## || Chemical Kinetics ||

#### **Introduction to Chemical Kinetics**

Chemical kinetics is a branch of physical chemistry that explores how fast chemical reactions occur and what factors influence their rates. Unlike thermodynamics, which tells us whether a reaction is possible and how much energy it involves, kinetics explains **how quickly** that reaction proceeds and through **what mechanism**.

Imagine striking a match—thermodynamics tells us that it *can* burn, but kinetics explains *how long it takes* and *why* it happens faster under certain conditions, like higher temperatures or in the presence of oxygen. Similarly, some reactions, such as rusting of iron, happen slowly, while others, like explosions, are nearly instantaneous.

Understanding chemical kinetics is essential for controlling reaction speeds in real-life applications—from designing better catalysts in industrial processes to optimizing reaction conditions in pharmaceuticals and environmental chemistry.

This topic forms the foundation for advanced studies in reaction dynamics, catalysis, enzyme kinetics, and materials science.

## **Teaching Content**

- Conceptual explanations
- Complete derivations for rate laws
- Graphical methods and analysis
- Theories (Collision, Transition State)
- Arrhenius equation with interpretation
- Numerical problem with full solution

## **Required Conceptual Foundations**

#### Reaction Rate

The rate of a chemical reaction measures the speed at which reactants are converted into products.

Rate = -d[Reactant]/dt = d[Product]/dt

Units: mol L<sup>-1</sup> s<sup>-1</sup>

#### Importance of Studying Reaction Rates

- Industrial Chemistry: Optimize conditions for better yield.
- Biochemistry: Understand enzyme activity.
- Environmental Chemistry: Predict pollutant degradation.
- Safety Engineering: Prevent uncontrolled fast reactions.

#### Factors Affecting the Rate of Reaction

- Concentration
- Temperature
- Catalyst
- Surface Area
- Pressure (for gases)
- Nature of Reactants

#### Elementary vs. Complex Reactions

Elementary Reaction: A single-step process.

Complex Reaction: Multiple steps; rate depends on the slowest step.

#### Reaction Mechanism

The reaction mechanism is the step-by-step pathway by which a reaction proceeds. Includes intermediates and transition states.

#### Molecularity

Number of molecules involved in an elementary step.

Types: Unimolecular, Bimolecular, Termolecular (rare).

#### Order of Reaction

Determined experimentally. Indicates the power to which a reactant concentration is raised in the rate law.

#### Order vs. Molecularity

Order is empirical and can be fractional or zero; applies to overall reactions.

Molecularity is theoretical and always a whole number; applies to elementary steps.

#### Activation Energy (Ea)

The minimum energy needed for a reaction to occur. Even thermodynamically favorable reactions may need high Ea to proceed.

#### Transition State and Activated Complex

High-energy, unstable configuration at the energy barrier's peak. Exists momentarily and leads to products.

### Catalysis and Reaction Rate

Catalyst: Increases rate by lowering Ea, not consumed in reaction. Types: Homogeneous, Heterogeneous, Enzyme Catalysis.

# Out of these today we will focus only on the Derivation of simplified rate law equations

#### Derivations of Rate Laws in Chemical Kinetics

#### Zero Order Reaction

Rate Law: Rate = k

For a zero-order reaction: Rate = -d[A]/dt = k

Integrating:

 $\int d[A] = -\int k dt$ 

[A] = -kt + C

Using initial condition  $[A] = [A]_0$  at t = 0:

 $\Rightarrow$  C = [A]<sub>o</sub>

So,  $[A] = [A]_0 - kt$ 

Half-life:  $t_1/_2 = [A]_0 / 2k$ 

#### First Order Reaction

Rate Law: Rate = -d[A]/dt = k[A]

Rearranging and integrating:

 $\int d[A]/[A] = -\int k \, dt$ 

ln[A] = -kt + C

Using [A] = [A]<sub>0</sub> at t =  $0 \Rightarrow C = In[A]_0$ 

So,  $In[A] = In[A]_o - kt$ 

or,  $ln([A]_0/[A]) = kt$ 

or,  $[A] = [A]_0 e^{-kt}$ 

Half-life:  $t_1/_2 = 0.693 / k$ 

## Second Order Reaction (Single Reactant)

Rate Law: Rate =  $-d[A]/dt = k[A]^2$ 

Rearranging:

 $\int d[A]/[A]^2 = -\int k dt$ 

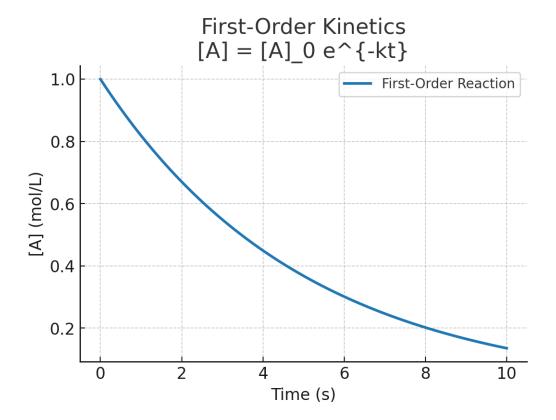
$$-1/[A] = -kt + C$$
Using [A] = [A]<sub>0</sub> at t = 0  $\Rightarrow$  C = -1/[A]<sub>0</sub>
So, -1/[A] = -kt - 1/[A]<sub>0</sub>
or, 1/[A] = kt + 1/[A]<sub>0</sub>
Half-life:  $t_1/2 = 1$  / (k[A]<sub>0</sub>)
Second Order Reaction (Two Reactants A and B)
Rate = -d[A]/dt = k[A][B]
When [A]<sub>0</sub>  $\neq$  [B]<sub>0</sub>:
Let [A] = a - x, [B] = b - x
 $dx/dt = k(a - x)(b - x)$ 
Integration depends on initial concentrations (complex form).
When [A]<sub>0</sub> = [B]<sub>0</sub> = a:
Rate = k(a - x)<sup>2</sup>  $\Rightarrow$  same as single reactant second order:
 $1/(a - x) = kt + 1/a$ 
Pseudo First Order Reaction
For a reaction: A + B  $\Rightarrow$  Products, with [B] in large excess,
[B]  $\approx$  constant  $\Rightarrow$  Rate = k[A][B]  $\approx$  k'[A]
This behaves like a first-order reaction:
 $ln([A]_0/[A]) = k't$ 
Units of Rate Constant
| Order | Rate Law | Units of k |

 $| 0 | Rate = k | mol L^{-1} s^{-1} |$ 

 $| 2 | Rate = k[A]^2 \text{ or } k[A][B] | L \text{ mol}^{-1} \text{ s}^{-1} |$ 

 $| 1 | Rate = k[A] | s^{-1}$ 

## Plot of Reaction Kinetics (Let say the first order reaction)



## Classroom Engagement Activities for Chemical Kinetics

## 1. Concept Mapping Challenge

- **Objective:** Students create a visual map connecting core topics like rate laws, order, molecularity, reaction mechanism, activation energy, etc.
- Instructions:
  - Divide students into small groups.
  - Provide chart paper or digital tools (like Padlet or Miro).
  - Ask them to map relationships using arrows and brief definitions.
- Outcome: Encourages students to visualize how kinetics concepts interrelate.

#### 2. Reaction Rate Race (Think-Pair-Share)

- Objective: Reinforce understanding of factors affecting reaction rates.
- Instructions:
  - Pose a real-life scenario (e.g., "Why does food spoil faster in summer?").
  - Students first write their thoughts individually.
  - Then, pair up to compare ideas.
  - Finally, share as a class.
- Variation: Assign different factors (temperature, catalyst, concentration) to different pairs.

#### 3. Live Demonstration + Prediction

- Objective: Observe the effect of various conditions on reaction rate.
- Instructions:
  - Perform a simple experiment, like the decomposition of  $H_2O_2$  with MnO<sub>2</sub> as a catalyst.
  - Ask students to predict how changes (like adding ice or increasing concentration) will affect rate.
  - Perform and then discuss outcomes.
- Extension: Use virtual lab simulations (e.g., PhET) if live setup isn't feasible.

#### 4. Rate Law Derivation Relay

- Objective: Reinforce integration of rate laws (zero, first, second order).
- Instructions:
  - Break the derivation steps into parts and write each on a card.
  - Distribute cards randomly to student groups.
  - Ask them to come to the board and arrange the steps in correct order.
- Outcome: Helps recall and structure derivations.

#### 5. Quiz-Bowl: "Order or Disorder?"

- Objective: Review order vs. molecularity, units, rate laws.
- Instructions:
  - Divide class into teams.
  - Ask rapid-fire questions: "What is the unit of k for second-order reaction?"
  - Use buzzers or bells for added fun.
- Optional: Include diagrams and ask students to interpret them.

#### 6. Error Hunt

- Objective: Identify and correct common misconceptions.
- Instructions:
  - Show incorrect statements like:
    - "Molecularity can be zero."
    - "Order of a reaction is always equal to the sum of stoichiometric coefficients."
  - Ask students to find and correct errors.
- Outcome: Sharpens conceptual clarity.

## 7. Role Play: Molecule Meeting

- Objective: Explain collision theory and transition state theory creatively.
- Instructions:
  - Assign roles: Molecule A, Molecule B, Activated Complex, Product, Catalyst.
  - Let students act out the process of a reaction with/without catalyst.
- Outcome: Makes abstract theories memorable.

#### 8. Kinetics Escape Room (Mini Game)

- Objective: Solve clues related to kinetics to "escape the room."
- Instructions:
  - Prepare a sequence of clues like:
    - "Solve the half-life of a zero-order reaction with  $[A]_0 = 0.2 \text{ mol/L}$ ,  $k = 0.01 \text{ mol L}^{-1} \text{ s}^{-1}$ "
    - "Identify the order from the given data."
  - Each correct answer reveals the next step.
- Outcome: Collaborative problem-solving under time pressure.

## 9. Rate Law Data Analysis

- Objective: Use experimental data to determine reaction order.
- Instructions:

- Give students data tables (time vs. [A], or rate vs. [A]).
- Ask them to plot graphs and determine order based on linearity.
- Tools: Graph paper or Excel/Google Sheets.
- Outcome: Builds analytical and graph interpretation skills.

## 10. Debate: Collision Theory vs. Transition State Theory

- Objective: Compare two major theories of reaction rates.
- Instructions:
  - Split students into two groups.
  - One defends Collision Theory, the other Transition State Theory.
  - Debate on applicability, limitations, and experimental evidence.
- Outcome: Deepens understanding through argument and defense.

## A. 20 Multiple Choice Questions (MCQs) with Answers

- 1. What is the unit of the rate constant for a zero-order reaction?
  - A.  $s^{-1}$
  - B.  $mol^{-1} L s^{-1}$
  - C.  $mol L^{-1} s^{-1}$
  - D. L<sup>2</sup> mol<sup>-2</sup> s<sup>-1</sup>

Answer: C

- 2. Which of the following reactions shows a linear plot of [A] vs. time?
  - A. First order
  - B. Second order
  - C. Zero order
  - D. Pseudo-first order

Answer: C

- 3. For a first-order reaction, the half-life is:
  - A. Proportional to  $[A]_0$
  - B. Independent of  $[A]_0$
  - C. Inversely proportional to  $[A]_0$
  - D. Depends on temperature only

**Answer:** B

- 4. What is the molecularity of the reaction:  $A \rightarrow Products$ ?
  - A. Zero
  - B. One
  - C. Two
  - D. Depends on the rate law

**Answer:** B

- 5. Which of the following affects the rate of a chemical reaction?
  - A. Temperature
  - B. Catalyst
  - C. Concentration
  - D. All of the above

Answer: D

- 6. In a second-order reaction with equal initial concentrations, the rate law is:
  - A. Rate = k[A]
  - B. Rate =  $k[A]^2$
  - C. Rate = k[A][B]
  - D. Rate = k

**Answer**: B

- 7. The rate constant for a first-order reaction has the unit:
  - A. mol  $L^{-1}$  s<sup>-1</sup>
  - B.  $s^{-1}$
  - C. L mol<sup>-1</sup> s<sup>-1</sup>
  - D.  $mol^2 L^{-2} s^{-1}$

**Answer:** B

- 8. What is the slope of the plot of ln[A] vs. t for a first-order reaction?
  - A. +k
  - B. -k
  - C. 1/k

D. -1/k

**Answer:** B

#### 9. Pseudo-first-order reactions are those which:

- A. Are of first order only
- B. Appear to be first-order due to excess of one reactant
- C. Are second-order reactions
- D. Have zero order overall

**Answer:** B

#### 10. Which factor is not included in the rate expression?

- A. Product concentration
- B. Reactant concentration
- C. Rate constant
- D. Time

Answer: A

#### 11. The unit of rate constant for a second-order reaction is:

- A. L  $mol^{-1} s^{-1}$
- B.  $s^{-1}$
- C. mol L<sup>-1</sup> s<sup>-1</sup>
- D. No unit

Answer: A

#### 12. The half-life of a zero-order reaction is directly proportional to:

- A. Rate constant
- B. Temperature
- C. Initial concentration
- D. Activation energy

Answer: C

## 13. Which theory considers the formation of an activated complex?

- A. Collision Theory
- B. Transition State Theory
- C. Molecular Orbital Theory
- D. Thermodynamic Theory

**Answer:** B

#### 14. The term 'reaction mechanism' refers to:

- A. Catalyst used
- B. Series of elementary steps
- C. Thermodynamic feasibility
- D. Enthalpy changes only

**Answer:** B

#### 15. The order of a reaction can be determined from:

- A. Balanced equation
- B. Molecularity
- C. Experimental data
- D. Enthalpy changes

Answer: C

#### 16. Which of the following statements is true about molecularity?

- A. It can be fractional
- B. It refers to complex reactions
- C. It is always a whole number

D. It equals the reaction order

Answer: C

- 17. In a first-order reaction, if the concentration of reactant is halved, the rate:
  - A. Doubles
  - B. Quadruples
  - C. Halves
  - D. Remains constant

Answer: C

- 18. Which of the following is not a factor affecting reaction rate?
  - A. Nature of reactants
  - B. Pressure
  - C. Activation energy
  - D. Color of reactants

Answer: D

- 19. The unit of rate constant for a pseudo-first-order reaction is:
  - A.  $s^{-1}$
  - B.  $L \text{ mol}^{-1} \text{ s}^{-1}$
  - C.  $mol L^{-1} s^{-1}$
  - D.  $mol^2 L^{-2} s^{-1}$

Answer: A

- 20. For the reaction  $A + B \rightarrow Products$ , if B is in large excess, the rate law becomes:
  - A. k[A][B]
  - B. k[A]<sup>2</sup>
  - C. k'[A]
  - D. k[B]

Answer: C

## B. 5 Short Answer Type Questions with Answers

1. What is the difference between order and molecularity of a reaction?

**Answer:** Order is an experimentally determined quantity (can be fractional or zero), whereas molecularity is theoretical and always a whole number referring to elementary steps.

2. What does the Arrhenius equation explain?

Answer: It relates the rate constant (k) to temperature and activation energy:  $k = Ae^{-Ea/RT}$ 

3. What is the significance of activation energy?

**Answer:** It is the minimum energy required for reactants to form products. Higher Ea means a slower reaction.

4. Define half-life of a reaction.

**Answer:** It is the time required for the concentration of a reactant to reduce to half its initial value.

5. What is a pseudo-first-order reaction?

**Answer:** A reaction that is actually higher order but appears first order due to one reactant being in large excess.



## C. 2 Long Answer/Subjective Questions with Answers

### 1. Derive the integrated rate law for a first-order reaction.

#### Answer:

Consider a first-order reaction: A → Products

Rate = -d[A]/dt = k[A]

Rearranging and integrating:

$$\int \frac{d[A]}{[A]} = -\int kdt \Rightarrow \ln[A] = -kt + C$$

Using initial condition  $[A] = [A]_0$  at t = 0:

$$C = \ln[A]_0$$

So,

$$ln[A] = ln[A]_0 - kt$$
 or  $ln(\frac{[A]_0}{[A]}) = kt$ 

Taking exponent:

$$[A] = [A]_0 e^{-kt}$$

Half-life  $(t_1/2)$ :

$$t_{1/2} = \frac{0.693}{k}$$

#### 2. Discuss the Collision and Transition State Theories of reaction rates.

#### **Answer:**

#### Collision Theory:

Assumes that molecules must collide with proper orientation and sufficient energy to react. Reaction rate depends on collision frequency and fraction of collisions with energy ≥ activation energy (Ea). Limitation: fails for complex reactions.

#### Transition State Theory:

Proposes formation of an unstable high-energy activated complex (transition state), which then decomposes to products. Reaction rate is proportional to concentration of this activated complex and its rate of decomposition.

Mathematically:

$$k = \frac{k_B T}{h} e^{-Ea/RT}$$

where  $k_B$  = Boltzmann constant, h = Planck constant, T = temperature.

Exit Ticket – Chemical Kinetics		
Name:	Date:	Roll No.:
☐ Today's Focus:		
Rate laws, reaction order, mole	cularity, integrated rate lo	aws, and rate-determining step.
<ul><li>1. One Thing I Learned</li></ul>	-	
3. Answer the Followin	g:	
(a) Define the rate of a chemic		
(b) What is the difference betw		
4. Multiple Choice Que	estion (Circle the Corre	ect Answer):
The unit of rate constant (k) f A. mol L <sup>-1</sup> s <sup>-1</sup> B. s <sup>-1</sup> C. I Your Answer:		
5. Self-Check: How Co	nfident Do You Feel A	bout Today's Topic?
(✓ Tick one)		
<ul> <li>■ Very confident</li> </ul>		

- ☐ Somewhat confident
- ☐ A little confused
- □ Very confused