Q.10 For the reaction: $CaSO_{4(s)} \longrightarrow Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

Calculate $\Delta H^\circ, \Delta S^\circ$ and ΔG° at $25^\circ C$ using the following data; and discuss its spontaneity.

Enthalpy of Formation:

$$\Delta H^\circ_{f(CaSO_4(s))} = -1432.7\ kJ, \Delta H^\circ_{f(Ca^{2+}(aq))} = -543.0 kJ, \Delta H^\circ_{f(SO_4^{2-}(aq))} = -907.5 kJ$$

[Standard entropy: $S^\circ_{(CaSO_4(s))} = 106.7\ J/K, S^\circ_{f(Ca^{2+}(aq))} = -55.2\ J/K, S^\circ_{f(SO_4^{2-}(aq))} = +17.2\ J/K$

Given Data:

Enthalpies of Formation (ΔH_f°):

- $\Delta H_f^\circ (CaSO_{4(s)}) = -1432.7$ kJ/mol
- $\Delta H_f^\circ (Ca^{2+}{}_{(aq)}) = -543.0$ kJ/mol
- $\Delta H_f^\circ(SO_4^{2-}{}_{(aq)}) = -907.5$ kJ/mol

Reaction:

$$CaSO_{4(s)} \rightarrow Ca^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Step 1: Calculate ΔH° (Enthalpy Change)

Using Hess's Law:

$$\Delta H^\circ_{reaction} = \sum\Delta H_f^\circ(products) - \sum\Delta H_f^\circ\ reactants)$$
$$\Delta H^\circ_{reaction} = [\Delta H_f^\circ (Ca^{2+}) + \Delta H_f^\circ (SO_4^{2-})] - [\Delta H_f^\circ (CaSO_4)]$$
$$\Delta H^\circ_{reaction} = [(-543.0) + (-907.5)] - [-1432.7]$$
$$\Delta H^\circ_{reaction} = -1450.5 + 1432.7 = -17.8\ kJ/mol$$

(Negative sign indicates the reaction is **exothermic**.)

Step 2: Calculate ΔS° (Entropy Change)

Using standard entropies:

$$\Delta S^\circ_{reaction} = \sum S^\circ_{(products)} - \sum S^\circ_{(reactants)}$$
$$\Delta S^\circ_{reaction} = [S^\circ (Ca^{2+})) + S^\circ (SO_4^{2-})] - [S^\circ (CaSO_4)]$$
$$\Delta S^\circ_{reaction} = [(-55.2) + (17.2)] - [106.7]$$
$$\Delta S^\circ_{reaction} = -38.0 - 106.7 = -144.7$$

(Negative sign means the system becomes **more ordered**.)

Step 3: Calculate ΔG° (Gibbs Free Energy Change)

Using the Gibbs-Helmholtz equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S$$

Convert units for consistency:

$$\Delta H^\circ = -17.8\ kJ/mol = -17{,}800\ J/mol$$

Substitute values at T = 298 K

$$\Delta G^\circ = -17{,}800 - (298 \times -144.7)$$
$$\Delta G^\circ = -17{,}800 + 43{,}120.6 = +25{,}320.6\ J/mol$$
$$\Delta G^\circ = +25.32\ kJ/mol$$

(Positive sign means the reaction is **non-spontaneous** at 25°C.)

- **$\Delta H^\circ = -17.8$ kJ/mol** (Exothermic, favorable)
- **$\Delta S^\circ = -144.7$ J/K·mol** (Decrease in entropy, unfavorable)
- $\Delta G^\circ = +25.32$ kJ/mol (Positive, non-spontaneous at 25°C)

ADDITIONAL SLOs BASED MCQs

1. **Which of the following substances have zero value for their standard enthalpy of formation?**
A. O_3 B. H_2O C. ZnO D. None of these

2. **Calorie is equivalent to:**
A. 4.18J B. 4.18kJ C. 0.418J D. 0.418kJ

3. **Enthalpy of neutralization of all the strong acids and strong basis has the same value due to:**
A. The formation of salt and water
B. The formation of salt
C. The complete ionization of acids and bases
D. The combination of H^+ and OH^- ions to form water

4. **Total heat content of a system is called:**
A. Enthalpy B. Internal energy C. Heat D. State function

5. **Heat of______ a substance is always negative:**
A. Formation B. Combustion C. Decomposition D. Solution

6. **A balloon filled with oxygen is placed in a freezer. Identify system:**
A. Balloon B. Oxygen C. Freezer D. All of these

7. **A bomb calorimeter is used in _____ calorimetry:**
A. Constant volume B. Constant pressure C. Both a and b D. Constant temperature

8. **Born Haber cycle is used to determine lattice energies of:**
A. Molecular solids B. Ionic solids C. Covalent solids D. Metallic solids

9. **Enthalpy of combustion for C is $-393.5\ kJ\ mol^{-1}$**
$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$
$\Delta H^\circ_{Combustion} = -393.5\ kJmol^{-1}$
Enthalpy of formation of CO_2 would be:
A. +393.5 kJ
B. −393.5 kJ
C. Zero
D. Cannot be predicted form the given equation

10. **Which of the following is not a state function of a system:**
A. Thermal energy at constant pressure
B. Enthalpy
C. Internal energy
D. Work done

11. **For writing a thermochemical equation for enthalpy of combustion of an element requires:**
A. 1 mole of element as reactant
B. 1 mole of oxide of element as product
C. Standard states of all the substances
D. Balanced equation of 1 mole of element

12. **For the reaction $NaCl_{(s)} \xrightarrow{water} Na^+_{aq} + Cl^-_{aq}$ the change in enthalpy is called:**
A. Heat of reaction B. Heat of formation C. Heat of combustion D. Heat of solution

13. **Which one of the following equations correctly defines the enthalpy change of formation of carbon monoxide?**
A. $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$
B. $C_{(s)} + O_{(g)} \longrightarrow CO_{(g)}$
C. $C_{(s)} + CO_{2(g)} \longrightarrow 2CO_{(g)}$
D. $C_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$

14. **ΔH will be given a negative sign in:**
A. Exothermic reactions
B. Dissociation reactions
C. Decomposition reactions
D. Endothermic reactions

15. **Hess's law may be represented mathematically as:**
A. $\Sigma\Delta H \neq 0$ B. $\Sigma\Delta G > 0$ C. $\Sigma\Delta H = 0$ D. $\Sigma\Delta H < 0$

Answer Key with Explanations

Q.#	Ans.	Explanations
1.	C	The standard enthalpy of formation of an element in molecular form is zero. Ozone (O_3) is molecular form of oxygen so its standard enthalpy of formation is zero.
2.	A	1 Calorie = 4.184 Joules 1J = 0.2390 cal
3.	D	Enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components. $H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$ $\Delta H^\circ_n = -57.4$ kJ mol^{-1} Enthalpy of neutralization for any strong acid with a strong base is approximately the same i.e. -57.4 kJ mole^{-1}.
4.	A	The sum of internal energy (E) and the product of pressure and volume (PV) is called enthalpy of the system." $H = E + PV$ • Enthalpy is a state function. • Enthalpy is measured in "Joules."
5.	B	All combustion reactions are exothermic in nature so enthalpy of combustion is always negative.
6.	B	Oxygen is the system while balloon, freezer etc are surroundings.
7.	A	Constant volume calorimetry is used for accurate determination of the enthalpy of combustion for food, fuel and other compounds. A bomb calorimeter is used for this purpose. Chemical reaction in a bomb calorimeter takes place under constant volume conditions.
8.	B	Born Haber cycle is used to calculate lattice energy of binary ionic compounds like M^+X^-.
9.	B	The given reaction is combustion of carbon as well as formation of CO_2 from its elements. So 393.5 kJ mol^{-1} is not only enthalpy of combustion of carbon but also enthalpy of formation of CO_2
10.	D	Work done depends upon path adopted to bring about change, so it is not state function. Similarly, heat, emf of cell are also not state functions.
11.	D	For writing thermochemical equation for enthalpy of combustion: (I) Write I mole of the element of compound and oxygen as reactant. (ii) Write oxides of the given element or oxides of elements present in the compound as products. (iii) Show standard states of all the substances. (iv) Finally, balance the atoms.
12.	D	1 mol of ionic solid is completely dissolved in minimum amount of H_2O so energy change is called enthalpy of solution.
13.	A	According to definition 1mol of CO is being formed from element in their standard state.
14.	A	For exothermic reaction, enthalpy of reaction is shown by negative sign.
15.	C	Definition of Hess's law, summation of enthalpies of cyclic process must be equal to zero.

ADDITIONAL SHORT ANSWER QUESTIONS

Q.1 Define electron affinity. Give example.

Ans. Electron Affinity (ΔH°_{ea})

The **first electron affinity** is the enthalpy change involved when 1 mole of electrons is added to 1 mole of gaseous atoms to form 1 mole of gaseous uni-negative ions under standard conditions.

Example:

Electron affinity of chlorine atom.

$$Cl_{(g)} + e^- \longrightarrow Cl^- \qquad \Delta H = -348.8 \text{ kJ mol}^{-1}$$

Since, energy is released, so first electron affinity carries negative sign.

Q.2 What is calorie content?

Ans. **Calorie content:** The calorie content of food is a measure of the energy **'released'** when the food is completely consumed in the body.

- This energy is typically expressed in units of kilocalories (k cal) or joules (J).

Q.3 What is meant by lattice energy? Give example.

Ans. Lattice Energy (ΔH_{latt})

"The lattice energy of an ionic crystal is the enthalpy change involved when one mole of the ionic compound is formed from gaseous ions under standard conditions."

Example:

$$Na^+_{(g)} + Cl^-_{(g)} \longrightarrow NaCl_{(s)} \qquad \Delta H = -747 \text{kJmol}^{-1}$$

Q.4 What do you know about entropy?

Ans. Entropy is a measure of the number of ways energy can be distributed within a system at a specific temperature.

(OR)

Entropy can also be thought of as a measure of the randomness or disorder of a system.

- When the energy is distributed in more ways, a system is more stable.
- The higher the randomness or disorder, the greater the entropy of the system.

Q.5 The sign of change in free energy (ΔG) of a process can be used to predict the spontaneity of that process. How?

Ans. The sign of change in free energy (ΔG) of a process can be used to predict the spontaneity of that process, when;

(i) **If $\Delta G < 0$ (–ve),** the given process may occur spontaneously

(ii) **If $\Delta G > 0$ (+ve),** the indicated process cannot occur spontaneously; instead, the reverse of it may occur.

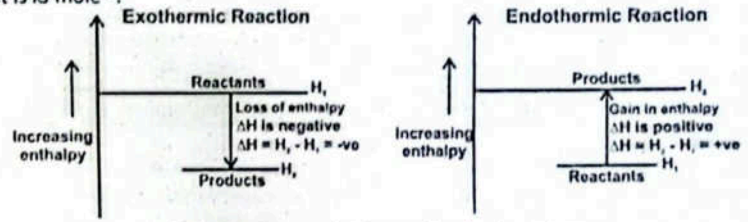
(iii) **If $\Delta G = 0$,** neither the indicated process nor reverse of it can occur spontaneously. The system is in a state of equilibrium

Q.6 Define: (I) Standard Enthalpy of reaction with one example.
(II) Enthalpy of a system with an example.

Ans. (I) Standard Enthalpy of a Reaction:

"The enthalpy change which occurs when the certain number of moles of reactants react together completely to give the products under standard conditions i.e. 25°C (298K) and one atmosphere pressure is called standard enthalpy of reaction." It is represented by ΔH°. All the reactants and products must be in their standard physical states.

- Its unit is kJ mole^{-1}.



Enthalpy changes in thermochemical reactions

Example:

$$H_{2(g)} + 1/2\, O_{2(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H^\circ = -285.8 \text{ kJ mol}^{-1}$$

-285.8kJ mol^{-1} is standard enthalpy of reaction.

(ii) Enthalpy of the system:

"The sum of internal energy (E) and the product of pressure and volume (PV) is called enthalpy of the system."

Formula: $H = E + PV$

Q.7 Define enthalpy of formation (ΔH_f°). Give two example.

Ans. Enthalpy of Formation (ΔH_f°):

"The amount of heat evolved or absorbed when one mole of compound is formed from its elements under standard conditions of temperature and pressure is called standard enthalpy of formation (ΔH_f°) of a compound."

- All the substances involved are in their standard physical states.
- The reaction is carried at standard conditions i.e. at 25oC (298K) and one atmospheric pressure.

Examples: (i) $Mg_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow MgO_{(s)} \quad \Delta H_f^\circ = -692\ kJ\ mol^{-1}$

(ii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_f^\circ = -393.7\ kJ\ mol^{-1}$

Q.8 State with one example enthalpy of combustion.

Ans. Enthalpy of Combustion:

"The amount of heat evolved when one mole of a substance is completely burnt in excess of oxygen under standard conditions is called standard enthalpy of combustion of a substance (ΔH_c°)."

- Its unit is kJ mol⁻¹.

Example:

Standard enthalpy of ethanol is –1368 kJ mol⁻¹.

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \qquad \Delta H_c^\circ = -1368\ kJ\ mol^{-1}$$

Enthalpy of Solution:

"The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change is called standard enthalpy of solution (ΔH_{sol}°)."

- Its unit is kJ mol⁻¹.

Examples: (i) Enthalpy of a solution of NH_4Cl = +16.2 kJ mol⁻¹.

(ii) Enthalpy of solution of Na_2CO_3 = –25.0 kJ mol⁻¹.

Q.9 Define enthalpy of neutralization. Why is enthalpy of neutralization of strong acid and strong base is always –57.5 kJ mol⁻¹?

Ans. Enthalpy of Neutralization:

Enthalpy of neutralization is the amount of heat evolved when one mole of hydrogen ions H^+ from an acid, react with one mole of hydroxide OH^- ions from a base to form one mole of water.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \quad \Delta H = -57.4\ kJ\ mol^{-1}$$

All strong acids and bases ionize completely in aqueous solutions providing equal number of H^+ and OH^- ions depending upon concentration of solutions.

So a net result of neutralization is just the formation of water from its ionic components.

For all strong acids and bases with equimolar concentrations of ions, the value of heat of neutralization is same i.e., –57.4 kJ mol⁻¹ or 13.2 Kcal mol⁻¹,

Q.10 Define the terms standard enthalpy of neutralization and standard enthalpy of atomization.

Ans. Enthalpy of Neutralization:

"The amount of heat evolved when one mole of hydrogen ions (H^+) from an acid, react with one mole of hydroxide ions (OH^-) from a base to form one mole of water under standard conditions is called standard enthalpy of neutralization (ΔH_n°)."

Example:

A strong acid HCl and a strong base NaOH ionize completely in dilute solutions as follows:

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

$$NaOH_{(aq)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$

When these solutions are mixed together during the process of neutralization, the only change that actually occurs is the formation of water molecules leaving the sodium ions and the chloride ions as free ions in solution. Thus, enthalpy of neutralization is merely the heat of formation of one mole of liquid water from its ionic components.

$$H^+_{(aq)} + Cl^-_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)} \quad \Delta H_n^\circ = -57.4\ kJ\ mol^{-1}$$

Enthalpy of neutralization for any strong acid with a strong base is approximately the same.

i.e. –57.4 kJ mole⁻¹.

Enthalpy of Atomization:

"The amount of heat absorbed when one mole of gaseous atoms is formed from the element under standard conditions is called standard enthalpy of atomization of that element (ΔH_{at}°)."

- Its unit is kJ mol⁻¹.

Example: The standard enthalpy of atomization of hydrogen is

$$\tfrac{1}{2}H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H_{at}^\circ = 218\ kJ\ mol^{-1}$$

A wide range of experimental techniques are available for determining enthalpies of atomization of elements.

Q.11 Define Hess's law of constant heat summation.

Ans. Hess's Law:

"If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same."

Mathematical Form: $\Sigma\Delta H(\text{cycle}) = 0$

Examples:

(i) **Formation of Na_2CO_3:**

Single Step Process:

$$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad \Delta H = -89.08\ kJ$$

Two Steps Process:

$$NaOH_{(aq)} + CO_{2(g)} \longrightarrow NaHCO_{3(aq)} \qquad \Delta H_1 = -48.06\ kJ$$

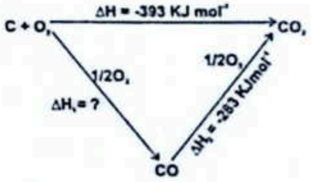
$$NaHCO_{3(aq)} + NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \quad \Delta H_2 = -41.02\ kJ$$

According to Hess's law $\Delta H = \Delta H_1 + \Delta H_2$

Putting the values of ΔH, ΔH_1 and ΔH_2 in the equation.

$$-89.08 = -48.06 - 41.02$$

$$-89.08 = -89.08\ kJ$$



(ii) **Enthalpy of Formation of CO:**

Single Step Process:

$$C_{(graphite)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_{(graphite)} = -393.7\ kJ\ mol^{-1}$$

Two Steps Process:

$$C_{(graphite)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \qquad \Delta H\ (CO) = ?$$

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H_2(CO_2) = -283\ kJ\ mol^{-1}$$

According to Hess's law

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = \Delta H_2 - \Delta H$$

$$= -393 - (-283)$$

$$= -110\ kJ\ mol^{-1}$$

So, the enthalpy change for the formation of $CO_{(g)}$ = –110.0 kJ mol⁻¹

Q.12 Differentiate between Atomization energy and Lattice energy.

Ans. Atomization Energy:

The energy required to convert a substance in atomic state is called atomization energy. It is always endothermic in nature.

$$\frac{1}{2}H_{2(g)} \longrightarrow H_{(g)} \qquad \Delta H^{\circ}_{at} = 218\ kJ\ mol^{-1}$$

Lattice Energy:

"Enthalpy of formation of one mole of crystalline ionic compound from gaseous ions under standard conditions is called lattice energy."

$$Na^{+}_{(g)} + C\ell^{-}_{(g)} \longrightarrow NaC\ell_{(s)} \qquad \Delta H_{latt} = -787\ kJ\ mol^{-1}$$

OR

"Energy required to break one mole of crystalline ionic compound into its gaseous ions at standard conditions is called lattice energy."

$$NaC\ell_{(s)} \longrightarrow Na^{+}_{(g)} + C\ell^{-}_{(g)} \qquad \Delta H = +787\ kJ\ mol^{-1}$$

Q.13 Define heat capacity of a body. Give its mathematical expressions.

Ans. Heat Capacity: "The product of mass and specific heat of water is called heat capacity of the whole system." It is represented by 'c'.

$$c = m \times s$$

◆ ◆ ◆ ◆ ◆

SELF-ASSESSMENT Chapter # 06

Total Mark: 30

Q.1 Encircle the correct option. **(1 × 6 = 6)**

(i) **Which of the following reactions is exothermic?**
A. Photosynthesis B. Electrolysis of water C. Combustion of methane D. Melting of ice

(ii) **The enthalpy change for a reaction depends on:**
A. Pathway taken from reactants to products
B. Presence of a catalyst
C. Initial and final states of the reactants and products
D. Rate of the reaction

(iii) **Which statement about bond energy is true?**
A. All bond energies are exact B. Bond energy is always negative
C. Some bond energies are average values D. Bond energy equals entropy change

(iv) **Which of the following processes would typically result in an increase in entropy of the system?**
A. Freezing of water
B. Condensation of steam
C. Dissolving a solid in a liquid
D. Formation of a crystal from a saturated solution

(v) **For a reaction to occur spontaneously,**
A. $(\Delta H - T\Delta S)$ must be negative B. $(\Delta H + T\Delta S)$ must be negative.
C. ΔH must be negative. D. ΔS must be negative.

(vi) **The term "standard conditions" means:**
A. 273 K and 2 atm B. 100°C and 1 mol C. 298 K and 1 atm D. 298 K and 760 mmHg

Q.2 Write short answers of the following questions. **(2 × 8 = 16)**

(i) Define Standard enthalpy of atomization.
(ii) Explain why energy is released when new bonds are formed.
(iii) How does ionic radius affect the enthalpy change of hydration?
(iv) Write down the formula for calculating heat using mass, specific heat capacity, and temperature change.
(v) Differentiate clearly between entropy (S) and Gibbs free energy (G).
(vi) What factors influence the magnitude of the lattice enthalpy?
(vii) The enthalpy of solution can be either positive or negative. Explain what a positive ΔH_{sol} and a negative ΔH_{sol} indicate about the energy changes during the dissolution process.
(viii) How the calorie value of food is related to enthalpy change?

Q.3 Extensive Questions. **(2 × 4 = 8)**

(a) State and explain Hess's law. Give its two applications.
(b) When 0.400 g NaOH is dissolved in 100.0 g of water, the temperature rises from 25.00 to 26.03°C. Calculate: (i) q_{water}, (ii) ΔH for the solution process

◆

Chapter 07 REACTION KINETICS

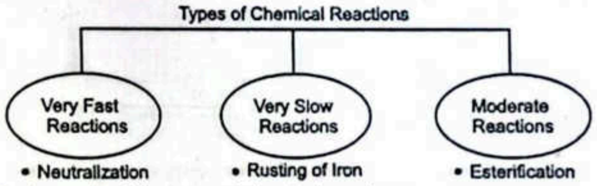
Student Learning Outcomes

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)**

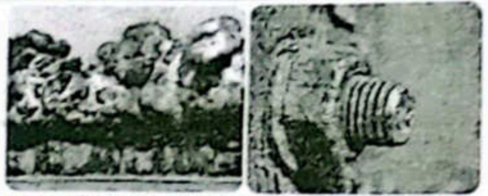
It is a common observation that rates of different chemical reactions differ greatly for example, the reaction of $NaCl$ with $AgNO_3$ is very fast. The hydrolysis of ester proceeds at a moderate rate. Whereas, rusting of iron is a slow process.

- **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.



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

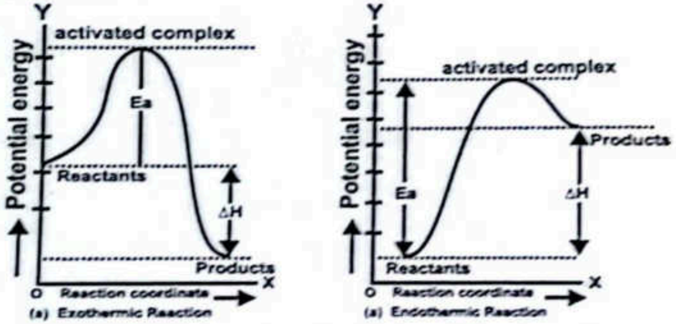
Rack Your Mind!

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

(i) 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.

(ii) 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.



(a) Exothermic Reaction

(a) Endothermic Reaction

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.

☑ 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 ≥ 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 → Fewer molecules have enough energy → Slower reaction.
   - Lower E_a → More molecules can react → 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):

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

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 ≥ E_a can overcome the barrier and form products.
2. **Boltzmann Distribution:**
   - At a given temperature, fewer molecules have energy ≥ E_a **if E_a is high** → slower reaction.
   - Lowering E_a (e.g., with a catalyst) increases the fraction of "successful" collisions → faster reaction.
3. **Arrhenius Equation:**

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

   - **Higher E_a** → Exponential decrease in rate.
   - **Lower E_a** → Exponential increase in rate.

Example:

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

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:

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

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

Rack Your Mind!

2. If the concentration of HCl decreases from 1.0 mol/dm³ to 0.6 mol/dm³ in 20 seconds, what is the rate of reaction?

A) 0.02 mol/dm³·s B) 0.04 mol/dm³·s
C) 0.06 mol/dm³·s D) 0.08 mol/dm³·s

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.

  $$A \longrightarrow B$$

  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.

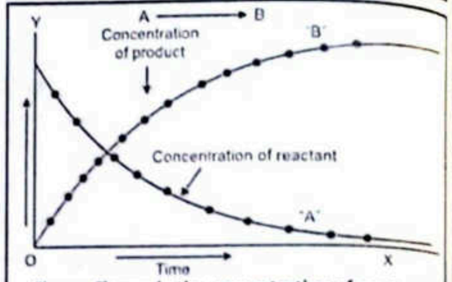


Figure: Change in the concentration of reactants and products with time for the reaction A → B

- **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 mol dm^{-3} s^{-1}.

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

- **Units for Slow Reactions:**

  For a slow reaction the units may be mol dm^{-3}min^{-1} or even mol dm^{-3} 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 → 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 one 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.

- 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:

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

i. **Calculate the instantaneous rate after 1.0 min**

ii. **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 mol dm^{-3} after 1.0 min and 6.2 mol.dm^{-3} after 4.0 minutes?

Solution:

$$\Delta C = \Delta[NH_3] = (6.2 - 3.5)\text{moldm}^{-3}; \qquad \Delta c = 2.7\ \text{moldm}^{-3}$$

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

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

The rate of production of NH_3 gas over the given time interval is 0.90 mol dm^{3} 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 moldm^{-3} to 0.0080 moldm^{-3}. What is the average rate of reaction during this period?

Given Data:

Reaction:

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

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

Step 1: Calculate Δ[I_2] (Change in Concentration)

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

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

$$\begin{aligned}\text{Average rate} &= -\Delta[I_2]/\Delta t \\ &= -(-0.0020\ \text{mol dm}^{-3}/100.0\ \text{s}) \\ &= +2.0\times10^{-5}\ \text{mol dm}^{-3}\,\text{s}^{-1}\end{aligned}$$

The average rate of reaction during this period is: 2.0×10^{-5} mol dm^{-3} s^{-1}

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 508°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 moldm⁻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

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

$$\text{Rate} = \frac{0.04\ \text{moldm}^{-3}}{100\ \text{sec}} = 4\times10^{-4}\ \text{moldm}^{-3}\text{s}^{-1}$$

This value of rate means that the concentration of HI is decreasing by 2.5 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 4×10^{-4} moldm⁻³ s⁻¹.

Figure: The change in the HI concentration with time for the reaction $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$ at 508°C

QUICK CHECK 7.3

a) **Plot the data in Table 7.1 for HI in your note book.**

Ans. There is no relevant data available in 7.1

b) **Calculate the rate after 300 sec (when the concentration is 0.03 moldm⁻³) by drawing a tangent.**

Ans. **Calculating Reaction Rate at 300 sec Using a Tangent**

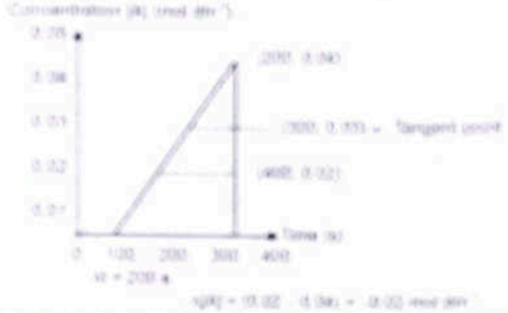
Given:

- 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.

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 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):

$$\text{Rate} = \frac{\Delta[\text{Conc.}]}{\Delta\text{Time}} = \frac{(0.02-0.04)}{(400-200)} = \frac{0.02}{200} = 1.0\times10^{-4}\ \text{moldm}^{-3}\text{s}^{-1}$$



c) **Use the same method to calculate the rate of reaction at HI concentrations of 0.10 moldm⁻³, 0.050 moldm⁻³ and 0.02 moldm⁻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 (Δ[HI]/Δt).

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

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

   - **HI formation rate** is twice the I_2 consumption rate (stoichiometry).
2. **Rate Calculations**

(a) At [HI] = 0.10 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):

$$\text{Rate} = \frac{\Delta[HI]}{\Delta t} = \frac{0.12-0.08}{250-150} = \frac{0.04}{100} = 4.0\times10^{-4}\ \text{mol dm}^{-3}\text{s}^{-1}$$

(b) At [HI] = 0.050 mol dm⁻³

Tangent points (example):

- (100 s, 0.03 mol dm⁻³)
- (200 s, 0.07 mol dm⁻³)

Slope:

$$\text{Rate} = \frac{0.07-0.03}{200-100} = \frac{0.04}{100} = 4.0\times10^{-4}\ \text{moldm}^{-3}\text{s}^{-1}$$

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

Tangent points (example):

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

Slope:

$$\text{Rate} = \frac{0.04-0.00}{150-50} = \frac{0.04}{100} = 4.0\times10^{-4}\,\text{mol dm}^{-3}\text{s}^{-1}$$

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 mol dm^{-3} 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 mol dm^{-3}:** 4.0×10^{-4} moldm^{-3} s^{-1}
- **At [HI] = 0.050 mol dm^{-3}:** 4.0×10^{-4} moldm^{-3} s^{-1}
- At [HI] = 0.02 mol dm^{-3}: 4.0×10^{-4} moldm^{-3} 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 (4.0×10^{-4} moldm^{-3} 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** (4.0×10^{-4} mol dm^{-3} 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 → more frequent collisions.

2. **Lowest Rate:**
   - At high [HI] (e.g., 0.10 mol dm^{-3}) later in the reaction.
   - Reactants are depleted → 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.

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \xrightarrow{H^+} CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$

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.

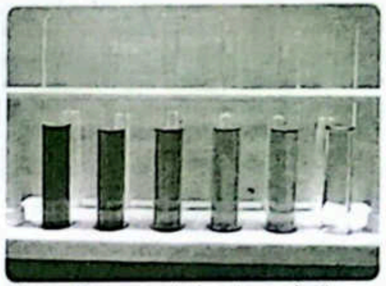


Figure: The concentration change for this reaction can be determined using colorimetry.

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.

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.

Electrical Conductivity ∝ 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

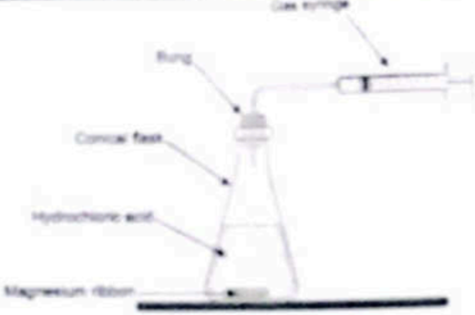


Figure: Rate of reaction can be followed by measuring the change in volume of a gas given off in a reaction.

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:

- i. Concentrations of the reactants
- ii. Temperature of the system
- iii. Surface area
- iv. Catalyst

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 → More collisions → High rate of reaction

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.

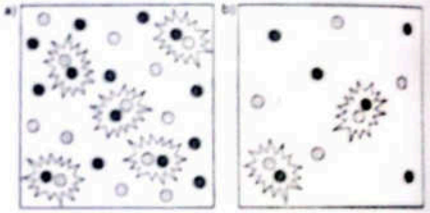


Figure: The reaction in box a) will occur faster than that in b) due to the higher concentration.

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.

Rock Your Mind!

3. Explain how temperature affects the Boltzmann distribution curve.

- **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 Figure7.6, 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 7.6 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.

Higher Temperature → More Energetic Collisions → Faster Rate of Reaction

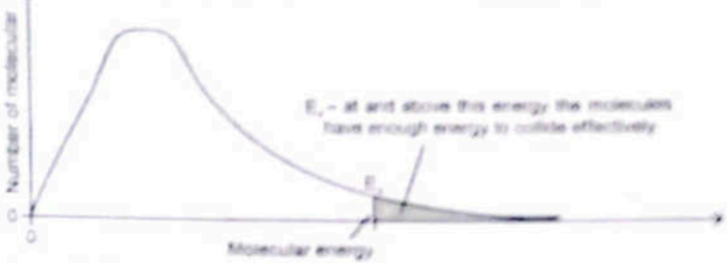


Figure: The Boltzmann distribution of molecular energies showing the activation energy

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.

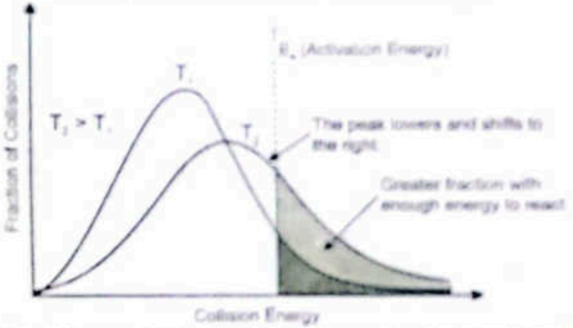


Figure: The Boltzmann distribution of molecular energies at temperatures T_1 and T_2

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:

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

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 K → 308 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 ~2 × (for typical E_a).
3. **Example Calculation**
   For E_a = 50 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 LQ5)

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, $KClO_3$ decomposes much more rapidly in the presence of a small amount of MnO_2.HCl is oxidized to Cl_2 in the presence of $CuCl_2$.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$
$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$
$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

"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.

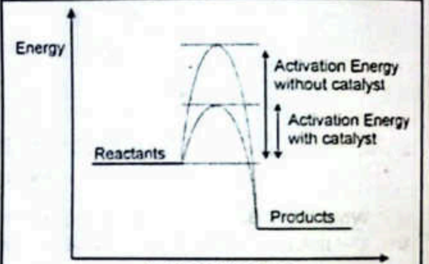


Figure: The energy path diagram for an uncatalyzed and a catalyzed reaction

Rock 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

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 $SO_{3(g)}$ from $SO_{2(g)}$ and $O_{2(g)}$ in the contact process for the manufacture of sulphuric acid, needs $NO_{(g)}$ as a catalyst. Both the reactants and the catalyst are gases.
$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO} 2SO_{3(g)}$$
- Esters are hydrolyzed in the presence of H_2SO_4. Both the reactants and the catalyst are in the solution state.
$$\underset{\text{Ethyl ethanoate}}{CH_3COOCH_2CH_{3(l)}} + H_2O_{(l)} \xrightarrow{H^+} \underset{\text{Ethanoic acid}}{CH_3COOH_{(l)}} + \underset{\text{Ethanol}}{CH_3CH_2OH_{(l)}}$$

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.
$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt,\ 800\ °C} 4NO_{(g)} + 6H_2O_{(g)}$$
- **Hydrogenation of unsaturated organic compounds** are catalysed by finely divided Ni, Pd or Pt.
$$C_2H_{4(g)} + H_{2(g)} \xrightarrow{Ni,\ 150\ °C} C_2H_{6(g)}$$

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?

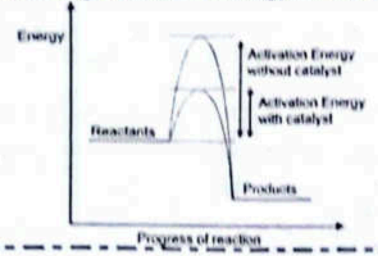
Ans. No, a catalyst is not consumed in a reaction.
1. **Regeneration:** Catalysts participate in intermediate steps but are reformed unchanged at the end generally.
   - **Example:** In the decomposition of H_2O_2, MnO_2 speeds up the reaction but remains intact.
2. **Role:** Lowers activation energy (E_a) by providing an alternative pathway

b) Explain whether the reaction below is an example of heterogeneous or homogeneous catalysis:
$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5\ (\text{solid})} 2SO_{3(g)}$$

Ans. The reaction $2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)}$ 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:
i) Catalysed reaction ii) Uncatalysed reactions

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.

Rack Your Mind!

5. What does the order of a reaction indicate in the rate law expression?

➢ **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 .

$$aA + bB \longrightarrow cC + dD$$

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 $[A] = 1\ \text{moldm}^{-3}$ and $[B] = 1\ \text{moldm}^{-3}$

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".

➢ **Explanation:**

Reaction order tells how rate changes with reactants concentrations.

- 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.

Example: Take equation for the reaction of nitrogen (II) oxide (NO) with H_2 and oxygen:

$$2H_{2(g)} + 2NO_{(g)} \longrightarrow N_{2(g)} + H_2O_{(g)}$$

$$\text{Rate} = k[H_2][NO]^2$$

This reaction is:

I. first-order with respect to H_2
II. second-order with respect to NO
III. third-order overall (1 + 2 = 3)

KEEP IN MIND

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. Steps to Determine Reaction Order

- **Write the Rate Law:**

  For a reaction: aA+bB → Products,

  the rate law is: Rate = $k[A]^a[B]^b$

  - k = rate constant
  - a, b = **orders** with respect to A and B
- **Experimental Data:**

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

  Overall order = a + b

$$2H_{2(g)} + 2NO_{(g)} \rightarrow N_{2(g)} + H_2O_{(g)}$$

Example:

For the rate law Rate = Rate = $k[H_2][NO]^2$

- **Overall third-order** = 1 + 2 = 3

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)

- 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.
- **Representation in Rate Equation:**

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

- k is specific to the reaction and temperature.

Units of Rate constants = various order

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

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:

$$A \rightarrow Product$$

$$Rate = k[A]^0$$

Examples:

i) $H_{2(g)} + C\ell_2 \longrightarrow 2HC\ell_{(g)}$

$$Rate = k[H_2]^0[C\ell_2]^0 = k$$

ii) $2NH_3 \longrightarrow N_2 + 3H_2$

$$Rate = k[NH_3]^0 = k$$

iii) Photochemical reactions are usually zero order.

Rock 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 → Product	Uni – molecular	Rate = k [A]
A + A → Product	Bi – molecular	Rate = k [A]^2
A + B → Product	Bi – molecular	Rate = k [A] [B]
A + B + C → Product	Ter – molecular	Rate = k [A]^2[B]

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.

$$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

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

$$Rate = k[N_2O_5]\ (n=1)$$

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

First order means rate ∝ [Reactant]

Smart Thinking

Units of Rate constants = various order

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

Second Order Reaction:

Definition:

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

(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: $Rate = k[A]^2$ (n = 2)

Example: $Rate = k[A]^1[B]^1$ (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 O_3. The sum of the individual orders gives the overall order of reaction as two.

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)} \quad Rate = k[NO][O_3]$$

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: $Rate = k[A]^3\ (n=3)$

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

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

Example: $2FeC\ell_{3(aq)} + 6KI_{(aq)} \longrightarrow 2FeI_{2(aq)} + 6KC\ell_{(aq)} + I_2$

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

$$Rate = k[FeC\ell_3][KI]^2$$

also, the following reaction is third order

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \qquad Rate = k[NO]^2[O_2]^1$$

Rock Your Mind!

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

A) 1 B) 2

C) 3 D) 4

Fractional Order Reaction:

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

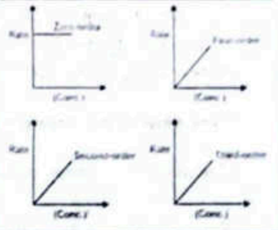
Example: Consider the formation of carbon tetrachloride from chloroform.

$$CHC\ell_{3(\ell)} + C\ell_{2(g)} \longrightarrow CC\ell_{4(\ell)} + HC\ell_{(g)}$$

$$Rate = k[CHC\ell_3][C\ell_2]^{1/2} \qquad n = 1 + 1/2 = 1.5$$

- Reactions involving free radicals frequently exhibit fractional orders.

Graphs for Entry Tests



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 $mol\ dm^{-3}\ s^{-1}$. The units for k depend on the order of the reaction and the units of time.

General Equation:

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

$$k = \frac{Rate}{(Rectants)^n} = \frac{(moldm^{-3})s^{-1}}{(moldm^{-3})^n}$$

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

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

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

For a zero order reaction (n = 0),

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

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

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

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

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

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

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

Rock Your Mind!

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

For a second order reaction (n = 2),

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

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

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

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

For a third order reaction (n = 3),

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

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

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

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

☑ QUICK CHECK 7.7

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

i) rate $= k[NO]^2[NH_3]^0$

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

ii) rate $= k[BrO_3][Br^-][H^+]^2$

Ans. Rate $= k[BrO_3^-][Br^-][H^+]^2$

$$BrO_3^- + 5Br^- + 6H^+ \longrightarrow 3Br^2 + 3H_2O$$

Experimentally Determined Rate Law:

$$Rate = k[BrO_3^-][Br^-][H^+]^2$$

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

i) Calculate the overall order of reactions.

Ans. The given rate law is:

$$Rate = k\left[BrO_3^-\right]\left[Br^-\right]\left[H^+\right]^2$$

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 exeeds 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. Rate $= k\left[BrO_3^-\right]\left[Br^-\right]\left[H^+\right]^2$
- The exponent of $\left[BrO_3^-\right] = 1$
- The exponent of $\left[Br^-\right] = 1$
- The exponent of $[H^+] = 2$

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.

e.g., $2H_2 + 2NO_2 \longrightarrow 2H_2O_2 + N_2$

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:

$$Rate \propto [H_2]^1[NO_2]^2$$
$$Rate = k[H_2]^1[NO_2]^2$$

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

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

DETERMINATION OF RATE CONSTANT

Exercise LQ.4

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

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:

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow 2H_2O_{(l)} + I_{2(aq)}$$

The rate equation for this reaction is:

$$\text{Rate of reaction} = \frac{k[H_2O_2]}{[I^-]}$$

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.

$$\text{Rate of reaction} = \frac{k[H_2O_2]}{[I^-]}$$

Step 2: Rearrange the equation in terms of k

$$k = \frac{rate \times [I^-]}{[H_2O_2]}$$

Step 3: Substitute the values

$$k = \frac{3.50 \times 10^{-6} \times (0.0100)}{(0.0200)}$$

$$= 1.75 \times 10^{-6} dm^3 mol^{-1} s^{-1}$$

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

Experiment	$[H_2O_2]/mol dm^{-3}$	$[I^-]/mol dm^{-3}$	$[H^+]/mol dm^{-3}$	Initial rate of reaction/ $mol dm^{-3} s^{-1}$
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 $[H^+]$ does not appear in the rate equation. The reaction is zero order with respect to $[H^+]$.

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:

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

Rock Your Mind!

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

A) $9.63 \times 10^{-5} s^{-1}$ B) $0.000072 s^{-1}$
C) $0.00128 s^{-1}$ D) $0.0036 s^{-1}$

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:

$$2 \times 60 \times 60 = 7200 s$$

We then simply substitute this value into the equation:

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

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

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:

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

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

☑ 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 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 mol dm^{-3}

Formula for First-Order Half-Life:

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

Step 1: Solve for k

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

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

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.

$$N_2O_{5(g)} \longrightarrow NO_{2(g)} + NO_{3(g)}$$

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

- For example;

$$CO_{(g)} + NO_{3(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$$

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

- **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.

$$2O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)} + O_{2(g)}$$

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:

$$2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$$

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.

$$Rate \propto [H_2]$$

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.

$$Rate \propto [NO]^2$$

The overall rate equation of reaction is,

$$Rate \propto [H_2][NO]^2$$

or

$$Rate = k[H_2]^1[NO]^2$$

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	0.0075
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.

Step 1: $2NO_{(g)} + H_{2(g)} \xrightarrow{Slow} N_{2(g)} + H_2O_{2(g)}$ (rate determining step)

Step 2: $H_2O_{2(g)} + H_{2(g)} \xrightarrow{Fast} 2H_2O_{(g)}$

The step 1 is slow and rate determining.

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

$$2NO_{2(g)} + F_{2(g)} \longrightarrow 2NO_2F_{(g)}$$

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:

$$Rate = k[NO_2][F_2] \qquad \text{(Observed)}$$

The accepted mechanism for the reaction is:

Step 1: $NO_{2(g)} + F_2 \xrightarrow{Slow} NO_2\ F_{(g)} + F_{(g)}$ $\qquad$ $Rate = k_1[NO_2][F_2]$

Step 2: $NO_{2(g)} + F^{\bullet}_{(g)} \xrightarrow{Fast} NO_2\ F_{(g)}$ $\qquad$ $Rate = k_2[NO_2][F^{\bullet}]$

- 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.**

$$H_2O_{2(aq)} + 2H^+_{(aq)} + 2I^-_{(aq)} \longrightarrow 2H_2O_{(\ell)} + I_{2(aq)}$$

The rate equation for this reaction = $[H_2O_2][I^-]$

The mechanism below has been proposed for this reaction.

$H_2O_2 + I^- \xrightarrow{Slow} H_2O + IO^-$

$H^+ + IO^- \xrightarrow{Fast} HIO$

$HIO + H^+ + I^- \xrightarrow{Fast} I_2 + H_2O$

Explanation of this mechanism's consistency with the rate equation.

Ans. The proposed mechanism is consistent with the experimentally determined rate equation rate = $k[H_2O_2][I^-]$ because:

Rate-Determining Step (RDS):

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

$$H_2O_2 + I^- \xrightarrow{Slow} H_2O + IO^-$$

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

$$Rate = k_1[H_2O_2][I^-]$$

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.
- 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.

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/dm³·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. $H_2 + Cl_2 \xrightarrow{sunlight} 2HCl$ iv. $2NH_3 \xrightarrow{Pt} N_2 + 3H_2$ v. $2HI \xrightarrow{Au} H_2 + I_2$ 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),** $k = (mol \cdot dm^{-3})^{1-0} s^{-1}$ $k = mol^1 \cdot dm^{-3} s^{-1}$ **For a first order reaction (n = 1),** the rate is directly proportional to the concentration of one reactant. $k = (mol \cdot dm^{-3})^{1-1} s^{-1}$ $k = (mol \cdot dm^{-3})^0 s^{-1}$ $k = s^{-1}$
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 $k = 0.3465/3600 = 9.625 \times 10^{-5} s^{-1}$.
10.	D	The slowest step determines the overall rate of the reaction.

Exercise

MULTIPLE CHOICE QUESTIONS (MCQs)

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 $NO_2 + CO \rightarrow NO + CO_2$ occurs in two steps. What is the rate law equation for this reaction?

$$2NO_2 \longrightarrow NO + NO_3 \ (k_1) \quad \text{slow}$$
$$NO_3 + CO \longrightarrow CO_2 + NO_2 \ (k_2) \quad \text{fast}$$

a) $R = k_1[NO_2]^3$ b) $R = k_2[NO_3][CO]$ c) $R = k_1[NO_2]$ d) $R = k_1[NO_2]^2$

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.

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	• Rate ∝ [Reactant]2 → 4 × 22 = rate increase.
VIII.	c	The slowest step	• The slowest step limits the overall rate.
IX.	d	$R = k_1[NO_2]^2$	• The slow step involves $2NO_2 \rightarrow$ products, so rate depends on $[NO_2]^2$.
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 $mol^{1-}nLn^{-1}s^{-1}$.
XIII.	c	0.0347 min^{-1}	• $k = \frac{ln(2)}{t_{1/2}} = \frac{0.693}{20} = 0.0347 min^{-1}$

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:

$$\text{Rate of reaction} = \frac{\text{Changeinconcentrationofthrsubstance}}{\text{Time taken for the change}}$$

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

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: $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ 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 → products, if rate = $k[A]^2$, the order is 2.	For A+B → 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.

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 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 ⇒ 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 ⇒ 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: 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.

- 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:

$$C_6H_{10}O_5 + O_2 \rightarrow CO_2 + H_2O$$

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

Ans. It seems to a reaction with a given rate constant ($k = 3.5 \times 10^{-4}\ s^{-1}$) 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:

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, $3.5 \times 10^{-4}\ s^{-1}$)
- [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 ($dm^3\ mol^{-1} s^{-1}$):** Rate depends on concentration squared (Rate = $k[A]^2$).
- **Zero-order ($k = mol.dm^{-3}\ s^{-1}$):** 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 $3.5 \times 10^{-4}\ s^{-1}$)
- [A] is the initial concentration of the reactant (given as $0.50\ mol/dm^3$).

Substitute the Given Values:

$$\text{Rate} = (3.5 \times 10^{-4} s^{-1}) \times (0.50\ mol/dm^3)$$
$$\text{Rate} = 1.75 \times 10^{-4}\ mol/dm^3 s$$

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 $2.5 \times 10^{-3}\ s^{-1}$. Calculate the half-life of the reaction in minutes.

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

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

Where:
$t_{1/2}$ = half-life,
$\ln 2 \approx 0.693$
$k = 2.5 \times 10^{-3}\ s^{-1}$

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

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

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

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

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

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

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

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:

Step 1: $H_2O_2 + I^- \longrightarrow H_2O + OI^-$ (slow)

Step 2: $OI^- + H^+ \longrightarrow HOI$ (fast)

Step 3: $HOI + I^- + H^+ \longrightarrow H_2O + I_2$ (fast)

i) Write the overall balanced equation for the reaction.

ii) Identify any intermediates and catalysts in this mechanism.

iii) What is the rate-determining step?

iv) 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:

$$MoO_4^{2-} \text{ or } Fe^{3+}$$

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 $M^{-2}s^{-1}$. Given the rate law for a reaction: Rate = $k[A][B]^2$.

Given Data:

Rate law = $k[A][B]^2$

Rate constant (k) = $4.0\ M^{-2}\ s^{-1}$

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:

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

Substitute the Given Values

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

Now, multiply all the terms step by step:

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

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

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

Q.7 A first order reaction is found to have a rate constant, k = $5.5\times10^{-14}s^{-1}$. Find the half-life of the reaction.

Temp. (K)	Rate constant ($cm^3\ mol^{-1}s^{-1}$)(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) = $5.5 \times 10^{-1}4\ s^{-1}$

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:

$$t_{1/2} = \frac{0.693}{5.5\times10^{-1}4s^{-1}}$$

Step 3: Calculation

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

Answer: The half-life of the reaction is **1.26×10^{13} s.**

Q.8 Three experiments that have identical conditions were performed to measure the initial rate of the reaction. $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$

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:

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

Step 1: Rate Law Form

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

.Use the data to find the order n.

Step 2: Determine Reaction Order (n)

Use experiments 1 and 2:

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

$$\frac{4.4\times10^{-3}}{1.1\times10^{-3}} = \left(\frac{0.030}{0.015}\right)^n \quad \Rightarrow 4 = 2^n \quad \Rightarrow n = 2$$

Order = 2

Step 3: Rate Law

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