# CHEMICAL KINETICS

## CHAPTER 04

## INTRODUCTION

Chemical kinetics is the study of the rates of chemical reactions and the factors that affect them. It examines how fast or slow reactions occur and explores the influence of variables such as concentration, temperature, catalysts, surface area, and pressure. By understanding reaction rates, scientists can optimize conditions, design processes, and develop new materials and drugs.

## RATE OF REACTION

The rate of a chemical reaction measures how quickly reactants are converted into products. It can be determined by measuring changes in concentration, pressure, mass, or pH over time. Factors such as reactant nature, concentration, temperature, and catalysts influence the reaction rate. Units of the rate of reaction are mol $L^{-1}$ time$^{-1}$ or for gaseous reaction, these are atm time$^{-1}$.

(i) For the reaction $PCl_5 \rightarrow PCl_3 + PCl_2$.

$$\text{Rate} = -\frac{\Delta[PCl_5]}{\Delta t} = +\frac{\Delta[PCl_3]}{\Delta t} = +\frac{\Delta[Cl_2]}{\Delta t}$$

## INSTANTANEOUS RATE OF REACTION

The instantaneous rate of a chemical reaction refers to the rate at a specific moment during the reaction. It is calculated by measuring the change in concentration of a reactant or product over a small time interval. This rate can vary throughout the reaction and is useful for studying reaction mechanisms and determining rate laws.

(i) For a reaction of the type $aA + bB \rightarrow xX + yY$

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{x}\frac{d[X]}{dt} = +\frac{1}{y}\frac{d[Y]}{dt}$$

(ii) For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$

$$\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

Rate of disappearance of $N_2 = -\frac{d[N_2]}{dt}$

Rate of disappearance of $H_2 = -\frac{d[H_2]}{dt}$

Rate of formation of $NH_3 = +\frac{d[NH_3]}{dt}$

## FACTORS DEPENDS ON RATE OF REACTION

- **Concentration:** Higher concentrations of reactants generally result in a faster reaction rate due to more frequent collisions.
- **Temperature:** Increasing the temperature increases the kinetic energy of molecules, leading to more energetic collisions and a higher reaction rate.
- **Pressure (for gas reactions):** Higher pressures can increase the reaction rate, especially when the number of gaseous molecules changes during the reaction.
- **Surface area:** Reactions involving solid reactants tend to proceed faster when the surface area is increased, as it provides more contact points for reactant molecules to collide.
- **Catalysts:** Catalysts speed up the reaction rate by providing an alternative reaction pathway with lower activation energy, allowing more reactant molecules to participate in successful collisions.
- **Nature of reactants:** Different reactants have varying inherent reactivities, resulting in different reaction rates.
- **Presence of inhibitors:** Inhibitors decrease the reaction rate by interfering with the reaction mechanism or reducing the effective concentration of reactants.

- ✓ *Arrhenius derived* a mathematical expression to give a quantitative relationship between rate constant and temperature. The expression is

  $$K = A.e^{-E_a/RT}$$

  (Here, A = Frequency factor; $E_a$ = activation energy; $R$ = gas constant and $T$= temperature).
- ✓ Arrhenius equation may also be written as $\log K = \log A - E_a / 2.303\,RT$. A plot of $\log K$ with $\frac{1}{T}$ gives a straight line with slope $= -\frac{E_a}{2.303\,R}$

If $K_2$ and $K_1$ are rate constant at temperature $T_2$ and $T_1$ then.

$$\log\frac{K_2}{K_1}=\frac{E_a}{2.303\,R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

Arrhenius equation can also be written in the form $\frac{d\ln K}{dT}=\frac{E_a}{RT^2}$

## RATE CONSTANT

The rate constant, in short, is a proportionality constant that relates the rate of a chemical reaction to the concentrations of the reactants. It represents the speed at which the reaction occurs and is specific to a particular reaction at a given temperature. The rate constant is typically denoted by the symbol "k" and is determined experimentally. It is used in rate equations to mathematically describe the relationship between reactant concentrations and the rate of reaction.

The units of the rate constant of a reaction depends on the order of the reaction. For an $n^{th}$ order reaction

$$dx/dt=k(\text{conc.})^n$$

$$\therefore \quad k=\frac{dx}{dt}\times\frac{1}{(\text{conc.})^n}=\frac{\text{conc.}}{\text{time}}\times\frac{1}{(\text{conc.})^n}=\frac{1}{\text{time}}\times\frac{1}{(\text{conc})^{n-1}}$$

For zero order, first order and second order reaction ($n$=0, 1, 2 respectively) units of rate constant, $K$ are $mol\ L^{-1}\ \text{time}^{-1}$, $\text{time}^{-1}$ and $L\,mol^{-1}\ \text{time}^{-1}$ respectively.

## ORDER OF REACTION AND MOLECULARITY

| Aspect | Order of Reaction | Molecularity |
|---|---|---|
| Definition | Mathematical relationship between reactant concentrations and reaction rate | Number of molecules involved in an elementary step of a reaction |
| Determination | Experimentally determined through rate data analysis | Theoretical concept based on proposed reaction mechanism |
| Values | Can be zero, first, second, fractional, or negative | Can be unimolecular, bimolecular, termolecular |
| Relationship to stoichiometry | May or may not correspond to stoichiometric coefficients in the balanced chemical equation | Not related to stoichiometric coefficients |
| Experimental Observance | Determined from experimental rate data and concentration changes | Not directly observable experimentally |
| Representation | Represented by small integers (0, 1, 2, etc.) or other numerical values | Represented by "uni-", "bi-", or "termolecular" |

## Types of order of reactions:

| Order of Reaction | Rate Equation | Rate Constant Units |
|---|---|---|
| Zeroth Order | Rate = k | Molarity per unit time (M/s) |
| First Order | Rate = k[A]^1 or Rate = k[B]^1 | Per unit time (1/s or s^-1) |
| Second Order | Rate = k[A]^2 or Rate = k[B]^2 or Rate = k[A][B] | Molarity per unit time (M^-1s^-1) |

(1) **Zero order reaction:**

Rate $= K[\ ]^{0}$ For $A \rightarrow$ product

i.e. $\frac{dx}{dt} = K$ $t = 0$ $a$ $0$

$t = t$ $(a - x)$ $x$

On integrating $\frac{x}{t} = K$

**Characteristics:**

- Rate remains constant throughout the course of reaction.
- Unit of rate constant $= \frac{\text{mol}}{\text{litre} \times \text{time}}$
- Half-life period $t_{1/2} \propto (a)$, Where $a$ is initial concentration.

(2) **1st order reaction:**

Rate $= [K]^{1}$ For $A \rightarrow$ product

i.e. $\frac{dx}{dt} = K\ [\ ]^{1}$ $t = 0$ $a$ $0$

$= K[a - x]^{1}$ $t = t$ $(a - x)$ $x$

On integrating, we get $K \times t = 2.303 \log_{10} \frac{a}{(a - x)}$

**Characteristics:**

- Rate continuously decreases with time.
- Unit of rate constant is time$^{-1}$
- Half-life period: $t_{1/2} \propto (a)^{o}$, *i.e.*, half-life for $1^{st}$ order is independent of initial conc.

### (3) 2nd order reaction:

**Case I**: If one reactant or two reactants with same initial concentration:

$$\begin{array}{lll} \text{For} & A \rightarrow & \text{Product} \\ t=0 & a & 0 \\ t=t & (a-x) & x \end{array}$$

Rate $= K[\ ]^2$ or $\frac{dx}{dt} = K(a-x)^2$

On integrating, we get, $K \times t = \frac{1}{a}\frac{x}{(a-x)}$

**Case II:** If reactant are two and initial concentrations are different.

$$\begin{array}{llll} & \text{For} & A + B \rightarrow & \text{Products} \\ \text{at} & t=t & (a-x) & (b-x) \end{array}$$

Rate $= K[\ ]^1\ [\ ]^1$

$$\frac{dx}{dt} = K[a-x][b-x]$$

on integrating, we get $K \times t = \frac{2.303}{(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$

**Characteristics:**

- Rate continuously decreases with time
- Unit of rate constant : $mol^{-1}\ litre^{-1}\ \ time^{-1}$
- Half life period : $t_{1/2} \propto (a)^{-1}$ or $t_{1/2} \propto \frac{1}{a}$

## Salient features of rate constant and half-life period.

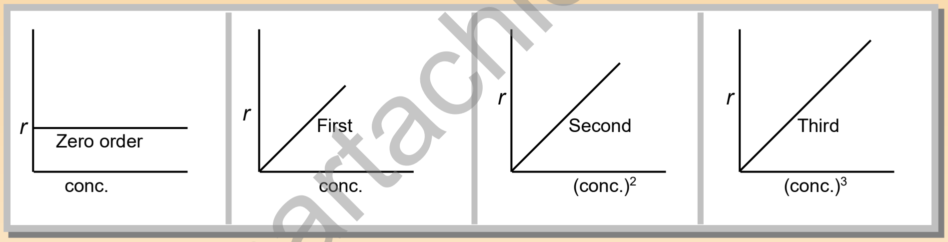
| Order of reaction | Half life | Unit of rate constant |
|---|---|---|
| 0 | $t_{1/2} \propto (a)$ | $mol\ litre^{-1}\ time^{-1}$ |
| 1 | $t_{1/2} \propto (a)^0$ | $time^{-1}$ |
| 2 | $t_{1/2} \propto (a)^{-1}$ | $mol^{-1}\ litre^{+1}\ time^{-1}$ |
| 3 | $t_{1/2} \propto (a)^{-2}$ | $mol^{-2}\ litre^{2}\ time^{-1}$ |
| $N$ | $t_{1/2} \propto (a)^{1-n}$ | $mol^{1-n}\ \ litre^{n-1}\ time^{-1}$ |

## Method of determination of order of reaction.

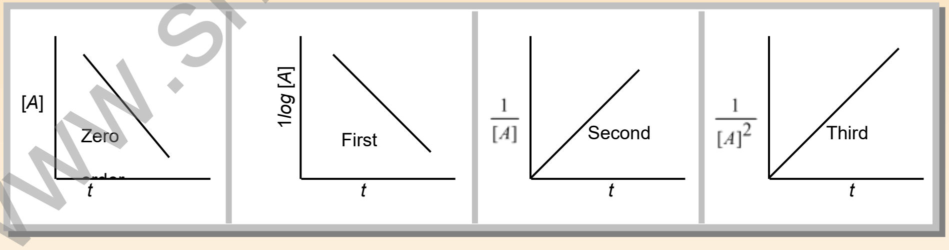
The determination of the order of a reaction involves analyzing experimental data to establish the relationship between the concentrations of reactants and the rate of the reaction. There are a few methods commonly used to determine the order of reaction

**1. Graphical method :**

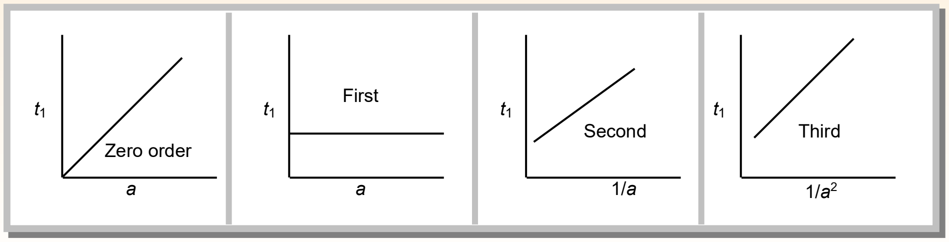
a. Plots of rate vs concentration for different order reactions [Rate =k (conc.)$^n$]



b. Plots of conc., [$A$] vs. time, for different order reactions on the basis of integrated rate laws



c. Plots of $t_{1/2}$ vs. initial concentration, a for different order reactions [$t_{1/2} \alpha\ a^{1-n}$]



### 2. Initial Rate Method:

- This method involves measuring the initial rates of the reaction under different initial concentrations of the reactants.
- By changing the concentration of one reactant while keeping others constant, the order with respect to that reactant can be determined.
- Experiments are performed where the reactant concentrations are varied (e.g., doubled or halved), and the corresponding changes in the initial rate are observed.
- The order of reaction is determined by comparing the ratio of the rate changes to the ratio of the concentration changes.

### 3. Integrated Rate Law Method:

- This method involves determining the order of reaction by integrating the rate equation and comparing the experimental data to various integrated rate laws.
- The integrated rate laws describe how the concentration of a reactant changes with time for a specific order of reaction.
- Experimental data is collected over a period of time, and the concentrations are measured at different time intervals.
- By plotting the concentration data and comparing it with the integrated rate laws, the order of reaction can be determined.

### 4. Half-Life Method:

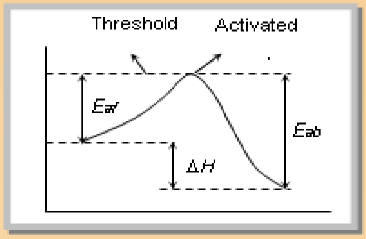
- The half-life method involves determining the order of reaction by comparing the half-lives of the reaction under different initial concentrations.
- The half-life is the time required for the concentration of a reactant to decrease by half.
- By measuring the half-life at different initial concentrations, the order of reaction can be determined.
- For example, if the half-life is constant regardless of the initial concentration, it indicates a zeroth order reaction. If the half-life is constant when the concentration is halved, it suggests a first order reaction. If the half-life is constant when the initial concentration is doubled, it suggests a second order reaction.

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \quad \text{or} \quad n = 1 + \frac{\log(t_{1/2})_1 - \log(t_{1/2})_2}{\log a_2 - \log a_1};$$ $n$ is the order of reaction.

5. **Van’t hoff differential method:** For the different initial concentrations $c_1$ and $c_2$ equations can be written in the form $-\frac{dc_1}{dt} = Kc_1^n$ and $-\frac{dc_2}{dt} = Kc_2^n$

Taking logarithms of two equations and then subtracting, $n = \dfrac{\log\left(\frac{dc_1}{dt}\right) - \log\left(\frac{dc_2}{dt}\right)}{\log c_1 - \log c_2}$

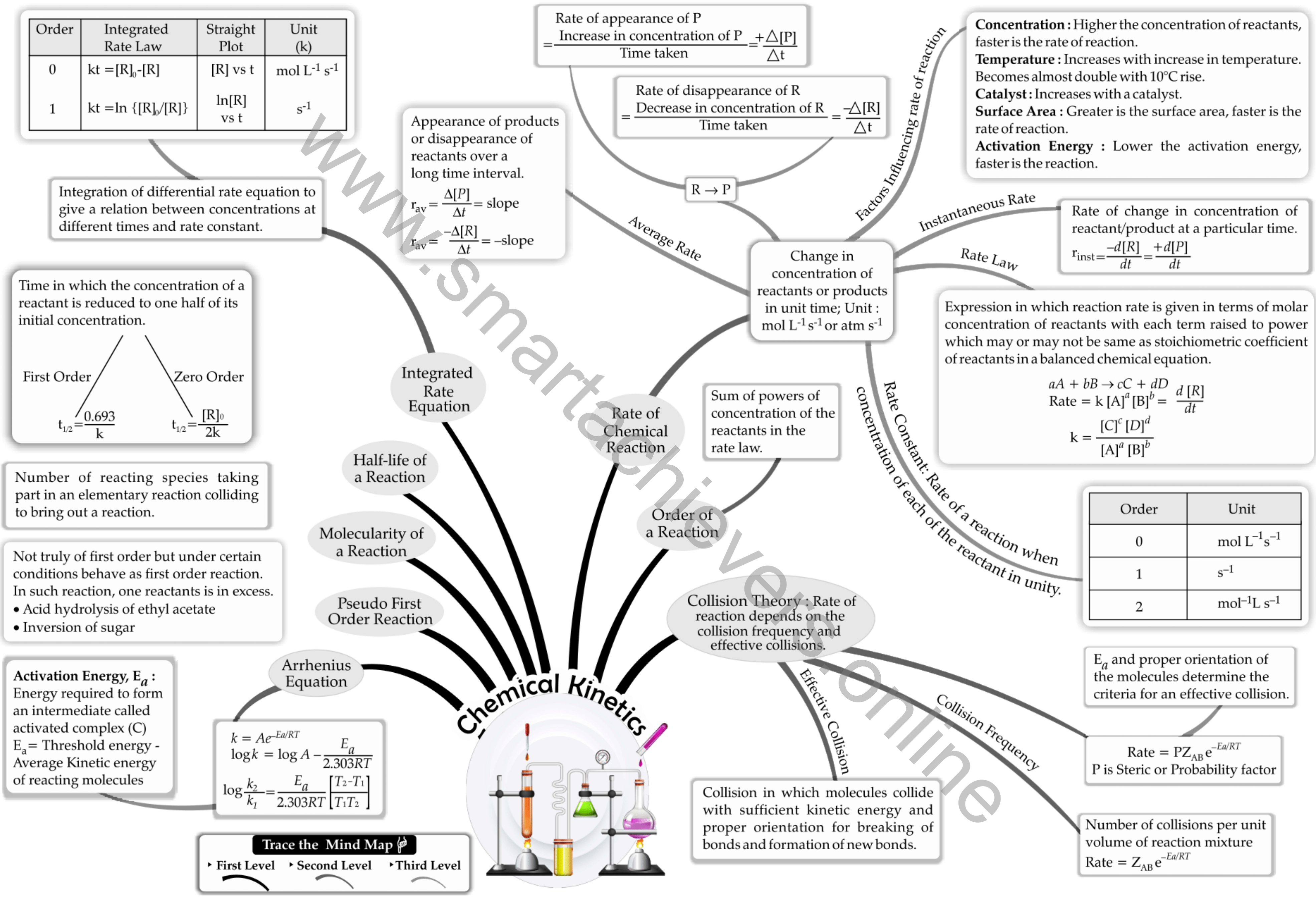
## Activated complex theory.



The activated complex theory, or transition state theory, explains that during a chemical reaction, reactant molecules must collide with enough energy to overcome an activation energy barrier. This leads to the formation of an activated complex, which is a short-lived, high-energy species representing the transition state. The theory suggests that the rate of a reaction is determined by the frequency of successful collisions and the stability of the activated complex. It provides a molecular-level understanding of reaction kinetics and helps explain factors like temperature dependence, activation energy, and the role of catalysts.

## Photochemical reactions.

Photochemical reactions are chemical reactions that are initiated or influenced by the absorption of light. These reactions occur when molecules absorb photons, which are particles of light, and undergo changes in their electronic and structural states. The absorbed light energy excites electrons in the molecules, leading to electronically excited states. These excited molecules can then undergo various processes, such as bond breaking, bond formation, isomerization, or electron transfer, resulting in the formation of new chemical species. Photochemical reactions often occur at higher energy levels compared to thermal reactions and exhibit different reaction pathways and products. They are typically faster and more selective than traditional thermal reactions. The specific wavelength of light and the molecular structure of the reactants are important factors that determine the type and efficiency of the photochemical reaction. Photochemical reactions find applications in diverse fields, including photography, solar energy conversion, and atmospheric chemistry.



# Chemical Kinetics

| Order | Integrated Rate Law | Straight Plot | Unit (k) |
|---|---|---|---|
| 0 | kt =$[R]_0$-[R] | [R] vs t | mol $L^{-1}$ $s^{-1}$ |
| 1 | kt =ln {$[R]_0$/[R]} | ln[R] vs t | $s^{-1}$ |

Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

**Integrated Rate Equation**

Time in which the concentration of a reactant is reduced to one half of its initial concentration.

First Order

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

Zero Order

$t_{1/2} = \frac{[R]_0}{2k}$

**Half-life of a Reaction**

Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.

**Molecularity of a Reaction**

Not truly of first order but under certain conditions behave as first order reaction. In such reaction, one reactants is in excess.
- Acid hydrolysis of ethyl acetate
- Inversion of sugar

**Pseudo First Order Reaction**

**Arrhenius Equation**

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

$\log k = \log A - \frac{E_a}{2.303RT}$

$\log\frac{k_2}{k_1} = \frac{E_a}{2.303RT}\left[\frac{T_2-T_1}{T_1T_2}\right]$

**Activation Energy, $E_a$ :** Energy required to form an intermediate called activated complex (C)
$E_a$= Threshold energy - Average Kinetic energy of reacting molecules

**Rate of Chemical Reaction**

Change in concentration of reactants or products in unit time; Unit : mol $L^{-1}$ $s^{-1}$ or atm $s^{-1}$

Average Rate

Appearance of products or disappearance of reactants over a long time interval.

$r_{av} = \frac{\Delta[P]}{\Delta t}$ = slope

$r_{av} = \frac{-\Delta[R]}{\Delta t}$ = –slope

R → P

Rate of appearance of P $= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\Delta[P]}{\Delta t}$

Rate of disappearance of R $= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = \frac{-\Delta[R]}{\Delta t}$

Factors Influencing rate of reaction

**Concentration :** Higher the concentration of reactants, faster is the rate of reaction.
**Temperature :** Increases with increase in temperature. Becomes almost double with 10°C rise.
**Catalyst :** Increases with a catalyst.
**Surface Area :** Greater is the surface area, faster is the rate of reaction.
**Activation Energy :** Lower the activation energy, faster is the reaction.

Instantaneous Rate

Rate of change in concentration of reactant/product at a particular time.

$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$

Rate Law

Expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation.

$aA + bB \rightarrow cC + dD$

Rate $= k[A]^a[B]^b = \frac{d[R]}{dt}$

$k = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Rate Constant: Rate of a reaction when concentration of each of the reactant in unity.

| Order | Unit |
|---|---|
| 0 | mol $L^{-1}s^{-1}$ |
| 1 | $s^{-1}$ |
| 2 | $mol^{-1}L\ s^{-1}$ |

**Order of a Reaction**

Sum of powers of concentration of the reactants in the rate law.

**Collision Theory :** Rate of reaction depends on the collision frequency and effective collisions.

Effective Collision

Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.

$E_a$ and proper orientation of the molecules determine the criteria for an effective collision.

Rate = $PZ_{AB}e^{-Ea/RT}$
P is Steric or Probability factor

Collision Frequency

Number of collisions per unit volume of reaction mixture
Rate = $Z_{AB}e^{-Ea/RT}$

**Trace the Mind Map**
- First Level
- Second Level
- Third Level

# PRACTICE QUESTIONS

1. Which of the following factors does not affect the rate of a chemical reaction?

a) Temperature b) Concentration of reactants
c) Presence of a catalyst d) Volume of the reaction vessel

2. The rate of a reaction can be determined by measuring the:

a) Change in temperature
b) Change in volume
c) Change in pressure
d) Change in concentration of reactants or products over time

3. The rate of a chemical reaction is usually expressed in terms of:

a) Moles per liter b) Grams per liter
c) Molar concentration d) All of the above

4. The order of a reaction can be determined experimentally by:

a) Measuring the initial rate of reaction
b) Measuring the rate constant
c) Analyzing the integrated rate equation
d) All of the above

5. The rate constant of a reaction is affected by:

a) Temperature b) Presence of a catalyst
c) Activation energy d) All of the above

6. In a first-order reaction, the rate constant has the unit of:

a) $\frac{M}{s}$ b) $\frac{1}{s}$ c) $M^{-1}s^{-1}$ d) $S^{-1}$

7. A zeroth-order reaction has a rate equation of the form:

a) $Rate = k[A]^{\circ}$ b) Rate = k[A]
c) $Rate = k[A]^{2}$ d) Rate = k

8. Which type of reaction order is characterized by a linear relationship between the concentration and time?

a) Zeroth order b) First order
c) Second order d) None of the above

9. The rate-determining step of a reaction is:

a) The slowest step in a reaction mechanism
b) The fastest step in a reaction mechanism
c) The step with the highest activation energy
d) The step with the lowest activation energy

10. The rate of a reaction is halved when the concentration of a reactant is halved. The reaction order with respect to that reactant is:

| | | | |
|---|---|---|---|
| a) Zeroth order | b) First order | c) Second order | d) Third order |

11. Which of the following factors can increase the rate of a reaction?

| | |
|---|---|
| a) Increasing temperature | b) Increasing concentration of reactants |
| c) Adding a catalyst | d) All of the above |

12. The collision theory of chemical kinetics states that a reaction is more likely to occur when:
   a) The reactant molecules collide with sufficient energy
   b) The reactant molecules collide with proper orientation
   c) Both a) and b)
   d) None of the above

13. The activation energy of a reaction is defined as:
   a) The energy required to break the bonds of reactant molecules
   b) The energy released during a reaction
   c) The energy difference between the reactants and the products
   d) The energy barrier that must be overcome for a reaction to occur

14. Which of the following factors does not affect the rate constant of a reaction?

| | |
|---|---|
| a) Temperature | b) Presence of a catalyst |
| c) Initial concentration of reactants | d) Pressure |

15. The rate constant of a reaction:
   a) Increases with increasing temperature
   b) Decreases with increasing temperature
   c) Is not affected by temperature
   d) Varies randomly with temperature

16. Which of the following statements about elementary reactions is correct?
   a) They are single-step reactions with a single transition state.
   b) They are multi-step reactions with multiple transition states.
   c) They are reversible reactions.
   d) They are always first-order reactions.

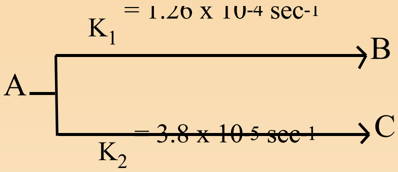
17. The overall order of a reaction is determined by:
   a) Adding the orders of each reactant in the rate equation
   b) Taking the product of the exponents in the rate equation
   c) Determining the slowest step in the reaction mechanism
   d) None of the above

18. The Arrhenius equation relates the rate constant (k) of a reaction to:
   a) The activation energy (Ea) and the rate of reaction
   b) The temperature (T) and the rate of reaction
   c) The concentration of reactants and products
   d) The stoichiometry of the reaction

19. A catalyst increases the rate of a reaction by:
   a) Decreasing the activation energy
   b) Increasing the concentration of reactants
   c) Increasing the temperature
   d) Changing the reaction mechanism

20. The half-life of a reaction is the time required for:
   a) The concentration of reactants to decrease by half
   b) The concentration of products to increase by half
   c) The rate of reaction to reach its maximum value
   d) The reaction to reach equilibrium

21. A substance undergoes first order decomposition. The decomposition follows to parallel fir order reactions as:



The percentage distribution of $B$ and $C$ are:
   a) 80% $B$ and 20% $C$
   b) 76.83% $B$ and 23.17% $C$
   c) 90% $B$ and 10% $C$
   d) 60% $B$ and 40% $C$

22. In Arrhenius plot intercept is equal to
   a) $-E_a/R$   b) $\ln A$   c) $\ln k$   d) $\log_{10} a$

23. Half-life period of a first order reaction is 1386 seconds. The specific rate constant of th reaction is:
   a) $5.0 \times 10^{-2} s^{-1}$   b) $5.0 \times 10^{-3} s^{-1}$   c) $0.5 \times 10^{-2} s^{-1}$   d) $0.5 \times 10^{-3} s^{-1}$

24. On addition of $AgNO_3$ to NaCl, white ppt. occurs:
   a) Instantaneously
   b) With a measurable speed
   c) Slowly
   d) None of these

25. Which is correct about zero order reaction?
    a) Rate of reaction depends on decay constant.
    b) Rate of reaction is independent of concentration.
    c) Unit of rate constant is $conc^{-1}$
    d) Unit of rate constant is $conc^{-1}\ time^{-1}$

26. The half-life period of a first order reaction is 1 min 40 s. Calculate its rate constant.
    a) $6.93 \times 10^{-3} min^{-1}$ b) $6.93 \times 10^{-3} s^{-1}$ c) $6.93 \times 10^{-3} s$ d) $6.93 \times 10^{3} s$

27. The reaction $2A + B + C \rightarrow D + E$ is found to be first order in A, second in B and zero order in C. What is the effect on the rate of increasing concentration of A, B and C two times?
    a) 72 times b) 8 times c) 24 times d) 36 times

28. In a reaction, the threshold energy is equal to:
    a) Activation energy + normal energy of reactants
    b) Activation energy − normal energy of reactants
    c) Activation energy
    d) Normal energy of reactants

29. Which one is not correct?
    a) Rate of zero order reaction depends upon initial concentration of reactant
    b) Rate of zero order reaction does not depend upon initial concentration of reactant
    c) $t_{1/2}$ of first order reaction is independent of initial concentration of reaction
    d) $t_{1/2}$ of zero order reaction is dependent of initial concentration of reaction

30. A reaction proceeds by first order, 75% of this reaction was completed in 32 min. the time required for 50% completion is
    a) 8 min b) 16 min c) 20 min d) 24 min

31. The rate of the reaction
    $\mathrm{CCl_3CHO + NO \rightarrow CHCl_3 + NO + CO}$ is equal to rate $k[\mathrm{CCl_3CHO}][\mathrm{NO}]$. If concentration is expressed in mol/L. The unit of $k$ is
    a) $\mathrm{L\ mol^{-1}\ s^{-1}}$ b) $\mathrm{mol\ L^{-1}\ s^{-1}}$ c) $\mathrm{L^2\ mol^{-2}\ s^{-1}}$ d) $\mathrm{s^{-1}}$

32. Observe the following reaction,
    $2A + B \rightarrow C$
    The rate of formation of C is $2.2 \times 10^{-3} mol\ L^{-1}\ \overset{-1}{\text{min}}$.
    What is the value of $-\frac{d[A]}{dt}$ $(mol\ L^{-1}\ \overset{-1}{\text{min}})$ ?
    a) $2.2 \times 10^{-3}$ b) $1.1 \times 10^{-3}$ c) $4.4 \times 10^{-3}$ d) $5.5 \times 10^{-3}$

33. The unit of rate constant of a third order chemical reaction is
a) $\text{mol}^{-1}\ \text{L}\ \text{s}^{-1}$
b) $\text{mol}^{-1}\ \text{s}^{-2}$
c) mol L
d) $\text{s}^{-1}\ \text{mol}^{-2}\ \text{L}^2$

34. $CH_3COOC_2H_5 + H_2O \xrightarrow{H+} CH_3COOH + C_2H_5OH$ is an example of …… order.
a) Zero
b) Second
c) Third
d) Pseudo first order

35. Collision theory is applicable to
a) First order reactions
b) Zero order reactions
c) Bimolecular reactions
d) Intra-molecular reactions

36. For the first order reaction with the rate constant $k$, which expression gives the rate half-li period? (Initial conc. = $a$)
a) $\frac{3}{2}ka^2$
b) $\frac{1}{ka}$
c) $\frac{1}{k}$
d) $\frac{0.693}{k}$

37. The rate constant $(k')$ of one of the reaction is found to be double that of the rate constant $(k'$ of another reaction. Then the relationship between the corresponding activation energies the two reaction ($E_a'$ and $E_a''$) can be represented as
a) $E_a' > E_a''$
b) $E_a' = 4E''$
c) $E_1' = E_a''$
d) $E_a' < E_a''$

38. For a given reaction of first order, it takes 15 minutes for the concentration to drop fro $0.8\ M$ litre$^{-1}$ to $0.4\ M$ litre$^{-1}$. The time required for the concentration to drop fro $0.1\ M$ litre$^{-1}$ to $0.025\ M$ litre$^{-1}$ will be:
a) 60 minutes
b) 15 minutes
c) 7.5 minute
d) 30 minutes

39. The rate constant for a second order reaction is $8 \times 10^{-5} M^{-1}\text{min}^{-1}$. How long will it take $1M$ solution to be reduced to $0.5M$?
a) $8.66 \times 10^3$ minute
b) $8 \times 10^{-5}$ minute
c) $1.25 \times 10^4$ minute
d) $4 \times 10^{-5}$ minute

40. The slope in Arrhenius plot, is equal to
a) $-\frac{E_a}{2.303\ R}$
b) $\frac{E_a}{R}$
c) $-\frac{R}{2.303\ E_a}$
d) None of the above

41. The rate constants $k_1$ and $k_2$ for two different reactions are $10^{16}e^{-2000/T}$ and $10^{15}e^{-1000/}$ respectively. The temperature at which $k_1 = k_2$ is:
a) $\frac{2000}{2.303}$ K
b) 2000 K
c) $\frac{1000}{2.303}$ K
d) 1000 K

42. If the volume of the vessel in which the reaction $2NO + O_2 \rightarrow 2NO_2$ is occurring is diminishe to 1/3rd of its initial volume. The rate of the reaction will be increased by

a) 3 times b) 9 times c) 27 times d) 36 times

43. The time for half-life period of a creation reaction $A$ →products is 1 h. when the initi concentration of the reactant 'A', is $2.0\, mol\, L^{-1}$, how much time does it take for i concentration to come from 0.50 to 0.25 $mol\, L^{-1}$, if it is a zero order reaction?

a) 4 h b) 0.5 h c) 0.25 h d) 1 h

44. For a reaction $A + B \rightarrow C + D$, if the concentration of A is doubled without altering t concentration of B, the rate gets doubled. If the concentration of B is increased by nine tim without altering the concentration of A, the rate gets tripled. The order of the reaction is

a) 2 b) 1 c) 3/2 d) 4/3

45. What fraction of a reactant showing first order remains after 40 minute if $t_{1/2}$ is 20 minute?

a) ¼ b) $1/2$ c) $1/8$ d) $1/6$

46. At 500 k, the half-life period of a gaseous reaction at an initial pressure of 80 kPa is 350 when the pressure is 40 kPa, the half-life period is 175 s. The order of the reaction is

a) Zero b) One c) Two d) Three

47. Which of the following statements are incorrect?

a) Rate of the reaction involving conversion of *ortho* hydrogen to *para* hydrogen $= -\frac{d[\mathrm{H_2}]}{dt}$ $k[\mathrm{H_2}]^{3/2}$

b) Rate of the reaction involving the thermal decomposition of acetaldehyde $= k[\mathrm{CH_3CHO}]^{1}$

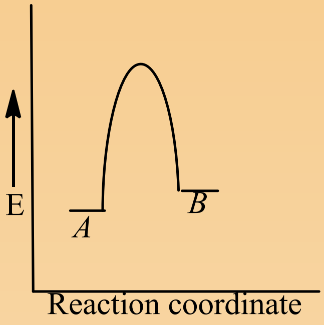
c) In the formation of phosgene from CO and $\mathrm{Cl_2}$, the rate of the reaction $= k[\mathrm{CO}][\mathrm{Cl_2}]^{1/2}$

d) In the decomposition of $\mathrm{H_2O_2}$, the rate of reaction $= k[\mathrm{H_2O_2}]$

48. At 373 K, a gaseous reaction $A \rightarrow 2B + C$ is found to be of first order. Starting with pure the total pressure at the end of 10 min was 176 mm and after a long time when $A$ w completely dissociated, it was 270 mm. The pressure of $A$ at the end of 10 min was

a) 94 mm b) 47 mm c) 43 mm d) 90 mm

49. For a reversible reaction, $A \rightleftharpoons B$, which one of the following statements is wrong from the give energy profile diagram?



a) Activation energy of forward reaction is greater than backward reaction
b) The forward reaction is endothermic
c) The threshold energy is less than that of activation energy
d) The energy of activation of forward reaction is equal to the sum of heat of reaction ar the energy of activation of backward reaction

50. According to the Arrhenius equation a straight line is to be obtained by plotting the logarithm of the rate constant of a chemical reaction ($\log\ k$) against

a) $T$
b) $\log T$
c) $\frac{1}{T}$
d) $\log \frac{1}{T}$

51. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one is true for rate of three reaction?

a) $r_1 = r_2 = r_3$
b) $r_1 > r_2 > r_3$
c) $r_1 < r_2 < r_3$
d) All of these

52. Mathematical expression for $t_{1/4}$ i.e., when (1/4)th reaction is over following first order kinetics can be given by

a) $t_{1/2} = \frac{2.303}{k} \log 4$
b) $t_{1/2} = \frac{2.303}{k} \log 2$
c) $t_{1/2} = \frac{2.303}{k} \log \frac{4}{3}$
d) $t_{1/2} = \frac{2.303}{k} \log \frac{3}{4}$

# HINTS AND SOLUTION

1. d) Volume of the reaction vessel: The volume of the reaction vessel does not directly affect the rate of a chemical reaction.

2. d) Change in concentration of reactants or products over time: The rate of a reaction is determined by measuring the change in concentration of reactants or products over time.

3. d) All of the above: The rate of a chemical reaction can be expressed in terms of moles per liter, grams per liter, or molar concentration.

4. d) All of the above: The order of a reaction can be determined experimentally by measuring the initial rate of reaction, the rate constant, or analyzing the integrated rate equation.

5. d) All of the above: The rate constant of a reaction is affected by temperature, presence of a catalyst, and activation energy.

6. b) 1/s: In a first-order reaction, the rate constant has the unit of 1/s.

7. d) Rate = k: A zeroth-order reaction has a rate equation of the form Rate = k.

8. b) First order: First-order reactions exhibit a linear relationship between the concentration and time.

9. a) The slowest step in a reaction mechanism: The rate-determining step is the slowest step in a reaction mechanism and determines the overall rate of the reaction.

10. b) First order: When the rate of a reaction is halved with the halving of reactant concentration, it indicates a first-order reaction.

11. d) All of the above: Increasing temperature, concentration of reactants, and adding a catalyst can all increase the rate of a reaction.

12. c) Both a) and b): According to the collision theory, a reaction is more likely to occur when reactant molecules collide with sufficient energy and proper orientation.

13. d) The energy barrier that must be overcome for a reaction to occur: Activation energy is the energy barrier that must be overcome for a reaction to occur.

14. c) Initial concentration of reactants: The rate constant of a reaction is not affected by the initial concentration of reactants.

15. a) Increases with increasing temperature: The rate constant of a reaction generally increases with increasing temperature.

16. a) They are single-step reactions with a single transition state: Elementary reactions are single-step reactions that occur through a single transition state.

17. a) Adding the orders of each reactant in the rate equation: The overall order of a reaction is determined by adding the orders of each reactant in the rate equation.

18. b) The temperature (T) and the rate of reaction: The Arrhenius equation relates the rate constant (k) of a reaction to the temperature (T) and the rate of reaction.

19. a) Decreasing the activation energy: A catalyst increases the rate of a reaction by decreasing the activation energy required for the reaction to occur.

20. a) The concentration of reactants to decrease by half: The half-life of a reaction is the time required for the concentration of reactants to decrease by half.

21 **(b)**

For parallel path reaction

$K_{\text{average}} = K_1 + K_2 = 1.26 \times 10^{-4} + 3.8 \times 10^{-5}$

$= 1.64 \times 10^{-4} \text{sec}^{-1}$

Also fractional yield of $B = \frac{K_B}{K_{\text{av}}} = \frac{1.26\times10^{-4}}{1.64\times10^{-4}} = 0.7683$

Fractional yield of $A = \frac{K_A}{K_{\text{av}}} = \frac{3.8\times10^{-5}}{1.64\times10^{-4}} = 0.2317$

23 **(d)** For first order : $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386} = 5 \times 10^{-4} \text{s}^{-1}$

24 **(a)**Ionic reactions are instantaneous one.

25 **(b)**For zero order reaction, rate of reaction is independent of concentration i.e., rate of reaction does not depend upon the concentration of reactant.

$$\frac{dx}{dt} = k[A]^0$$

26 **(c)**$t_{1/2} = 100s$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100}$$

$$k = 6.93 \times 10^{-3} s^{-1}$$

27 **(b)** The rate law for the reaction is as

r=$\frac{dx}{dt}$=k(A)$(B)^2(C)^0$=$k(A)(B)^2$

on increasing the concentration of A,B and C two times.

r'=$\frac{dx}{dt}$=k(2A)$(2B)^2(2C)^0$

=8k(A)$(B)^2$

Thus, the rate increases eight times.

28 **(a)**Activation energy is the needed by reactant molecules to gain threshold energy level.

29 **(a)**The rate of zero order reaction is independent of the concentration of the reactants or the concentration of the reactant do not change with time. Thus, the rate of reaction remains constant.

$$\frac{dx}{dt} = k(a-x)^0 \Rightarrow \frac{dx}{dt} = k$$

Or Rate=k

30 **(b)** For first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

Where, a= initial concentration

X= change in concentration during time‘t’.

If 75% of the reaction was completed in 32 min, then

$$k = \frac{2.303}{32} \log_{10} \frac{100}{100-75} = \frac{2.033}{32} \log_{10} 4$$

$$k = 0.0433 \text{min}^{-1}$$

Hence, time required for the completion of 50% reaction.

$$t = \frac{2.303}{0.0433} \log_{10} \frac{100}{100-75}$$

$$= \frac{2.033}{32} \log_{10} 2 = 16\, min$$

31 **(a)**For the reaction :

$$\mathrm{CCl_3CHO + NO \rightarrow CHCl_3 + NO + CO}$$

$$\text{Rate} = \frac{dx}{dt} = k[\mathrm{CCl_3CHO}][\mathrm{NO}]$$

$$k = \frac{dx}{dt \times [\mathrm{CCl_3CHO}][\mathrm{NO}]}$$

$$= \frac{\mathrm{mol/L}}{\mathrm{s \times mol/L \times mol/L}}$$

$$k = \mathrm{L\, mol^{-1}\, s^{-1}}$$

32 **(c)** $2A + B \rightarrow C$

Rate of reaction,

$$= -\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

$$\therefore -\frac{d[A]}{dt} = 2\frac{d[C]}{dt}$$

$$= 2 \times 2.2 \times 10^{-3}$$

$$= 4.4 \times 10^{-3} mol\, L^{-1} \text{min}^{-1}$$

33 **(d)** For third order reaction,

$$\text{rate} = k[A]^3$$

$$\frac{\mathrm{mol\ L^{-1}}}{\mathrm{s}} = k(\mathrm{mol - L^{-1}})^3$$

$$k = \frac{1}{\mathrm{mol^2\ L^{-2}\ s}}$$

$$= \mathrm{mol^{-2}\ L^2\ s^{-1}}$$

34

**(d)**$CH_3COOC_2H_5 + H_2O \xrightarrow{H+} CH_3COOH + C_2H_5OH$

Since, in this reaction, water is excess, it is an example of psedo first order reaction (as rate depends only on the concentration of $CH_3COOC_2H_5$).

35.(C)

36 **(d)**$k = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$

For half-life period, $x = \frac{a}{2}$

$$t = \frac{2.303}{k}\log_{10}\frac{a}{a-\frac{a}{2}}$$

$$t = \frac{2.303}{k}\log_{10} 2$$

$$\because t = t_{1/2}$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k}$$

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

37 **(d)**$\because$ Rate constant $(k')$ > rate constant $(k'')$

Greater the rate constant lesser will be the activation energy

$$\therefore E_a' < E_a''$$

38 **(d)**The reactant concentration drop from 0.8 to $0.4\,M$, i.e., 50% takes place in 15 minute.

$$K = \frac{2.303}{15}\log\frac{0.8}{0.4} = \frac{0.693}{15} = 0.0462\text{ min}^{-1}$$

$$\text{Also, } t = \frac{2.303}{K}\log\frac{0.1}{0.025} = \frac{2.303}{0.0462}\log\frac{0.1}{0.025} = 30\text{ min}$$

39 **(c)**For II order, $t = \frac{1}{Ka}\frac{x}{(a-x)}$

$$\therefore \quad t = \frac{1}{8 \times 10^{-5} \times 1}\left(\frac{0.5}{0.5}\right)$$

$$= 1.25 \times 10^{-4} \text{ minute}$$

40 **(a)**The Arrhenius equation can be written as

$$\log k = \log A - \frac{E_a}{2.303\ RT}$$

On comparing this equation with standard equation of straight line

$y = mx + c$, we get,

$y = \log k$

$x = \frac{1}{T}$

$m = -\frac{E_a}{2.303R}$

$c = \log A$

Hence, on plotting graph between $\log k$ ($y -$ axis)and $\frac{l}{T}$ ($x$-axis), we get a line with slope equal to

$$m = -\frac{E_a}{2.303\ R}$$

41 **(c)** $K_1 = 10^{16}e^{-2000/T}; K_2 = 10^{15}e^{-1000/T}$

if $\quad K_1 = K_2$ then $10^{16}e^{-2000/T} = 10^{15}e^{-1000/T}$

or $\quad \log 10 - \frac{2000}{T} = -\frac{1000}{T}$ or $T = \frac{1000}{2.303}$ K

42 **(c)**As we know that, rate of reaction is directly proportional to concentration of reactant and inversely proportional to the volume of vessel.

$i.e.$,concentration$\alpha \propto \frac{n}{v}$

For a given reaction,

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

Rate of reaction=$k[NO]^2[O_2]$

If volume of vessel is reduced by $\frac{1}{3}rd$ of its initial value, then concentration of compound is increase by 3 times. Hence, the rate of reaction will be increased by 27 times.

43 **(c)** For a zero-order reaction

$$k_0 = \frac{[A_0]}{2t_{1/2}}$$

Since,$[A]_0 = 2\ M, t_{1/2} = 1\ h$

So, $k_0 = 1$ and

$$k_0 = \frac{\Delta x}{t}\ or\ t = \frac{0.50 - 0.25}{1} = 0.25\ h$$

44 **(c)**$A + B \rightarrow C + D$

Rate ($r$)=$k[A]^a[B]^b$ …(i)

$2r$=$k[2A]^a[B]^b$ ... (ii)

$3r$=$k[A]^a[9B]^b$ …(iii)

Dividing eq.(ii) by eq.(i)

$2 = 2^a$or a=1

Dividing eq (iii)by eq.(i)

$3 = 9^b\ or\ 3 = 3^{2b}\ \ or\ 2b = 1\ or\ b = 1/2$

So order of reaction $= 1 + \frac{1}{2} = \frac{3}{2}$

45 **(a)** $N = \frac{N_0}{2^n}$

$$n = \frac{T}{t_{1/2}} = \frac{40}{20} = 2$$

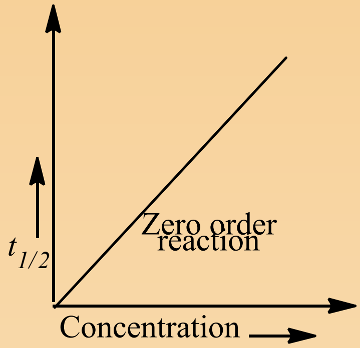
$$\therefore \quad N = \frac{N_0}{2^2} = \frac{N_0}{4}$$

46 **(a)**

$p_1 = 80\text{ kPa}, \left(\mathrm{t}_{1/2}\right)_1 = 350s$

$p_1 = 40\text{ kPa}, \left(\mathrm{t}_{1/2}\right)_1 = 175s$

$\frac{80}{40} = \frac{350}{175} = 2$



$\because \frac{p_1}{p_2} = \frac{\left(\mathrm{t}_{1/2}\right)_1}{\left(\mathrm{t}_{1/2}\right)_2} = \frac{a_1}{a_2}$

$\left(\mathrm{t}_{1/2}\right) \propto a(\text{zero order reaction})$

47 **(b)**Thermal decomposition,

$$\mathrm{CH_3CHO} \xrightarrow{\Delta} \mathrm{CH_4} + \mathrm{CO}$$

$$\frac{dx}{dt} = k[\mathrm{CH_3CHO}]^{3/2}$$

48 **(b)**For the reaction : $A \rightarrow 2B + C$

| | $A$ | $2B$ | $C$ |
|---|---|---|---|
| | $p_1$ | $0$ | $0$ |
| After 10 min | $p_1 - p$ | $2p$ | $p$ |
| After long time | $0$ | $2p_1$ | $p_1$ |

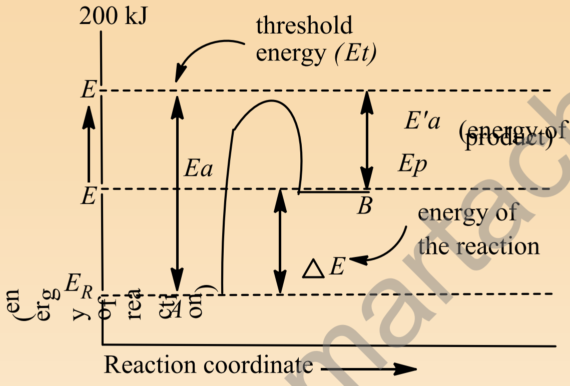
Total pressure $= (p_1 - p + 2p + p) = 176$ mm

Total pressure after long time

$= 2p_1 + p_1 = 270$ mm

Calculate the value of $p$ from above two equation and then the difference of $p_1$ and $p$ will be the pressure of $A$

49. (c)



Where,

$E_a$ =activation energy of forward reaction

$E_a''$=activation energy of backward reaction

The above energy profile diagram shows that

$E_a > E_a''$

The potential energy of the product is greater than that of the reactant, so the reaction is endothermic.

$E_a = E_a'' + \Delta E$

$E_t = E_a$ or $E_t > E_a''$

50 (a)$K = Ae^{-E_a/RT}$

51 (d) $r_1 = K[A]^1$; $r_2 = K[A]^2, r_3 = K[A]^3$

if $[A] >$ t; $r_3 > r_2 > r_1$

52 (c) $t = \frac{2.303}{k} log \frac{a}{(a-x)}$

If $t = t_{1/4}$; $x = a/4$

$\therefore t_{1/4} = \frac{2.303}{k} log \frac{a}{(a-1/4)}$

$\frac{2.303}{k} \log \frac{4}{3}$