

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Chapter

07

REACTION KINETICS

Student Learning Outcomes

After studying this chapter, students will be able to:

- Explain the rate of reaction, and rate constant. (Understanding)
- Use experimental data to calculate the rate of a chemical reaction. (Application)
- Use the Boltzmann distribution curve to explain the effect of temperature on the rate of a reaction. (Understanding)
- Describe the effect of temperature change on the rate constant and rate of reaction. (Understanding)
- Explain the concept of activation energy and its role in chemical reactions. (Understanding)
- Explain the concept of catalyst and how they increase the rate of a reaction by lowering the activation energy. (Understanding)
- Interpret reaction pathway diagrams, including in the presence and absence of catalysts. (Application)
- Use rate equations, including orders of reaction and rate constant. (Application)
- Calculate the numerical value of a rate constant using the initial rates and half-life method. (Application)
- Suggest a reaction mechanism that is consistent with a given rate equation and rate determining step. (Understanding)
- Explain the relationship between Gibbs free energy change, ΔG° and the feasibility of a reaction. (Understanding)

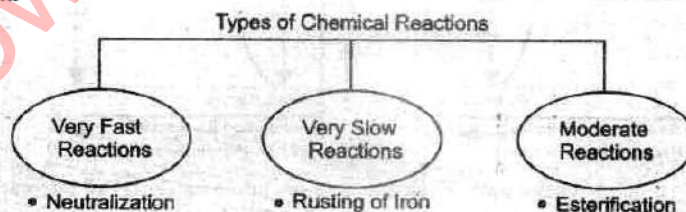
It is a common observation that rates of different chemical reactions differ greatly for example, the reaction of NaCl with AgNO_3 is very fast. The hydrolysis of ester proceeds at a moderate rate. Whereas, rusting of iron is a slow process.

➤ Reaction Kinetics:

"The branch of chemistry which deals with rates of chemical reactions, factors that affect the rates of chemical reactions and the mechanisms of reactions is called reaction kinetics."

➤ Chemical Reaction:

"The breaking of pre-existing bonds and the formation of new bonds is called chemical change or chemical reaction."



Reaction kinetics is the study of the rates of chemical reactions.

➤ Domain of Reaction Kinetics:

It includes a variety of experimental methods for measuring reaction rates, orders and mechanisms of reactions.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)



An explosion is a swift reaction that happens within a fraction of a second, the rusting of iron is a slow process that may take days or months. The rates of reactions occurring during the explosion are enormous.

The rates of reactions and their control are often important in industry. They might be the deciding factors that determine whether a certain chemical reaction may be used economically or not. Many factors influence the rate of a chemical reaction. It is important to discover the conditions under which the reaction will proceed most economically.

COLLISION THEORY

Collision theory explains how reactions occur.

○ Main Postulates of Collision Theory

- According to this theory, for a chemical reaction to take place, the particles atoms, ions or molecules of reactants must form a homogeneous mixture and collide with one another. These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective, they give rise to the products, otherwise the colliding particles just bounce back.
- The effective collisions can take place only when the colliding particles possess certain amount of energy and they approach each other with the proper orientation.

Activation Energy: The minimum amount of energy, required for an effective collision between the reacting species, is called activation energy. Most of the reactions are slow, showing that all the collisions are not equally effective.

**Rock Your Mind!**

1. What conditions must be met for a collision to be effective according to collision theory?

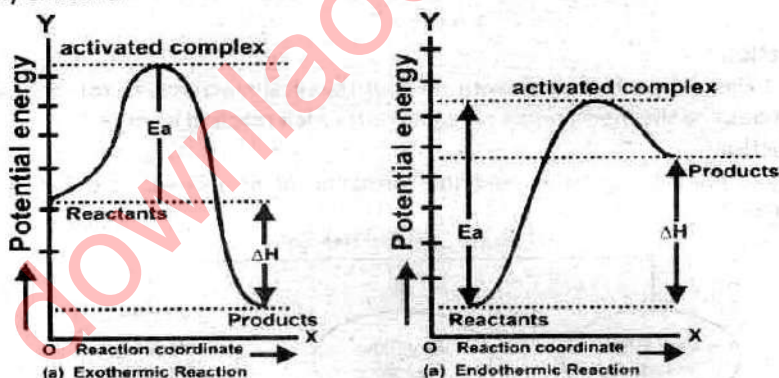


Figure: A graph between path of reaction and the potential energy of the reaction

It is important to note that the process can be understood with the help of a graph between the path of reaction and the potential energy of the reacting molecules. If the collision is effective, then the molecules flying apart are chemically different otherwise the same molecules just bounce back. The reactants reach the peak of the curve to form the activated complex. Only, the colliding molecules with proper activation energy, will be able to climb up the hill and give the products.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

QUICK CHECK-7.1

a) What role does the activation energy play in chemical reactions?

Ans. **Role of Activation Energy in Chemical Reactions**

Activation energy (E_a) is the minimum energy required for reactant molecules to undergo a successful collision and form products. It plays three key roles:

1. **Determines Reaction Feasibility**

- Only molecules with energy $\geq E_a$ can overcome the energy barrier and react.
- Example:** Combustion of paper requires heat (E_a) to start, even though it's exothermic.

2. **Controls Reaction Rate**

- Higher $E_a \rightarrow$ Fewer molecules have enough energy $\rightarrow$ Slower reaction.
- Lower $E_a \rightarrow$ More molecules can react $\rightarrow$ Faster reaction.

3. **Explains Temperature Dependence**

- Increasing temperature raises the fraction of molecules with $E \geq E_a$ (per the Boltzmann distribution), speeding up reactions.
- Catalysts lower E_a to accelerate reactions (e.g., enzymes in biology).
- Explosions occur when E_a is very low (rapid release of energy).

Equation (Arrhenius):

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

Where:

- k = Rate constant
- A = Frequency factor (collision/orientation)
- R = Gas constant
- T = Temperature

In short: Activation energy is the "gatekeeper" of chemical reactions.

b) How does the activation energy affect the rate of reaction?

Ans. **Effect of Activation Energy on Reaction Rate**

Activation energy (E_a) directly controls how fast a reaction proceeds by determining the fraction of molecules with enough energy to react. Here's how:

1. **Energy Barrier:**

- Only molecules with kinetic energy $\geq E_a$ can overcome the barrier and form products.

2. **Boltzmann Distribution:**

- At a given temperature, fewer molecules have energy $\geq E_a$ if E_a is **high** $\rightarrow$ slower reaction.
- Lowering E_a (e.g., with a catalyst) increases the fraction of "successful" collisions $\rightarrow$ faster reaction.

3. **Arrhenius Equation:**

$$\text{Rate} \propto e^{-E_a/RT}$$

- Higher $E_a \rightarrow$ Exponential decrease in rate.
- Lower $E_a \rightarrow$ Exponential increase in rate.

Example:

- Combustion (low E_a):** Fast at room temperature.
- Diamond $\rightarrow$ Graphite (high E_a):** Extremely slow (takes billions of years).

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

RATE OF REACTION

During a chemical reaction, reactants are converted into products. So, the concentration of the products increases with the corresponding decrease in the concentration of the reactants as they are being consumed.

Definition:

"The rate of a reaction is defined as the change in the concentration of a reactant or a product divided by the time taken for the change."

Formula:

$$\text{Rate of reaction} = \frac{\text{change in concentration of the substance}}{\text{time taken for the change}}$$

$$\text{Rate of reaction} = \frac{\Delta x}{\Delta t}$$

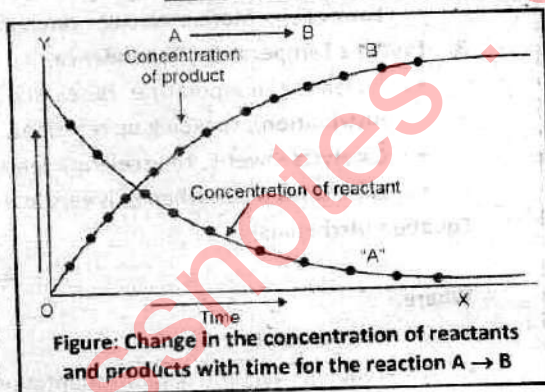
Where Δx is a very small change in the concentration of a reactant or a product in a very small time interval Δt .

➤ Explanation with the Help of Graph:

The situation is explained graphically in Figure for the reactant A which is changing irreversibly to the product B.



The slope of the graph for the reactant or the product is steepest at the beginning. This shows a rapid decrease in the concentration of the reactant and consequently, a rapid increase in the concentration of the product. As the reaction proceeds, the slope becomes less steep indicating that the reaction is slowing down with time, ultimately both the curves become parallel. It means that the rate of a reaction is changing every moment. This is the stage of completion of reaction.



➤ Units of Reaction Rate:

The rate of reaction has the units of concentration divided by time. Usually, the concentration is expressed in mol dm^{-3} and the time in second, thus the units for the reaction rate are $\text{mol dm}^{-3} \text{s}^{-1}$.

$$\text{Rate of reaction} = \frac{\text{mol.dm}^{-3}}{\text{seconds}} = \text{mol dm}^{-3} \text{s}^{-1}$$

➤ Units for Slow Reactions:

For a slow reaction the units may be $\text{mol dm}^{-3} \text{min}^{-1}$ or even $\text{mol dm}^{-3} \text{h}^{-1}$. For a gas phase reaction, units of pressure are used in the place of molar concentrations.

➤ Rate of General Reaction:

The rate of a general reaction, $A \rightarrow B$, can be expressed in terms of rate of disappearance of the reactant A or the rate of appearance of the product B mathematically, where $[A]$ and $[B]$ are the concentrations of A and B, respectively.

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

- The negative sign with indicates a decrease in the concentration of the reactant A.
- Since the concentration of product increases with time, the sign in rate expression involving the change of concentration of product is positive.

➤ Instantaneous and Average Rate

- **Instantaneous Rate:** The rate at any instant during the interval is called the instantaneous rate.
- **Average Rate:** The average rate of reaction is defined as, "The rate of reaction between two specific time intervals or the rate over a time period". The average rate and instantaneous rate are equal for only one instant in any time interval.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

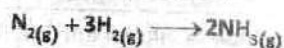
- At first, the instantaneous rate is higher than the average rate.
- At the end of the interval the instantaneous rate becomes lower than the average rate.

Differences Between Instantaneous Rate And Average Rate

Instantaneous rate	Average rate
• The rate at any one instant during the interval is called the instantaneous rate.	• The rate of reaction between two specific time intervals is called average rate.
• Instantaneous rate = $\frac{dx}{dt}$	• Average rate = $\frac{\Delta x}{\Delta t}$
• At first, the instantaneous rate is higher than the average rate.	• At the end, average rate is higher than instantaneous rate.

Sample Problem 7.1

The reaction for the formation of ammonia in Haber process is:



- Calculate the instantaneous rate after 1.0 min
- What is the average rate of production of ammonia for the system, between 1.0 and 4.0 minutes?

Solution:

The instantaneous rate at 1.0 min can be calculated as:

$$\text{Instantaneous Rate} = \frac{\Delta C}{\Delta t} = \frac{2.7 \text{ mol} \cdot \text{dm}^{-3}}{1 \text{ min}} = 2.7 \text{ mol} \cdot \text{dm}^{-3} \text{ min}^{-1}$$

If the concentration of ammonia is $3.5 \text{ mol} \cdot \text{dm}^{-3}$ after 1.0 min and $6.2 \text{ mol} \cdot \text{dm}^{-3}$ after 4.0 minutes?

Solution:

$$\Delta C = \Delta [NH_3] = (6.2 - 3.5) \text{ mol} \cdot \text{dm}^{-3}; \quad \Delta C = 2.7 \text{ mol} \cdot \text{dm}^{-3}$$

$$\Delta t = (4.0 - 1.0); \quad \Delta t = 3.0 \text{ min}$$

$$\text{Rate of formation of } NH_3 = \frac{\Delta C}{\Delta t} = \frac{\Delta [NH_3]}{\Delta t} = \frac{2.7 \text{ mol} \cdot \text{dm}^{-3}}{3 \text{ min}} = 0.90 \text{ mol} \cdot \text{dm}^{-3} \text{ min}^{-1}$$

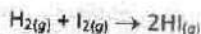
The rate of production of NH_3 gas over the given time interval is $0.90 \text{ mol} \cdot \text{dm}^{-3} \text{ min}^{-1}$.

QUICK CHECK 7.2

The reaction of hydrogen and iodine to make hydrogen iodide at a particular temperature, $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ was studied at various times. At 100.0 s after the start of the reaction, the iodine concentration had fallen from $0.010 \text{ mol} \cdot \text{dm}^{-3}$ to $0.0080 \text{ mol} \cdot \text{dm}^{-3}$. What is the average rate of reaction during this period?

Given Data:

Reaction:



- Initial $[I_2]$ (at $t = 0 \text{ s}$): $0.010 \text{ mol} \cdot \text{dm}^{-3}$
- Final $[I_2]$ (at $t = 100.0 \text{ s}$): $0.0080 \text{ mol} \cdot \text{dm}^{-3}$
- Time interval (Δt): 100.0 s

Step 1: Calculate $\Delta[I_2]$ (Change in Concentration)

$$\Delta[I_2] = [I_2]_{\text{final}} - [I_2]_{\text{initial}} = 0.0080 - 0.010 = -0.0020 \text{ mol} \cdot \text{dm}^{-3}$$

Step 2: Average Rate of Reaction (w.r.t. I_2)

$$\begin{aligned} \text{Average rate} &= -\Delta[I_2]/\Delta t \\ &= -(-0.0020 \text{ mol} \cdot \text{dm}^{-3}/100.0 \text{ s}) \\ &= +2.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \text{ s}^{-1} \end{aligned}$$

The average rate of reaction during this period is: $2.0 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3} \text{ s}^{-1}$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

➤ Measuring the Rate of a Chemical Reaction

The measurement of rate of a chemical reaction involves the determination of the concentration of reactants or products at regular time intervals as the reaction progresses.

➤ Graph of Concentration Vs Time

To determine the rate of reaction for a given length of time, a graph is plotted between time on x-axis and concentration of a reactant on y-axis, whereby a curve is obtained.

➤ Decomposition of HI:

To illustrate it, let us investigate the decomposition of HI to H_2 and I_2 at $50^\circ C$. By using the data, a graph is plotted as shown in Fig. The graph is between time on x-axis and concentration of HI in mol dm^{-3} on y-axis. Since HI is a reactant, so it is a falling curve. The steepness of the concentration-time curve reflects the progress of reaction. Greater the slope of curve near the start of reaction, greater is the rate of reaction.

Table: Change in concentration of HI with regular intervals

$$2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$$

Concentration of HI (mol dm^{-3})	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300

In order to measure the rate of reaction, draw a tangent say, at 100 seconds, on the curve and measure the slope of that tangent. The slope of the tangent is the rate of reaction at that point i.e., after 100 seconds. A right-angled triangle ABC is completed with a tangent as hypotenuse. Figure shows that in 100 sec, the change in concentration is 0.04 mol dm^{-3} .

➤ Rate Calculation Formula:

The rate is then calculated by using the following expression.

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta T}$$

$$\text{Rate} = \frac{0.04 \text{ mol dm}^{-3}}{100 \text{ sec}} = 4 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

This value of rate means that the concentration of HI is decreasing by $2.5 \text{ moles per dm}^{-3}$ every second during the given interval.

If we plot a graph between time on x-axis and concentration of any of the products i.e., H_2 or I_2 , then a rising curve is obtained. The value of the tangent at 100 seconds will give the same value of rate of reaction as $4 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$.

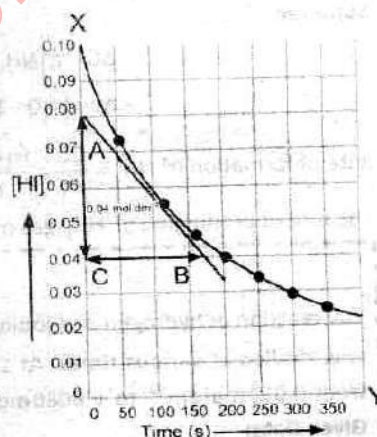


Figure: The change in the HI concentration with time to the reaction $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$ at $50^\circ C$

☑ QUICK CHECK 7.3

a) Plot the data in Table 7.1 for HI in your notebook.

Ans. There is no relevant data available in 7.1.

b) Calculate the rate after 300 sec (when the concentration is 0.03 mol dm^{-3}) by drawing a tangent.

Ans. Calculating Reaction Rate at 300 sec Using a Tangent

Given:

- At 300 sec, concentration of reactant = 0.03 mol dm^{-3} .

- Goal: Find the instantaneous rate at this point by drawing a tangent to the concentration-time curve.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Steps:

1. Plot the Graph

- X-axis: Time (sec)
- Y-axis: Concentration (mol dm^{-3})
- Mark the point (300 sec, 0.03 mol dm^{-3}) on the curve.

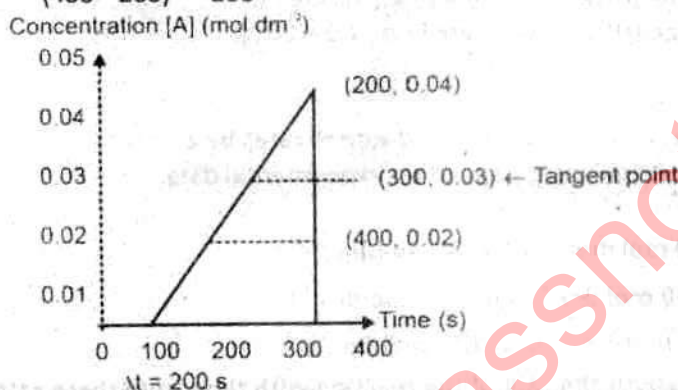
2. Draw the Tangent

- At $t = 300 \text{ sec}$, sketch a straight line that *just touches* the curve (no crossing).

3. Calculate Slope (Rate)

- Choose two points on the tangent line (e.g., (200 sec, 0.04) and (400 sec, 0.02)).
- Slope (rate)

$$\text{Rate} = \frac{\Delta[\text{Conc.}]}{\Delta \text{Time}} = \frac{(0.02 - 0.04)}{(400 - 200)} = \frac{0.02}{200} = 1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$



$$\Delta[A] = (0.02 - 0.04) = -0.02 \text{ mol dm}^{-3}$$

- c) Use the same method to calculate the rate of reaction at HI concentrations of 0.10 mol dm^{-3} , $0.050 \text{ mol dm}^{-3}$ and 0.02 mol dm^{-3} .

Ans.

1. General Approach

For each HI concentration:

- Locate the point on the concentration-time curve.
- Draw a tangent at that point.
- Calculate the slope of the tangent ($\Delta[\text{HI}]/\Delta t$).

Since the exact curve isn't provided, we'll assume typical behaviour for the reaction:



- HI formation rate is twice the I_2 consumption rate (stoichiometry).

2. Rate Calculations

(a) At $[\text{HI}] = 0.10 \text{ mol dm}^{-3}$

Tangent points (example):

- (150 s, 0.08 mol dm^{-3})
- (250 s, 0.12 mol dm^{-3})

Slope (rate of HI formation):

$$\text{Rate} = \frac{\Delta[\text{HI}]}{\Delta t} = \frac{0.12 - 0.08}{250 - 150} = \frac{0.04}{100} = 4.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

(b) At $[\text{HI}] = 0.050 \text{ mol dm}^{-3}$

Tangent points (example):

- (100 s, 0.03 mol dm^{-3})
- (200 s, 0.07 mol dm^{-3})

Slope:

$$\text{Rate} = \frac{0.07 - 0.03}{200 - 100} = \frac{0.04}{100} = 4.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

(c) At $[HI] = 0.02 \text{ mol dm}^{-3}$

Tangent points (example):

- (50 s, 0.00 mol dm^{-3})
- (150 s, 0.04 mol dm^{-3})

Slope:

$$\text{Rate} = \frac{0.04 - 0.00}{150 - 50} = \frac{0.04}{100} = 4.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

3. Observations

- Constant rate? The examples assume a linear concentration-time curve (constant rate).
- Real-world cases: Rates typically decrease over time as reactants deplete. If the curve is nonlinear:
- Early stage (low $[HI]$): Faster rate (e.g., 6.0×10^{-4}).
- Late stage (high $[HI]$): Slower rate (e.g., 2.0×10^{-4}).

4. Key Notes

- Units: Always in $\text{mol dm}^{-3} \text{ s}^{-1}$.
- Stoichiometry: For I_2 consumption, divide HI rates by 2.
- Assumptions: Actual rates depend on experimental data.

Final Answers:

- At $[HI] = 0.10 \text{ mol dm}^{-3}$: $4.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
- At $[HI] = 0.050 \text{ mol dm}^{-3}$: $4.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$
- At $[HI] = 0.02 \text{ mol dm}^{-3}$: $4.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$

d) What do you deduce about the rate of the reaction with time from these calculations?

Ans. From these calculations, we can deduce the following about the reaction rate over time:

1. Constant Rate (Linear Concentration-Time Curve)

If the rate is the same ($4.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$) at all concentrations (0.02, 0.05, and 0.10 mol dm^{-3}), this suggests:

- Zero-order kinetics with respect to HI (rate is independent of $[HI]$).
- The reaction does not slow down as products accumulate or reactants deplete.

2. Practical Implications

Likely controlled by external factors:

- Example: A catalyst surface is saturated (e.g., $H_2 + I_2$ on platinum), where the rate depends only on catalyst sites, not concentrations.
- Uncommon for elementary reactions: Most reactions slow over time due to fewer reactant collisions.

3. If Rates Were Different (Nonlinear Curve)

In real-world cases (nonlinear $[HI]$ vs. time):

- Decreasing rate over time: Indicates first/second-order kinetics (rate depends on $[reactants]$).
- Early stage (low $[HI]$): Faster rate (more reactants).
- Late stage (high $[HI]$): Slower rate (reactants deplete).

The constant rate here implies a zero-order mechanism for HI formation under these conditions.

e) At which concentration, the rate is highest, and lowest?

Ans. Highest and Lowest Reaction Rates

From the given calculations (assuming a linear concentration-time curve):

- Rate is constant ($4.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$) at all $[HI]$ (0.02, 0.05, 0.10 mol dm^{-3}).
- No difference in rate—neither highest nor lowest.

If the Curve is Nonlinear (Typical Behavior):

1. Highest Rate:

- At low $[HI]$ (e.g., 0.02 mol dm^{-3}) early in the reaction.
- Reactants (H_2 and I_2) are abundant $\rightarrow$ more frequent collisions.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

2. Lowest Rate:

- At high $[HI]$ (e.g., 0.10 mol dm^{-3}) later in the reaction.
- Reactants are depleted $\rightarrow$ fewer collisions.

Key Idea:

- For non-zero-order reactions, rate decreases over time as reactants are consumed.
- The example assumes **zero-order kinetics** (rate = constant), which is rare unless conditions are controlled (e.g., catalyst saturation).

Final Answer:

- If **zero-order**: Rate is identical at all concentrations.
- **Otherwise**: Highest at low $[HI]$, lowest at high $[HI]$.

➔ Measurement of Concentration

The change in concentrations of reactants or products can be determined by both physical and chemical methods depending upon the type of reactants or products involved.

a) **Chemical Method**

This is particularly suitable for reactions in solution. In this method, we do the chemical analysis of a reactant or a product.

Example:

The acid hydrolysis of an ester (ethyl acetate) in the presence of a small amount of an acid is one of the best examples.



In case of hydrolysis of an ester, the solution of ester in water and the acid acting as a catalyst are allowed to react. After some time, a sample of reaction mixture is withdrawn by a pipette and run into about four times its volume of ice-cold water. The dilution and chilling stop the reaction. The acid formed is titrated against a standard alkali, say NaOH, using phenolphthalein as an indicator.

The analysis is repeated at various time intervals after the start of reaction. This would provide an information about the change in concentration of acetic acid formed during the reaction at different time intervals.

b) **Physical Methods**

Some of the methods used for the measurement of concentration are as follows:

i) **Spectrophotometry or Colorimetry**

This method is applicable if a reactant or a product absorbs ultraviolet, visible or infrared radiation. The rate of reaction can be measured by measuring the amount of radiations absorbed. For the reaction shown in Figure, the concentration can be measured using the colorimetry.

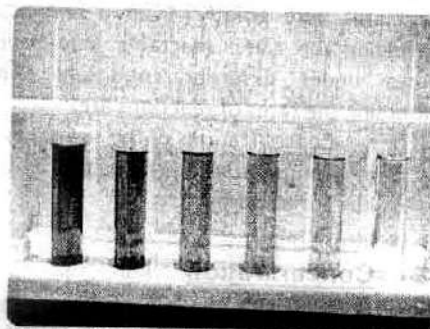


Figure: The concentration change for this reaction can be determined using colorimetry.

ii) **Electrical Conductivity Method**

The rate of a reaction involving ions can be studied by electrical conductivity method. The conductivity of such a solution depends upon the rate of change of concentration of the reacting ions or the ions formed during the reaction. The conductivity will be proportional to the rate of change in the concentration of such ions.

$$\text{Electrical Conductivity} \propto \text{Rate of change of concentration of ions}$$

iii) **Volume Change Method**

This method is useful for those reactions, which involve changes in volumes of gases as shown in Figure. The volume change is directly proportional:

- The extent of reaction
- Changes in concentration

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

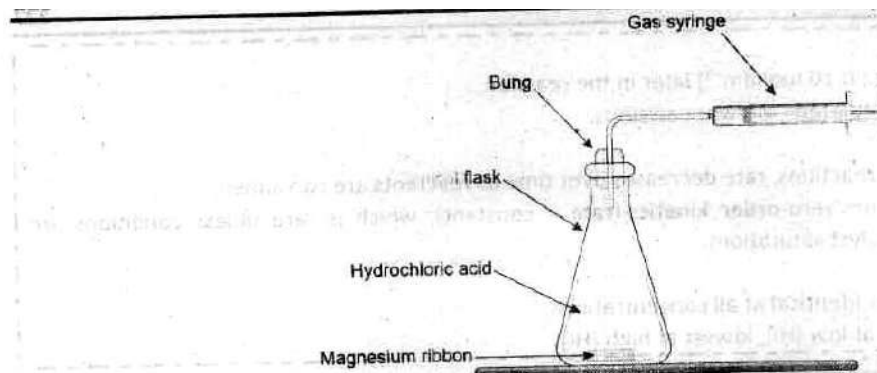


Figure: Rate of reaction can be followed by measuring the change in volume of a gas given off in a reaction.



Interesting Information!

Stopped-Flow Spectrophotometry

The rates of some very fast reactions can be monitored using stopped-flow spectrophotometry. In this technique, very small volumes of reactants are driven at high speed into a mixing chamber. From here they go to an observation cell, where the progress of the reaction is monitored (usually by measuring the transmission of ultraviolet radiation through the sample). A graph of rate of reaction against time can be generated automatically.

FACTORS AFFECTING RATE OF A CHEMICAL REACTION

In general, the rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Even a chemical reaction involving the same reactants may have different rates under different conditions. The factors affecting the rates of reactions are:

- Concentrations of the reactants
- Temperature of the system
- Surface area
- Catalyst

➤ Concentration

According to the law of mass action, the greater the concentration of the reactants, the more rapidly the reaction proceeds. When the concentration of one or more reactants increases, rate of reaction increases. This is because increasing the concentration results in more collisions between the reacting particles, which speeds up the reaction.

➤ Temperature

(Maxwell-Boltzmann Distribution Curve)

- Increase in temperature increases the reaction rate. It has been observed that rate either doubles or triples for every 10°C rise in temperature.
- Temperature usually has a major effect on the rate of reaction. Molecules at higher temperatures have more thermal energy. So, they collide more frequently and with greater energy.



Did You Know?

Effect of Pressure on Rate of Reaction:

In the case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction. However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.

Higher concentration $\rightarrow$ More collisions $\rightarrow$ High rate of reaction

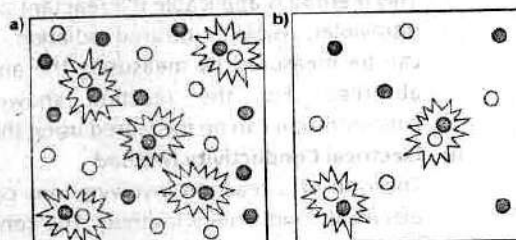


Figure: The reaction in box a) will occur faster than that in b) due to the higher concentration.



Rock Your Mind!

- Explain how temperature affects the Boltzmann distribution curve.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

- The **Boltzmann distribution curve** is a graph that shows the distribution of energies at certain temperature. In a reaction, a few particles will have very low energy, a few particles will have very high energy, and many particles will have energy in between. The distribution of energies at a given temperature can be shown on a graph as shown in Figure, this is called the Boltzmann distribution.
- The **activation energy** is the minimum energy required for colliding particles fruitfully to convert into the product. The shaded area under the graph as shown in Figure represents the proportion of molecules that have enough energy to cause a chemical change when they collide. The area under the curve represents the number of particles. The shaded area shows the number of particles with energy greater than the activation energy, E_a .

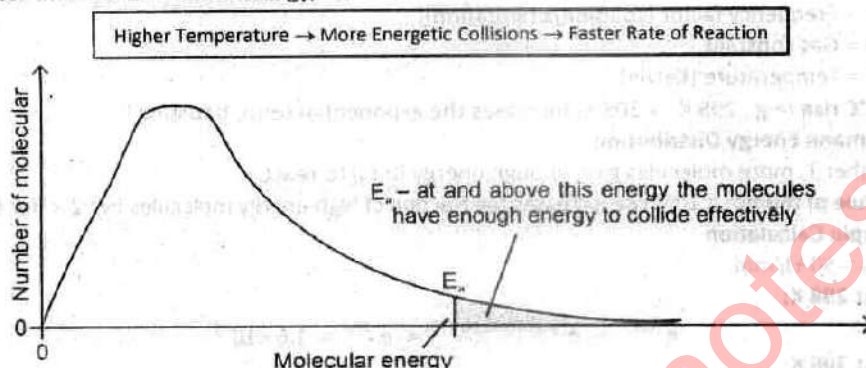


Figure: The Boltzmann distribution of molecular energies showing the activation energy

➤ When Temperature Increases:

As the temperature of a reaction mixture is raised, the average kinetic (movement) energy of the particles increases. The reacting particles move around more quickly at a higher temperature, resulting in more frequent collisions. Therefore, the proportion of successful collisions also increases greatly as shown in Figure. The curve showing the Boltzmann distribution at the higher temperature flattens and the peak shifts to the right. For 10°C rise in temperature, the shaded area under the curve approximately doubles. In conclusion, increasing the temperature increases the rate of a reaction.

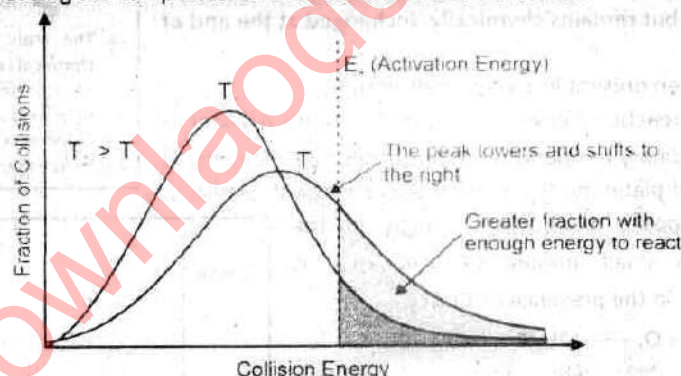


Figure: The Boltzmann distribution of molecular energies at temperatures T_1 and T_2

☑ QUICK CHECK 7.4

a) What is the Boltzmann distribution curve?

Ans. The Boltzmann distribution curve is a fundamental concept in statistical mechanics that describes the distribution of kinetic energies among particles (e.g., molecules in a gas) at a given temperature.

Mathematical Form

The fraction of particles with energy E at temperature T is given by:

$$f(E) \propto e^{-E/kBT}$$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

where:

- k_B = Boltzmann constant (1.38×10^{-23} J/K)
- T = Absolute temperature (Kelvin)

b) Explain why a 10°C rise in temperature approximately doubles the rate of a reaction.

Ans. The doubling of reaction rates with a 10°C temperature rise is explained by the Arrhenius equation and the Boltzmann distribution of molecular energies. Here's why:

1. Arrhenius Equation

The rate constant (k) depends on temperature (T) and activation energy (E_a):

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

- A = Frequency factor (collision/orientation),
- R = Gas constant,
- T = Temperature (Kelvin).

A 10°C rise (e.g., $298\text{ K} \rightarrow 308\text{ K}$) increases the exponential term, boosting k.

2. Boltzmann Energy Distribution

At higher T, more molecules gain enough energy ($\geq E_a$) to react.

- **Rule of thumb:** A 10°C rise increases the fraction of high-energy molecules by $\sim 2 \times$ (for typical E_a).

3. Example Calculation

For $E_a = 50\text{ kJ/mol}$:

- At 298 K :

$$e^{-E_a/RT} = e^{-50000/(8.314 \times 298)} \approx e^{-20.2} \approx 1.6 \times 10^{-9}$$

- At 308 K :

$$e^{-50000/(8.314 \times 308)} \approx e^{-19.5} \approx 3.2 \times 10^{-9}$$

Result: The exponential term doubles, doubling the rate.

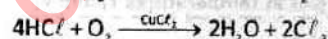
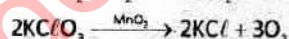
[Exercise 1.Q.5]

Q. How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?

Catalyst

A catalyst is defined as a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction.

- A catalyst is often present in a very small amount.
- **Example:** The reaction between H_2 and O_2 to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst. Similarly, KCIO_3 decomposes much more rapidly in the presence of a small amount of MnO_2 . HCl is oxidized to Cl_2 in the presence of CuCl_2 .



"The process, which takes place in the presence of a catalyst, is called catalysis."

Functions of Catalyst:

A catalyst provides a new reaction path with a low activation energy barrier. A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.



Rack Your Mind!

4. The main role of a catalyst in a chemical reaction is to:

- A) Increases activation energy
- B) Lowers activation energy
- C) Increases enthalpy
- D) Raises temperature

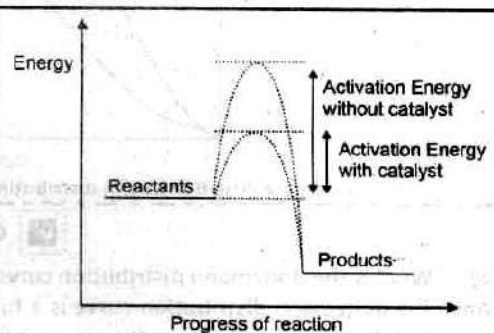


Figure: The energy path diagram for an uncatalyzed and a catalyzed reaction

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Types of Catalysis

i) Homogeneous Catalysis

In this process, the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout. The catalyst is distributed uniformly throughout the system.

For example:

- The formation of $\text{SO}_3(\text{g})$ from $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$ in the contact process for the manufacture of sulphuric acid, needs $\text{NO}(\text{g})$ as a catalyst. Both the reactants and the catalyst are gases.



- Esters are hydrolyzed in the presence of H_2SO_4 . Both the reactants and the catalyst are in the solution state.

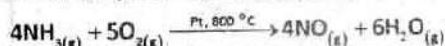


ii) Heterogeneous Catalysis

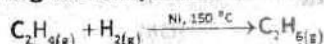
In such systems, the catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase, while the reactants are in the gaseous or liquid phase.

For example:

- Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3 .



- Hydrogenation of unsaturated organic compounds are catalysed by finely divided Ni , Pd or Pt .



Interesting Information!

Vitamins:

Vitamins are organic compounds that act as catalysts in biochemical reactions, especially when they function as coenzymes.

Coenzymes:

Coenzymes are organic molecules that help enzymes catalyze reactions more efficiently.

For example: Vitamin K, is necessary for blood clotting. Low levels of vitamin K can cause bleeding diathesis. A lack of vitamins can disrupt metabolic balance in cells and organisms. Vitamin deficiency is an example of a cofactor deficiency.



Did You Know?

Enzymes:

Biochemical catalysts, commonly known as enzymes (nature's catalyst) are essential molecules in living organisms.

Function: Its function is to lower the activation energy required for a chemical reaction to proceed, thereby increasing the reaction rate.

Enzymes are typically proteins.

Factors such as pH, temperature, and the concentration of substrate molecules can influence enzyme activity.



QUICK CHECK 7.5

- a) Can a catalyst be consumed in a chemical reaction? Why or why not?

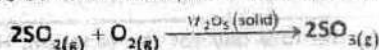
Ans. No, a catalyst is not consumed in a reaction.

- Regeneration:** Catalysts participate in intermediate steps but are reformed unchanged at the end generally.

▪ **Example:** In the decomposition of H_2O_2 , MnO_2 speeds up the reaction but remains intact.

- Role:** Lowers activation energy (E_a) by providing an alternative pathway

- b) Explain whether the reaction below is an example of heterogeneous or homogeneous catalysis:



Ans. The reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$ is typically an example of heterogeneous catalysis.

Reactants are in gaseous form and the catalysts Vanadium (V) oxide (V_2O_5) or platinum are in the solid form.

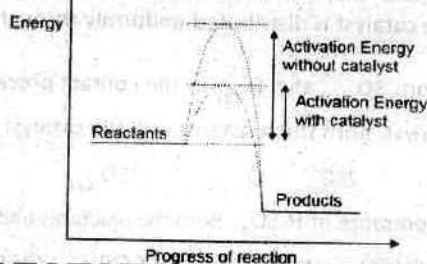
- c) Draw an energy profile diagram to show a typical uncatalysed reaction and an enzyme-catalysed reaction.

On your diagram show the activation energy for:

- Catalysed reaction
- Uncatalysed reactions

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Ans. A catalyst provides a new reaction path with a low activation energy barrier, as shown in figure. A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.



RATE LAW, RATE CONSTANT AND ORDER OF REACTION

➤ Rate Law and Rate Constant

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products.

➤ Rate Law:

"The representation of rate of a reaction in terms of concentration of the reactants is known as rate law."

(OR)

"A rate law is an equation that relates the rate of a reaction to the concentrations of reactants raised to various powers according to the experimental data."

➤ General Reaction:

For a general reaction between A and B where 'a' moles of A and 'b' moles of B react to form 'c' moles of C and 'd' moles of D.



We can write the rate equation as:

$$\text{Rate} = k[A]^x [B]^y$$

Where x and y are the experimentally determined values that may or may not be equal to the coefficient of reactants in the balanced chemical equation, as 'a' and 'b' in the above equation. This expression is called rate equation.

- The brackets [] represent the molar concentrations.
- The proportionality constant k is called rate constant for the reaction.

If $[A] = 1 \text{ mol dm}^{-3}$ and $[B] = 1 \text{ mol dm}^{-3}$

Rate of reaction $= k \times 1^x \times 1^y = k$

Rate Constant: It can be defined as "The specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity".

- Under the given conditions, k remains constant, but it changes with temperature.

(Exercise L.Q.3)

Q. Relate the order of a reaction to the rate law for the reaction. How do you distinguish between zero order, first order and second order reaction?

➤ Reaction Order

The exponents 'x' or 'y' in the above equation give the order of reaction with respect to the individual reactants.

"The order of a reaction with respect to a specific reactant is the exponent applied to that reactant's concentration within the rate equation".

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

➤ Explanation:

- Thus, the reaction is of order 'x' with respect to A and of order 'y' with respect to B.
- The overall order of reaction = x + y.
- The order of a reaction defines how the reactant concentration influences its rate.
- For a single-reactant, the order is simply the concentration's power in the rate equation.
- The chemical reactions are classified as zero, first, second and third order reactions.
- The order of reaction provides valuable information about the mechanism of a reaction.
- It is crucial to differentiate between the order concerning a single reactant and the overall reaction order.

Reaction order tells how rate changes with reactants concentrations.

Example: Take equation for the reaction of nitrogen (II) oxide (NO) with H₂ and oxygen:



$$\text{Rate} = k[\text{H}_2][\text{NO}]^2$$

This reaction is:

- first-order with respect to H₂
- second-order with respect to NO
- third-order overall (1 + 2 = 3)



Order of Reaction:

- The order of reaction is given by the sum of all the exponents to which the concentrations in the rate equation are raised.
- It is important to note that the order of a reaction is an experimentally determined quantity and cannot be inferred simply by looking at the reaction equation.
- The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation.



QUICK CHECK 7.6

a) **How order of reaction is derived from the rate law?**

Ans. The order of reaction is derived from the rate law by analyzing how the reaction rate depends on the concentrations of reactants.

Steps to Determine Reaction Order

1. Write the Rate Law:

For a reaction: $a\text{A} + b\text{B} \rightarrow \text{Products}$,

the rate law is: $\text{Rate} = k[\text{A}]^m[\text{B}]^n$

- k = rate constant,
- m, n = orders with respect to A and B (often integers, but can be fractions or zero).

2. Experimental Data:

Measure how the **initial rate** changes when varying one reactant's concentration while keeping others constant.

3. Derive Orders (m, n):

- If doubling [A] doubles the rate: m = 1 (first-order in A).
- If doubling [A] quadruples the rate: m = 2 (second-order in A).
- If rate is unchanged when [A] changes: m = 0 (zero-order in A).

4. Overall Order:

Sum of individual orders:

$$\text{Overall order} = m + n + \dots$$

Example:

For the rate law $\text{Rate} = k[\text{A}][\text{B}]^2$:

- First-order in A (exponent = 1),
- Second-order in B (exponent = 2),
- Overall third-order (1 + 2 = 3).

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

b) Explain what is meant by the specific rate (rate constant) of a reaction and how it is represented in rate equation.

Ans. **Specific Rate (Rate Constant, k)**

- **Definition:** The rate constant (k) is a proportionality factor in the rate law that quantifies the reaction's speed at a given temperature, independent of reactant concentrations.

- **Role in Rate Equation:**

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

- k is specific to the reaction and temperature.

Units of Rate constants = various order

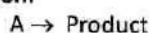
Order	Unit of K
nth	$\frac{1}{(\text{mol} \cdot \text{dm}^{-3})^{1-n}} \cdot \text{sec}^{-1}$
Zero	$\text{mol dm}^{-3} \text{ s}^{-1}$
First	s^{-1}
Second	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Third	$\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

Types of Reaction Order

Zero Order Reaction:

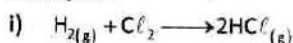
The rate of a zero order reaction is independent of the concentration of the reactants. A change in the concentration has no effect on the speed of the reaction.

General Reaction:



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

Examples:



$$\text{Rate} = k[\text{H}_2]^0 [\text{Cl}_2]^0 = k$$



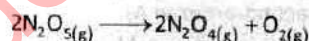
$$\text{Rate} = k[\text{NH}_3]^0 = k$$

iii) Photochemical reactions are usually zero order.

First Order Reaction:

In these reactions, there may be multiple reactants present, but concentration of only one reactant will change during the reaction.

Examples: Decomposition of nitrogen pentoxide involves the following equation.



The experimentally determined rate equation for this reaction is as follows:

$$\text{Rate} = k[\text{N}_2\text{O}_5] \quad (n=1)$$

This equation suggests that the reaction is first order with respect to the concentration of N_2O_5 .

Second Order Reaction:

Definition:

"A reaction for which sum of the exponents of the concentrations in the rate equation is 2."



Rack Your Mind!

6. Give at least four examples of zero order reaction.



Interesting Information!

Rate laws for Elementary Reaction

Elementary Reaction	Molecularity	Rate Law
$A \rightarrow \text{Product}$	Uni-molecular	$\text{Rate} = k[A]$
$A + A \rightarrow \text{Product}$	Bi-molecular	$\text{Rate} = k[A]^2$
$A + B \rightarrow \text{Product}$	Bi-molecular	$\text{Rate} = k[A][B]$
$A + B + C \rightarrow \text{Product}$	Ter-molecular	$\text{Rate} = k[A]^2[B]$

First order means $\text{rate} \propto [\text{Reactant}]$



Smart Thinking

Units of Rate constants = various order

Order	Unit of K
nth	$\frac{1}{(\text{mol} \cdot \text{dm}^{-3})^{1-n}} \cdot \text{sec}^{-1}$
Zero	$\text{mol dm}^{-3} \text{ s}^{-1}$
First	s^{-1}
Second	$\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
Third	$\text{dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

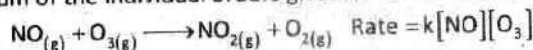
(OR)

"A second order reaction is a reaction whose rate depends either on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power." The simpler type of reaction involves one kind of reactant molecule.

Rate Equation: $\text{Rate} = k[A]^2$ ($n = 2$)

Example: $\text{Rate} = k[A]^1[B]^1$ ($n = 1 + 1 = 2$)

Oxidation of nitric oxide with ozone has been shown to be first order with respect to NO and first order with respect to O₃. The sum of the individual orders gives the overall order of reaction as two.



➤ Third Order Reaction:

A third order reaction is the reaction for which sum of the exponents of the concentrations in the rate equation is three.

Rate Equation: $\text{Rate} = k[A]^3$ ($n = 3$)

or $\text{Rate} = k[A]^2[B]^1$ ($n = 2 + 1 = 3$)

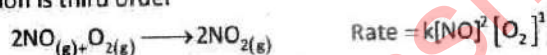
or $\text{Rate} = k[A]^1[B]^1[C]^1$ ($n = 1 + 1 + 1 = 3$)

Example: $2\text{FeCl}_{3(aq)} + 6\text{KI}_{(aq)} \longrightarrow 2\text{FeI}_{2(aq)} + 6\text{KCl}_{(aq)} + \text{I}_2$

This reaction involves eight reactant molecules but experimentally it has been found to be a third order reaction.

$$\text{Rate} = k[\text{FeCl}_3][\text{KI}]^2$$

also, the following reaction is third order



➤ Fractional Order Reaction:

"A reaction in which the sum of exponents of rate equation is in fraction, is called the fractional order reaction."

Example: Consider the formation of carbon tetrachloride from chloroform.



$$\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2} \quad n = 1 + 1/2 = 1.5$$

- Reactions involving free radicals frequently exhibit fractional orders.

➤ Units of Rate Constant

The rate constant is specific for a particular reaction at a certain temperature. Since concentrations are in mol dm^{-3} and the reaction rate is in units of $\text{mol dm}^{-3} \text{s}^{-1}$. The units for k depend on the order of the reaction and the units of time.

General Equation:

$$\text{Rate} = k[\text{Reactants}]^n \quad \text{where } n = \text{order of reaction}$$

$$k = \frac{\text{Rate}}{(\text{Reactants})^n} = \frac{(\text{mol dm}^{-3}) \text{s}^{-1}}{(\text{mol dm}^{-3})^n}$$

or $k = (\text{mol} \cdot \text{dm}^{-3})^{1-n} \text{s}^{-1}$

or $k = (\text{concentration})^{1-n} \text{s}^{-1}$

This equation can be used to determine units of any order of reaction.

For a zero order reaction ($n = 0$),

$$k = (\text{mol} \cdot \text{dm}^{-3})^{1-0} \text{s}^{-1}$$

$$k = \text{mol}^1 \cdot \text{dm}^{-3} \text{s}^{-1}$$

For a first order reaction ($n = 1$), the rate is directly proportional to the concentration of one reactant.

$$k = (\text{mol} \cdot \text{dm}^{-3})^{1-1} \text{s}^{-1}$$

$$k = (\text{mol} \cdot \text{dm}^{-3})^0 \text{s}^{-1}$$

$$k = \text{s}^{-1}$$

Therefore, the units of k for a first order rate constant are s^{-1} .



Rock Your Mind!

7. Given $\text{Rate} = k[A]^2[B]$, what is the overall order of reaction?

- A) 1 B) 2
C) 3 D) 4



Rock Your Mind!

8. What are units for Zero and first order Reaction?

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

For a second order reaction ($n = 2$),

$$k = (\text{mol dm}^{-3})^{1-2} \text{s}^{-1}$$

$$= \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$$

$$k = \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$$

The units of k for a second order rate constant are $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

For a third order reaction ($n = 3$),

$$k = (\text{mol dm}^{-3})^{1-3} \text{s}^{-1}$$

$$= \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$$

$$k = \text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$$

Therefore, the units of k for a third order rate constant are $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$.



QUICK CHECK 7.7

a) Calculate the overall order of reactions which have the rate expressions:

i) $\text{rate} = k[\text{NO}]^2[\text{NH}_3]^0$

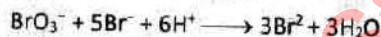
Ans. $\text{Rate} = k[\text{NO}]^2[\text{NH}_3]^0$

- Order with respect to NO: 2 (exponent of [NO]).
- Order with respect to NH_3 : 0 (exponent of [NH₃]).
- Overall order: $2 + 0 = 2$ (Second-order overall).

As per text book order of reaction usually does not exceeds 3.

ii) $\text{rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$

Ans. $\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$



Experimentally Determined Rate Law:

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

i) Calculate the overall order of reactions.

Ans. The given rate law is:

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

Overall order is the sum of these exponents: $1 + 1 + 2 = 4$

Note: Overall order reaction comes out to be 4 but as per our syllabus order of reaction never exceeds 3. So, 3 is the maximum order the reaction and it is 3 for the above.

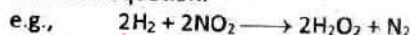
ii) What are the orders with respect to each reactant in the expression.

Ans. $\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$

- The exponent of $[\text{BrO}_3^-] = 1$
- The exponent of $[\text{Br}^-] = 1$
- The exponent of $[\text{H}^+] = 2$

b) Why the sum of the coefficients of a balanced chemical equation is not necessarily important to give the order of a reaction?

Ans. Order of a chemical reaction is not necessarily the sum of the coefficients of the balanced chemical equation because the order of reaction is determined experimentally and not from the balanced chemical equation.



For this reaction, the sum of coefficients of balanced equation is $2 + 2 = 4$ but the reaction is 3rd order. It is experimentally verified that rate of reaction is directly related to conc. of H_2 and to the square of concentration of NO_2 . So the rate equation of this reaction is:

$$\text{Rate} \propto [\text{H}_2]^1[\text{NO}_2]^2$$

$$\text{Rate} = k[\text{H}_2]^1[\text{NO}_2]^2$$

Order of reaction is sum of exponents of rate equation. So

$$\text{Order of reaction} = 1 + 2 = 3$$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

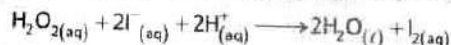
DETERMINATION OF RATE CONSTANT

Q. How do you find the numerical value of a rate constant by initial and half-life methods? (Exercise L.Q.4)

The rate constant (k) of a reaction can be calculated using the following two methods:

➤ Initial Concentration Method

In the presence of hydrogen ions, hydrogen peroxide, H_2O_2 , reacts with iodide ions to form water and iodine:



The rate equation for this reaction is:

$$\text{Rate of reaction} = \frac{k[\text{H}_2\text{O}_2]}{[\text{I}^-]}$$

The progress of the reaction can be followed by measuring the initial rate of formation of iodine. Table shows the rates of reaction obtained using various initial concentrations of each reactant. The procedure for calculating k is shown below, using the data for experiment 1.

Step 1: Write out the rate equation.

$$\text{Rate of reaction} = \frac{k[\text{H}_2\text{O}_2]}{[\text{I}^-]}$$

Step 2: Rearrange the equation in terms of k

$$k = \frac{\text{rate} \times [\text{I}^-]}{[\text{H}_2\text{O}_2]}$$

Step 3: Substitute the values

$$k = \frac{3.50 \times 10^{-6} \times (0.0100)}{(0.0200)} \\ = 1.75 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Table: Effect of change in concentrations of reactants on the rate of reaction

Experiment	$[\text{H}_2\text{O}_2] / \text{mol dm}^{-3}$	$[\text{I}^-] / \text{mol dm}^{-3}$	$[\text{H}^+] / \text{mol dm}^{-3}$	Initial rate of reaction / $\text{mol dm}^{-3} \text{ s}^{-1}$
1.	0.0200	0.0100	0.0100	3.5×10^{-6}
2.	0.0300	0.0100	0.0100	5.3×10^{-6}
3.	0.0050	0.0200	0.0200	1.75×10^{-6}

The concentration of hydrogen ions is ignored because $[\text{H}^+]$ does not appear in the rate equation. The reaction is zero order with respect to $[\text{H}^+]$.

➤ Half-Life Method

"Half-life, $t_{1/2}$, is the time taken for the concentration of a reactant to fall to half of its original value".

➤ Calculation of Rate Constant:

Calculating the rate constant (k) using the half-life method involves measuring the time it takes for the concentration of a reactant to decrease by half.

If the reaction is first-order, then the rate constant and the half-life of the reaction are related in the following way:

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

Example: A sample of hydrogen peroxide has a half-life of 2 hours. It decomposes in a first-order reaction. Calculate the rate constant, k, for this reaction.

To calculate k, we first need to convert the half-life, which is 2 hours, into seconds:

$$2 \times 60 \times 60 = 7200 \text{ s}$$



Rack Your Mind!

9. Hydrogen peroxide decomposes by a first-order reaction. If its half-life is 2 hours, what is the rate constant (k)?

- A) $9.63 \times 10^{-5} \text{ s}^{-1}$ B) 0.00072 s^{-1}
C) 0.00139 s^{-1} D) 0.0036 s^{-1}

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

We then simply substitute this value into the equation:

$$k = \frac{0.693}{7200 \text{ s}}$$

$$k = 9.6 \times 10^{-5} \text{ s}^{-1}$$

Sample Problem 7.2

The first-order reaction cyclopropane to propene, for which the half-life is 17.0 min, Calculate the rate constant of this reaction.

Solution:

Step 1: convert minutes to seconds

Step 2: substitute the half-life into the expression:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{17 \times 60 \text{ s}}$$

$$k = 6.79 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$



QUICK CHECK 7.8

Consider a first-order reaction with a half-life of 15 minutes. If the initial concentration of the reactant is $0.100 \text{ mol dm}^{-3}$, calculate the rate constant (k) for the reaction.

Solution:

- Half-life ($t_{1/2}$) = 15 minutes
- Initial concentration ($[A]_0$) = $0.100 \text{ mol dm}^{-3}$

Formula for First-Order Half-Life:

$$t_{1/2} = \ln(2)/k$$

Step 1: Solve for k

- $k = \ln(2)/t_{1/2} = 0.693/15 \text{ min}$
- $k = 0.0462 \text{ min}^{-1}$

REACTION MECHANISM

➤ **Definition:**

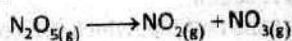
"A reaction mechanism is a detailed, step by step description of how a chemical reaction occurs at the molecular level to yield the product(s)."

- Unlike the overall balanced chemical equation, which only shows the reactants and products, the reaction mechanism reveals the actually happening individual steps (called elementary steps) that lead to the formation of products.
- Each of these steps represents a single molecular event, such as the breaking or forming of bonds.
- Many reactions do not occur in a single step, but rather proceed through a series of steps.
- Each step is called an elementary reaction and is directly caused by the collision of atoms, ions or molecules.

➤ **Molecularity:**

The number of reactant molecules involved in an elementary step is called its molecularity.

- A unimolecular elementary reaction involves only a single reactant molecule.
- **Example:** Decomposition of N_2O_5 .



- An elementary reaction that involves two atoms, ions or molecules and is called bimolecular.



Rack Your Mind!

10. Which of the following is most likely to be the rate-determining step in a multi-step reaction?

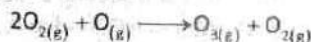
- A) The fastest step
- B) The step with the lowest activation energy
- C) The step forming the product
- D) The slowest step

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

- For example;



- A **ter-molecular reaction step** involves the simultaneous reaction of three molecules. Such reactions are rare. An example is the reaction between oxygen molecules and atomic oxygen to form ozone in the stratosphere or during smog formation.



➤ Intermediates:

Intermediates are short lived species (ions or free radicals) that are produced in one step of the mechanism and consumed in a subsequent step. They do not appear in the overall balanced equation because they are not stable products.

➤ Rate Determining Step:

In many reaction mechanisms, one step is significantly slower than all the others, this step is called the rate-determining step.

- This step controls the overall rate of the reaction because it limits the speed at which the reaction can proceed.
- The balanced equation for the overall reaction is equal to the net result of all the individual steps. In a chemical reaction, any step that occurs after the rate-determining step will not affect the rate, provided that it is compared with the rate-determining step.
- The atoms, ions or molecules taking part in the mechanism after the rate-determining step do not appear in the rate expression.
- All reactants that appear in the rate-determining step will also appear in the rate equation. Because the rate-determining step limits the rate of the overall reaction, the order of a reaction can be deduced from the rate determining step.

Example 1: Consider the following reaction:



Table shows the results of six experiments. In the first three experiments the concentration of H_2 is increased by keeping the concentration of NO constant. By doubling the concentration of H_2 , the rate is doubled and by tripling the concentration of H_2 , the rate is tripled. So, the rate of reaction is directly proportional to the first power of concentration of H_2 .

$$\text{Rate} \propto [\text{H}_2]$$

In the next three experiments, the concentration of H_2 is kept constant. By doubling the concentration of NO , the rate increases four times and by tripling the concentration of NO the rate is increased nine times. So, the rate is proportional to the square of concentration of NO .

$$\text{Rate} \propto [\text{NO}]^2$$

The overall rate equation of reaction is,

$$\text{Rate} \propto [\text{H}_2][\text{NO}]^2$$

or

$$\text{Rate} = k[\text{H}_2]^1[\text{NO}]^2$$

Table: Effect of change in concentrations of reactants on the rate of reaction

[NO] in (mol dm^{-3})	[H ₂] in (mol dm^{-3})	Initial rate (atm min^{-1})
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

Hence, the reaction is a third order one.

- This final equation is the rate law for this reaction.
- It should be kept in mind that rate law cannot be predicted from the balanced chemical equation.
- The possible mechanism consisting of two steps for the reaction is as follows.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Step 1: $2\text{NO}_{(g)} + \text{H}_2_{(g)} \xrightarrow{\text{Slow}} \text{N}_2_{(g)} + \text{H}_2\text{O}_{2(g)}$ (rate determining step)

Step 2: $\text{H}_2\text{O}_{2(g)} + \text{H}_2_{(g)} \xrightarrow{\text{Fast}} 2\text{H}_2\text{O}_{(g)}$

The step 1 is slow and rate determining.

Example 2: The reaction between nitrogen dioxide and fluorine gas:



This reaction is first order in NO_2 , first order in F_2 and second order overall.

Rate Law: The experimental rate law is first order in NO_2 and in F_2 :

$$\text{Rate} = k[\text{NO}_2][\text{F}_2] \quad (\text{Observed})$$

The accepted mechanism for the reaction is:

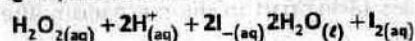
Step 1: $\text{NO}_{2(g)} + \text{F}_2 \xrightarrow{\text{Slow}} \text{NO}_2\text{F}_{(g)} + \text{F}_{(g)}$ $\text{Rate} = k_1[\text{NO}_2][\text{F}_2]$

Step 2: $\text{NO}_{2(g)} + \text{F}_{(g)} \xrightarrow{\text{Fast}} \text{NO}_2\text{F}_{(g)}$ $\text{Rate} = k_2[\text{NO}_2][\text{F}]$

- The first step is slow and determines the rate, in agreement with the observed rate expression.
- The second and fast step does not affect the reaction rate because fluorine atoms react with NO_2 as soon as they are produced.

QUICK CHECK 7.9

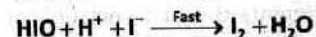
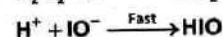
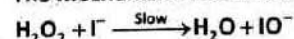
Q. An acidified solution of hydrogen peroxide reacts with iodide ions.



The rate equation for this reaction is

$$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$$

The mechanism below has been proposed for this reaction.



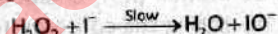
Explain why this mechanism is consistent with the rate equation.

Ans. The proposed mechanism is consistent with the experimentally determined rate equation

$\text{rate} = k[\text{H}_2\text{O}_2][\text{I}^-]$ because:

Rate-Determining Step (RDS):

- The slow step involves only H_2O_2 and I^- :



Since the RDS determines the rate law, it directly gives:

$$\text{rate} = k_1[\text{H}_2\text{O}_2][\text{I}^-]$$

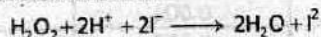
1. Fast Steps:

The subsequent fast steps involve H^+ and IO^-/HIO , but these do not affect the rate law because:

- They occur after the RDS.
- H^+ acts as a catalyst (regenerated in the mechanism) and does not appear in the rate law.

2. Consistency with Stoichiometry:

The mechanism sums to the overall reaction:



Why H^+ Doesn't Appear in the Rate Law:

- H^+ participates only in fast steps (after RDS) and is not involved in the slow step.
- Its concentration does not influence the rate.

Conclusion:

The mechanism aligns perfectly with the observed rate equation because:

- The slow step involves only the reactants that appear in the rate law (H_2O_2 and I^-).
- The fast steps reconcile the intermediates (IO^- , HIO) with the overall reaction.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Solution File Rack Your Brain!

Sr. #	Option	Explanation
1.	S.Q	The conditions must be met for a collision to be effective according to collision theory are given below; A collision is effective only if; - The reacting particles have enough activation energy - Collide with the correct orientation
2.	A	0.02 mol/l.s
3.	S.Q	Temperature affects the Boltzmann distribution curve because higher temperature - shifts the curve to the right and flattens it, - increasing the number of particles with energy greater than the activation energy, - speeds up the reaction.
4.	B	A catalyst speeds up a reaction by providing an alternative reaction pathway with lower activation energy, allowing more reactant molecules to overcome the energy barrier and form products.
5.	S.Q	It shows how the concentration of a reactant affects the rate of the reaction. For example, if rate = $k[A]^2[B]$, the reaction is second order with respect to A and first order with respect to B.
6.	S.Q	Examples i. Photochemical reactions are usually zero order reactions. ii. Enzyme catalysed reactions iii. $H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$ iv. $2NH_3 \xrightarrow{Pt} N_2 + 3H_2$ v. $2HI \xrightarrow{Al_2O_3} H_2 + I_2$ vi. $N_2O \xrightarrow{Pt} N_2 + \frac{1}{2} O_2$
7.	C	Order of reaction = 2 + 1 = 3
8.	S.Q	For a zero order reaction ($n = 0$), $k = (\text{mol} \cdot \text{dm}^{-3})^{1-0} \text{s}^{-1}$ $k = \text{mol}^1 \cdot \text{dm}^{-3} \text{s}^{-1}$ For a first order reaction ($n = 1$), the rate is directly proportional to the concentration of one reactant. $k = (\text{mol} \cdot \text{dm}^{-3})^{1-1} \text{s}^{-1}$ $k = (\text{mol} \cdot \text{dm}^{-3})^0 \text{s}^{-1}$ $k = \text{s}^{-1}$
9.	A	For a first-order reaction, the half-life ($t_{1/2}$) is related to the rate constant (k) by the equation: $t_{1/2} = 0.693/k$. Rearranging this equation give $k = 0.693 / t_{1/2}$. The rate constant k is calculated as 0.3465 h^{-1} . To convert this to seconds, we multiply by (1h/3600s) giving $k = 0.3465/3600 = 9.625 \times 10^{-5} \text{ s}^{-1}$.
10.	D	This step determines the overall rate of the reaction, as the reaction cannot proceed faster than its slowest step.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

16
10

Q.1 Four choices are given for each question. Select the correct choice.

- I. The rate of reaction:
 - a) Increases as the reaction proceeds
 - b) Decreases as the reaction proceeds
 - c) Remains the same as the reaction proceeds
 - d) May decrease or increase as the reaction proceeds
- II. Increasing the temperature of a chemical reaction increases the rate of reaction because:
 - a) Both the collision frequency and collision energies of reactant molecules increase
 - b) Collision frequency of reactant molecules increases
 - c) Activation energy increase
 - d) Activation energy decrease
- III. Consider two reactions with different activation energies at the same temperature. The reaction with the lower activation energy will have:
 - a) A smaller rate constant
 - b) A larger rate constant
 - c) The same rate constant
 - d) A rate constant that depends on the enthalpy change
- IV. The order of a chemical reaction, that is independent of concentration is:
 - a) Second order reaction
 - b) First order reaction
 - c) Zero order reaction
 - d) Pseudo first order reaction
- V. On a Boltzmann distribution curve, the area under the curve represents:
 - a) Activation energy of the reaction.
 - b) Total number of molecules in the sample.
 - c) Average kinetic energy of the molecules.
 - d) Rate constant of the reaction.
- VI. On a Boltzmann distribution curve, the activation energy (E_a) is represented by:
 - a) The height of the peak
 - b) The area under the entire curve
 - c) A vertical line drawn at a specific kinetic energy value
 - d) The difference between the peak and the X-axis
- VII. If we double the concentration of a reactant, the rate increases by four times, the reaction is:
 - a) Second order
 - b) First order
 - c) Third order
 - d) Zero order
- VIII. The rate determining step in a multi-step reaction is:
 - a) Always the first step
 - b) Always the last step
 - c) The slowest step
 - d) The fastest step
- IX. The reaction $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ occurs in two steps. What is the rate law equation for this reaction?

$$2\text{NO}_2 \longrightarrow \text{NO} + \text{NO}_3 \quad (k_1) \quad \text{slow}$$

$$\text{NO}_3 + \text{CO} \longrightarrow \text{CO}_2 + \text{NO}_2 \quad (k_2) \quad \text{fast}$$

 - a) $R = k_1[\text{NO}_2]^3$
 - b) $R = k_2[\text{NO}_3][\text{CO}]$
 - c) $R = k_1[\text{NO}_2]$
 - d) $R = k_1[\text{NO}_2]^2$
- X. How does the presence of a catalyst affect the rate of a chemical reaction?
 - a) It always decreases the rate of the reaction.
 - b) It always increases the rate of the reaction.
 - c) It increases the rate of the forward and decreases the rate of the reverse reaction.
 - d) It increases the rate of both the forward and reverse reactions.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

243

- XI. On an energy profile diagram, the presence of a catalyst is represented by:**
 a) A higher peak representing the activation energy.
 b) A lower peak representing the activation energy.
 c) A change in the energy level of the reactants or products.
 d) A shift in the equilibrium position.
- XII. The units of the rate constant (k) for a reaction depend on the:**
 a) Activation energy of the reaction
 b) Temperature of the reaction
 c) Overall order of the reaction
 d) Stoichiometry of the balanced chemical equation
- XIII. A first-order reaction has a half-life ($t_{1/2}$) of 20 minutes. What is the value of its rate constant (k)?**
 a) 0.05 min^{-1} b) 0.693 min^{-1} c) 0.0347 min^{-1} d) 13.86 min^{-1}

Answer Key with Explanations

Sr.No.	Option	Answer	Explanation
I.	b	Decreases as the reaction proceeds	• Reactant concentrations decrease over time, reducing collision frequency and rate.
II.	a	Both the collision frequency and collision energies of reactant molecules increase	• Higher temperature boosts molecular speed (more collisions) and energy (more exceed E_a).
III.	b	A larger rate constant	• Lower E_a means more molecules have sufficient energy to react (faster rate, larger k).
IV.	c	Zero order reaction	• Zero-order rates are constant (e.g., catalytic surface reactions).
V.	b	Total number of molecules in the sample	• The integral of the curve equals the total molecules.
VI.	c	A vertical line drawn at a specific kinetic energy value	• E_a is the threshold energy (vertical line) beyond which molecules can react.
VII.	a	Second order	• $\text{Rate} \propto [\text{Reactant}]^2 \rightarrow 4 \times 22 = \text{rate increase}$.
VIII.	c	The slowest step	• The slowest step limits the overall rate.
IX.	d	$R = k_1[\text{NO}_2]^2$	• The slow step involves $2\text{NO}_2 \rightarrow \text{products}$, so rate depends on $[\text{NO}_2]^2$.
X.	d	It increases the rate of both the forward and reverse reactions	• Catalysts lower E_a for both directions, speeding up equilibrium attainment.
XI.	b	A lower peak representing the activation energy	• Catalysts provide an alternative pathway with reduced E_a .
XII.	c	Overall order of the reaction	• For order n, k has units of $\text{mol}^{1-n}\text{L}^n\text{s}^{-1}$.
XIII.	c	0.0347 min^{-1}	• $k = \frac{\ln(2)}{t_{1/2}} = \frac{0.693}{20} = 0.0347 \text{ min}^{-1}$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a. What do you understand by the rate of a reaction?

Ans. The rate of a reaction refers to how fast or slow a chemical reaction occurs. It is defined as the change in concentration of a reactant or product per unit time.

Mathematically, the rate of reaction can be expressed as:

$$\text{Rate of reaction} = \frac{\text{Change in concentration of substance}}{\text{Time taken for the change}}$$

$$\text{Rate of reaction} = \frac{\Delta x}{\Delta t}$$

b. Give the difference between enthalpy change of reaction and energy of activation of reaction.

Ans. Difference between Enthalpy Change of Reaction and Energy of Activation of Reaction:

Property	Enthalpy Change of Reaction (ΔH)	Activation Energy (E_a)
Definition	The total heat change during a chemical reaction at constant pressure.	The minimum energy required for a reaction to occur.
Significance	It indicates whether a reaction is exothermic ($\Delta H < 0$) or endothermic ($\Delta H > 0$).	It represents the energy barrier that must be overcome for a reaction to proceed.
Effect on Reaction	Reflects the overall energy change between products and reactants.	Affects the rate of the reaction; higher E_a means slower reaction.
Energy Direction	ΔH can be positive (endothermic) or negative (exothermic).	E_a is always positive, indicating an energy input is needed.
Measurement	It is the difference in the enthalpy between reactants and products.	It is determined experimentally by studying reaction rates.
Example	In the combustion of methane: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ ΔH is negative (exothermic).	For a reaction to occur, molecules must first overcome the activation energy, which can be lowered by a catalyst.

c. Differentiate clearly between order and molecularity of a reaction.

Ans. Differentiate between Order and Molecularity

Property	Order of a Reaction	Molecularity of a Reaction
Definition	The power to which the concentration of a reactant is raised in the rate law expression.	The number of reacting species (atoms, molecules, or ions) involved in the elementary step of a reaction.
Dependence on Concentration	Order depends on the experimental observation of how reaction rate changes with concentration of reactants.	Molecularity is based on the stoichiometric coefficients in the elementary reaction step.
Nature	Experimental: Determined by experimental data, can be fractional or zero.	Theoretical: Based on the nature of the reaction mechanism and the elementary steps.
Units	Depends on the rate law and overall reaction rate, and can vary with different reactions.	Always an integer (1, 2, 3, etc.), indicating the number of molecules or ions reacting in an elementary step.
Examples	For $A \rightarrow \text{products}$, if $\text{rate} = k[A]^2$, the order is 2.	For $A+B \rightarrow \text{products}$, the molecularity is 2 (because two molecules are involved).
Can It Be Fractional?	Yes, order can be fractional, zero, or a whole number.	No, molecularity must always be a whole number (1, 2, 3, ...).
Reactions	The order applies to overall reactions and depends on how concentration affects the rate.	Molecularity applies to the elementary step of a reaction mechanism.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

=====

d. Why the instantaneous rate changes during a reaction?

Ans. The instantaneous rate of a reaction changes during the course of the reaction because:

1. Concentration of Reactants Changes:

- As the reaction proceeds, reactant molecules are consumed to form products. This causes a decrease in the concentration of the reactants over time.
- According to the rate law, the rate of reaction depends on the concentration of reactants. As the concentration decreases, the rate of the reaction generally slows down (in the case of most reactions).

2. Effect on Rate Law:

- The rate of the reaction is often directly proportional to the concentration of reactants raised to some power (the order of the reaction).
- For example, if the rate law is $\text{rate} = k[A]^n$, as $[A]$ decreases, the rate will decrease accordingly. This change in concentration over time causes the instantaneous rate to change as well.

3. Transition from Fast to Slow Reactions:

- In initial stages, when reactants are present in higher concentrations, the reaction proceeds faster.
- As reactants are consumed and their concentrations drop, the rate of reaction decreases.

4. Reverse Reaction (if applicable):

- In reversible reactions, as products form, they can also react to regenerate reactants. This can affect the overall rate, especially as the reaction approaches equilibrium.

e. Briefly summarize the effects of temperature and surface area on the rates of reactions.

Ans.

1. Effect of Temperature on Reaction Rate:

- Increase in Temperature $\Rightarrow$ Increase in Rate of reaction.
- At higher temperatures, molecules have more kinetic energy, leading to:
 - More frequent collisions between reactant molecules.
 - More energetic collisions, increasing the chances of successful reactions (i.e., collisions with enough energy to overcome the activation energy barrier).
- **Arrhenius Equation:** The rate constant (k) increases with temperature, generally leading to a faster reaction.

2. Effect of Surface Area on Reaction Rate:

- Increase in Surface Area $\Rightarrow$ Increase in Rate of reaction.
- Smaller particles or larger surface area of reactants result in:
 - More surface contact between reactants, leading to more collisions.
 - Faster reaction rate as more reactant particles are exposed to react with the other reactant molecules.
- **Example:** Powdered solid reactants react faster than large chunks of the same substance because of the greater surface area available for collisions.

f. Justify that the radioactive decay is always a first order reaction.

Ans. Radioactive decay is always a first-order reaction due to the nature of the process, which can be justified as follows:

First-Order Reaction:

- A first-order reaction is one where the rate of reaction depends on the concentration of a single reactant raised to the power of 1.
- Mathematically: $\text{rate} = k[A]$, where $[A]$ is the concentration of the reactant, and k is the rate constant.

Dependence on the Number of Radioactive Nuclei:

- In radioactive decay, the rate at which a substance decays depends on the number of radioactive nuclei present at any given time.
- The probability that a single nucleus will decay within a given time interval is constant and independent of the number of decays that have already occurred.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

- The rate of decay is proportional to the number of radioactive atoms that are still intact at any moment, i.e., the concentration of the substance.
- The half-life remains constant regardless of how much material is left, further proving that radioactive decay is a first-order process.

g. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration is doubled and reduced to half?

Ans. For a second-order reaction with respect to a reactant, the rate of the reaction is proportional to the square of the concentration of that reactant. This means that the rate law can be expressed as:

$$\text{Rate} = k[A]^2$$

Where:

- k is the rate constant,
- $[A]$ is the concentration of the reactant.

h. What is meant by half-life and what is it used for?

Ans. Half-Life ($T_{1/2}$):

The half-life of a reaction is the time required for the concentration of a reactant to decrease to half of its initial value. It is a measure of how quickly a reaction occurs or how long it takes for a substance to undergo a certain amount of decay or transformation.

Uses:

It is used in various fields like radioactive decay, chemical reactions, and pharmacokinetics to measure the rate of processes or determine safe and effective dosages in medicine.

i. Why does wood burn more rapidly in pure oxygen than in air?

Ans.

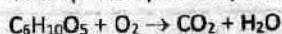
1. Increased Oxygen Concentration:

- In air, oxygen makes up about 21% of the atmosphere, with the rest primarily consisting of nitrogen and trace gases.
- In pure oxygen, the oxygen concentration is 100%, meaning there is a much higher availability of oxygen molecules to react with the wood during combustion.
- More oxygen molecules allow the combustion reaction to proceed more quickly and at a higher rate, as there are more molecules available to support the chemical reaction.

2. Increased Rate of Combustion:

- Combustion is a chemical reaction between the fuel (in this case, wood) and oxygen. The reaction rate increases when the concentration of oxygen is higher.
- Since the combustion of wood involves breaking bonds in the wood's cellulose structure, more oxygen molecules allow the reaction to happen more efficiently and rapidly.

The general combustion reaction of wood (which primarily consists of cellulose) is:



In pure oxygen, this reaction can proceed much faster than in air.

j. A catalyst lowers the activation energy of a chemical reaction. Illustrate it.

Ans. A catalyst is a substance that lowers the activation energy of a chemical reaction, thereby increasing the reaction rate without being consumed in the process.

k. The rate constant for a certain reaction is $3.5 \times 10^{-4} \text{ s}^{-1}$ at 25°C . What is the order of the reaction? Explain based on the units of the rate constant.

Ans. It seems to be a reaction with a given rate constant ($k = 3.5 \times 10^{-4} \text{ s}^{-1}$) at a specific temperature (25°C). This rate constant suggests that the reaction may follow first-order kinetics, where the rate of reaction depends linearly on the concentration of the reactant.

Here are some key points about rate constants and their interpretation:

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

First-Order Kinetics:

For a reaction with first-order kinetics, the rate law is given by:

$$\text{rate} = k[A]$$

where:

- k is the rate constant (in this case, $3.5 \times 10^{-4} \text{ s}^{-1}$)
- $[A]$ is the concentration of the reactant.

The units of k for a first-order reaction are s^{-1} seconds inverse, which is consistent with the given rate constant.

"The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction."

OR

"The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction."

Order of a reaction decides the units of rate constant a reaction.

Explanation:

The units of the rate constant (k) reveal the reaction order:

- First-order (s^{-1}): Rate depends linearly on concentration (Rate = $k[A]$).
- Second-order ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$): Rate depends on concentration squared (Rate = $k[A]^2$).
- Zero-order ($k = \text{mol} \cdot \text{dm}^{-3} \text{ s}^{-1}$): Rate is independent of concentration.

l. If the initial concentration of the reactant is 0.50 mol dm^{-3} , calculate the initial rate of the reaction.

Ans. For a first-order reaction, the rate law is:

$$\text{Rate} = k[A]$$

Where:

- Rate is the initial rate of the reaction,
- k is the rate constant (given as $3.5 \times 10^{-4} \text{ s}^{-1}$)
- $[A]$ is the initial concentration of the reactant (given as 0.50 mol/dm^3).

Substitute the Given Values:

$$\text{Rate} = (3.5 \times 10^{-4} \text{ s}^{-1}) \times (0.50 \text{ mol/dm}^3)$$

$$\text{Rate} = 1.75 \times 10^{-4} \text{ mol/dm}^3 \text{ s}$$

m. How would the rate of this reaction change if the concentration of the reactant were doubled?

Ans. The reaction is first-order, the rate is directly proportional to the concentration of the reactant.

Rate law:

$$\text{Rate} = k[A]$$

If the initial concentration is doubled, say from $[A]$ to $2[A]$, then:

$$\text{New rate} = k(2[A]) = 2 \cdot (k[A]) = 2 \times \text{original rate}$$

n. A certain first-order reaction has a rate constant of $2.5 \times 10^{-3} \text{ s}^{-1}$. Calculate the half-life of the reaction in minutes.

Ans. Half-life formula (for first-order reactions):

$$t_{1/2} = \ln 2 / k$$

Where:

$$t_{1/2} = \text{half-life,}$$

$$\ln 2 \approx 0.693$$

$$k = 2.5 \times 10^{-3} \text{ s}^{-1}$$

$$\text{Calculate in seconds: } t_{1/2} = 0.693 / 2.5 \times 10^{-3} = 277.2 \text{ seconds}$$

$$\text{Convert seconds to minutes: } t_{1/2} = 277.2 / 60 \approx 4.62 \text{ minutes}$$

o. A radioactive isotope decays by a first-order process with a half-life of 12 hours. Calculate the rate constant for the decay in s^{-1} .

$$\text{Ans. } k = \ln 2 / t_{1/2}$$

$$\text{Given: } t_{1/2} = 12 \text{ hours}$$

$$\text{Convert to seconds: } 12 \text{ hours} = 12 \times 60 \times 60 = 43,200 \text{ s}$$

$$k = 0.693 / 43,200 \text{ s} \approx 1.60 \times 10^{-5} \text{ s}^{-1}$$

The rate constant k is approximately $1.60 \times 10^{-5} \text{ s}^{-1}$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

DESCRIPTIVE QUESTIONS

Q.3 Relate the order of a reaction to the rate law for the reaction. How do you distinguish between zero order, first order and second order reaction?

Ans. See Page No. (232)

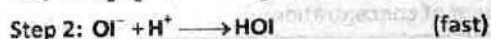
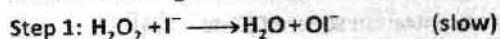
Q.4 How do you find the numerical value of a rate constant by initial and half-life methods?

Ans. See Page No. (237)

Q.5 How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?

Ans. See Page No. (230)

Q.6 The reaction between hydrogen peroxide (H_2O_2) and iodide ions (I^-) in acidic solution is believed to occur via the following mechanism:



- Write the overall balanced equation for the reaction.
- Identify any intermediates and catalysts in this mechanism.
- What is the rate-determining step?
- Write the rate equation for the reaction, expressing it in terms of the reactants in the overall reaction.

Ans. See Quick Check 7.9

(ii) Possible Intermediates:

- Hypoiodous Acid (HOI) – May form transiently during iodide oxidation.
- Iodine Radical (I^*) – A short-lived species in electron transfer steps.

And Catalysts for This Mechanism:



NUMERICAL PROBLEMS

Q.6 Calculate the reaction rate if the concentration of A is 0.5 M, the concentration of B is 0.2 and the rate constant k is $4.0 \text{ M}^{-2}\text{s}^{-1}$. Given the rate law for a reaction: $\text{Rate} = k[\text{A}][\text{B}]^2$.

Given Data: Rate law = $k[\text{A}][\text{B}]^2$
Rate constant (k) = $4.0 \text{ M}^{-2}\text{s}^{-1}$
Concentration of A ([A]) = 0.5 M
Concentration of B ([B]) = 0.2 M

To find: Reaction rate = ?

Solution:

The rate of the reaction is given by:

$$\text{Rate} = k[\text{A}][\text{B}]^2$$

Substitute the Given Values

$$\text{Rate} = (4.0 \text{ M}^{-2}\text{s}^{-1}) \times (0.5 \text{ M}) \times (0.2 \text{ M})^2$$

Now, multiply all the terms step by step:

$$\text{Rate} = 4.0 \times 0.5 \times 0.04$$

$$\text{Rate} = 0.08 \text{ Ms}^{-1}$$

The reaction rate is: 0.08 M s^{-1}

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Q.7 A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14} \text{ s}^{-1}$. Find the half-life of the reaction.

Temp. (K)	Rate constant ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)(K)
500	6.814×10^{-4}
550	2.64×10^{-2}
600	0.56×10^0
650	7.31×10^0
700	66.67×10^0

Given Data: Rate constant (k) = $5.5 \times 10^{-14} \text{ s}^{-1}$

Reaction order = First-order

To find: Half-life ($t_{1/2}$) = ?

Solution:

Step 1 write formula

For a first-order reaction, the half-life is given by:

$$t_{1/2} = \frac{\ln(2)}{k}$$

where:

- $\ln(2) \approx 0.693$
- k is the rate constant.

Step 2: Substitute the Given Rate Constant

By putting the value of k :

$$t_{1/2} = \frac{0.693}{5.5 \times 10^{-14} \text{ s}^{-1}}$$

Step 3: Calculation

$$t_{1/2} = 1.26 \times 10^{13} \text{ s}$$

Answer: The half-life of the reaction is $1.26 \times 10^{13} \text{ s}$.

Q.8 Three experiments that have identical conditions were performed to measure the initial rate of the reaction. $2\text{HI}_{(g)} \longrightarrow \text{H}_{2(g)} + \text{I}_{2(g)}$

Experiment	[HI](M)	Rate (M/s)
1.	0.015	1.1×10^{-3}
2.	0.030	4.4×10^{-3}
3.	0.045	9.9×10^{-3}

Write the rate law for the reaction. Find the value and units of the specific rate constant, k .

Given Reaction:



Step 1: Rate Law Form

$$\text{Rate} = k[\text{HI}]^n$$

Use the data to find the order n .

Step 2: Determine Reaction Order (n)

Use experiments 1 and 2:

- Exp 1: $[\text{HI}] = 0.015$ Rate = 1.1×10^{-3}
- Exp 2: $[\text{HI}] = 0.030$ Rate = 4.4×10^{-3}

$$\frac{4.4 \times 10^{-3}}{1.1 \times 10^{-3}} = \left(\frac{0.030}{0.015} \right)^n \Rightarrow 4 = 2^n \Rightarrow n = 2$$

Order = 2

Step 3: Rate Law

$$\text{Rate} = k[\text{HI}]^2$$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

Step 4: Rate constant (k)

Use any experiment (e.g., Exp 1):

$$\begin{aligned}\text{Rate} &= k[\text{HI}]^2 \\ 1.1 \times 10^{-3} &= k(0.015)^2 \\ k &= \frac{1.1 \times 10^{-3}}{0.000225} \approx 4.89 \text{ M}^{-1} \text{ s}^{-1}\end{aligned}$$

Answer:

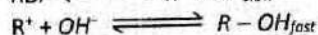
- **Rate Law:** $\text{Rate} = k[\text{HI}]^2$
 $k = 4.89 \text{ M}^{-1} \text{ s}^{-1}$
- **Order:** Second order

ADDITIONAL SLOs BASED MCQs

1. The rate of a reaction ----- as the reaction proceeds.
 - A. Increases
 - B. Decreases
 - C. Remains the same
 - D. May increase or decrease
2. The unit of the rate constant is the same as that of the rate of reaction in ----- order reaction.
 - A. First
 - B. Second
 - C. Third
 - D. Zero
3. For the reaction:
 $2\text{A} + \text{B} \xrightarrow{\text{slow}} \text{C}$, the rate law for the reaction is
 - A. $\text{rate} = k[\text{A}]^2 [\text{B}]$
 - B. $\text{rate} = k[\text{A}][\text{B}]$
 - C. $\text{rate} = k[\text{C}]$
 - D. None of these
4. For the reaction: $2\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$
The expression for the rate law is, $\text{rate} = k[\text{A}]^2$, the order of reaction in B is
 - A. First
 - B. Second
 - C. Third
 - D. Zero
5. The activation energy for a reaction can be:
 - A. Increased by increasing temperature
 - B. Increased by decreasing temperature
 - C. Decreased by increasing concentration of reactants
 - D. None of these
6. Rate law for the reaction
 $\text{R-X} + \text{H}_2\text{O} \rightarrow \text{R-OH} + \text{HX}$ is, $\text{rate} = k[\text{R-X}]$. The rate of reaction will be doubled when
 - A. Concentration of H_2O is doubled
 - B. Concentration of R-X is reduced to half
 - C. Concentration of both R-X and H_2O is doubled
 - D. None of these
7. The rate of a catalyzed reaction is independent of the concentration of
 - A. Reactants
 - B. Products
 - C. Catalyst
 - D. Zero
8. If a reaction proceeds in such a way that order of reaction is independent of the reactants concentration, the overall order of reaction would be
 - A. First
 - B. Second
 - C. Third
 - D. Zero
9. Reactions with high activation energy are usually
 - A. Fast
 - B. Slow
 - C. Exothermic
 - D. Reversible
10. In a reversible reaction, catalyst lowers the activation energy of the
 - A. Forward reaction
 - B. Reverse reaction
 - C. Forward as well as reverse reaction
 - D. Forward reaction but increases for the reverse reaction
11. If rate of reaction doubles for every 10°C rise in temperature what is the increase in rate of reaction if temperature rises from 10°C to 100°C
 - A. 112 times
 - B. 100 times
 - C. 400 times
 - D. 512 times
12. Order of reaction is the number of reacting molecules whose concentration alters as a result of chemical change for which order of reaction the unit of rate constant (k) is the same as that of rate of reaction?
 - A. 1st order reaction
 - B. 2nd order reaction
 - C. Zero order reaction
 - D. 3rd order reaction

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

13. The hydrolysis of $(\text{CH}_3)_3\text{CBr}$ by OH^- ion proceed in two steps:



Which of the following rate equation is consistent with this scheme?

- A. rate = $k[\text{RBr}]^2$ B. rate = $k[\text{RBr}][\text{OH}^-]$ C. rate = $k[\text{RBr}][\text{OH}^-]^2$ D. rate = $k[\text{RBr}]$
14. Which one of the following correctly represents the units of the rate constant k for a first order reaction?
 A. s^{-1} B. $\text{mol dm}^{-3}\text{s}$ C. $\text{mol dm}^{-3}\text{s}^{-1}$ D. $\text{mol}^{-1}\text{dm}^3\text{s}$
15. If the rate of decay of a radioactive isotope decreases from 200 counts per minutes to 25 counts per minute after 24 hours. What is half life?
 A. 3 hours B. 4 hours C. 6 hours D. 8 hours

Answer Key with Explanations

Q.#	Ans.	Explanations
1.	B	The rate of reaction is directly proportional to concentration of reactant. As reaction goes the amount of reactant decrease hence the rate of reaction decreases.
2.	D	$\text{A} \longrightarrow \text{Product}$ Rate = $k[\text{A}]^0$ So, Rate = $k = \text{mol dm}^{-3} \text{s}^{-1}$
3.	A	$2\text{A} + \text{B} \xrightarrow{\text{slow}} \text{C}$ Since two molecules of 'A' and one molecule of 'B' participate, so rate equation will be Rate = $k[\text{A}]^2[\text{B}]$ Order of reaction = $2 + 1 = 3$
4.	D	Rate equation shows that concentration of reactant 'B' does not affect reaction rate. Therefore the order of reaction in 'B' is zero.
5.	B	$k = \text{Ae}^{-\text{E}_a/\text{RT}}$ $\text{E}_a \propto 1/T$
6.	D	(i) Rate $\propto [\text{R} - \text{X}]$. It means when concentration of $\text{R} - \text{X}$ doubles, rate of reaction also doubles. (ii) Concentration of H_2O does not affect the rate of reaction. So to increase rate of reaction, it is not necessary to increase conc. of H_2O .
7.	B	According to Law of mass action: The rate of a chemical reaction is directly proportional to the active mass of the reactant or to the product of active masses if more than one reactants are involved in a chemical reaction. As the concentration of a catalyst increases its catalytic activity also increase.
8.	D	Such a reaction is zero order reaction: $\text{A} + \text{B} \longrightarrow \text{Product}$ Rate = $k[\text{A}]^0[\text{B}]^0$ Order of reaction = zero
9.	B	According to Arrhenius equation: $k = \text{Ae}^{-\text{E}_a/\text{RT}}$ k = Rate of reaction (when molar concentration of reactants are in unity) Rate = $\text{Ae}^{-\text{E}_a/\text{RT}}$ Rate $\propto 1/\text{E}_a$
10.	C	A catalyst cannot affect the equilibrium constant of a reaction but it helps the equilibrium to be established earlier. The rates of forward and backward steps are increased equally.
11.	D	For every 10°C Risk rate of reaction become double temp is increase $10^\circ - 100^\circ (9\text{Time}) 2^9 = 515$ Time rate of reaction will increase
12.	C	$\text{R} = \text{K}[\text{cosec}]^0$ $\frac{\text{mole/dm}^3}{\text{sec}} = k$

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

13.	D	Rate expression is always according to slow step
14.	A	$R = K[\text{conc}]^1$ $\text{mol/dm}^3/\text{sec} = k.\text{mole/dm}^3$ $K = \text{sec}^{-1}$
15.	D	$200 \rightarrow 100 \rightarrow 50 \rightarrow 25$ Total 3 half-life = 24 hours 1 Half-life = 8 hours

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Differentiate between instantaneous and average rate of reaction.

Ans. Differences between Instantaneous and Average Rate of Reaction:

Average Rate	Instantaneous Rate
"The rate at any one instant during the interval is called the instantaneous rate".	"The rate of reaction between two specific time intervals is called average rate".
Instantaneous rate = $\frac{dx}{dt}$	Average rate = $\frac{\Delta x}{\Delta t}$
At first instantaneous rate is higher than average rate.	At the end, average rate is higher than instantaneous rate.

Q.2 Differentiate between rate and rate constant of a reaction.

Ans. Differences between rate and rate constant of a reaction:

Rate of reaction	Rate constant
(i) It is the speed at which the reactants are converted into the products.	It is a constant of proportionality in the rate law expression.
(ii) Rate = $\frac{\Delta x}{\Delta t}$	Rate = $k[\text{Reactants}] \Rightarrow k = \frac{\text{Rate}}{[\text{Reactants}]}$
(iii) It depends upon the concentration of reactant species at that moment.	It refers to the rate of reaction at specific point when concentration of every reacting species is unity.
(iv) It decreases with the progress of reaction generally.	It is a constant and does not depend on the progress of the reaction.

Q.3 Radioactive decay is always first order reaction. Justify.

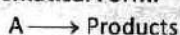
Ans. A radioactive substance has a single species at a moment, whose nucleus under goes disintegration. As only one reactant is involved, so it follows 1st order mechanism.

e.g., Half-life of $^{235}_{92}\text{U}$ is 710 million years. It means if one kg uranium is present at start, after 710 million years, 0.5 kg of it will disintegrate and after next 710 million years 0.25 kg of it will disintegrate and so on. Therefore we can say that half-life of a radioactive decay is always a 1st order reaction.

Q.4 What is zero order reaction? Give one example.

Ans. Zero Order Reaction: "The reaction which is entirely independent of the concentration of reactant molecules is called zero order reaction"

Mathematical Form:



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

$$\text{Rate} = k$$

Example: All photosynthetic reactions are usually zero order reactions.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

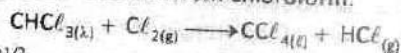
Q.5 The order of reaction may be in fraction. Explain.

Ans. Fractional Order Reaction:

The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value.

Example:

Consider the formation of carbon tetrachloride from chloroform.



$$\text{Rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$$

The sum of exponents will be $1 + 1/2 = 1.5$ so,

Order of reaction = 1.5

Q.6 Differentiate between order of reaction and rate of reaction.

Ans. Order of Reaction:

"The number of reacting molecules whose concentration alters as a result of the chemical change is called order of reaction."

OR

"The sum of all the exponents to which the concentrations in the rate equation are raised is called order of reaction."

Rate of Reaction:

(i) It is the speed at which the reactants are converted into the products.

(ii) $\text{Rate} = \frac{\Delta x}{\Delta t}$

(iii) It depends upon the concentration of reactant species at that moment.

(iv) It decreases with the progress of reaction generally.

Q.7 Define half-life period of a reaction. Give one example.

Ans. Half-Life Period:

"The time which is required to convert 50% of the reactants into products is called half-life period ($t_{1/2}$)."

Example:

Decomposition of N_2O_5

The half-life period for the decomposition of N_2O_5 at 45°C is 24 minutes.



Importance:

- We can use the rate of decay of an item to determine the age of item.
- We can predict the amount of radioactive material that will remain after a given amount of time.

Half-Life and Order of Reaction:

"Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction."

$$[t_{1/2}] \propto \frac{1}{a^{n-1}}$$

Half-Life and 2nd Order of Reaction:

For Second Order Reaction: $n = 2$

$$[t_{1/2}]_2 \propto \frac{1}{a^{2-1}} \text{ or } [t_{1/2}]_2 \propto \frac{1}{a^1}; \quad \text{Since } [t_{1/2}]_2 = \frac{1}{ka}$$

Note: In case of second order reaction, the half-life period is inversely proportional to the initial concentration of the reactant.

Half-Life and 3rd Order of Reaction:

For Third Order Reaction: $n = 3$

$$[t_{1/2}]_3 \propto \frac{1}{a^{3-1}} \text{ or } [t_{1/2}]_3 \propto \frac{1}{a^2}; \quad \text{Since } [t_{1/2}]_3 = \frac{1.5}{ka^2}$$

For a third order reaction, the half-life period is inversely proportional to the square of initial concentration of reactants.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

254

Q.8 What is rate determining step? Give a suitable example.

Ans. Rate Determining Step:

"A slowest step in reaction mechanism which can determine the overall rate of reaction is called rate determining step."

Rate Determining Step:

"Rate-determining step is that step of a chemical reaction which controls the rate of reaction."

- If a reaction occurs in several steps, one of the steps is the slowest.
- The rate of this step determines the overall rate of reaction.
- This slowest step is called the rate determining or rate limiting step.
- The total number of molecules taking part in the rate determining step appear in the rate equation of the reaction.
- Let us consider the following reaction



The rate equation of the reaction is found to be:

$$\text{Rate} = k[\text{NO}_2]^2$$

- The reaction is second order with respect to $\text{NO}_2(\text{g})$. Experiment shows that $\text{CO}(\text{g})$ is not taking part in the rate determining step. The proposed mechanism for this reaction is as follows:

Step 1: $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \xrightarrow{\text{Slow}} \text{NO}_3(\text{g}) + \text{NO}(\text{g})$ (It is a slow hence rate determining step)

Step 1: $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \xrightarrow{\text{fast}} \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$

- The first step is the rate determining step and NO_3 which does not appear in the balanced equation, is called the reaction intermediate.
- The reaction intermediate has a temporary existence and it is unstable relative to the reactants and the products.

Q.9 Differentiate between fast step and the rate determining step.

Ans.	Fast Step	Rate Determining Step
i.	A step in a chemical reaction which proceeds so fastly that we are unable to determine the rate of reaction is called fast step. It has no effect on overall rate of reaction.	A slowest step in reaction mechanism which can determine the overall rate of reaction is called rate determining step.
ii.	For example: For a reaction $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{g}) + \text{N}_2(\text{g})$ The steps of reaction mechanisms are a. $2\text{NO}(\text{g}) + \text{H}_2 \xrightarrow{\text{Slow}} \text{H}_2\text{O}_2(\text{g}) + \text{N}_2(\text{g})$ b. $\text{H}_2(\text{g}) + \text{H}_2\text{O}_2(\text{g}) \xrightarrow{\text{fast}} 2\text{H}_2\text{O}(\text{g})$ Step (b) is fast step.	In the example given in left column, step (a) is the rate determining step. $2\text{NO}(\text{g}) + \text{H}_2(\text{g}) \xrightarrow{\text{slow}} \text{H}_2\text{O}_2(\text{g}) + \text{N}_2(\text{g})$ It is experimentally determined. It involves 2 moles NO and one mole H_2 .
iii.	Reactants of fast step are eliminated from rate equation. Moreover, in a multistep reaction, number of fast steps can be one or more than one.	Reactants of slow step are present in rate equation i.e., $\text{Rate} = k[\text{H}_2][\text{NO}]^2$. Moreover there is only one rate determining step in a multistep reaction.
iv.	Fast step is unable to determine order of reaction.	Sum of reactant coefficients of slowest step is the order of reaction. e.g. in the above reaction: Order of reaction = $2 + 1 = 3$.

Q.10 The sum of the co-efficient of a balanced chemical equation is no necessarily important to give the order of reaction. Give reasons in support of your answer.

Ans. Order of a chemical reaction is not necessarily the sum of the coefficients of the balanced chemical equation because the order of reaction is determined experimentally and not from the balanced chemical equation.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

e.g., $2\text{H}_2 + 2\text{NO}_2 \longrightarrow 2\text{H}_2\text{O}_2 + \text{N}_2$

For this reaction, the sum of coefficients of balanced equation is $2 + 2 = 4$ but the reaction is 3rd order. It is experimentally verified that rate of reaction is directly related to conc. of H_2 and to the square of concentration of NO_2 . So the rate equation of this reaction is

$$\text{Rate} \propto [\text{H}_2]^1 [\text{NO}_2]^2$$

$$\text{Rate} = k[\text{H}_2]^1 [\text{NO}_2]^2$$

Order of reaction is sum of exponents of rate equation. So,

$$\text{Order of reaction} = 1 + 2 = 3$$

Q.11 Define energy of activation. How is it affected by temperature?

Ans. Energy of Activation:

The minimum amount of energy in addition to average kinetic energy which is just sufficient to convert the reactants into products is called energy of activation (E_a).

Effect of Temperature:

According to Arrhenius Equation:

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

k is exponentially related to activation energy E_a and temperature T . The equation shows that the increase in temperature, increase the rate constant and the reaction of high activation energy have low " k " values. It means that if we increase the temperature the activation energy of the reaction decreases.

Activated complex is an unstable combination of all the atoms involved in the reaction for which the energy is maximum. It is a short lived species and decomposes into products immediately. It has a transient existence that is why it is also called a transition state.

Q.12 Describe Half Life Method to determine order of reaction.

Ans. Half-Life Method:

"Half-life of a reaction is inversely proportional to the initial concentration of reactants raised to the power one less than the order of reaction."

$$[t_{1/2}] \propto \frac{1}{a^{n-1}}$$

Let us perform a reaction twice by taking two different initial concentrations a_1 and a_2 and their half-life periods are found to be t_1 and t_2 respectively.

$$t_1 \propto \frac{1}{a_1^{n-1}} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}}$$

Dividing the above two equations:

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1} \right)^{n-1}$$

Taking log on both sides, we have

$$\log \left(\frac{t_1}{t_2} \right) = \log \left[\left(\frac{a_2}{a_1} \right)^{n-1} \right]$$

$$\log \left(\frac{t_1}{t_2} \right) = (n-1) \log \left(\frac{a_2}{a_1} \right)$$

$$n = 1 + \frac{\log \frac{t_1}{t_2}}{\log \frac{a_2}{a_1}}$$

Where,

n = order of reaction

Q.13 Define Catalysis. Write two characteristics of a catalyst.

Ans. Catalysis:

"The process, which takes place in the presence of a catalyst, is called catalysis."

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

256

Characteristics of a Catalyst:

1. Unchanged Chemical Composition:

A catalyst remains unchanged in mass and chemical composition at the end of reaction. It may not remain in the same physical state.

Examples:

- (i) MnO_2 is added as a catalyst for the decomposition of KClO_3 . But MnO_2 is regenerated at the end in the form of a fine powder.
- (ii) In some cases, the shining surfaces of the solid catalyst become dull.

2. Effectiveness of a Catalyst:

Sometimes, we use a trace of a metal catalyst to effect very large amount of reactants.

Examples:

- (i) 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.
- (ii) Dry HCl and NH_3 don't combine, but in the presence of trace of moisture, they give dense white fumes of NH_4Cl .
- (iii) Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.

Q.14 Define catalysis. Give its different types with one example in each case.

Ans. Catalysis:

"The process, which takes place in the presence of a catalyst, is called catalysis."

Types of Catalysis:

(a) Homogeneous Catalysis

(a) Homogeneous Catalysis:

"When the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout, then it is called homogeneous catalysis."

The catalyst is distributed uniformly throughout the system.

Examples:

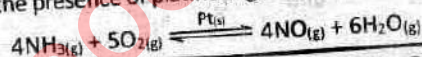
The formation of SO_3 from SO_2 and O_2 in the lead chamber process for the manufacture of sulphuric acid needs NO as a catalyst. Both the reactants and the catalyst are gases.

(b) Heterogeneous Catalysis:

"When the catalyst and the reactants are in different phases, then it is called heterogeneous catalysis."

Examples:

Oxidation of ammonia to NO in the presence of platinum gauze helps us to manufacture HNO_3 .



Q.15 Differentiate between homogeneous and heterogeneous catalysis. Give example.

Ans.

Homogeneous Catalysis	Heterogeneous Catalysis
(i) It is catalysis in which the catalyst and reacting substances are in same physical state/phase.	(i) It is catalysis in which the catalyst and reacting substances are in different phases.
(ii) Catalyst is uniformly distributed.	(ii) No uniform distribution of catalyst.
(iii) Mostly liquid or gaseous catalysts are used in homogeneous catalysis.	(iii) Catalyst is solid and reacting substances are either liquids or gases.
(iv) e.g., $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{\text{NO}(\text{g})} 2\text{SO}_3(\text{g})$	(iv) e.g., $4\text{NH}_3(\text{g}) + 5\text{O}_2(\text{g}) \xrightarrow{\text{Pt(s)}} 4\text{NO}(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

Q.16 Describe the effects of catalyst on reversible reaction.

Ans. Effect of Catalyst on Rate of Reversible Reaction:

In reversible chemical reaction, a catalyst, suitable for forward reaction may be used to carry out back reaction as it increases the rate of both forward and reverse processes by lowering the activation energy of both forward and reverse steps by giving new path to the reaction. This reduces the time to attain the equilibrium state. It does not affect the equilibrium state K_c .

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

SELF-ASSESSMENT

Chapter # 07

Q.1 Encircle the correct option.

Total Mark: 30

(1 × 6 = 6)

- (i) The rate of reaction:
- Increases as the reaction proceeds
 - Decreases as the reaction proceeds
 - Remains the same as the reaction proceeds
 - May decrease or increase as the reaction proceeds
- (ii) On a Boltzmann distribution curve, the area under the curve represents:
- Activation energy of the reaction.
 - Total number of molecules in the sample.
 - Average kinetic energy of the molecules.
 - Rate constant of the reaction.
- (iii) How does the presence of a catalyst affect the rate of a chemical reaction?
- It always decreases the rate of the reaction.
 - It always increases the rate of the reaction.
 - It increases the rate of the forward and decreases the rate of the reverse reaction.
 - It increases the rate of both the forward and reverse reactions.
- (iv) A first-order reaction has a half-life ($t_{1/2}$) of 20 minutes. What is the value of its rate constant (k)?
- 0.05 min^{-1}
 - 0.693 min^{-1}
 - 0.0347 min^{-1}
 - 13.86 min^{-1}
- (v) The reaction pathway diagram with a lower peak represents:
- A slower reaction
 - A reaction with no catalyst
 - A catalyzed reaction
 - A reversible reaction
- (vi) The order of a chemical reaction, that is independent of concentration is:
- Second order reaction
 - First order reaction
 - Zero order reaction
 - Pseudo first order reaction

Q.2 Write short answers of the following questions.

(2 × 8 = 16)

- Differentiate clearly between order and molecularity of a reaction.
- How does increasing temperature affect the rate of a reaction?
- What is the significance of the rate constant in a rate equation?
- Can a catalyst be consumed in a chemical reaction? Why or why not?
- The shape of the Boltzmann distribution curve change with temperature. How?
- What is the order of the reaction? Explain based on the units of the rate constant.
- Calculate the rate of reaction from the following data: 0.5 mol of reactant consumed in 10 s.
- A radioactive isotope decays by a first-order process with a half-life of 12 hours. Calculate the rate constant for the decay in s^{-1} .

Q.3 Extensive Questions.

(2 × 4 = 8)

- How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?
- Calculate the reaction rate if the concentration of A is 0.5 M, the concentration of B is 0.2 and the rate constant k is $4.0 \text{ M}^{-2}\text{s}^{-1}$. Given the rate law for a reaction: $\text{Rate} = k[\text{A}][\text{B}]^2$.

CHEMISTRY NOTES FOR CLASS - 11 (FOR PUNJAB)

=====

17

