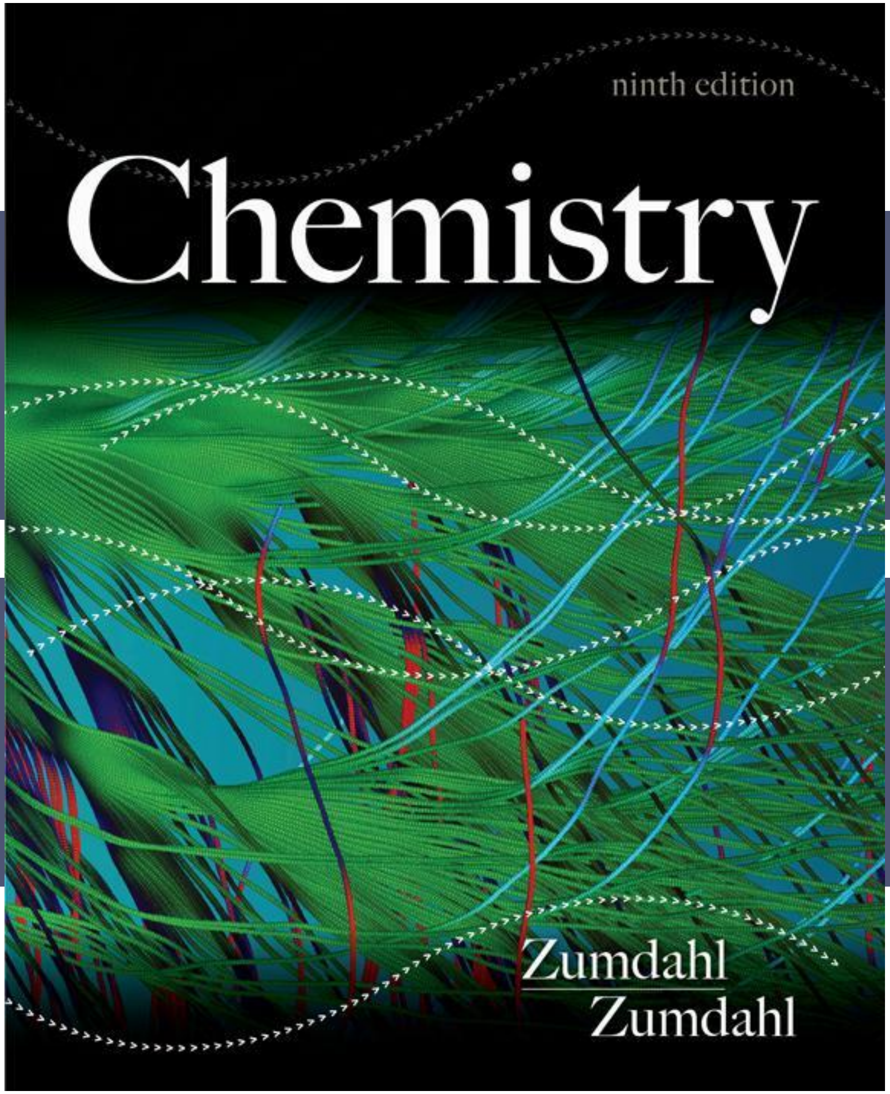


Chapter 12

Chemical Kinetics

Rate Law

- Chemical reactions are reversible
  - As NO and O_2 accumulate, they can react to re-form NO_2

$$O_2(g) + 2NO(g) \longrightarrow 2NO_2(g)$$

- When gaseous NO_2 is placed in an otherwise empty container, initially the dominant reaction is

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

Rate Law (Continued)

- Change in the concentration of NO_2 depends only on the forward reaction
- Expression to be used if the reverse reaction is to be neglected

$$\text{Rate} = k\,[NO_2]^n \qquad (12.1)$$

  - *k* = **rate constant**
  - *n* = **order** of the reactant

Rate Law - Key Points

- The concentrations of the products do not appear in the rate law
- The value of the exponent *n* must be determined by experiment
  - Cannot be written from the balanced equation

Rate Constant

- Definition of reaction rate in terms of the consumption of NO_2

$$\text{Rate} = -\frac{\Delta\,[\mathrm{NO_2}]}{\Delta t} = k\,[\mathrm{NO_2}]^n$$

Types of Rate Laws

- **Differential rate law** (**rate law**)
  - Expresses how the rate depends on the concentration of the reactant
- **Integrated rate law**: Expresses how the concentration depends on time

Do in your notes, compare with partner

- Using the following information, find the reaction order with respect to each reactant.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(l) + 3H_2O(l)$$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

First-Order Rate Laws

- Rate law for the decomposition of dinitrogen pentoxide

$$\text{Rate} = -\frac{\Delta[\mathrm{N_2O_5}]}{\Delta t} = k[\mathrm{N_2O_5}]$$

  - This is a **first-order reaction**
    - Rate of formation of products increases with the increase in the concentration of the reactant

Integrated First-Order Rate Law

- Consider a reaction with the following rate law

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

- The integrated first-order rate law is

$$\ln\,[\text{A}] = -kt + \ln\,[\text{A}]_0 \qquad (12.2)$$

Integrated First-Order Rate Law - Key Points (Continued)

- The equation can be expressed in terms of a ratio of [A] and $[A]_0$

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]}\right) = kt$$

Do in notes, compare with partner

- Calculate $[N_2O_5]$ at 150 s after the start of the following reaction:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

  - Use the following information:

$[N_2O_5]$ (mol/L)	Time (s)
0.1000	0
0.0707	50
0.0500	100
0.0250	200
0.0125	300
0.00625	400

Half-Life of a First-Order Reaction

- **Half-life of a reactant** ($t_{1/2}$): Time required for a reactant to reach half its original concentration
- Consider the general reaction aA → products
  - If the reaction is first order in [A], then

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

  - When $t = t_{1/2}$,

$$[A] = \frac{[A]_0}{2}$$

Half-Life of a First-Order Reaction (Continued 1)

- For $t = t_{1/2}$, the integrated rate law becomes

$$\ln\left(\frac{[\mathrm{A}]_0}{[\mathrm{A}]_0/2}\right) = kt_{1/2} \qquad \text{or} \qquad \ln(2) = kt_{1/2}$$

- Substituting the value for ln(2) and solving for $t_{1/2}$

$$t_{1/2} = \frac{0.693}{k} \qquad (12.3)$$

Do in notes, compare with partner

- A certain first-order reaction has a half-life of 20.0 minutes
  a. Calculate the rate constant for this reaction
  b. How much time is required for this reaction to be 75% complete?

Interactive Example 12.4 - Solution (a)

- Solving equation (12.3) for *k* gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{20.0\ \text{min}} = 3.47 \times 10^{-2}\ \text{min}^{-1}$$

Interactive Example 12.4 - Solution (b)

- We use the integrated rate law in the form

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

  - If the reaction is 75% complete, 75% of the reactant has been consumed, leaving 25% in the original form

$$\frac{[A]}{[A]_0} \times 100\% = 25\%$$

Interactive Example 12.4 - Solution (b) (Continued 1)

$$\frac{[A]}{[A]_0} = 0.25 \text{ or } \frac{[A]_0}{[A]} = \frac{1}{0.25} = 4.0$$

$$\ln\left(\frac{[A]_0}{[A]}\right) = \ln(4.0) = kt = \left(\frac{3.47 \times 10^{-2}}{\text{min}}\right)t$$

$$t = \frac{\ln(4.0)}{\frac{3.47 \times 10^{-2}}{\text{min}}} = 40 \text{ min}$$

- It takes 40 minutes for this particular reaction to reach 75% completion

Interactive Example 12.4 - Solution (b) (Continued 2)

- Alternate way of solving the problem using the definition of half-life
  - After one half-life the reaction has gone 50% to completion
  - If the initial concentration were 1.0 mol/L, after one half-life the concentration would be 0.50 mol/L
    - One more half-life would produce a concentration of 0.25 mol/L

Interactive Example 12.4 - Solution (b) (Continued 3)

- Comparing 0.25 mol/L with the original 1.0 mol/L shows that 25% of the reactant is left after two half-lives
- What percentage of reactant remains after three half-lives?
    - Two half-lives for this reaction is 2(20.0 min), or 40.0 min, which agrees with the preceding answer

Second-Order Rate Laws

- Consider a general reaction

  aA → products

  - Rate law for a second-order reaction

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2 \qquad (12.4)$$

  - The **integrated second-order rate law** has the form

$$\frac{1}{[\text{A}]} = kt + \frac{1}{[\text{A}]_0} \qquad (12.5)$$

Half-Life for a Second-Order Reaction

- When one half-life of the second-order reaction has elapsed ($t = t_{1/2}$), by definition,

$$[\mathrm{A}] = \frac{[\mathrm{A}]_0}{2}$$

  - Equation (12.5) becomes

$$\frac{1}{\frac{[\mathrm{A}]_0}{2}} = kt_{1/2} + \frac{1}{[\mathrm{A}]_0}$$

Zero-Order Rate Laws

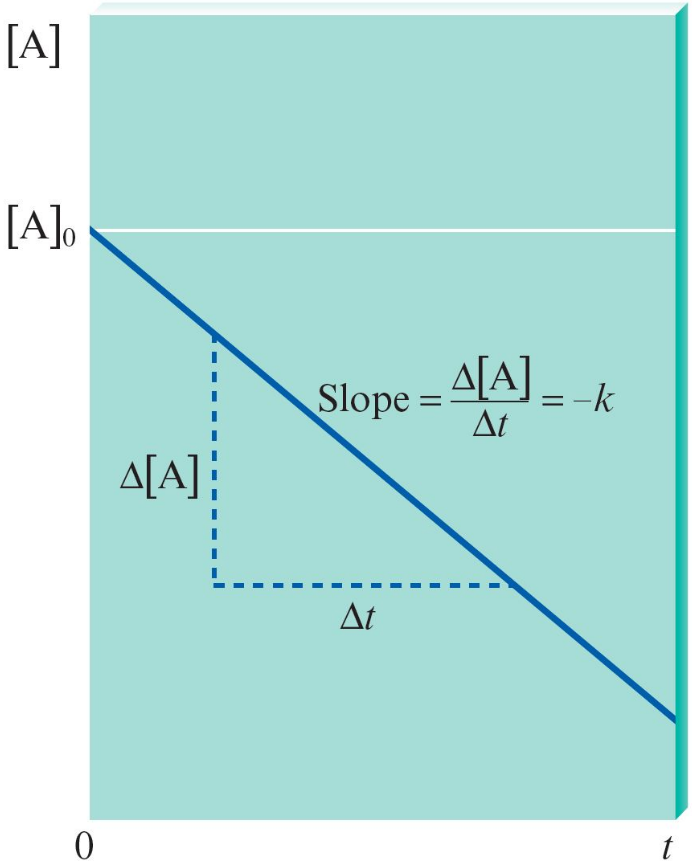
- Rate law for a **zero-order reaction**

  $$\text{Rate} = k[A]^0 = k(1) = k$$

  - The rate is constant

- **Integrated rate law for a zero-order reaction**

  $$[A] = -kt + [A]_0 \qquad (12.7)$$



Answer with partner, compare with another group

- Consider the simple reaction aA$\longrightarrow$ products
  - You run this reaction and wish to determine its order
  - What if you made a graph of reaction rate versus time?
    - Could you use this to determine the order?
    - Sketch the three plots of rate versus time for the reaction if it is zero, first, or second order
    - Sketch these plots on the same graph, compare them, and defend your answer

Reaction Mechanism

- Most chemical reactions occur by a series of steps
- Example - The reaction between nitrogen dioxide and carbon monoxide involves the following steps:

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)$$
$$NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$$

  - Where k_1 and k_2 are the rate constants of the individual reactions

Molecularity

- Number of species that must collide to produce the reaction represented by an elementary step
  - **Unimolecular**: Reaction that involves one molecule
  - **Bimolecular**: Reaction that involves the collision of two species
  - **Termolecular**: Reaction that involves the collision of three species

Requirements of a Reaction Mechanism

- The sum of the elementary steps must give the overall balanced equation for the reaction
- The mechanism must agree with the experimentally determined rate law

Do in your notes, compare with partner

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

- Experimentally determined rate law is

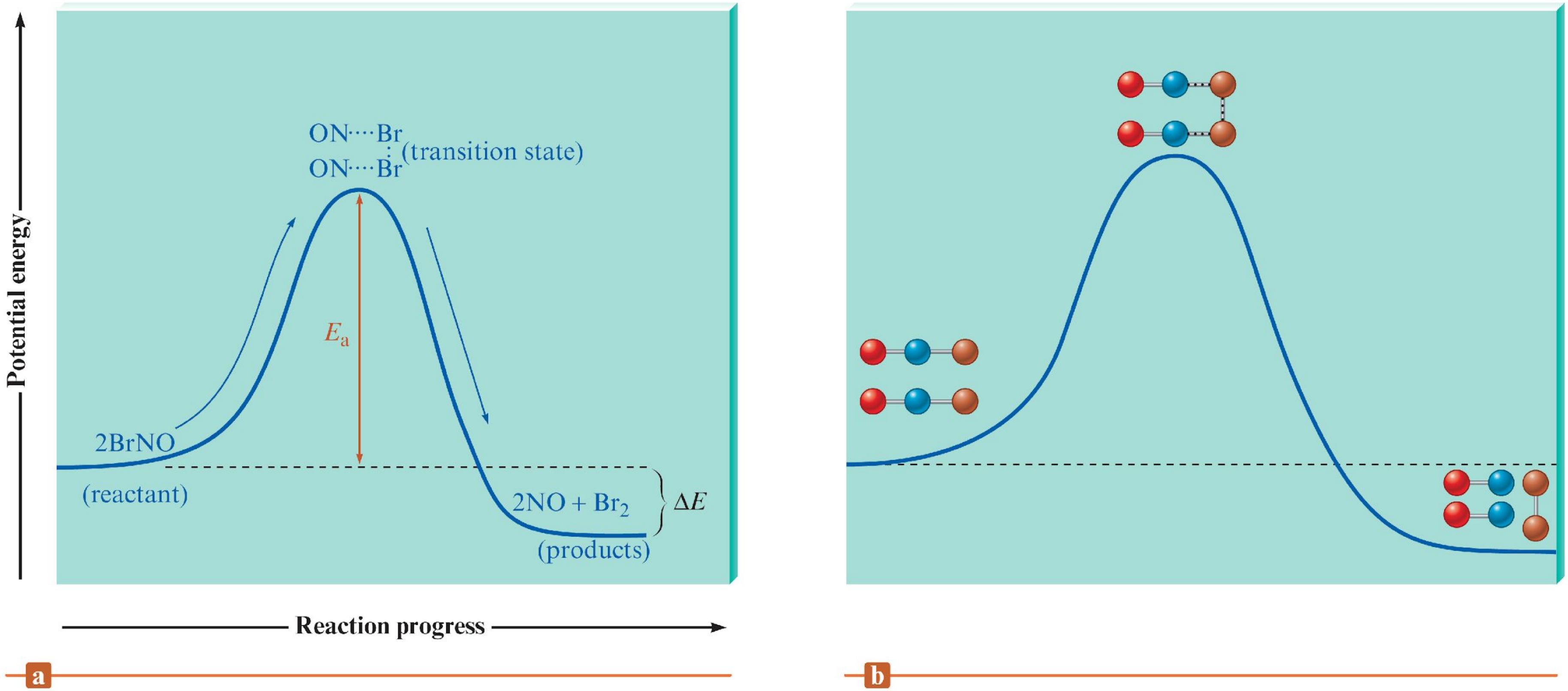
$$\text{Rate} = k[NO_2][F_2]$$

$$NO_2 + F_2 \xrightarrow{k_1} NO_2F + F \quad \text{(slow)}$$

$$F + NO_2 \xrightarrow{k_2} NO_2F \quad \text{(fast)}$$

- Is this an acceptable mechanism?

Figure 12.10 - Activated Complex/Transition State



Relation between Effective Collisions and Temperature

- The fraction of effective collisions increases exponentially with temperature

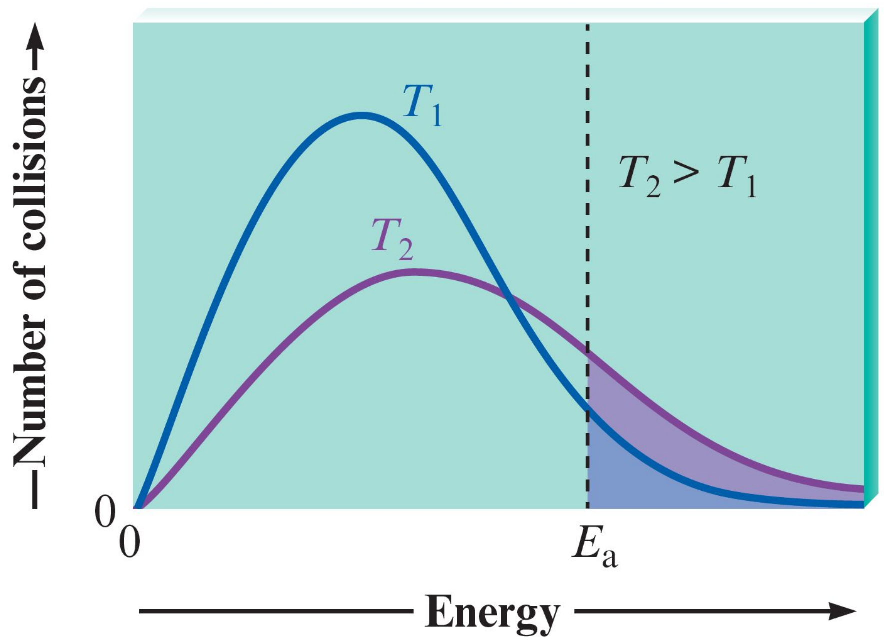
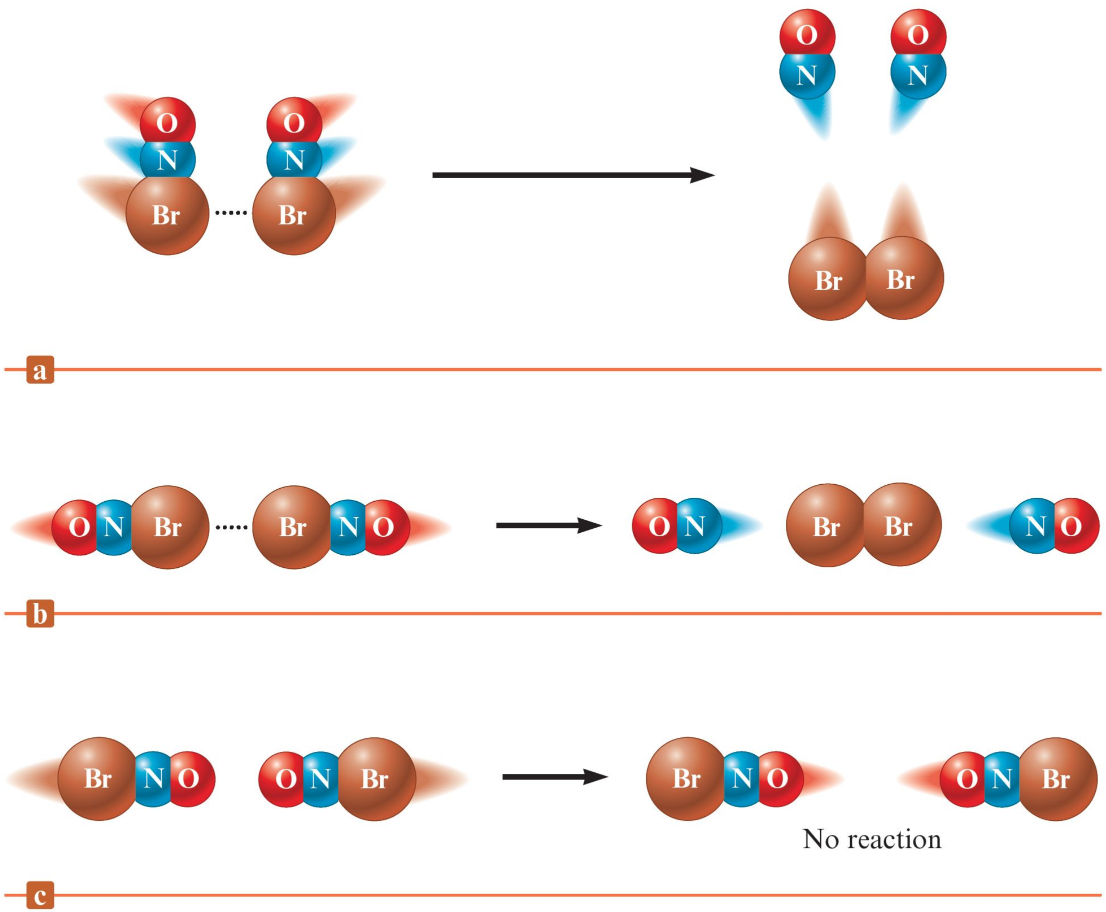


Figure 12.12 - Molecular Orientations



Requirements to be Satisfied for Reactants to Collide Successfully

- The collision energy must equal or exceed the activation energy
- The relative orientation of the reactants must allow the formation of any new bonds necessary to produce products

Discuss with partner, compare with another group

- There are many conditions that need to be met to result in a chemical reaction between molecules
  - What if all collisions between molecules resulted in a chemical reaction?
    - How would life be different?

Figure 12.14 - Effect of a Catalyst on the Number of Reaction-Producing Collisions