Dev Academy
Yamunanagar (Haryana)

Comprehensive Notes

Chemical Kinetics

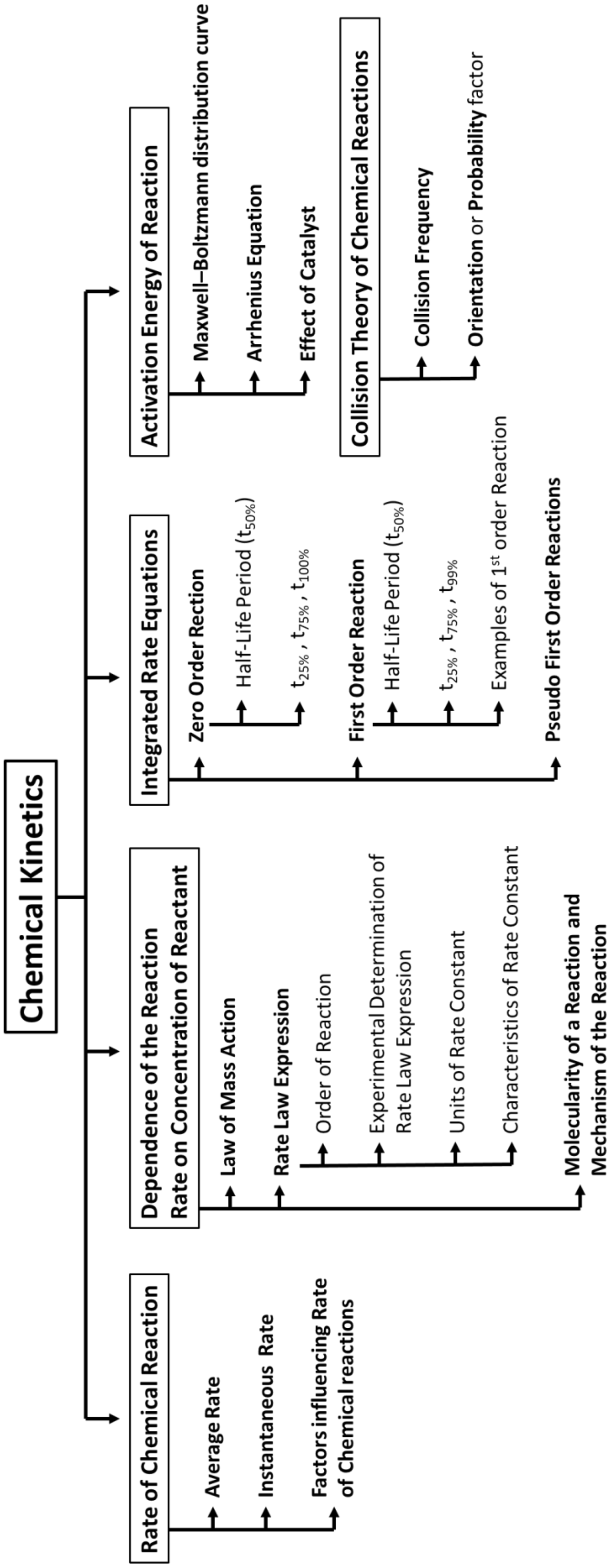
Class
12

CHEMISTRY

By
Mr. Hardev Singh Antal

Website: devacademy.click
Email id: devacademy.click@gmail.com

Ph.: 7404044544



Chemical Kinetics

- **Rate of Chemical Reaction**
  - Average Rate
  - Instantaneous Rate
  - Factors influencing Rate of Chemical reactions
- **Dependence of the Reaction Rate on Concentration of Reactant**
  - Law of Mass Action
  - Rate Law Expression
    - Order of Reaction
    - Experimental Determination of Rate Law Expression
    - Units of Rate Constant
    - Characteristics of Rate Constant
  - Molecularity of a Reaction and Mechanism of the Reaction
- **Integrated Rate Equations**
  - Zero Order Rection
    - Half-Life Period ($t_{50\%}$)
    - $t_{25\%}$, $t_{75\%}$, $t_{100\%}$
  - First Order Reaction
    - Half-Life Period ($t_{50\%}$)
    - $t_{25\%}$, $t_{75\%}$, $t_{99\%}$
    - Examples of 1st order Reaction
  - Pseudo First Order Reactions
- **Activation Energy of Reaction**
  - Maxwell–Boltzmann distribution curve
  - Arrhenius Equation
  - Effect of Catalyst
- **Collision Theory of Chemical Reactions**
  - Collision Frequency
  - **Orientation** or **Probability** factor

INDEX

Introduction

- Chemical kinetics is the branch of physical chemistry that deals with the study of (i) the **rates of chemical reactions**, (ii) the **factors affecting the reaction rate**, and (iii) the **mechanism of the chemical reaction**.
- In a spontaneous reaction, the **Gibbs free energy (ΔG)** must be **less than zero**.

Classification of Chemical Reactions Based on Rate

- **Fast (Instantaneous) Reactions:**
  - These occur extremely rapidly, typically within picoseconds (10^{-12} s) or femtoseconds (10^{-15} s).
  - Their rates are difficult to measure directly.
  - Examples: Ionic reactions (e.g., Double displacement reactions).
- **Slow Reactions:**
  - These proceed over long periods, from minutes to years.
  - Examples: Rusting of iron, conversion of diamond into graphite.
- **Moderately Slow Reactions:**
  - These occur at measurable rates, suitable for kinetic studies.
  - Examples: Hydrolysis of sucrose, decomposition of H_2O_2, hydrolysis of ethyl acetate.

Reasons for Differences in Reaction Rates

- **Activation Energy:**
  - Activation energy is the **minimum amount of energy** required to **initiate the reaction** (or the minimum energy needed to break old bonds and form new ones).
  - Reactions with a **higher activation energy** tend to be **slower**.
- **Ionic Reactions and Pre-existing Ions:**
  - Ionic reactions are fast because the ions are already free and available in the solution.
  - They do not need to break strong covalent bonds, which drastically lowers the energy barrier and allows the reaction to proceed quickly.

Rate of Chemical Reaction

- The rate of a chemical reaction is **not constant** throughout the process. It typically **decreases over time** as the **concentration of the reactants decreases**.
- **Average rate** is the rate measured over a **finite time interval** (**Δt**).
- Therefore, the **rate of a chemical reaction** is defined as the change in the concentration of any one of the reactants or products per unit time.

$$\text{Rate of Chemical Reaction} = \frac{\text{Change in } \textbf{Concentration} \text{ of Reactant or Product}}{\text{Change in } \textbf{Time}}$$

- For a Hypothetical Reaction:

$$\underset{\textbf{(Reactant)}}{\mathbf{R}} \xrightarrow{\qquad} \underset{\textbf{(Product)}}{\mathbf{P}}$$

  - The rate of reaction can be expressed in two ways:

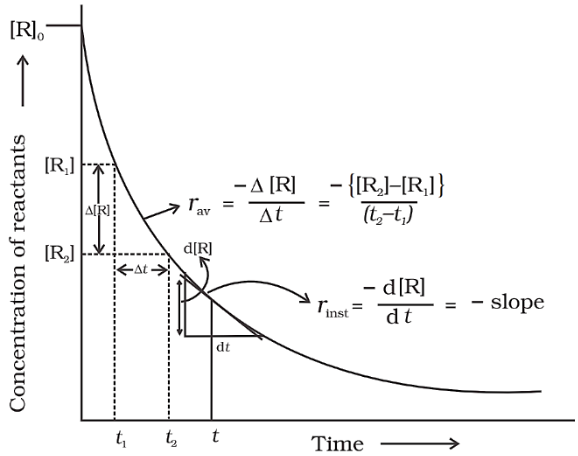
(a) In term of **Reactants**:

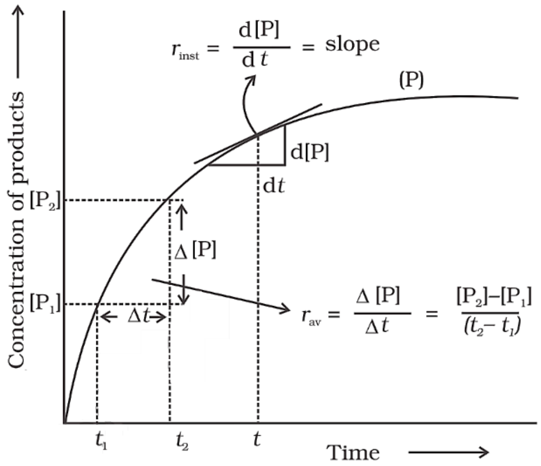
$$\text{Rate of Reaction} = \frac{\textbf{Decrease in Concentration of Reactant}}{\text{Change in Time}} = -\frac{\Delta[\mathbf{R}]}{\Delta \mathbf{t}} = -\frac{[\mathbf{R_2}] - [\mathbf{R_1}]}{\boldsymbol{t_2 - t_1}}$$

- ➢ **Note:** Because the concentration of a reactant decreases over time, **Δ[R] is a negative value**. A **negative sign** is added to make **overall rate a positive quantity**.

(b) In term of **Products**:

$$\text{Rate of Reaction} = \frac{\textbf{Increase in Concentration of Products}}{\text{Change in Time}} = \frac{\Delta[\mathbf{P}]}{\Delta \mathbf{t}} = \frac{[\mathbf{P_2}] - [\mathbf{P_1}]}{\boldsymbol{t_2 - t_1}}$$





Rate of a Chemical Reaction Vs Rate of Disappearance or Appearance of a component

- For a balanced Hypothetical Reaction: $$\underbrace{\mathbf{aA + bB}}_{\textbf{(Reactants)}} \longrightarrow \underbrace{\mathbf{cC + dD}}_{\textbf{(Products)}}$$
  - The **Rate of Disappearance of reactants** can be written as:
    - Rate of Disappearance of **component 'A'** = $\frac{\textbf{Decrease in Concentration of A}}{\text{Change in Time}} = -\frac{\Delta[\mathbf{A}]}{\Delta \mathbf{t}}$
    - Rate of Disappearance of **component 'B'** = $\frac{\textbf{Decrease in Concentration of B}}{\text{Change in Time}} = -\frac{\Delta[\mathbf{B}]}{\Delta \mathbf{t}}$
  - The **Rate of Appearance of products** can be written as:
    - Rate of Appearance of **component 'C'** = $\frac{\textbf{Increase in Concentration of C}}{\text{Change in Time}} = \frac{\Delta[\mathbf{C}]}{\Delta \mathbf{t}}$
    - Rate of Appearance of **component 'D'** = $\frac{\textbf{Increase in Concentration of D}}{\text{Change in Time}} = \frac{\Delta[\mathbf{D}]}{\Delta \mathbf{t}}$
- As we know, **all the components** of a reaction have **different rates** of appearance or disappearance. However, these can be **related to** the overall **rate of the reaction** using their **stoichiometric coefficients**. Therefore, the **Rate of a chemical reaction** can be expressed as:

$$\textbf{Rate of Reaction} = \frac{\textbf{Rate of Appearance or Disappearance of a Component}}{\textbf{Stochiometric Coefficient}} = -\frac{1}{\mathbf{a}}\frac{\Delta[\mathbf{A}]}{\Delta \mathbf{t}} = -\frac{1}{\mathbf{b}}\frac{\Delta[\mathbf{B}]}{\Delta \mathbf{t}} = \frac{1}{\mathbf{c}}\frac{\Delta[\mathbf{C}]}{\Delta \mathbf{t}} = \frac{1}{\mathbf{d}}\frac{\Delta[\mathbf{D}]}{\Delta \mathbf{t}}$$

Example 1: $2HI \longrightarrow H_2 + I_2$

Rate of reaction $= -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$

Rate of Disappearance of HI = 2 × Rate of Reaction $= 2 \times \left(-\frac{1}{2}\frac{\Delta[HI]}{\Delta t}\right) = -\frac{\Delta[HI]}{\Delta t}$

Example 2: $4\,NH_3 + 5\,O_2 \longrightarrow 4\,NO + 6H_2O$

Rate of reaction = $-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t} = -\frac{1}{5}\frac{\Delta[O_2]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO]}{\Delta t} = \frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$

Rate of Disappearance of NH_3 = 4 × Rate of Reaction = $4 \times \left(-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t}\right) = -\frac{\Delta[NH_3]}{\Delta t}$

Rate of Disappearance of O_2 = 5 × Rate of Reaction = $5 \times \left(-\frac{1}{5}\frac{\Delta[O_2]}{\Delta t}\right) = -\frac{\Delta[O_2]}{\Delta t}$

Rate of Appearance of NO = 4 × Rate of Reaction = $4 \times \left(\frac{1}{4}\frac{\Delta[NO]}{\Delta t}\right) = \frac{\Delta[NO]}{\Delta t}$

Rate of Appearance of H_2O = 6 × Rate of Reaction = $6 \times \left(\frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}\right) = \frac{\Delta[H_2O]}{\Delta t}$

Units of the Rate of Reaction

- As we know,

$$\textbf{Rate} = \frac{\text{Change in }\textbf{Concentration}}{\text{Change in }\textbf{Time}} = \frac{\text{mol L}^{-1}}{\text{Sec}} = \text{mol L}^{-1}\ \text{sec}^{-1}$$

Note:

- For reactions involving gases, **pressure (in atm)** is often used instead of molar concentration.
- In such cases, the unit of rate becomes: **atm sec^{-1}**

Instantaneous Rate of Reaction

- It can be defined as the **change in concentration** of any one of the reactants or products **at a particular instant of time**, i.e., when **Δt approaches zero** (as small as 10^{-12} or 10^{-14} sec).
  - In practice, it is not possible to determine the instantaneous rate directly.
  - It is determined **graphically** by plotting the concentration of reactant or product against time.
  - The **instantaneous rate** at time **'t'** is obtained by drawing a **tangent** to the curve at that point and calculating its **slope**.

- **For instance, consider the hydrolysis of butyl chloride:** $C_4H_9Cl + H_2O \longrightarrow C_4H_9OH + HCl$

  The concentration of butyl chloride (C_4H_9Cl) at different times is given below:

Time (sec)	0	50	100	150	200	300	400	700
C_4H_9Cl (mol L^{-1})	0.1	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210

Let us try to find the average rate of reaction at different time intervals and instantaneous rate of reaction at 600 sec.

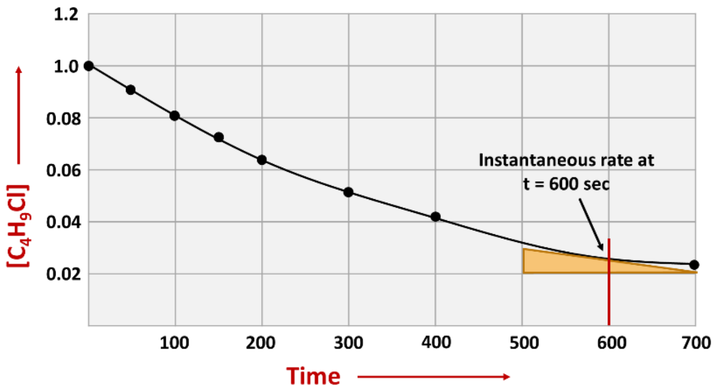
(a) Average Rate of Reaction $= -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{[C_4H_9Cl]_{t2} - [C_4H_9Cl]_{t1}}{t_2 - t_1}$

t_1	t_2	$[C_4H_9Cl]$ at t_1	$[C_4H_9Cl]$ at t_2	Average Rate (mol L^{-1} sec^{-1})
0	50	0.100	0.0905	1.90×10^{-4}
50	100	0.0905	0.0820	1.70×10^{-4}
100	150	0.0820	0.0741	1.58×10^{-4}
150	200	0.0741	0.0671	1.40×10^{-4}
200	300	0.0671	0.0549	1.22×10^{-4}
300	400	0.0549	0.0439	1.10×10^{-4}
400	700	0.0439	0.0210	0.76×10^{-4}

As seen from the table, the average rate decreases over time, which is expected as the reactant concentration falls.

(b) Instantaneous Rate at 600 sec

To find the instantaneous rate at 600 sec, a graph of $[C_4H_9Cl]$ vs time is plotted, and the tangent line at time = 600 sec is drawn. The slope of this tangent gives the instantaneous rate.



From the graph, the tangent is calculated using two points on the line: (500, 0.03) and (700, 0.02).

Instantaneous Rate at 600 sec $-\frac{d[C_4H_9Cl]}{dt} = -\frac{(0.02-0.03)}{700-500} = 5 \times 10^{-5}$ mol L^{-1} sec^{-1}

Practice Problems

1. The Reaction, $2N_2O_5 \rightleftharpoons 4NO_2 + O_2$ was studied in a closed vessel. It was found that the concentration of NO_2 increase by 2.0×10^{-2} molL^{-1} in five seconds. Calculate (i) the rate of reaction, and (ii) the rate of change of concentration of N_2O_5.
2. A chemical reaction, $2A \longrightarrow 4B + C$, was studied in a closed vessel. The concentration of 'B' was found to be increased by 5×10^{-3} mol L^{-1} sec^{-1} in 10 seconds. Calculate (i) the rate of appearance of B, and (ii) the rate of disappearance of A.
3. $A + 2B \longrightarrow 3C + 2D$. The rate of disappearance of B is 1×10^{-2} mol L^{-1} sec^{-1}. What will be (i) Rate of the reaction, and (ii) Rate of change in concentration of A and C ?
4. Express the relationship between the rate of formation of water and rate of disappearance of oxygen in the following reaction: $2H_2 + O_2 \longrightarrow 2H_2O$

5. For a reaction, $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2} O_2$; the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol L^{-1} sec^{-1}. Calculate the rate of formation of NO_2 and O_2.
6. For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$; if rate of appearance of $NH_3 = 4 \times 10^{-8}$ mol L^{-1} sec^{-1}. What is the rate of disappearances of H_2 ?
7. For the chemical decomposition of SO_2Cl_2 , its initial concentration is 0.842 mol L^{-1} and the concentration after two hours is 0.210 mol L^{-1}. What is the average rate of reaction ?
8. For the elementary reaction, $2A + B \longrightarrow 3C$; if the rate of appearance of 'C' at time 't' is 1.3×10^{-4} mol L^{-1} sec^{-1}. Calculate (i) rate of the reaction, and (ii) rate of disappearance of 'A'.
9. The following reaction was carried at 300 K: $2SO_2 + O_2 \rightleftharpoons 2SO_3$
   The concentration of SO_3 gas is 5×10^{-3} moles after 7.5 minutes of the start of the reaction. Calculate the average rate of formation of SO_3 during the reaction.

Factors Influencing the Rate of Chemical Reactions

- **Temperature**
  - The rate of reaction increases with an increase in temperature.
  - In most cases, the reaction rate **approximately doubles** for every **10 °C rise in temperature**.
- **Presence of a Catalyst**
  - A **catalyst** increases the rate of reaction without undergoing any permanent chemical change itself.
  - It provides an **alternative reaction pathway** with lower activation energy, thus making the reaction faster.
- **Concentration of Reactants**
  - The rate of reaction is **directly proportional** to the concentration of reactants: **Rate ∝ [Reactants]**
  - **Higher conc.** means **more frequent collisions** between reactant particles, leading to faster reaction.
- **Nature of Reactants**
  - The rate of reaction depends on the nature/type of bonds being broken and formed. The energy required for this process (known as the **activation energy**) depends on the type and strength of the chemical bonds in the reactants.

    Example:
    - Oxidation of CO to CO_2 is **slow**. $CO + O_2 \longrightarrow CO_2$ (slow)
    - Oxidation of NO to NO_2 is **fast**. $NO + O_2 \longrightarrow NO_2$ (fast)
- **Surface Area of Reactants**
  - The rate of reaction increases with an increase in **surface area** of the reactants.
  - More surface area provides **more sites for collisions**, thus speeding up the reaction.

    Example: Powdered zinc reacts faster with acid than a zinc granule.
- **Exposure to Radiation (Photochemical Effect)**
  - Some reactions are accelerated by the absorption of light energy.
  - Photons of light provide sufficient energy (E=hv) to break chemical bonds, initiating reactions. Such reactions are called **photochemical reactions**.

    Example:
    - $AgBr \xrightarrow{h\upsilon} 2Ag + Br_2$
    - $H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$

Dependence of Rate of Reaction on Concentration of Reactant

- When a chemical reaction proceeds, **reactants are consumed** and **products are formed**.
  - The concentration of reactants decreases, and the concentration of products increases with time.
  - The **rate of reaction also decreases** with time, indicating that the **reaction rate is directly related** to the concentration of the reactants.

Law of Mass Action

- The quantitative relationship between the rate of a reaction and the molar concentrations of reactants was given by **Guldberg and Waage (1867)**.
- **Statement:**
  At a given temperature, the rate of a chemical reaction is **directly proportional** to the product of the molar **concentrations of the reactants**, each raised to a power **equal to** its stoichiometric coefficient.
  - For a general reaction: $aA + bB \longrightarrow \text{Products}$

    $\text{Rate} \propto [A]^a [B]^b$

    $\textbf{Rate} = \mathbf{K [A]^a [B]^b}$

Rate Law Expression

- Experimental studies show that the actual dependence of rate on concentrations of reactant **may differ from the stoichiometric coefficients**.
  - For the same reaction: $aA + bB \longrightarrow \text{Products}$

    The Rate Law expression is: $\text{Rate} \propto [A]^x [B]^y$

    $\textbf{Rate} = \mathbf{K [A]^x [B]^y}$
  - Here, x and y are experimentally determined powers. They may or may not be equal to the stoichiometric coefficients (**a** and **b**).
- Therefore, a **rate law expression** (or **rate equation**) is the mathematical expression that relates the rate of reaction to the molar concentrations of reactants, raised to experimentally determined powers.

- **Order of a Reaction**
  - The order of a reaction is the **sum of the powers** to which the concentration terms are raised in the rate law expression.
  - For example: $\textbf{Rate} = \mathbf{K [A]^x [B]^y}$

    Order of Reaction = $x + y$

- **Examples of Reactions of Different Orders**
  - **Zero** Order Reactions
    - $2NH_3 \xrightarrow{\text{W or Mo}} N_2 + 3H_2$ Rate = $K [NH_3]^0 = K$

      [Note: Reaction becomes of First order at low pressure and in absence of catalyst]
    - $H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$ Rate = $K [H_2]^0 [Cl_2]^0 = K$

      [Note: All photochemical reactions follow zero order kinetics]
  - **First** Order Reactions
    - $2N_2O_5 \longrightarrow 4NO_2 + O_2$ Rate = $K [N_2O_5]^1$
    - $2N_2O \longrightarrow 2N_2 + O_2$ Rate = $K [N_2O]^1$
    - $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ Rate = $K [SO_2Cl_2]^1$

- **Second** Order Reactions
  - $2HI \longrightarrow H_2 + I_2$ Rate = $K [HI]^2$
  - $NO_2 + CO \longrightarrow NO + CO_2$ Rate = $K [NO_2]^2$
  - $2H_2O_2 \xrightarrow{KI} 2H_2O + O_2$ Rate = $K [H_2O_2]^1[KI]^1$
- **Third** Order Reactions
  - $2NO + Br_2 \longrightarrow 2NOBr$ Rate = $K [NO]^2[Br]^1$
  - $2NO + O_2 \longrightarrow 2NO_2$ Rate = $K [NO]^2 [O_2]^1$
- **Fractional** Order Reactions
  - $H_2 + Br_2 \longrightarrow 2HBr$ Rate = $K [H_2]^1 [Br_2]^{1/2}$
  - $CO + Cl_2 \longrightarrow COCl_2$ Rate = $K [CO]^2 [Cl_2]^{1/2}$
  - $CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$ Rate = $K [CHCl_3]^1 [Cl_2]^{1/2}$

- <u>**Determining Rate Law Expression from Experimental Data**</u>
  - Consider a reaction: $2NO + O_2 \longrightarrow 2NO_2$
  - The following experimental data was collected:

Exp No.	**Initial [NO] (mol L^{-1})**	**Initial [O_2] (mol L^{-1})**	**Rate of formation of NO_2 (mol L^{-1} sec $^{-1}$)**
1.	0.30	0.30	0.096
2.	0.60	0.30	0.384
3.	0.30	0.60	0.196
4.	0.60	0.60	0.768

  - **To Find the order with respect to NO**:
    - Compare experiments where **[O_2] is constant** (e.g., Exp. 1 & 2).
    - When **[NO] is doubled** (0.30 to 0.60), the **rate increases by a factor of 4** (0.384/0.096 = 4).
    - This indicates the rate depends on **$[NO]^2$**.
  - **To find the order with respect to O_2:**
    - Compare experiments where **[NO] is constant** (e.g., Exp. 1 & 3).
    - When **[O_2] is doubled** (0.30 to 0.60), the **rate also doubles** (0.196/0.096 ≈ 2).
    - This indicates the rate depends on **$[O_2]^1$**.
  - Thus, the Rate Law Expression is: **Rate = $K [NO]^2 [O_2]^1$**
  - The overall order of the reaction is: Order = 2 + 1 = 3

- <u>**Units of the Rate Constant (K)**</u>
  - The unit of the rate constant depends on the **overall order of the reaction**.
  - For a hypothetical reaction ; **$rR \longrightarrow$ Product**
    - The Rate Law Expression is: **Rate = $K [R]^n$** {Where, **n** = order of the reaction.}
    - Therefore, $K = \frac{\text{Rate}}{[R]^n} = \frac{\text{mol L}^{-1}\text{ sec}^{-1}}{[\text{mol L}^{-1}]^n} = (\text{mol L}^{-1})^{1-n}\text{ sec}^{-1}$
    - For gaseous phase reactions, **mol L^{-1}** is **substituted** with pressure unit '**atm**'.
    - Therefore, **$K = (atm)^{1-n}\ sec^{-1}$**

- For Example:

Order of the Reaction (n)	Units of K (In liquid Phase)	Units of K (In Gaseous Phase)
0	mol L^{-1} sec^{-1}	atm sec^{-1}
1	sec^{-1}	sec^{-1}
2	mol^{-1} L sec^{-1}	atm^{-1} sec^{-1}
3	mol^{-2} L^2 sec^{-1}	atm^{-2} sec^{-1}
4	mol^{-3} L^3 sec^{-1}	atm^{-3} sec^{-1}
n	$(mol\ L^{-1})^{1-n}$ sec^{-1}	$(atm)^{1-n}$ sec^{-1}

- **Characteristics of the Rate Constant (K):**
  - A **larger value** of the rate constant indicates a **faster reaction** rate.
  - Different reactions have **different values** of rate constant (K).
  - For a given reaction, the value of the rate constant is **constant at a fixed temperature**.
  - For a given reaction, the value of the rate constant **changes with temperature**.
  - The value of the rate constant does **not depend** on the **initial concentrations of the reactants**.
  - **The unit** of the rate constant **depends on the order** of the reaction.

Practice Problems

1. State the order with respect to each reactant and overall order for the reaction;
   $2H_2 + 2NO \longrightarrow 2H_2O + N_2$; Rate = K $[H_2]$ $[NO]^2$. Calculate the units for the rate constant.
2. For the reaction, $A + B \longrightarrow AB$, rate law expression is: Rate = K [A] $[B]^2$. If the volume of the vessel is reduced to 1/3 of its original volume, them what will be the effect on the rate of reaction ?
3. Calculate the overall order of a reaction and dimensions of rate constant which has rate expression:
   (a) Rate = K $[A]^{1/2}$ $[B]^{3/2}$ (b) Rate = K $[A]^{3/2}$ $[B]^{-1}$
4. Identify the order of a reaction for each of the following rate constants:
   (a) K = 2.3 × 10^{-5} mol^{-1} L sec^{-1} (b) K = 3 × 10^{-4} sec^{-1}
5. The rate of decomposition of a substance 'A' becomes eight times when its concentration is doubled. What is the order of reaction ?
6. The rate of formation of dimer in second order dimerization reaction is 9.5 × 10^{-5} mol L^{-1} sec^{-1} at 0.01 mol L^{-1} monomer concentration. Calculate the rate constant.
7. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half ?
8. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y ?
9. The rate of reaction; $2NO + Cl_2 \longrightarrow 2NOCl$ is doubled when concentration of Cl_2 is doubled and becomes eight times when concentration of both NO and Cl_2 are doubled. Determine the order of reaction.
10. Consider the following data for the reaction ; $A + B \longrightarrow$ Products

Experiment	Initial [A]	Initial [B]	Initial Rate (mol $L^{-1}sec^{-1}$)
1	0.10	1.0	2.1 × 10^{-3}
2	0.20	1.0	8.4 × 10^{-3}
3	0.20	2.0	8.4 × 10^{-3}

Determine the order of reaction with respect to A and with respect to B and overall order of the reaction.

Molecularity of a Reaction

- According to the **collision theory**, a chemical reaction occurs when **reactant molecules collide** with sufficient energy and in the correct orientation.
- The **molecularity** of an elementary reaction is defined as the **number of reacting species (atoms, ions, or molecules) that collide simultaneously** to bring about a chemical change or reaction.
    - **Example:**
        - $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ (Unimolecular reaction)
        - $O_2F_2 \longrightarrow O_2 + F_2$ (Unimolecular reaction)
        - $NO + O_3 \longrightarrow NO_2 + O_2$ (Bimolecular reaction)
        - $2NO + O_2 \longrightarrow 2NO_2$ (Trimolecular reaction)
- On the basis of collision theory, we can say that the **reaction involving three or more reacting particles** should be **slow**. However, it has been observed that some reaction involving more than three molecules are quite fast.
    - **Example:** $\mathbf{5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O}$
      The above reaction should have **molecularity 12** but in actually this reaction is **tetramolecular**. The experimentally measured rate law for this reaction is: **Rate = $k[Br^-][BrO_3^-][H^+]^2$**
    - The above reaction supposed to takes place in a **sequence of number of steps.** Therefore, the above reaction is **complex reaction**. Each of the reaction step is **elementary in nature**.
    - The **overall rate of reaction** depends upon the **slowest step**. Hence, the slowest step is called the **rate determining step**.
    - Therefore, **molecularity** can be defined only for an **elementary reaction**. It has **no meaning** for the **complex reaction**.
        - The reactions taking place in **one step** are called **elementary or simple reactions**.
        - The reactions taking place in **two or more steps** are called **complex reactions**.

Mechanism of a Reaction

- The **mechanism of a reaction** is the **detailed description of the various steps** by which reactants are converted into products. This can be explained using **intermediate formation theory**.
- In a multi-step reaction, the **rate of the overall reaction is determined by the slowest step**, which is called the **rate-determining step**.
- The **molecularity of the slowest step** dictates the **order** of the overall reaction.

Example 1.: Decomposition of N_2O_5 : $\mathbf{2N_2O_5 \longrightarrow 4NO_2 + O_2}$

- The experimentally determined rate law expression for the reaction is; **Rate = k $[N_2O_5]^1$**.
- This suggests a mechanism on the basis of **intermediate formation theory** where the **slowest step** involves a **single N_2O_5 molecule**.
    - Step 1. $N_2O_5 \longrightarrow NO_2 + NO_3$ (**slow**, unimolecular)
    - Step 2. $N_2O_5 + NO_3 \longrightarrow 3NO_2 + O_2$ (**fast**)
- The molecularity of the **rate-determining step** is **1**, so the reaction is unimolecular and **first order**.
- The NO_3 molecule is an **intermediate** (substances which are believed to be formed during the process but do not appear in the final product).

Example 2.: Reaction of NO_2 with CO : $NO_2 + CO \longrightarrow CO_2 + NO$

- The experimentally determined rate law expression for the reaction is; **Rate = k $[NO_2]^2$**.
- This suggests a mechanism where the **slowest step** involves **two molecules of NO_2**.
    - Step 1. $NO_2 + NO_2 \longrightarrow NO + NO_3$ (**slow**, bimolecular)
    - Step 2. $CO + NO_3 \longrightarrow NO_2 + CO_2$ (**fast**)
- The molecularity of the **rate-determining step** is **2**, so the reaction is bimolecular and **second order**.
- The NO_3 molecule is an **intermediate**.

Example 3.: Decomposition of ClO^{-1} : $3\ ClO^{-1} \longrightarrow ClO_3^{-1} + 2Cl^{-1}$

- The experimentally determined rate law expression for the reaction is; **Rate = k $[ClO^{-1}]^2$**.
- This suggests a mechanism where the **slowest step** involves **two molecules of ClO^{-1}**.
    - Step 1. $ClO^{-1} + ClO^{-1} \longrightarrow ClO_2^{-1} + Cl^{-1}$ (**slow**, bimolecular)
    - Step 2. $ClO^{-1} + ClO_2^{-1} \longrightarrow ClO_3^{-1} + Cl^{-1}$ (**fast**)
- The molecularity of the **rate-determining step** is **2**, so the reaction is bimolecular and **second order**.
- The ClO_2^{-1} molecule is an **intermediate**.

Example 4.: Reaction of NO_2 with F_2 : $2NO_2 + F_2 \longrightarrow 2NO_2F$

- The experimentally determined rate law expression for the reaction is; **Rate = k $[NO_2]^1[F_2]^1$**.
- This suggests a mechanism where the **slowest step** involves **one molecule of each NO_2 and F_2**.
    - Step 1. $NO_2 + F_2 \longrightarrow NO_2F + F$ (**slow**, bimolecular)
    - Step 2. $NO_2 + F \longrightarrow NO_2F$ (**fast**)
- The molecularity of the **rate-determining step** is **2**, so the reaction is bimolecular and **second order**.
- The F atom is an **intermediate**.

Example 5.: Decomposition of H_2O_2 : $2H_2O_2 \xrightarrow{\text{Alkaline Medium, } I^{-1}} 2H_2O + O_2$

- The rate of reaction may also depend upon the concentration of catalyst. Such rates are called **catalyst dependent rate of reactions**.
- The experimentally determined rate law expression for the reaction is; **Rate = k $[H_2O_2]^1\,[I^{-1}]^1$**.
- This suggests a mechanism where the **slowest step** involves a **one molecule of each H_2O_2 and I^{-1}**.
    - Step 1. $H_2O_2 + I^{-1} \longrightarrow H_2O + OI^{-1}$ (**slow**, bimolecular)
    - Step 2. $H_2O_2 + OI^{-1} \longrightarrow H_2O + O_2 + I^{-1}$ (**fast**)
- The molecularity of the **rate-determining step** is **2**, so the reaction is unimolecular and **second order**.
- The OI^{-1} molecule is an **intermediate**.

Practice Problems

1. For a hypothetical reaction, $2A + B \longrightarrow 3C$, the proposed mechanism is:
   Step 1: $A + B \rightleftharpoons D$ (**fast** equilibrium)
   Step 2: $D + A \longrightarrow 3C$ (**slow**)
   What is the overall rate law expression for this reaction?
2. The rate law for a reaction is given by Rate = $k[X]^1[Y]^2$. If the concentration of X is doubled and the concentration of Y is halved, what will be the effect on the reaction rate?

3. In the reaction mechanism given below, what it the overall rate law expression for this reaction ?

   Step 1: $O_{3\,(g)} \rightleftharpoons O_{2\,(g)} + O_{(g)}$ (**fast** equilibrium)

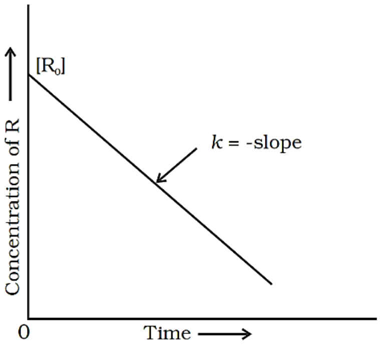
   Step 2: $O_{(g)} + O_{3\,(g)} \longrightarrow 2O_{2\,(g)}$ (**slow**)

4. Consider the following reaction; $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$, the rate law expression for the reaction is Rate = $K\,[NO]^2[H_2]^1$. Can you suggest the mechanism for the reaction?

Integrated Rate Equations

Zero Order Reactions

- Consider a hypothetical equation ; **R** ⟶ **Product**
  - Rate = $-\dfrac{d[R]}{dt}$ -----(i)
  - Rate = $K\,[R]^0 = K$ -----(ii)
- **Compare** the equation **(i) and (ii)** , we get,
  - $-\dfrac{d[R]}{dt} = K$ ------(iii)
- By **rearranging** the equation **(iii)**, we get,
  - $-d[R] = K \cdot dt$ -------(iv)
- **Integrating both sides** of equation **(iv)** ;
  - $-\int d[R] = K \int dt$
  - $-[R] = K \cdot t + I$ --------(v)



- Where '**I**' is the **constant of integration**. The value of 'I' can be calculated form initial concentration. The initial concentration of reactant (**[R] = [R₀]**) at time (**t = 0**). Put these values in equation (v), we get;
  - $-[R_0] = K \times 0 + I$
  - $-[R_0] = I$ ------- (vi)
- Substitute the **value of 'I' or equation (vi)** in equation **(v)**, we get:
  - $-[R] = K \cdot t - [R_0]$
  - $[R_0] - [R] = K \cdot t$
  - $\mathbf{\dfrac{[R_0] - [R]}{t} = K}$ --------(vii)

Time for 50% Completion or Half-Life Period ($t_{1/2}$) :

- The half-life period ($t_{1/2}$ or $t_{50\%}$) is the time required for the concentration of a reactant to be **reduced to half of its initial concentration**.
  - At $t_{1/2}$, the concentration of reactant [R] is 50% of its initial concentration ; $[R] = [R_0] \times 50\% = \dfrac{[R_0]}{2}$
- As we know; $\mathbf{t = \dfrac{[R_0] - [R]}{K}}$
- Hence, $t_{1/2} = \dfrac{[R]_0 - \frac{[R]_0}{2}}{k} = \dfrac{[R]_0}{2\,k}$; $\mathbf{t_{1/2} = \dfrac{[R]_0}{2\,k}}$

Time for 1/4 or 25% Completion :

- At $t_{1/4}$ or $t_{25\%}$, the concentration of reactant [R] is 75% of its initial concentration; $[R] = [R_0] \times 75\% = \frac{3[R_0]}{4}$
- Therefore ; $t_{1/4} = \frac{[R]_0 - \frac{3\,[R]_0}{4}}{k} = \frac{[R]_0}{4\,k}$; $\mathbf{t_{1/4} = \frac{[R]_0}{4\,k}}$

Time for 3/4 or 75% Completion :

- At $t_{3/4}$ or $t_{75\%}$, the concentration of reactant [R] is 25% of its initial concentration; $[R] = [R_0] \times 25\% = \frac{[R_0]}{4}$
- Therefore ; $t_{3/4} = \frac{[R]_0 - \frac{[R]_0}{4}}{k} = \frac{3\,[R]_0}{4\,k}$; $\mathbf{t_{3/4} = \frac{3\,[R]_0}{4\,k}}$

Time for 100% Completion :

- At $t_{100\%}$, the concentration of reactant [R] is 0; $[R] = [R_0] \times 0 = 0$
- Therefore ; $t_{100\%} = \frac{[R]_0 - 0}{k} = \frac{[R]_0}{k}$

Relation between half-life period and time 1/4 :

- $\frac{t_{1/2}}{t_{1/4}} = \frac{[R_0] \times 4K}{2K \times [R_0]} = 2$; $\mathbf{t_{1/2} = 2 \times t_{1/4}}$

Relation between half-life period and time 3/4 :

- $\frac{t_{3/4}}{t_{1/2}} = \frac{3[R_0] \times 2K}{4K \times [R_0]} = 2$; $\mathbf{t_{3/4} = \frac{3}{2} \times t_{1/2} = 1.5 \times t_{1/2}}$

Relation between time 1/4 and time 3/4 :

- $\frac{t_{3/4}}{t_{1/4}} = \frac{3[R_0] \times 4K}{4K \times [R_0]} = 3$; $\mathbf{t_{3/4} = 3 \times t_{1/4}}$

Time required for x amount completion

	Reactant $\longrightarrow$	Product
Initial conc. of reactant	$[R_0] = a$	
Final conc. of reactant (after 'x' amount completion)	$[R] = a - x$	x

- As we know that, $\mathbf{t = \frac{[R_0] - [R]}{K}}$
- Then, time required for 'x' amount completion ; $t_x = \frac{\mathbf{a - (a - x)}}{\mathbf{K}} = \frac{\mathbf{x}}{\mathbf{K}}$

NOTE

- Zero-order reactions are **relatively uncommon** but they occur under **special conditions**.
- In such reactions, the rate of reaction is **independent of the concentration of the reactant**.

Examples of Zero Order Reactions:

- ○ **Enzyme-catalysed reactions** under certain substrate-saturated conditions follow zero-order kinetics.

- **Surface-catalysed reactions (on metals)** may follow zero-order kinetics when the surface becomes saturated with reactant molecules.
  - **Example 1:** Decomposition of NH_3 on Platinum surface at 1130 K and high pressure.

    $$2NH_3 \xrightarrow{\text{Pt, 1130 K, High pressure}} N_2 + 3H_2 \quad ; \quad \text{Rate} = K[NH_3]^0$$

    Here, platinum acts as a catalyst. At **high pressure**, the platinum surface becomes saturated with ammonia molecules. As a result, increasing the concentration of ammonia does not increase the rate, making the reaction **independent of concentration**.
  - **Example 2:** The **thermal decomposition of hydrogen iodide (HI) on a gold surface** also follows zero-order kinetics under certain conditions.

Practice Problems

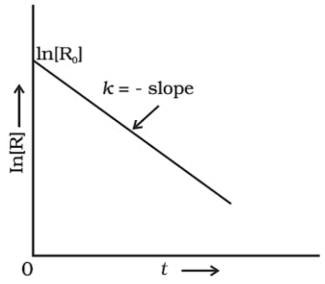
1. The rate constant of a reaction of zero order in A is 0.0030 $molL^{-1}$ sec^{-1}. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M ?
2. A zero-order reaction complete 20% in 5 minutes, calculate the time required for 75% completion.
3. The half-life period of a substance is 50 minutes at a certain initial concentration. When the concentration is reduced to one-half of the initial value, the half-life period is 25 minutes. Calculate the order of reaction?
4. During the decomposition of a gas on the surface of a solid catalyst, the pressure of the gas at different times was observed to be as follows:

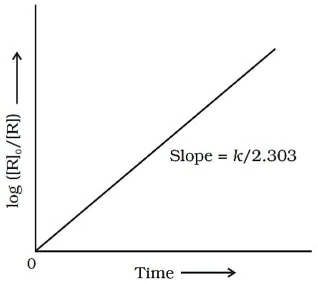
Time (sec)	0	100	200	300
Pressure (Pa)	5.00×10^3	4.20×10^3	3.40×10^3	2.60×10^3

Calculate order, rate constant and half-life period of this reaction.

First Order Reactions

- Consider a hypothetical equation ; **R** $\longrightarrow$ **Product**
  - $\text{Rate} = -\dfrac{d[R]}{dt}$ -----(i)
  - $\text{Rate} = K\,[R]$ -----(ii)
- **Compare** the equation **(i) and (ii)** , we get,
  - $-\dfrac{d[R]}{dt} = K\,[R]$ ------(iii)
- By **rearranging** the equation **(iii)**, we get,
  - $-\dfrac{d[R]}{[R]} = K \cdot dt$ -------(iv)
- **Integrating both sides** of equation **(iv)** ;
  - $-\int \dfrac{d[R]}{[R]} = K \int dt$
  - $-\ln[R] = K \cdot t + I$ --------(v)
- Where '**I**' is the **constant of integration**. The value of 'I' can be calculated form initial concentration. The initial concentration of reactant (**[R] = [R₀]**) at time (**t = 0**). Put these values in equation (v), we get;





  - ○ $-\ln[R_0] = K \times 0 + I$
  - ○ $-\ln[R_0] = I$ ------- (vi)
- Substitute the **value of 'I' or equation (vi)** in equation **(v)**, we get:
  - ○ $-\ln[R] = K \cdot t - \ln[R_0]$
  - ○ $\ln[R_0] - \ln[R] = K \cdot t$ $[\ln x - \ln y = \ln \frac{x}{y}]$
  - ○ $\ln \frac{[R_0]}{[R]} = K \cdot t$ $[\ln x = 2.303 \log x]$
  - ○ $2.303 \log \frac{[R_0]}{[R]} = K \cdot t$
  - ○ $\mathbf{\frac{2.303}{t} \log \frac{[R_0]}{[R]} = K}$ --------(vii)

Time for 50% Completion or Half-Life Period ($t_{1/2}$) :

- The half-life period ($t_{1/2}$ or $t_{50\%}$) is the time required for the concentration of a reactant to be **reduced to half of its initial concentration**.
  - ○ At $t_{1/2}$, the concentration of reactant [R] is 50% of its initial concentration ; $[R] = [R_0] \times 50\% = \frac{[R_0]}{2}$
- As we know; $t = \frac{2.303}{K} \log \frac{[R_0]}{[R]}$
- Therefore, $\mathbf{t_{1/2}} = \frac{2.303}{K} \log \frac{[R_0] \times 2}{[R_0]}$

$$= \frac{2.303}{K} \log 2 \qquad [\log 2 = 0.3010]$$

$$= \frac{2.303 \times 0.3010}{K} = \frac{0.693}{K}$$

- Hence, $\mathbf{t_{1/2} = \frac{0.693}{k}}$

Time for 1/4 or 25% Completion :

- At $t_{1/4}$ or $t_{25\%}$, the concentration of reactant [R] is 75% of its initial concentration; $[R] = [R_0] \times 75\% = \frac{3[R_0]}{4}$
- Therefore ; $\mathbf{t_{1/4}} = \frac{2.303}{K} \log \frac{[R_0] \times 4}{3\,[R_0]} = \frac{2.303}{K} \log \frac{4}{3}$

$$= \frac{2.303}{K} \log 1.33 \qquad [\log 1.333 = 0.124]$$

$$= \frac{2.303 \times 0.124}{K} = \frac{0.286}{K}$$

- Hence, $\mathbf{t_{1/4} = \frac{0.286}{k}}$

Time for 3/4 or 75% Completion :

- At $t_{3/4}$ or $t_{75\%}$, the concentration of reactant [R] is 25% of its initial concentration; $[R] = [R_0] \times 25\% = \frac{[R_0]}{4}$
- Therefore ; $\mathbf{t_{3/4}} = \frac{2.303}{K} \log \frac{[R_0] \times 4}{[R_0]}$

$$= \frac{2.303}{K}\log 4 \qquad [\log 4 = 0.6020]$$

$$= \frac{2.303 \times 0.6020}{K} = \frac{1.386}{K}$$

- Hence, $t_{3/4} = \frac{1.386}{k}$

Time for 100% Completion :

- For a first-order reaction, the time for **100% completion** is theoretically **infinite**. This is because the concentration of the reactant approaches zero asymptotically but never actually reaches it. The reaction rate, which **depends on the reactant concentration**, slows down as the concentration decreases, but it **never becomes zero**.

For 1/nth of the reaction complete :

- $t_{1/n} = \frac{2.303}{K}\log\frac{n}{n-1}$

Relation between half-life period and time 1/4 :

- $\frac{t_{1/2}}{t_{1/4}} = \frac{0.693 \times K}{K \times 0.286} = 2.42$; $t_{1/2} = 2.42 \times t_{1/4}$

Relation between half-life period and time 3/4 :

- $\frac{t_{3/4}}{t_{1/2}} = \frac{1.386 \times K}{K \times 0.693} = 2$; $t_{3/4} = 2 \times t_{1/2}$

Relation between time 1/4 and time 3/4 :

- $\frac{t_{3/4}}{t_{1/4}} = \frac{1.386 \times K}{K \times 0.286} = 4.85$; $t_{3/4} = 4.85 \times t_{1/4}$

Time required for x amount completion

	Reactant ⟶	Product
Initial conc. of reactant	$[R_0] = a$	
Final conc. of reactant (after 'x' amount completion)	$[R] = a - x$	x

- As we know that, $t = \frac{2.303}{K}\log\frac{[R_0]}{[R]}$
- Then, time required for 'x' amount completion ; $t_x = \frac{2.303}{K}\log\frac{a}{a-x}$

NOTE

- Integrated rate constant for **second order** reaction: $K = \frac{1}{t}\left(\frac{1}{[R]} - \frac{1}{[R_0]}\right)$
- Integrated rate constant for **third order** reaction: $K = \frac{1}{2t}\left(\frac{1}{[R]^2} - \frac{1}{[R_0]^2}\right)$

- Half-life period for **second order** reaction: $t_{1/2} = \frac{1}{K\,[R_0]}$
- Half-life period for **third order** reaction: $t_{1/2} = \frac{1}{K\,[R_0]^2}$
- Half-life period for **nth order** reaction: $t_{1/2} = \frac{1}{K\,[R_0]^{n-1}}$; or simply $t_{1/2} \propto \frac{1}{[R_0]^{n-1}}$

Practice Problems

1. A first order reaction is found to have a rate constant $K = 5.5 \times 10^{-14}\ \text{sec}^{-1}$. Find half-life of the reaction.
2. The 3/4 of a first order reaction is completed in 32 minutes. What is the half-life period of the reaction?
3. The rate constant of a first order reaction is $60\ \text{sec}^{-1}$. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?
4. A first order reaction is 20% complete in 10 minutes. Calculate the time for the completion of 75% of the reaction.
5. Find out two-third (2/3) life of a first order reaction in which $K = 4.89 \times 10^{-14}\ \text{sec}^{-1}$.
6. Show that for a first order reaction, time required for 99.9% of the reaction to take place 10 times of the time required for the completion of half of the reaction.
7. Show that the time required for 99% completion of a first order reaction is the twice of the time required for 90% completion of the reaction.
8. If half-life period for a first order reaction is 6 minutes, how long will it take to reach (i) 10% of its initial concentration, and (ii) 25% of its initial concentration.
9. The decomposition of N_2O_5 in CCl_4 solution follows the first order rate law. The concentration of N_2O_5 measured at different intervals are given below:

Time (min)	0	80	160	410	600	1130	1720
Mol L^{-1}	5.5	5.0	4.8	4.0	3.4	2.4	1.6

Calculate the rate constant at 410 sec and 1130 sec.

10. The rate constant for an isomerization reaction $A \longrightarrow B$ is $4.5 \times 10^{-3}\ \text{mol}^{-1}$. If the initial concentration of A is 1M, calculate the its concentration and rate of reaction after 1 Hr.
11. The rate of a first order reaction is $0.04\ \text{mol L}^{-1}\ \text{sec}^{-1}$ after 10 minutes, and $0.03\ \text{mol L}^{-1}\ \text{sec}^{-1}$ after 20 minutes. Find the half-life period of the reaction.
12. A first order reaction has rate constant of $0.005\ \text{min}^{-1}$. If we begin with 0.1 M concentration of the reactant, what concentration of reactant will remain in solution after 3 Hr.
13. With rate constant of $5 \times 10^{-4}\ \text{sec}^{-1}$ at 45 °C, If initial concentration of N_2O_5 is 0.25 M, calculate the concentration after 2 minutes. Also calculate half-life for the decomposition of N_2O_5 ?
14. H_2O_2 decomposes to H_2O and O_2 in a reaction that is of first order, and has a rate constant $K = 1.06 \times 10^{-3}\ \text{min}^{-1}$. (i) How long will it take 15% of a sample of H_2O_2 to decompose? (ii) How long will it take 85% of a sample of H_2O_2 to decompose?
15. The rate constant of a reaction with respect to the reactant 'A' is $6\ \text{min}^{-1}$. If we start with $[A] = 0.8\ \text{mol L}^{-1}$, when would [A] reach the value of $0.08\ \text{mol L}^{-1}$.
16. The initial concentration of N_2O_5 in the following first order reaction; $2N_2O_5 \longrightarrow 2NO_2 + O_2$ was $1.25 \times 10^{-2}\ \text{mol L}^{-1}$ at 318 K. The concentration of N_2O_5 after 60 minutes was $0.20 \times 10^{-2}\ \text{mol L}^{-1}$. Calculate the rate constant for the reaction at 318 K

17. A first order reaction is 20% complete in 5 min. Calculate time taken for the reaction to be 60% complete.
18. A first order reaction is found to have a rate constant ‘K’ 7.39×10^{-5} sec^{-1}. Find the half-life of the reaction.
19. For the first order reaction, the rate constant is 4.62×10^{-2} sec^{-1}. What will be the time required for the initial concentration 1.5 mole of the reactant to be reduced to 0.75 mole?
20. A first order reaction is 20% complete in 10 minutes. Calculate the time taken by the reaction for 75% completion.
21. A first order reaction is 75% complete in 60 min. Find the half-life period of the reaction.
22. Calculate the half-life period of a reaction of first order whose specific rate constant is 200 sec^{-1}.
23. 60% of first order reaction was complete in 60 minutes. When was it half completed?
24. Rate constant ‘K’ for a first order reaction has been found to be 2.54×10^{-3} sec^{-1}. Calculate three fourth and half-life period.
25. The decomposition of H_2O_2 is a first order reaction. Calculate the half-life the and rate constant for the decomposition from the fact that the fraction decomposed in 50 minutes is 0.75.
26. In a reaction, 5 gm of ethyl acetate is hydrolysed per litre in presence of dilute HCl in 300 minutes. If the reaction is of first order and the initial concentration of ethyl acetate is 22 gm/L. Calculate the rate constant of the reaction.
27. A first order reaction takes 40 minutes for 30% decomposition of reactants. Calculate its half-life period.
28. The half-life period of a radioactive element is 1.4×10^{10} years. Calculate the time in which the activity of the element is reduced to 90% of its original volume.
29. The half-life of radioisotope bromine-82 is 36 hours. Calculate the fraction of a sample of bromine that remains after one day.
30. A radioactive element has a rate constant $K = 2.31 \times 10^{-4}$ min^{-1}. Find its half-life period.
31. The half-life of ^{14}C is 5730 years. A wooden artifact shows only 40% of the original carbon-14 activity. Estimate the age of the artifact.
32. A fossil bone contains only 25% of the carbon-14 it would have contained if it were a living organism. Calculate the age of the bone (Half-life of ^{14}C = 5730 years).
33. A rock sample contains uranium-238 which decays with a half-life of 4.5×10^9 years. If the sample originally contained 10 g of U-238 but now contains only 2.5 g, calculate the age of the rock.
34. A dinosaur bone is found to contain only 1/16th of the original carbon-14. If the half-life of ^{14}C is 5730 years, calculate the approximate age of the bone.
35. A dinosaur bone contains only 20% of the original carbon-14. Estimate its age, given that the half-life of carbon-14 is 5730 years.
36. A fossilized dinosaur bone contains uranium-238, which decays to lead-206 with a half-life of 4.5×10^9 years. If the bone originally contained 12 g of U-238, but only 3 g remains, calculate the approximate age of the bone.
37. The half-life of phosphorus-32 is 14.3 days. Calculate the rate constant (k) for its decay.
38. A phosphorus-32 tracer is injected into a patient. After 43 days, only 12.5% of the isotope remains active in the body. Calculate the half-life of the isotope and check whether it matches 14.3 days.
39. A laboratory receives a 15 mg sample of P-32. After 21.45 days, only 5 mg remains. Calculate the half-life of P-32 from this data and compare with its actual value (14.3 days).
40. A sample of P-32 initially contains 80 mg. How much will remain after 28.6 days? (Half-life = 14.3 days)
41. The half-life of P-33 is 25.3 days. A 40 mg sample is taken. Calculate the time required for the sample to decay to 10 mg.

Method to calculate approx. value of Antilog:

- Step 1: antilog (y) = 10^y
- Step 2: Break into two parts; $10^y = 10^{a+b} = 10^a \times 10^b$
    - Example 1: antilog (2.3) = $10^{2.3} = 10^{2+0.3} = 10^2 \times 10^{0.3} = 100 \times 2 = 200$
    - Example 2: antilog (–1.7) = $10^{-1.7} = 10^{-2+0.3} = 10^{-2} \times 10^{0.3} = 0.01 \times 2 = 0.02$
- Step 3: Memorize a few decimal power values:

Decimal (b)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.1	1
10^b (antilog)	1.26	1.58	2.0	2.51	3.16	3.98	5.01	6.31	7.94	10.0

Method to calculate approx. value of Logs:

- Step 1: Representing a number as $N = a \times 10^b$; $250 = 2.5 \times 10^2$
- Step 2: Then, use formula $\log (N) = \log (a \times 10^b) = b + \log (a)$

  Example1: $\log (250) = \log (2.5 \times 10^2) = 2 + \log (2.5) = 2 + 0.398 = 2.398$

  Example2: $\log (550) = \log (5.5 \times 10^2) = 2 + \log (5.5) = 2 + 0.74 = 2.74$
- Step 3: Memorize logs of small numbers

(a)	1	2	3	4	5	6	7	8	9	10
log (a)	0.00	0.3	0.48	0.6	0.7	0.78	0.85	0.9	0.95	1

Examples of 1st Order Reaction

Example 1.: Decomposition of N_2O_5 :

- Nitrogen pentoxide (N_2O_5) is a **volatile solid** which decompose as follow:

  Step 1: $2\,N_2O_5 \longrightarrow 2\,N_2O_4 + O_2$

  Step 2: $2\,N_2O_4 \longrightarrow 4\,NO_2$
- When reaction is carried out in an inert solution, **N_2O_4 and NO_2 remain in the solution** and the **volume of oxygen gas collected is noted** at different intervals of time.
    - Volume of O_2 collected at ∞ time (V_∞) ∝ Amount of N_2O_5 initially taken (**a**)
    - Volume of O_2 collected at any time (V_T) ∝ Amount of N_2O_5 decompose (x)
- Substituting these values in first order equation: $K = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$ or $K = \frac{2.303}{t} \log \frac{a}{a - x}$
- We get , $K = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_T}$

Question : From the following data for the decomposition of N_2O_5 in CCl_4 solution at 321 K, show that the reaction is of first order and calculate the rate constant.

Time (min)	**10**	**15**	**20**	**25**	∞
Vol. of O_2 evolved (ml)	**6.30**	**8.95**	**11.40**	**13.50**	**34.75**

Answer : If the reaction is of the first order, it must obey the equation :

$$K = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_T}$$

Time (min)	V_T	$V_\infty - V_T$	$K = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_T}$
10	6.30	34.75 – 6.30 = 28.45	$K = \frac{2.303}{10} \log \frac{34.75}{28.45} = 0.01997\ min^{-1}$
15	8.95	34.75 – 8.95 = 25.80	$K = \frac{2.303}{15} \log \frac{34.75}{25.80} = 0.01985\ min^{-1}$
20	11.40	34.75 – 11.40 = 23.35	$K = \frac{2.303}{20} \log \frac{34.75}{23.35} = 0.01987\ min^{-1}$
25	13.50	34.75 – 13.50 = 21.25	$K = \frac{2.303}{25} \log \frac{34.75}{21.25} = 0.01967\ min^{-1}$

Since the value of 'K' comes to be nearly constant, hence given reaction is of the first order.

Example 2.: Decomposition of H_2O_2 :

- The decomposition of H_2O_2 in aqueous solution takes place as follow;
  - $2\ H_2O_2 \longrightarrow 2\ H_2O + O_2$
- The **kinetics** of this reaction may be studied in **two ways**:
  - By **collecting the volume of oxygen gas** produced at different intervals of time
  - By **titrating H_2O_2 solution against $KMnO_4$ solution** at different time intervals.
- Following conclusions can be drawn by **titrating H_2O_2 solution against $KMnO_4$ solution**:
  - Vol^m of $KMnO_4$ used before reaction (**V_0**) $\propto$ Initial conc. of H_2O_2 (**a**)
  - Vol^m of $KMnO_4$ used at any instant time (**V_T**) $\propto$ Amount of H_2O_2 present at that time (**$a - x$**)
- Substituting these values in first order equation: $K = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$ or $K = \frac{2.303}{t} \log \frac{a}{a-x}$
- We get, $\mathbf{K = \frac{2.303}{t} \log \frac{V_0}{V_T}}$

Question : From the following data, show that decomposition of hydrogen peroxide is 1st Order reaction:

Time (min)	**0**	**10**	**20**
Volume of $KMnO_4$ used (ml)	**46.1**	**29.8**	**19.3**

Answer : Volume of $KMnO_4$ used is directly proportional to the amount of H_2O_2 present. If the reaction is of the first order, it must obey the equation: $K = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{V_0}{V_T}$

Time (min)	V_T	$k = \frac{2.303}{t} \log \frac{V_0}{V_T}$
10	29.8	$K = \frac{2.303}{10} \log \frac{46.1}{29.8} = 0.0436\ min^{-1}$
20	19.3	$K = \frac{2.303}{20} \log \frac{46.1}{19.3} = 0.0435\ min^{-1}$

Since the value of 'k' comes to be nearly constant, hence given reaction is of the first order.

Example 3.: Decomposition of SO_2Cl_2 (A Gaseous Phase Reaction)

- The decomposition of SO_2Cl_2 in a closed vessel takes place as follow;

$$SO_2Cl_{2\,(g)} \longrightarrow SO_{2\,(g)} + Cl_{2\,(g)}$$

- Following conclusions can be drawn by **measuring the pressure inside the vessel**:

	$SO_2Cl_{2\,(g)}$ ⟶	$SO_{2\,(g)}$	+ $Cl_{2\,(g)}$
Initial Pressure in atm	P_0	0	0
Pressure at time ‘t’ in atm	$P_0 - p$	p	p

  - Initial pressure of SO_2Cl_2 **(P_0)** ∝ Initial concentration of SO_2Cl_2 **[R_0]**
  - Pressure of SO_2Cl_2 at time ‘t’ **($P_0 - p$)** ∝ Concentration of SO_2Cl_2 at time ‘t’ **[R]**

- Substituting these values in first order equation: $K = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$

  We get, $$K = \frac{2.303}{t} \log \frac{P_0}{P_0 - p}$$

- The **pressure (p) of product component** in reaction mixture can be calculated as follows:
  - The **total pressure (P_T)** of the reaction mixture after time ‘t’ will be :

$$P_T = (P_0 - p) + p + p$$
$$P_T = P_0 + p$$

  - Therefore, the **pressure (p) of product component** in reaction mixture is: $p = P_T - P_0$

- Now, substitute this value in first order equation: $K = \frac{2.303}{t} \log \frac{P_0}{P_0 - p}$

  We get, $$K = \frac{2.303}{t} \log \frac{P_0}{P_0 - (P_T - P_0)}$$

  Hence, $$K = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_T}$$

Question 1: Following data were obtained during the first order thermal decomposition of SO_2Cl_2 at constant volume:

Time (sec)	**0**	**100**
Total Pressure (atm)	**0.5**	**0.6**

Calculate the rate constant and rate of reaction when total pressure is 0.65 atm

Question 2: For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data were obtained at constant volume:

Time (sec)	**0**	**360**	**720**
Total Pressure (mmHg)	**35.0**	**54.0**	**63.0**

Calculate the rate constant if the reaction follows first order kinetics.

Question 3: The following data were obtained during the first order thermal decomposition of N_2O_5 at constant volume : $2N_2O_{5\,(g)} \longrightarrow 2N_2O_{4\,(g)} + O_{2\,(g)}$

Time (sec)	**0**	**100**
Total Pressure (atm)	**0.5**	**0.512**

Calculate the rate constant for the gaseous reaction.

Pseudo First Order Reaction

- Chemical reactions which are not truly first order but under certain conditions behave as first-order reactions are called **pseudo first-order reactions**.
- This usually occurs when one of the reactants is present in a **significantly large excess** as compared to the others, so that its **concentration remains essentially constant** throughout the reaction.
- The rate of the reaction, therefore, **depends only** on the concentration of the **limiting reactant**.

Example 1.: Acid Catalysed Hydrolysis of Ester (Ethyl Acetate)

- The reaction involves: $$\underset{\text{Ethyl Acetate}}{CH_3COOC_2H_5} + \underset{\text{Water}}{H_2O} \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$
  - The above reaction involves **two reactants** (ethyl acetate and water), hence the **molecularity is two**.
  - Its rate law expression can be written as: Rate = **K** $[CH_3COOC_2H_5]$ $\mathbf{[H_2O]}$
  - However, **water is present in very large excess**, so its concentration remains practically **constant** during the reaction.

    $$K' = K\,[H_2O]$$
  - Therefore, the rate of the reaction **depends only** on the **concentration of ethyl acetate**.

    $$\text{Rate} = K'\,[CH_3COOC_2H_5]$$
- Thus, the reaction appears to be **second order** but **follows the first order kinetics**. Such reactions which appear to be **higher order** but **follow lower order kinetics** are called **pseudo chemical reactions**.

Question 1 : Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The **concentration of ester at different times** is given below :

Time (min)	0	30	60	90
Concentration (mol L^{-1})	0.8500	0.8004	0.7538	0.7096

Show that it follows a pseudo first order reaction as the concentration of H_2O remains nearly constant during the course of the reaction. What is the value of K” in this equation? If : **Rate = K” $[CH_3COOCH_3]$ $[H_2O]$**

Answer : Let us calculate the value of K for the first order reaction:

Time (min)	Concentration (mol L^{-1})	$K = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$
0 to 30	0.8500 to 0.8004	$K = \frac{2.303}{30} \log \frac{0.8500}{0.8004} = 2.004 \times 10^{-3}\ \text{min}^{-1}$
0 to 60	0.8500 to 0.7538	$K = \frac{2.303}{60} \log \frac{0.8500}{0.7538} = 2.002 \times 10^{-3}\ \text{min}^{-1}$
0 to 90	0.8500 to 0.7096	$K = \frac{2.303}{90} \log \frac{0.8500}{0.7096} = 2.005 \times 10^{-3}\ \text{min}^{-1}$

Since the calculated values for **the rate constant (K)** are all **approximately the same** (≈ $2.004 \times 10^{-3}\ \text{min}^{-1}$), this confirms that the reaction follows **first-order kinetics** under the experimental conditions.

But the rate of reaction is given by the rate law expression : **Rate = K” [CH_3COOCH_3] [H_2O]**

It means the reaction is **pseudo-first order reaction**. Therefore, the **observed rate constant K** is given by:

$$K = K'' [H_2O] = 2.004 \times 10^{-3}\ \text{min}^{-1}$$

Let us, find K” (second-order rate constant) assuming [H_2O] = 55.5 mol L^{-1} (molarity of pure water)

$$K'' = \frac{K}{[H_2O]} = \frac{2.004 \times 10^{-3}\ \text{min}^{-1}}{55.5} = 3.6 \times 10^{-5}\ \text{mol}^{-1}\ \text{L}\ \text{min}^{-1}$$

Question 2 : 1.0 ml of ethyl acetate was added to 25 ml of N/2 HCl, 2 ml of the mixture were withdrawn from time to time during the progress of the hydrolysis of the ester and **titrated against standard NaOH solution**. The amount of **NaOH required for titration at various intervals** is given below:

Time (min)	**0**	**20**	**75**	**119**	**183**	**∞**
NaOH used (ml)	**20.24**	**21.73**	**25.20**	**27.60**	**30.22**	**43.95**

The value at ∞ time was obtained by completing the hydrolysis on boiling. Show that it is a reaction of first order and find the value of rate constant.

Answer : If the given reaction is first order, it must obey the equation:

$$K = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_T}$$

We know that :

$$V_0 = 20.24\ \text{ml and } V_\infty = 43.95\ \text{ml}, \quad \therefore\ V_\infty - V_0 = 43.95 - 20.24 = 23.71\ \text{ml}$$

Time (min)	V_T	$V_\infty - V_T$	$K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_T}$
20	21.73	43.95 – 21.73 = 22.22	$K = \frac{2.303}{20} \log \frac{23.71}{22.22} = 0.00324\ \text{min}^{-1}$
75	25.20	43.95 – 25.20 = 18.75	$K = \frac{2.303}{75} \log \frac{23.71}{18.75} = 0.00313\ \text{min}^{-1}$
119	27.60	43.95 – 27.60 = 16.35	$K = \frac{2.303}{119} \log \frac{23.71}{16.35} = 0.00312\ \text{min}^{-1}$
183	30.22	43.95 – 30.22 = 13.73	$K = \frac{2.303}{183} \log \frac{23.71}{13.73} = 0.00299\ \text{min}^{-1}$

Since the value of ‘K’ comes out to be nearly constant, hence given reaction is of the first order.

Reaction and Logical Basis:

- The acid-catalysed hydrolysis of Ethyl acetate takes place as follow:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

- The titration of the reaction mixture with NaOH at any time ‘t’ neutralises :
  - (i) the acid initially present/added as catalyst (H^+), and
  - (ii) the acetic acid (CH_3COOH) formed by hydrolysis.

- Let,
    - $\mathbf{V_0}$ = Volume of NaOH used in beginning when time = 0
    - $\mathbf{V_\infty}$ = Volume of NaOH used after complete hydrolysis
    - $\mathbf{V_T}$ = Volume of NaOH used during the reaction or at any time ‘t’

- When equal volumes of reaction mixture withdraw at different time, following conclusions are made:
    - $\mathbf{V_0} \propto$ Acid present as catalyst
    - $\mathbf{V_\infty} \propto$ Acid present as catalyst **+** Maximum amount of CH_3COOH produced in the reaction

      [Maximum amount of CH_3COOH produced in rec^n $\propto$ Initial conc. of $CH_3COOC_2H_5$ **(a)**]

      Therefore,

      $$\mathbf{V_\infty \propto V_0 + a} \qquad \textbf{OR} \qquad \mathbf{a \propto V_\infty - V_0}$$

    - $\mathbf{V_T} \propto$ Acid present as catalyst **+** Amount of CH_3COOH produced in the reaction at time ‘t’

      [Amount of CH_3COOH produced in the reaction $\propto$ Amount of $CH_3COOC_2H_5$ reacted (x)]

      Therefore,

      $$\mathbf{V_T \propto V_0 + x} \qquad \textbf{OR} \qquad \mathbf{x \propto V_T - V_0}$$

- From all above conclusions, we have:

  $$\mathbf{a \propto V_\infty - V_0}$$
  $$\mathbf{x \propto V_T - V_0}$$

- Substituting these values in 1st order equation: $K = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$ or $\mathbf{K = \frac{2.303}{t} \log \frac{a}{a-x}}$

  We get,

  $$\mathbf{K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{(V_\infty - V_0) - (V_T - V_0)}}$$

  $$\mathbf{K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_T}}$$

Example 2.: Acid Catalysed Hydrolysis of Cane Sugar (Inversion of Sucrose)

- The reaction involves:

  $$\underset{\substack{\text{Sucrose}\\ \text{dextro-rotatory}\\ (+\,66.5°)}}{\mathbf{C_{12}H_{22}O_{11}}} + \underset{\text{Water}}{\mathbf{H_2O}} \xrightarrow{\mathbf{H^+ \text{ or Invertase}}} \underset{\substack{\text{Glucose}\\ \text{dextro-rotatory}\\ (+\,52.5°)}}{\mathbf{C_6H_{12}O_6}} + \underset{\substack{\text{Fructose}\\ \text{laevo-rotatory}\\ (-\,92°)}}{\mathbf{C_6H_{12}O_6}}$$

    - The above reaction involves **two reactants** (sucrose and water), hence the **molecularity is two**.
    - Its rate law expression can be written as: Rate = **K** $[C_{12}H_{22}O_{11}]$ $\mathbf{[H_2O]}$
    - However, **water is present in very large excess**, so its concentration remains practically **constant** during the reaction.

      $$\mathbf{K' = K\,[H_2O]}$$

    - Therefore, the rate of the reaction **depends only** on the **concentration of sucrose**.

      $$\mathbf{Rate = K'\,[C_{12}H_{22}O_{11}]}$$

Question 1 : Optical rotation of sucrose in 1N HCl at various times was found and is shown below:

Time (sec)	**0**	**7.18**	**18**	**27.05**	**∞**
Rotation (degree)	**+24.09**	**+21.4**	**+17.7**	**+15.0**	**–10.74**

Show that the inversion of sucrose is a first order reaction.

Answer : If the given reaction is first order, it must obey the equation:

$$K = \frac{2.303}{t} \log \frac{[\mathbf{R_0}]}{[\mathbf{R}]} = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

We know that :

$$r_0 = +24.09 \text{ and } r_\infty = -10.74, \qquad \therefore r_0 - r_\infty = (+24.09) - (-10.74) = +34.83$$

Time (sec)	r_t	$r_t - r_\infty$	$K = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$
7.18	+21.4	21.4 – (– 10.74) = 32.14	$K = \frac{2.303}{7.18} \log \frac{34.83}{32.14} = 1.23 \times 10^{-3}\ \text{sec}^{-1}$
18	+17.7	17.7 – (– 10.74) = 28.44	$K = \frac{2.303}{18} \log \frac{34.83}{28.44} = 1.13 \times 10^{-3}\ \text{sec}^{-1}$
27.05	+15.0	15.0 – (– 10.74) = 25.74	$K = \frac{2.303}{27.05} \log \frac{34.83}{25.74} = 1.15 \times 10^{-3}\ \text{sec}^{-1}$

Since the value of 'K' comes out to be nearly constant, hence, the inversion of cane sugar is the reaction of first order.

Logical Basis:

- Let the optical rotations at various times be:
  - $\mathbf{r_0}$ = Optical rotation at time (t=0). This is proportional to the initial concentration of sucrose (a) and a specific rotation constant (c).
  - $\mathbf{r_t}$ = Optical rotation at time (t). This is due to the mixture of unreacted sucrose (a – x), and the products (glucose and fructose).
  - $\mathbf{r_\infty}$ = Optical rotation at infinite time (after the reaction is complete). This is due to the products only (glucose and fructose).

- The change in optical rotation from time, t = 0 to t = ∞ , is a measure of the total change possible. This total change is proportional to the initial concentration of sucrose (a).

$$a \propto (\mathbf{r_0} - \mathbf{r_\infty})$$

- The change in optical rotation from time, t = 0 to t = t , is a measure of the amount of sucrose that has reacted (x).

$$x \propto (\mathbf{r_0} - \mathbf{r_t})$$

- The concentration of sucrose remaining at time *t* is (a – x).

$$a - x = (\mathbf{r_0} - \mathbf{r_\infty}) - (\mathbf{r_0} - \mathbf{r_t}) = \mathbf{r_t} - \mathbf{r_\infty}$$

- From all above conclusions, we have:

$$a \propto r_0 - r_\infty$$

$$a - x \propto r_t - r_\infty$$

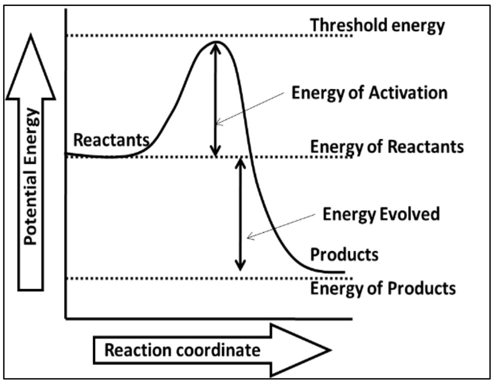
- Substituting these values in 1st order equation: $K = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$ or $K = \frac{2.303}{t} \log \frac{a}{a-x}$

  We get,

$$K = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

Activation Energy of Reactions

- The term **Activation Energy** was introduced in 1889 by **Svante Arrhenius**, a Swedish scientist.
- It is denoted by **Ea** and expressed in **kJ/mol**.
- **Activation Energy** is the minimum amount of energy required to start a chemical reaction.
  - In other words, it is the minimum energy absorbed by reactant molecules so that their energy becomes equal to the threshold energy (The minimum energy that colliding molecules must have for the collision to be effective).
  - **Activation energy = Threshold energy – Average kinetic energy of the reactants**



Relation Between Activation Energy and Rate of Reaction :

- Lower activation energy ⟶ Faster reaction.
- Higher activation energy ⟶ Slower reaction.
- For example:
  - $2\,NO + O_2 \longrightarrow 2\,NO_2$ (Reaction is fast because of low activation energy)
  - $2\,CO + O_2 \longrightarrow 2\,CO_2$ (Reaction is slow because of high activation energy)

Temperature Dependence of Reaction Rate (Arrhenius Equation)

- Temperature significantly affects reaction rate.
- For most reactions, the rate **approximately doubles** with every **10 °C rise** in temperature due to more effective collisions.
- **Example:**
  - Decomposition of N_2O_5 to half of its original volume takes about;

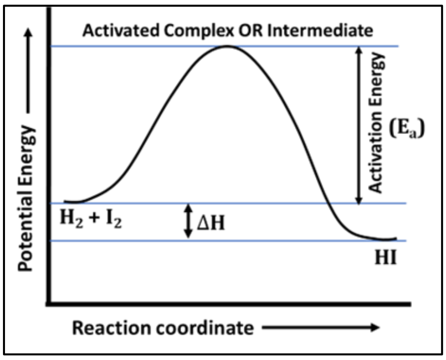
    - 12 minutes ⟶ at 50 °C
    - 5 Hours ⟶ at 25 °C
    - 10 days ⟶ at 0 °C

- **Temperature Coefficient (τ)**
  - Defined as the ratio of rate constants at two temperatures differing by 10°C.

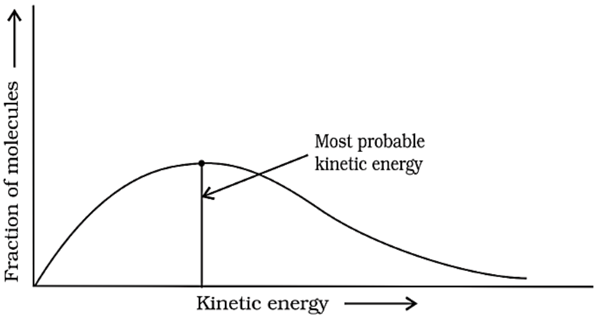
$$\text{Temperature coefficient } (\tau) = \frac{\text{Rate constant at } (T + 10) \text{ in Kelvin}}{\text{Rate constant at } T \text{ in Kelvin}}$$

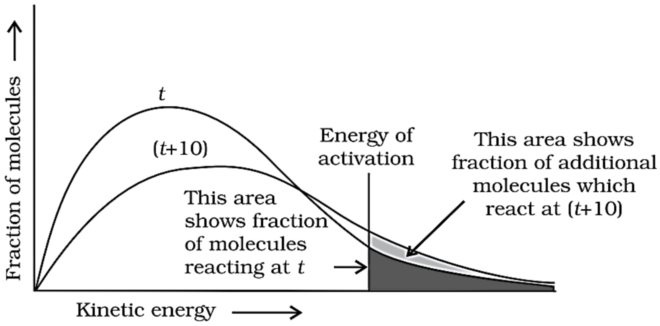
To understand, let us consider a chemical reaction: $H_{2\,(g)} + I_{2\,(g)} \longrightarrow 2\,HI_{(g)} + \text{Energy}$

- **According to Arrhenius:**
  - The reaction can take place only when **a molecule of H_2** and **a molecule of I_2** collide to form an **unstable intermediate** (**or Activated Complex**).
  - Energy required to form this intermediate (or activated complex) is known as **activation energy (Ea)**.
  - The intermediate (or activation complex) exists for a **very short time**. It decomposes to form products (two molecules of HI) and releasing energy.



- **Distribution of Kinetic Energy**
  - Not all molecules of a reacting components have the same kinetic energy.
  - The **Maxwell–Boltzmann distribution curve** shows the fraction of molecules (N_E / N_T) with different kinetic energies.
    - **Peak**: Most probable kinetic energy.
    - Fewer molecules have very low or very high energies.
  - On increasing **temperature:**
    - The curve shifts to the right (towards higher energies).
    - More molecules have energy greater than activation energy (Ea).
    - Therefore, the doubling of the area in curve (t + 10) after the activation energy doubles the rate of reaction.





Arrhenius Equation:

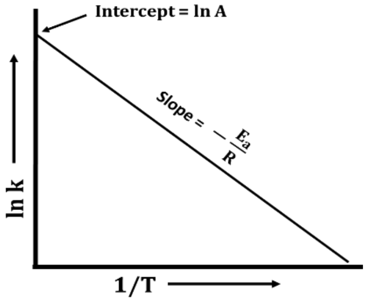
- The rate constant 'K' is related to activation energy by:

$$K = Ae^{-E_a/RT}$$

- Where:
    - A = Pre-exponential factor (frequency of collisions per second per litre)
    - Ea = Activation energy (J/mol)
    - R = Gas constant (8.314 J mol^{-1} K^{-1})
    - T = Absolute temperature (K)
    - $e^{-E_a/RT}$ is called **Boltzmann factor** (fraction of molecules having energy equal to or greater than the activation energy).

- **Linear Form of Arrhenius Equation**
    - Taking logarithm :

$$\ln K = \ln A - \frac{E_a}{RT}$$



- Plot of '**ln *K***' vs '**1/T**' gives a linear line.
- Slop = $-\frac{E_a}{R}$
- Increase in '**T**' or decrease in '**Ea**' will lead to an exponential increase in reaction rate.

- **Activation Energy from Two Temperatures**
    - If the value of the rate constants at temperature **T_1** and **T_2** are **K_1** and **K_2** respectively, then

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \quad \text{and} \quad \ln K_2 = \ln A - \frac{E_a}{RT_2}$$

- Subtracting the above two equations, we get (Since 'A' is constant for a given reaction):

$$\ln K_2 - \ln K_1 = -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$\ln K_2 - \ln K_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2}$$

$$\ln\frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad [\ \ln x = 2.303 \log x\ ]$$

$$2.303 \log\frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

Practice Problems

1. The reaction; $C_2H_5I \longrightarrow C_2H_4 + HI$, is of first order and its rate constant are 3.2 × 10^{-4} sec^{-1} at 600 K and 1.6 × 10^{-2} sec^{-1} at 1200 K. Calculate the energy of activation for the reaction. (Given, R = 8.314 J mol^{-1} K^{-1}).

2. A first order reaction is 50% complete in 30 minutes at 27 °C and in 10 minutes at 47 °C. Calculate the reaction rate constants at these temperatures and the energy of activation of the reaction in KJ/mole. (Given, R = 8.314 J mol^{-1} K^{-1}).
3. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is again 50% complete in 5 minutes at 350 K. Calculate the activation energy if the reaction is of first order. (Given, R = 8.314 J mol^{-1} K^{-1})
4. The rate constant of a reaction is 1.2×10^{-3} sec^{-1} at 30 °C and 2.1×10^{-3} sec^{-1} at 40 °C. Calculate the energy of activation for the reaction. (Given, R = 8.314 J mol^{-1} K^{-1}).
5. The rate of a particular reaction doubles when temperature changes from 27 °C to 37 °C. Calculate the energy of activation for the reaction. (Given, R = 8.314 J mol^{-1} K^{-1}).
6. The activation energy of a reaction is 94.14 KJ/mol and the value of rate constant at 313 K is 1.8×10^{-1} sec^{-1}. Calculate the frequency factor, A.

Effect of Catalyst on the Rate of Reaction

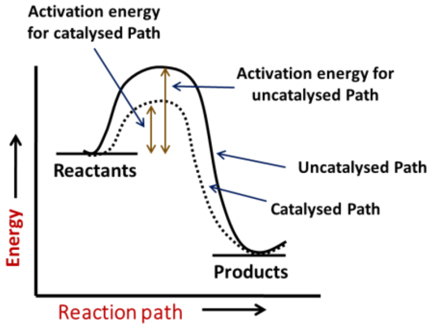
- A **catalyst** is a substance that **increases the speed of a chemical reaction** without itself undergoing any permanent chemical change.
- **Example: Decomposition of Potassium Chlorate ($KClO_3$)**
    - When heated strongly, $KClO_3$ decomposes slowly in the temperature range **653–873 K**.

$$2KClO_3 \xrightarrow{653-873\ K} 2KCl + 3O_2$$

    - On adding a small amount of **manganese dioxide (MnO_2)**, the decomposition occurs at a much lower temperature range (**473–633 K**). MnO_2 remains unchanged in mass and composition. Hence, MnO_2 acts as a **catalyst**. The process is called **catalysis**.

$$2KClO_3 \xrightarrow{473-633\ K,\ MnO_2} 2KCl + 3O_2$$

- **Action of a Catalyst :**
    - A catalyst provides an **alternative reaction pathway** with **lower activation energy (Ea)**. As a result, the **rate of reaction increases**.
    - Important points:
        - A catalyst does not change the **Gibbs free energy (ΔG)** of the reaction.
        - It cannot make a **non-spontaneous reaction spontaneous**.
        - Energies of **reactants and products remain unchanged**.
        - It accelerates **both forward and backward reactions equally**, so equilibrium is reached **faster** but is **not shifted**.



- **Characteristics of a Catalyst and Catalysed Reaction**
  - A **small amount** of catalyst is sufficient to bring about a reaction.
  - A catalyst **cannot initiate** a chemical reaction; it can only **accelerate** one.
  - A catalyst does not alter the **Gibbs free energy (ΔG)** of the reaction.
  - A catalyst does not alter the **enthalpy change (ΔH)** of the reaction.
  - A catalyst may participate in the reaction, but it is **regenerated** at the end, remaining unchanged in mass and composition.
  - A catalyst does not disturb the **equilibrium** of the reaction, but equilibrium is attained **more quickly**.

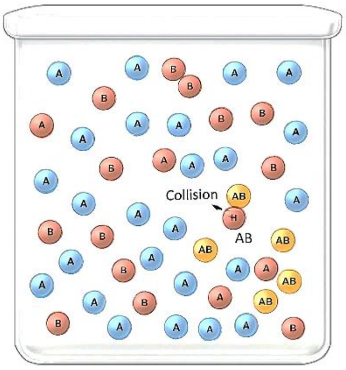
Collision Theory of Chemical Reactions

- According to this theory, reactant molecules are considered as **hard spheres**. A chemical reaction occurs **only when molecules collide** with each other.
  For a **collision to be effective or successful**, two conditions must be met:
  - The colliding molecules must have **energy greater than or equal to threshold energy**.
  - The molecules must have a **proper orientation** during collision.

- For an elementary reaction: $A + B \longrightarrow AB$
  - The **rate of reaction** directly depends on the **number of effective collisions**.
    This can be expressed as:

$$\text{Rate of reaction} = Z_{AB} \times f$$

    Where:
    - Z_{AB} = **Collision frequency**
      (**Number of collisions per second per unit volume** of the reaction mixture **(Z_{AB})**)
    - **f** = Fraction of molecules having **energy equal to or greater** than **Ea**.



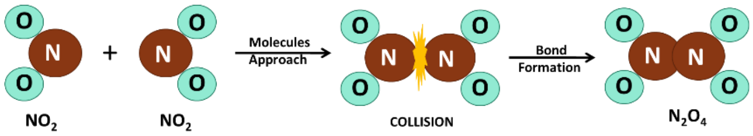
  - According to the **Kinetic Theory of Gases**, the fraction (**f**) of molecules having **energy equal to or greater** than **threshold value** at temperature ‘T’ is given by **Boltzmann factor**.

$$f = e^{-E/RT}$$

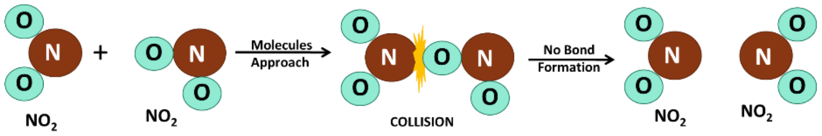
    Since, rate of reaction depends on **activation energy (Ea) :** $f = e^{-E_a/RT}$

  - Therefore, $\text{Rate of reaction} = Z_{AB} \times e^{-E_a/RT}$
  - As **rate of reaction** is directly related to **rate constant ‘K’**, we can say: $K = Z_{AB} \times e^{-E_a/RT}$

- **Orientation or Steric Factor (P) :**
    - Even if molecules have sufficient energy, a reaction will not occur unless they collide with the **proper orientation**.



In Proper Orientation



Not in Proper Orientation

-
    - To account for this, an additional factor **P** (**orientation** factor or **steric** factor or **Probability** factor) is introduced. Hence, equation can be modified as:

$$K = P \times Z_{AB} \times e^{-E_a/RT}$$

- **Relation with Arrhenius Equation :**
    - According to Arrhenius equation: $K = A\, e^{-E_a/RT}$
    - According to Collision Theory: $K = P \times Z_{AB} \times e^{-E_a/RT}$
    - By comparing the above equations, we get :

$$A\, e^{-E_a/RT} = P \times Z_{AB} \times e^{-E_a/RT}$$
$$A = P \times Z_{AB}$$

Limitations of Collision Theory

- Assumes molecules to be **hard spheres**, which is an oversimplification. Therefore, it gives **unsatisfactory results** for many reactions.
- Does not explain reactions involving **complex activated states**.
- To overcome these drawbacks, advanced theories such as **Transition State Theory (Activated Complex Theory)** are used.

NCERT : Intext Questions

1. For the reaction R $\xrightarrow{\quad}$ P, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.
2. In a reaction, 2A $\xrightarrow{\quad}$ Products, the concentration of *A* decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?
3. For a reaction, A + B $\xrightarrow{\quad}$ Product; the rate law is given by, rate = $k\,[A]^{1/2}\,[B]^2$. What is the order of the reaction?
4. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times, how will it affect the rate of formation of Y ?
5. A first order reaction has rate constant 1.15×10^{-3} sec^{-1}. How long will 5 g of reactant take to reduce to 3 g?
6. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.
7. What will be the effect of temperature on rate constant ?
8. The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298K. Calculate Ea .
9. The activation energy for the reaction: $2\,HI_{(g)} \xrightarrow{\quad} H_2 + I_{2\,(g)}$; is 209.5 kJ mol^{-1} at 581K.Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

NCERT : Exercise Questions

1. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.
   a. $3NO_{(g)} \xrightarrow{\quad} N_2O_{(g)}$; Rate = $k[NO]^2$
   b. $H_2O_{2\,(aq)} + 3I^{-1}_{(aq)} + 2H^{+1} \xrightarrow{\quad} 2H_2O_{(l)} + I_3^{-1}$; Rate = $k[H_2O_2][I^{-1}]$
   c. $CH_3CHO_{(g)} \xrightarrow{\quad} CH_{4\,(g)} + CO_{(g)}$; Rate = $k\,[CH_3CHO]^{3/2}$
   d. $C_2H_5Cl_{(g)} \xrightarrow{\quad} C_2H_{4\,(g)} + HCl_{(g)}$; Rate = $k\,[C_2H_5Cl]$
2. For the reaction: 2A + B $\xrightarrow{\quad}$ A_2B the rate = $k[A][B]^2$ with k = 2.0×10^{-6} $mol^{-2}\,L^2\,s^{-1}$. Calculate the initial rate of the reaction when [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1}. Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.
3. The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if rate constant 'k' = 2.5×10^{-4} mol^{-1} L sec^{-1}?
4. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction rate is given by ; Rate = $k\,[CH_3OCH_3\,]^{3/2}$
   The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e., Rate = $k\,(P_{CH_3OCH_3})^{3/2}$
   If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?
5. Mention the factors that affect the rate of a chemical reaction.
6. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled, and (ii) reduced to half ?
7. What is the effect of temperature on the rate constant of a reaction? How can this effect of temperature on rate constant be represented quantitatively?
8. In a pseudo first order reaction in water, the following results were obtained:

Time (sec)	0	30	60	90
[A] | mol L^{-1}	0.55	0.31	0.17	0.085

Calculate the average rate of reaction between the time interval 30 to 60 seconds.

9. A reaction is first order in *A* and second order in *B*.
   a. Write the differential rate equation.
   b. How is the rate affected on increasing the concentration of B three times?
   c. How is the rate affected when the concentrations of both A and B are doubled?
10. In a reaction between A and B, the initial rate of reaction (r0) was measured for different initial concentrations of A and B as given below:

A/ mol L^{-1}	0.20	0.20	0.40
B/ mol L^{-1}	0.30	0.10	0.05
r_0/mol $L^{-1}s^{-1}$	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B ?

11. The following results have been obtained during the kinetic studies of the reaction: $2A + B \longrightarrow C + D$

Experiment	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

12. The reaction between *A* and *B* is first order with respect to *A* and zero order with respect to *B*. Fill in the blanks in the following table:

Experiment	[A]/ mol L^{-1}	[B]/ mol L^{-1}	Initial rate/ mol L^{-1} min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	–	0.2	4.0×10^{-2}
III	0.4	0.4	–
IV	–	0.2	2.0×10^{-2}

13. Calculate the half-life of a first order reaction from their rate constants given below:
    (i) 200 sec^{-1} (ii) 2 min^{-1} (iii) 4 $years^{-1}$
14. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.
15. The experimental data for decomposition of N_2O_5 [$2N_2O_5 \longrightarrow 4NO_2 + O_2$] in gas phase at 318K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5]$/ mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot $[N_2O_5]$ against t.
(ii) Find the half-life period for the reaction.
(iii) Draw a graph between log$[N_2O_5]$ and t.
(iv) What is the rate law ?

(v) Calculate the rate constant.

(vi) Calculate the half-life period from k and compare it with (ii).

16. The rate constant for a first order reaction is 60 sec^{-1}. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?

17. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

18. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

19. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.

20. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t (sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

21. Following data were obtained during the first order thermal decomposition of SO_2Cl_2 at constant volume:

Time (sec)	0	100
Total Pressure (atm)	0.5	0.6

Calculate the rate constant and rate of reaction when total pressure is 0.65 atm

22. The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

$T/°C$	0	20	40	60	80
$10^5 \times k/s^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between 'ln *k*' and '1/T' and calculate the values of *A* and *Ea* .
Predict the rate constant at 30 °C and 50 °C.

23. The rate constant for the decomposition of hydrocarbons is 2.418×10^{-5} sec^{-1} at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

24. Consider a certain reaction $A \longrightarrow$ Products, with $k = 2.0 \times 10^{-2}$ sec^{-1}. Calculate the concentration of *A* remaining after 100 sec. if the initial concentration of *A* is 1.0 mol L^{-1}.

25. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2}$ = 3.00 hours. What fraction of sample of sucrose remains after 8 hours ?

26. The decomposition of hydrocarbon follows the equation; $k = (4.5 \times 10^{11}\ sec^{-1})\ e^{-28000\ K/T}$. Calculate Ea .

27. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4\ K/T$$

Calculate Ea for this reaction and at what temperature will its half-period be 256 minutes?

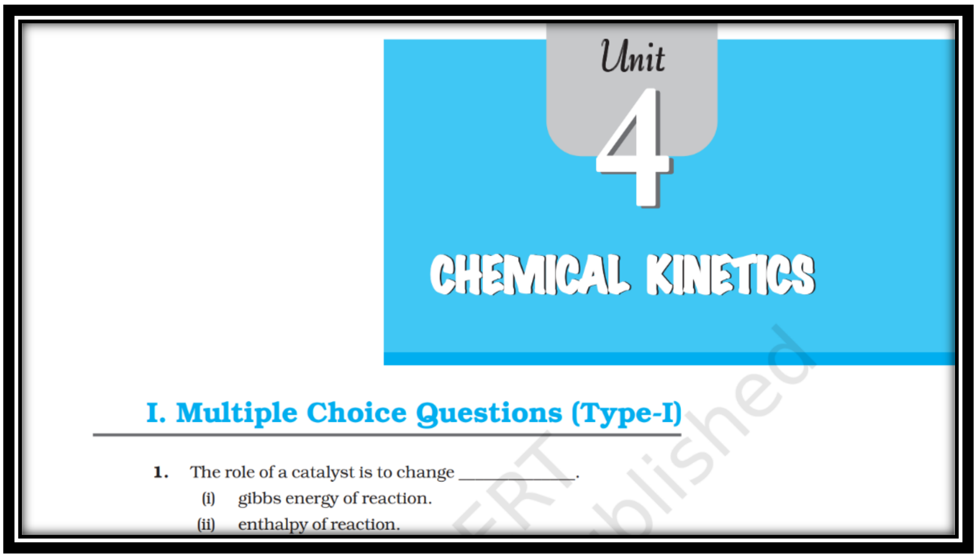
28. The decomposition of *A* into product has value of k as 4.5×10^3 sec^{-1} at 10 °C and energy of activation 60 kJ mol^{-1}. At what temperature would k be 1.5×10^4 sec^{-1}?

29. The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. If the value of *A* is 4×10^{10} sec^{-1}. Calculate k at 318K and Ea .

30. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

NCERT : Examplar

Click on the link below to download the pdf :
https://ncert.nic.in/pdf/publication/exemplarproblem/classXII/chemistry/leep504.pdf



Unit
4

CHEMICAL KINETICS

I. Multiple Choice Questions (Type-I)

1. The role of a catalyst is to change ______.
   - (i) gibbs energy of reaction.
   - (ii) enthalpy of reaction.

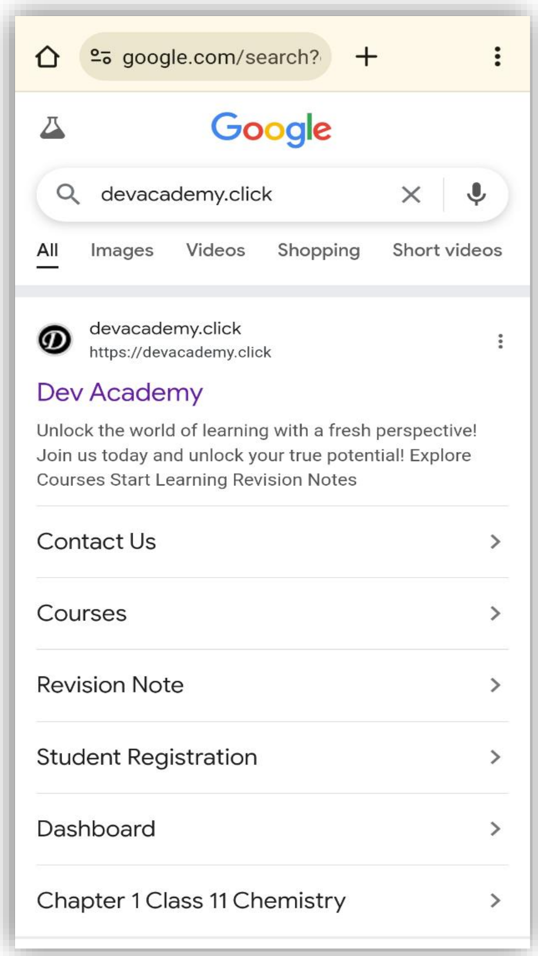
Scan QR Code

Click on the link to visit our website:

devacademy.click

OR

Scan QR Code



google.com/search?

devacademy.click

All Images Videos Shopping Short videos

devacademy.click
https://devacademy.click

Dev Academy

Unlock the world of learning with a fresh perspective! Join us today and unlock your true potential! Explore Courses Start Learning Revision Notes

Contact Us

Courses

Revision Note

Student Registration

Dashboard

Chapter 1 Class 11 Chemistry

Follow us on social media

YouTube
youtube.com/**@DevAcademy_edu**

Instagram
instagram.com/**devacademy_edu**

Telegram
t.me/**devacademy_edu**

X
x.com/**devacademy_edu**

Facebook
facebook.com/**devacademy.edu**

WhatsApp

WhatsApp

Click Here

YouTube

YouTube