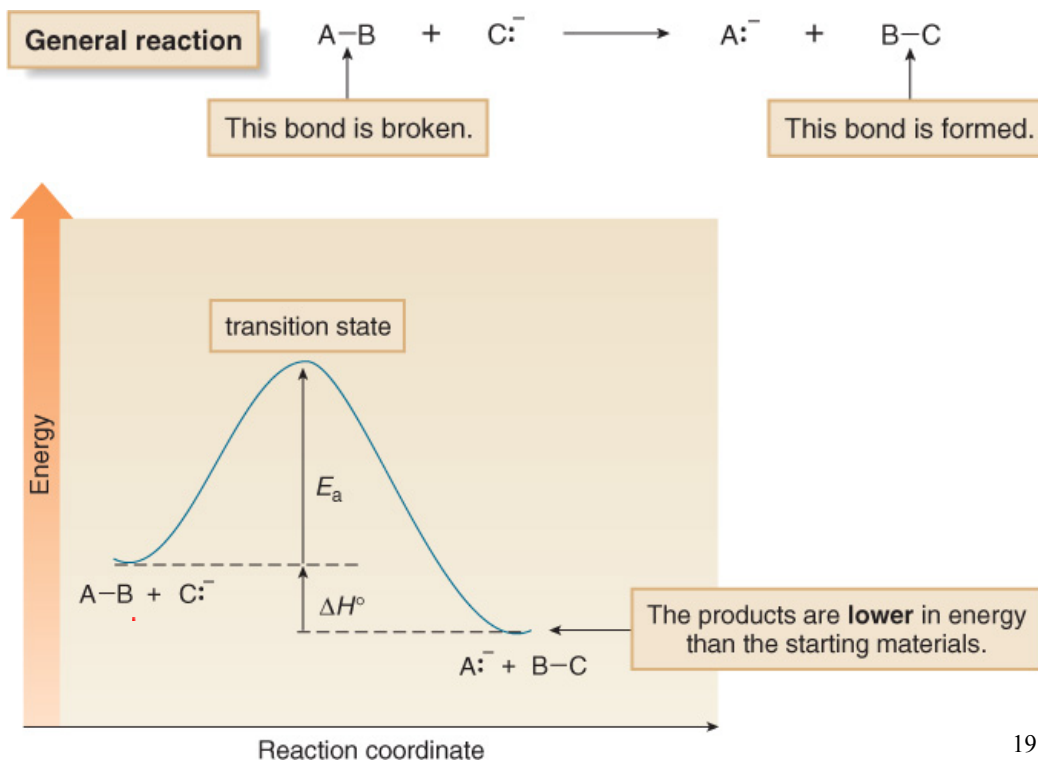
Total energy change $\rightarrow \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ [$T = \text{Kelvin temperature}$]

\uparrow
change in bonding energy
 \uparrow
change in disorder

- Free Energy (ΔG°) is due to two factors: the change in bonding energy/enthalpy (ΔH°) and the change in entropy (ΔS°).**
 - 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.
 - An acyclic molecule is cyclized to a cyclic one, or a cyclic molecule is converted to an acyclic one.

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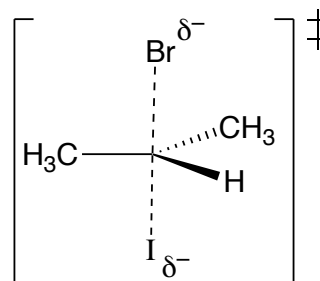
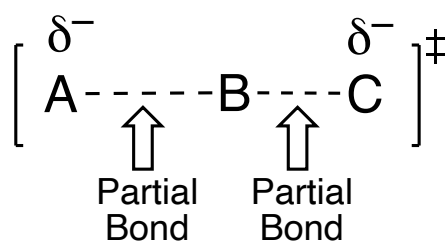
Energy Diagrams



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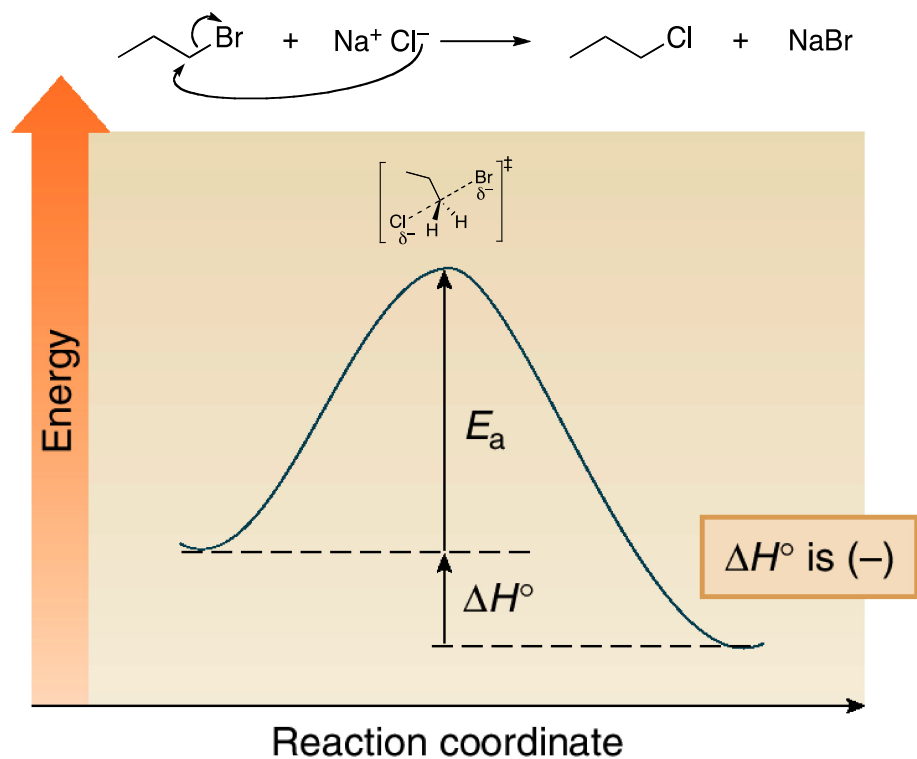
E_a and the Transition State

- E_a (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 (\ddagger).



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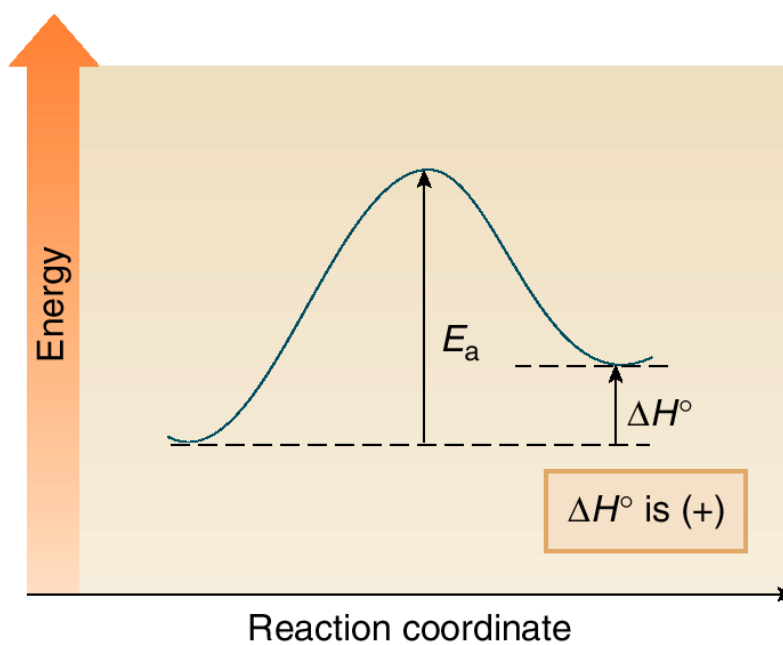
Energy Diagrams: An Example of a Substitution Reaction



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A Slow Endothermic Reaction

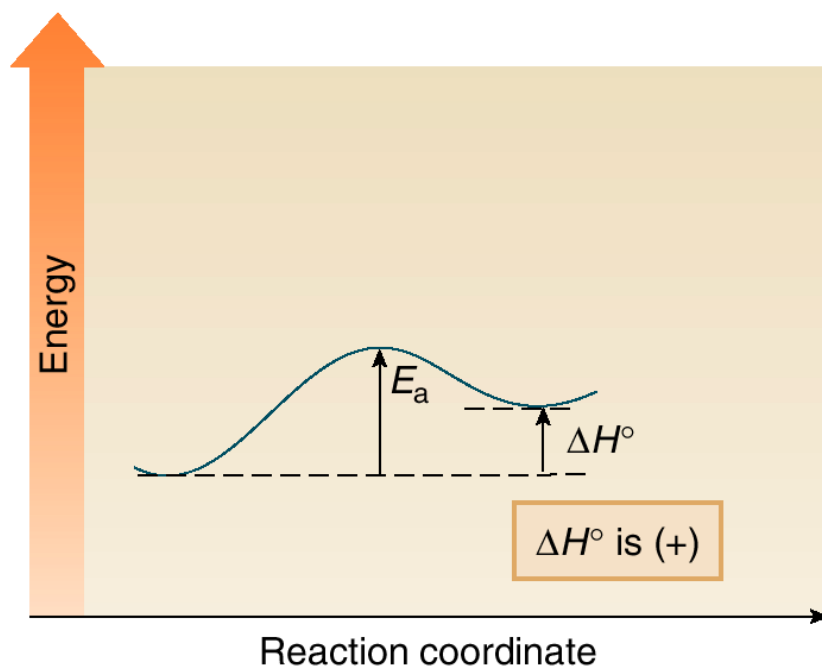
- Large $E_a \rightarrow$ slow reaction
- (+) $\Delta H^\circ \rightarrow$ endothermic reaction



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A Fast Endothermic Reaction

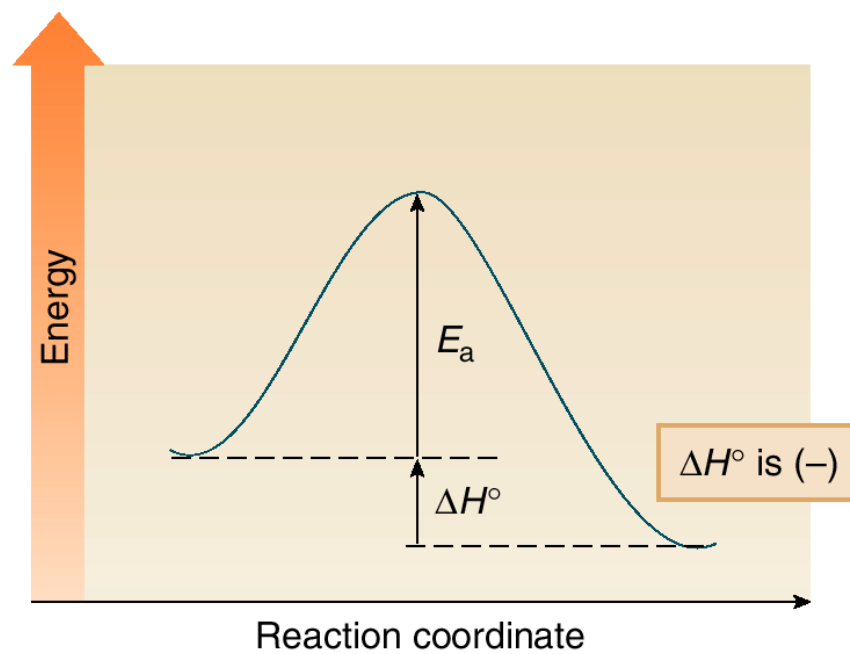
- Low E_a \rightarrow fast reaction
- (+) ΔH° \rightarrow endothermic reaction



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A Slow Exothermic Reaction

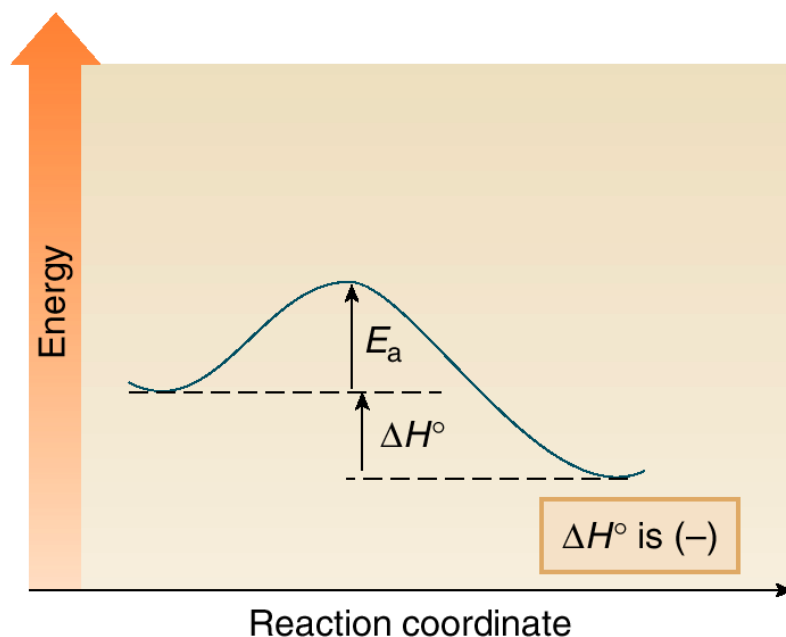
- Large E_a \rightarrow slow reaction
- (-) ΔH° \rightarrow exothermic reaction



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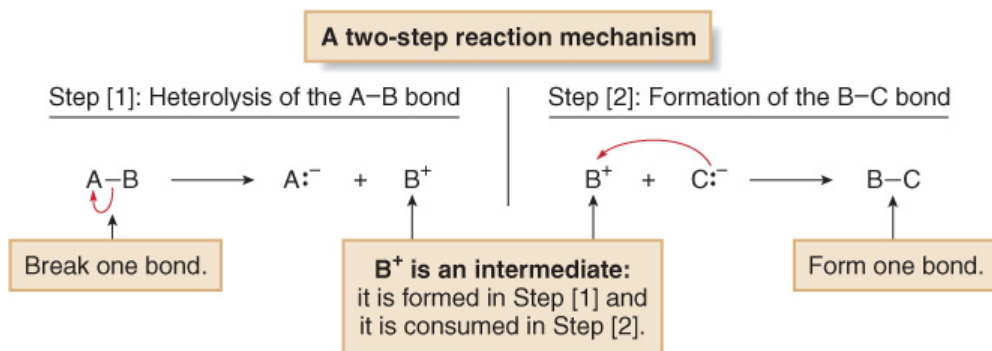
A Fast Exothermic Reaction

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



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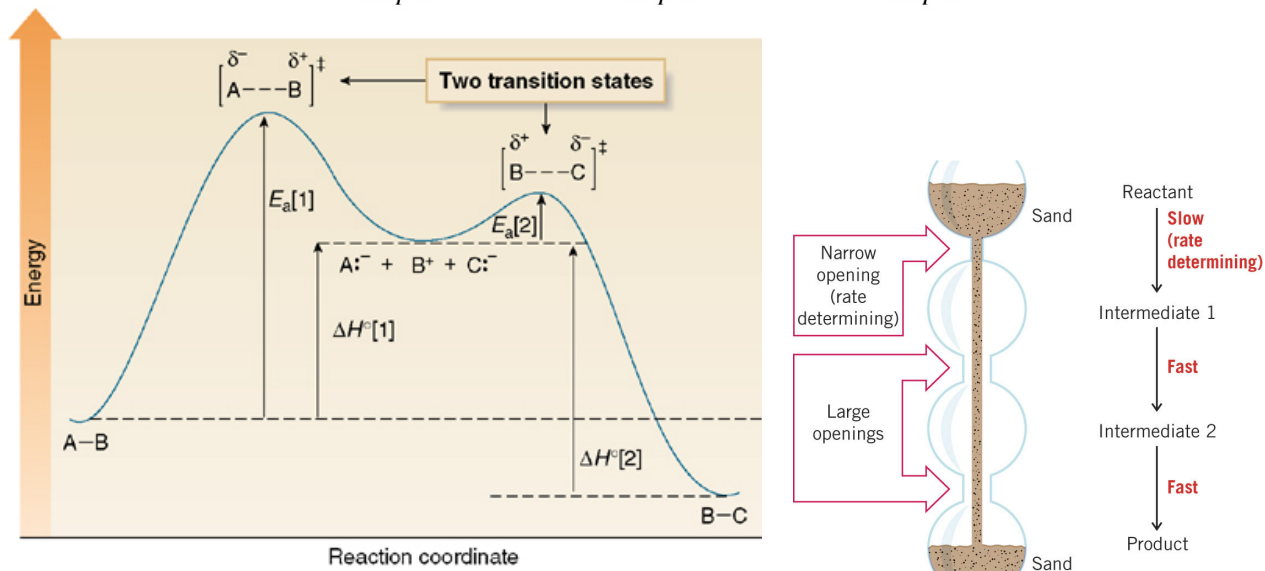
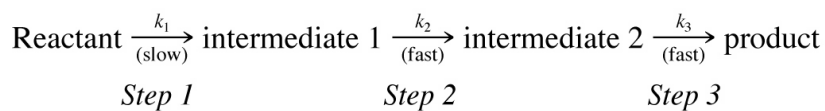
An Energy Profile Diagram for a 2-Step Reaction



- 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.

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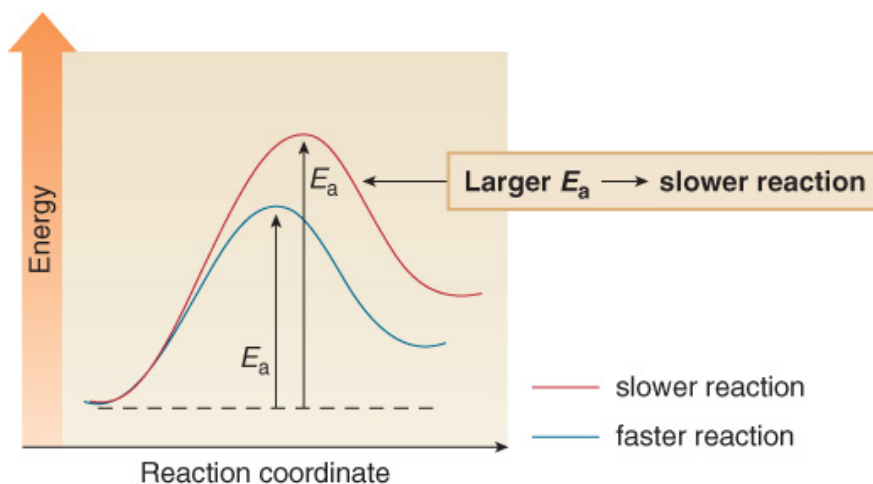
An Energy Profile Diagram for a 2-Step Reaction



- The overall rate of a multi-step reaction will be determined by the rate of the step with the highest E_a . 27

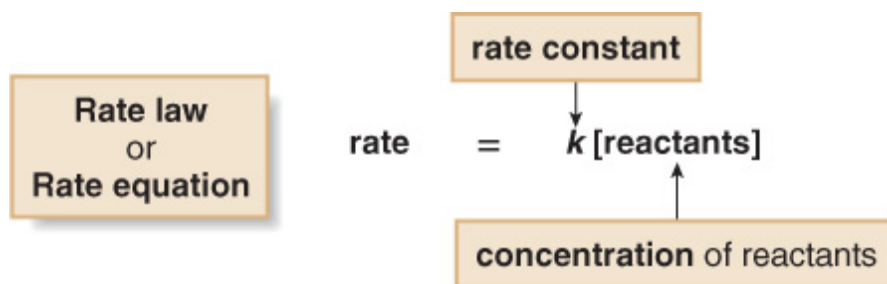
Kinetics (Reaction Rates)

- 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

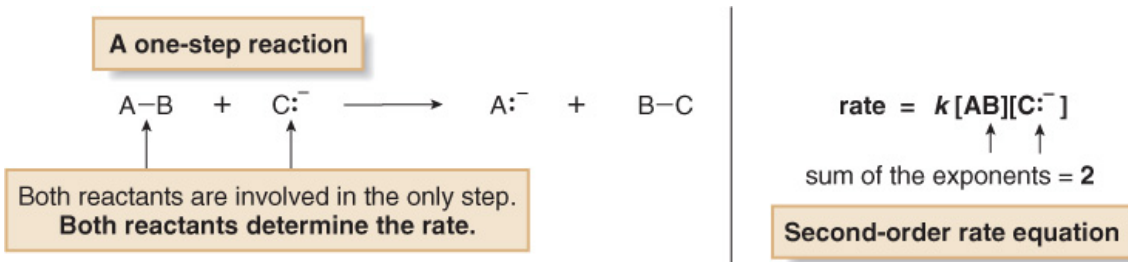
- The higher the concentration, the faster the rate.
- The higher the temperature, the faster the rate.
- ΔG° , ΔH° , and K_{eq} do not determine the rate of a reaction. These quantities indicate the direction of the equilibrium and the relative energy of reactants and products.
- The **rate law** or **rate equation** shows the relationship between the reaction rate and the concentration of the reactants. It is experimentally determined.



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The Rate Equation

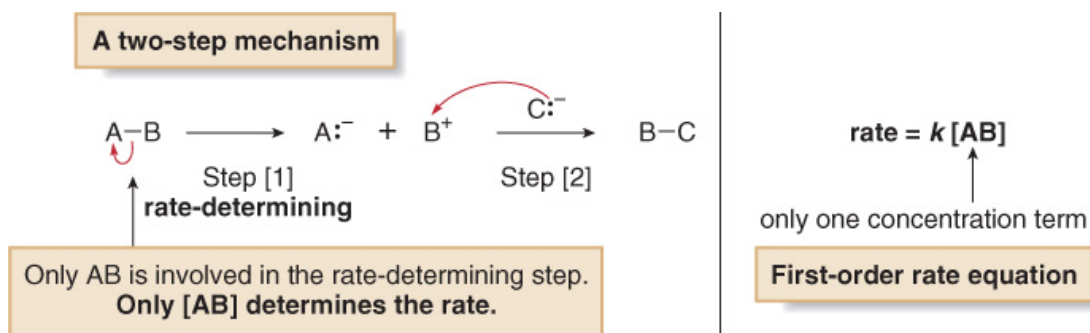
- Fast reactions have large rate constants.
- Slow reactions have small rate constants.
- The rate constant k and the energy of activation E_a are inversely related. A high E_a corresponds to a small k .
- A rate equation contains concentration terms for all reactants in the slowest step of the reaction.
- The **order** of a rate equation equals the sum of the exponents of the concentration terms in the rate equation.



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The Rate-Determining Step (RDS) of a Reaction

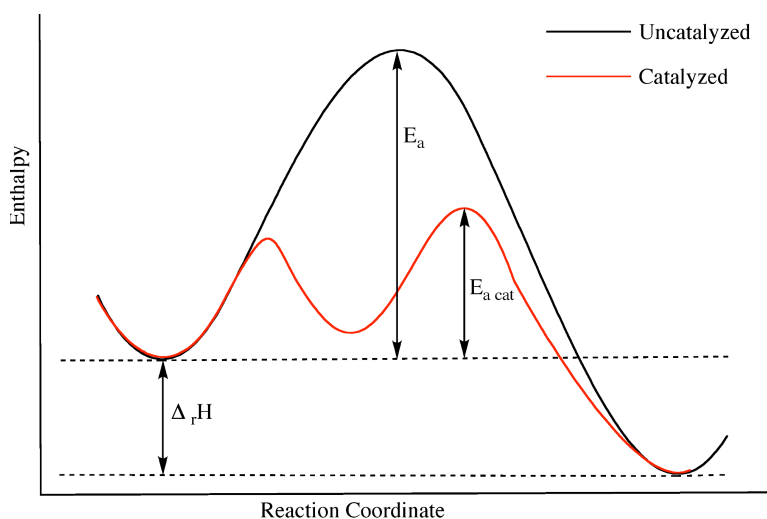
- Reactions have a rate-determining step in their mechanism. This is always the slowest step of the reaction.
- In a multi-step mechanism, the reaction can occur no faster than its rate-determining step.
- Only the concentration of the reactants in the rate-determining step are included in the rate equation.



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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.



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