

Chapter 17 Outline

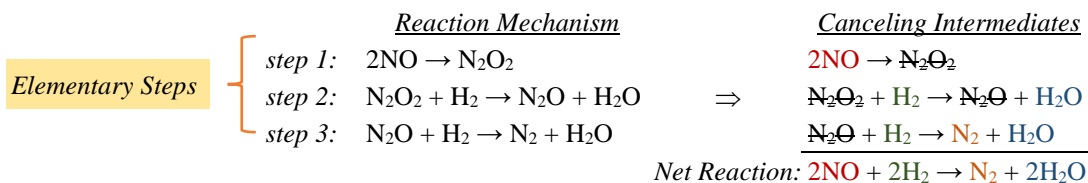
Reaction Kinetics

Main Ideas

I. The Reaction Process

A. Reaction Mechanism

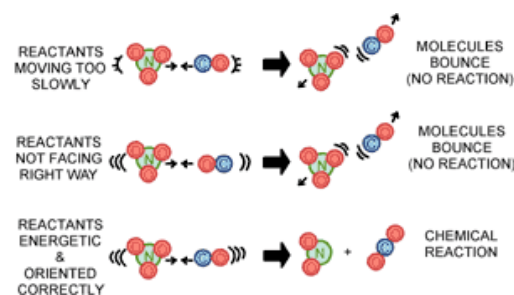
1. Reactions proceed by a series of individual *elementary steps* called the *reaction pathway*.
2. *Reaction mechanism* = step-by-step sequence representing the pathway of reactions by which the overall chemical change (or *net reaction*) occurs
 - a. *Intermediates* = species (*substances*) produced in one step, then consumed in another
 - b. *Net reaction* = combination and simplification of the reaction mechanism



3. *Homogeneous reaction* = a reaction whose reactants and products exist in the *same phase*

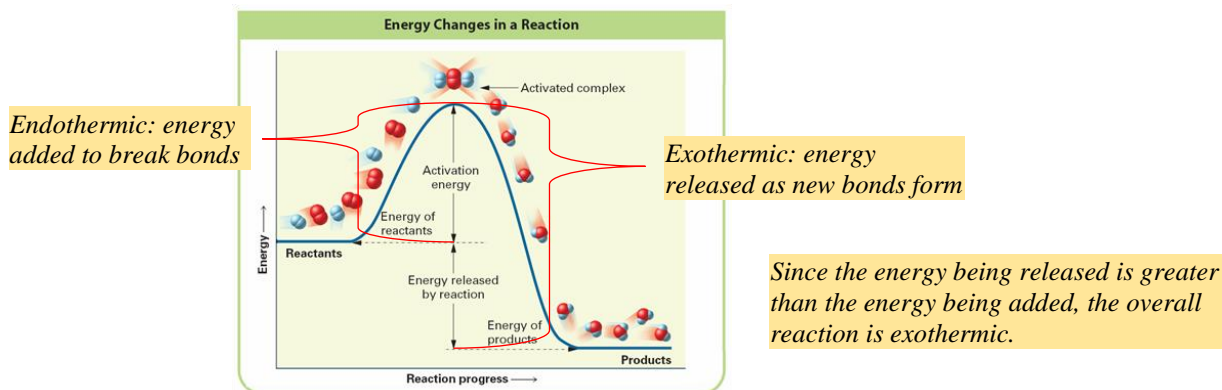
B. Collision Theory

1. In order for chemicals to react, they must collide
 - a. The nature and frequency of these collisions dictate the rate of a chemical reaction
2. Collision theory
 - a. Only certain collisions (*effective collisions*) will result in a reaction
 - b. *Effective collisions have:*
 - i. The *proper orientation* so that bonding sites align
 - ii. *Enough energy* to overcome electron cloud repulsion and disrupt existing electron arrangements (bonds)

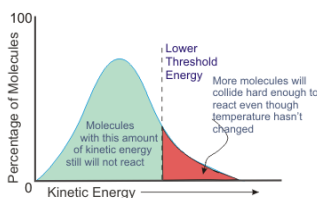


C. Activation Energy

1. *Activation energy* = the minimum energy required to achieve an effective collision
 - a. The electrons are disrupted and a high energy collection of particles (*activated complex*) is formed.
 - b. This occurs during a period of time in the reaction called the *transition state*.
 - i. Achieving the transition state is always an *endothermic process*.
 - ii. As the particles transition and new species are formed, energy is released in an *exothermic process*.
 - iii. The energy from this exothermic process sustains the reaction by activating other molecules



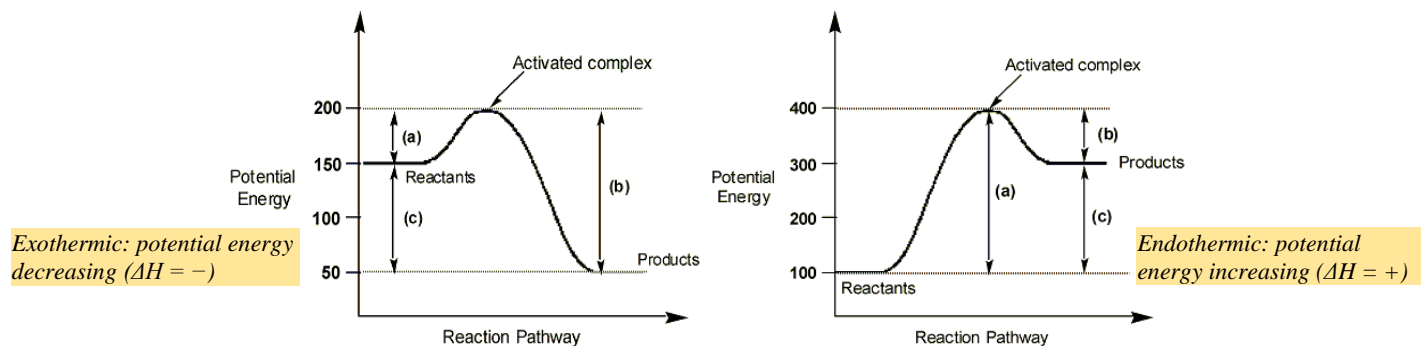
2. Activation energy is generally heat, but may be electricity, radiation, mechanical shock, etc.
3. The minimum amount of activation energy may be depicted using a Maxwell-Boltzmann distribution:



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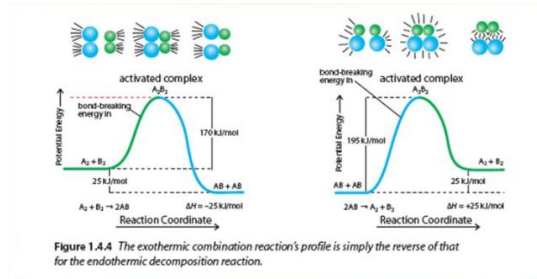
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D. Reaction Pathway Diagrams

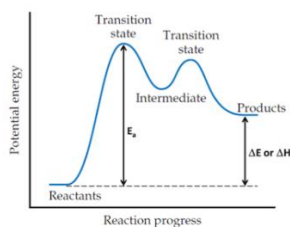


Where (a) = the activation energy, (b) = the energy released from bond formation, and (c) represents the change in potential energy (or change in enthalpy ΔH for our purposes)

1. The reaction pathway diagram will be flipped (mirror image) when reversing a reaction.



2. Reaction pathway diagrams may show the elementary steps of a reaction mechanism.



II. Reaction Rate

A. Factors Affecting Reaction Rate

1. Nature of the Reactants

- a. Some reactants have more stable bonds than others and require more energy to achieve an effective collision.
- b. Physical state (homogeneous v. heterogeneous reactants) will also affect the ability to collide.

2. Surface Area

- a. Greater surface area provides for **more frequent** collisions.
 - i. The more frequent the collisions, the more likely particles are to strike with the correct orientation and energy.
- b. Gases and liquids (including aqueous solutions) generally react more quickly due to increased surface interactions.

3. Temperature

- a. Temperature indicates kinetic energy, so the higher the temperature, the **greater the energy** of collision.
- b. At higher temperatures, collisions occur **more frequently**.
- c. Raising the temperature of a reaction by just **10°C will double the rate** of many reactions.

4. Concentration

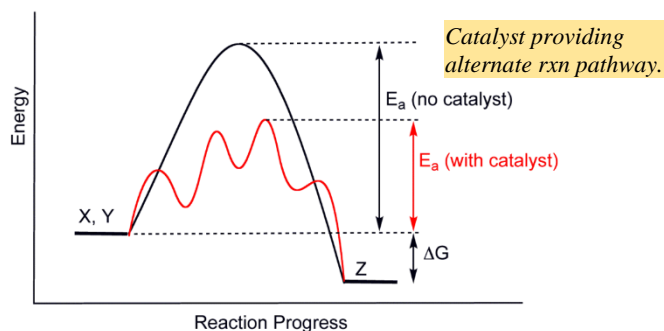
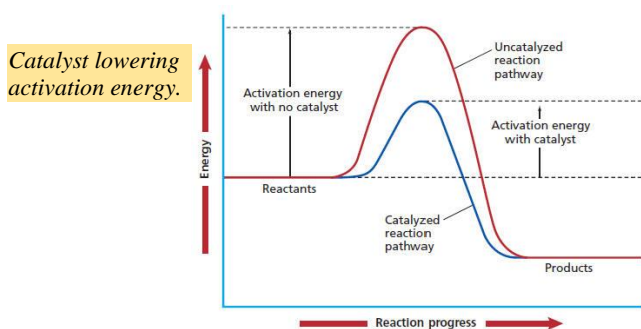
- a. Increasing the concentration of liquid or gaseous solutions puts more particles in proximity and **increases the frequency** of collisions, which **usually** increases the rate.
 - i. Not all reactants contribute equally to the production of effective collisions.
 - ii. The effect of a particular reactant in a particular reaction must be determined experimentally.

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5. Catalysts

- Catalyst** = a substance that increases the rate of a reaction without being permanently changed
 - Catalysts may **lower the activation energy** or one or more elementary steps, or
 - Catalysts may provide a completely **different pathway** for the reaction to follow
- Catalysts do not appear in a chemical equation but may be indicated above the arrow.
 - Homogeneous catalyst = catalyst in the same phase as the reactants
 - Heterogeneous catalyst = catalyst in a different phase as the reactants
- Enzymes** = biological catalysts
- Inhibitors** = substances that increase the activation energy of reaction and slow the reaction



B. Measuring Reaction Rates

- Rate** = change/unit of time
- Reaction rate** = rate at which reactants are turned into products.
 - Reaction rate may be expressed by rate at which **reactants are consumed** or **products are produced**.
 - Rates expressed in terms of reactant used are preceded by a ‘-’ sign.
 - This is expressed by using the change in concentration (molarity) of any reactant or product in a given amount of time – usually seconds (s).
 - Units of reaction rate = M/s or mol/L•s

$$\text{Average rate of reaction} = \frac{\Delta[\text{reactant or product}]}{\Delta\text{time}}$$

Brackets [] indicate concentration in mol/liter (M)

C. Rate Laws

- Rate Law** = equation that relates reaction rate and concentrations of reactants
 - Determined experimentally by running an experiment repeatedly while varying the concentration of **only one reactant at a time**.
- General format:

$$\text{Rate} = k[\text{reactant 1}]^x[\text{reactant 2}]^y[\text{reactant 3}]^z\dots$$

Where k = specific rate constant of the reaction,
 $x, y,$ and z = exponents determined by experiment.

Example: For the generic equation, $aA + bB \rightarrow cC + dD$, rate = $k[A]^x[B]^y$

3. Reactant order

- Reactant order** = the value of the exponent applied to the reactant concentration
 - The reactant order *must be determined experimentally*.
 - Higher order reactants have a greater effect on the reaction rate.
 - Orders are usually integers but may be fractions or even negative.
- The sum of the exponents is the **overall reaction order**.
- Determining Reactant Order (*Initial Rates Method*)
 - The concentration of one reactant is doubled (usually) in successive trials while all other reactants are held constant and the rate is measured. Rates will vary as exponentiation of 2 in those trials.
 - If the rate doesn't change, then the order (exponent) is zero (zeroth order) because $2^0 = 1$.
 - If the rate doubles, then the order is 1 (first order) because $2^1 = 2$.
 - If the rate quadruples, then the order is 2 (second order) because $2^2 = 4$.
 - If the rate octuples, then the order is 3 (third order) because $2^3 = 8$.
 - 3rd order is rare and orders above 3rd are practically nonexistent.

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4. k = the rate constant
 - a. k is specific to a reaction and **temperature dependent**.
 - b. The units of k vary with the overall order of the reaction.
 - c. Once the rate and orders of the reactants are known, they can be substituted into the rate law to determine k .
5. Rate-Determining Step
 - a. In any multi-step reaction mechanism, one step (the **rate-determining or rate-limiting step**) will limit the rate of the reaction.
 - b. **Rate-determining step** = slowest step in the mechanism

D. **Molecularity**

1. Rate laws can sometimes be written based on the stoichiometry of the reaction.
2. Single-step Reactions
 - a. When a reaction occurs in a single step (is an elementary reaction), the rate law can be predicted based on the moles of reactants that are present.

TABLE 14.3 • Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
Unimolecular	$A \longrightarrow \text{products}$	Rate = $k[A]$
Bimolecular	$A + A \longrightarrow \text{products}$	Rate = $k[A]^2$
Bimolecular	$A + B \longrightarrow \text{products}$	Rate = $k[A][B]$
Termolecular	$A + A + A \longrightarrow \text{products}$	Rate = $k[A]^3$
Termolecular	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
Termolecular	$A + B + C \longrightarrow \text{products}$	Rate = $k[A][B][C]$

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3. Multi-step Reactions
 - a. In multi-step reactions the rate law will be the rate law for the rate-determining step.
 - b. If the rate-determining step comes first, then the rate law can be determined from the molecularity of that step.
 - c. If the rate-determining step does not come first, then rate laws for the rate-determining step and those preceding it must be combined.