CHAPTER 04

Chemical Kinetics

1. **Chemical kinetics** is the branch of Chemistry which deals with the study of reaction rates and their mechanisms.
2. The **speed** or the **rate of a chemical reaction** can be defined as the change in concentration of reactants or products in unit time.
3. The **average rate of reaction** is the appearance of product or disappearance of reactants over a period of time interval.

$$r_{\text{av}} = -\frac{\Delta[R]}{\Delta t} = +\frac{\Delta[P]}{\Delta t}$$

4. Reaction rate, at a particular moment of time is called **instantaneous rate** of the reaction.

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

As, $\Delta t \to 0$

Average rate approaches to instantaneous rate.

Unit of the rate of reaction

$$\text{Rate of reaction} = \frac{dx}{dt} = \frac{\text{mol L}^{-1}}{\text{s}}$$

5. **Rate of a chemical reaction** depends upon the experimental conditions, like concentration of one or more reactants (pressure in case of gases), temperature, catalyst and surface area of the reactants.
6. **Rate law** is the expression in which the reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation. It cannot be decided from the balanced chemical equation, i.e. theoretically. It has to be determined experimentally.
7. The sum of the powers of the concentration of the reactants in the rate law expression is called the **order of that chemical reaction.**

   It can be zero or have fractional value but molecularity of a reaction cannot be zero or a non-integer.

   It is always an integer and cannot be more than three.
8. The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called **molecularity of a reaction.**
9. **Rate constant** (k) is the rate of chemical reaction when concentration of each reactant is unity.

   The rate constant is also called the **specific reaction rate**.

   For nth order of reaction,

   Units of $k = (\text{mol L}^{-1})^{1-n}\,(\text{time})^{-1}$, where, n = order of reaction.
10. **Half-life ($t_{1/2}$)** is the time in which the concentration of a reactant is reduced to one half of its initial concentration. For first order reaction, $t_{1/2} = 0.693/k$.
11. Given table summarises the mathematical features of integrated laws of zero and first order reactions.

Integrated Rate Laws for the Reactions of Zero and First Order

Order	Reaction type	Differential rate law	Integrated rate law	Straight line plot	Half-life	Units of k
0	$R \to P$	$d[R]/dt = -k$	$kt = [R]_0 - [R]$	$[R]$ vs t	$[R]_0/2k$	Conc. time^{-1} or mol L^{-1}s^{-1}
1	$R \to P$	$d[R]/dt = -k[R]$	$[R] = [R]_0 e^{-kt}$ or $kt = \ln\{[R]_0/[R]\}$	$\ln[R]$ vs t (with negative slope) $\log\frac{[R_0]}{[R]}$ vs t (with positive slope)	$\ln 2/k = \frac{0.693}{k}$	time^{-1} or s^{-1}

12. The reactions which are not actually of first order but behave, so due to changed conditions are called **pseudo first order reactions**. For example, hydrolysis of ethyl acetate, as in this case concentration of water is not considered in calculation because its concentration does not get changed much with time.

13. For a chemical reaction with rise in temperature by 10°, the rate constant is nearly doubled.

Temperature coefficient is the ratio of rate constant at temperature (T + 10) K to the rate constant at temperature T (K).

$$\text{Temperature coefficient} = \frac{\text{Rate constant } (k) \text{ at } (T+10) \text{ K}}{\text{Rate constant } (k) \text{ at } T \text{ K}}$$

14. The temperature dependence of rate for a chemical reaction is expressed by **Arrhenius equation**.

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

Where, A is the Arrhenius factor or the frequency factor, also called **pre-exponential factor**.

$$\ln\ k = \frac{-E_a}{RT} + \ln A$$

- The plot of ln k *vs* $1/T$ gives a straight line with slope $= -\frac{E_a}{R}$ and intercept $= \ln A$
- Rate constants k_1 and k_2 at two different temperatures T_1 and T_2 repectively can written as,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 \cdot T_2}\right]$$

15. **Activation energy** (E_a) is the extra energy required by the reactant molecules that results into effective collision between them to form the products.

16. **Threshold energy** is the minimum energy which the colliding molecules must have for effective collisions.

(Collisions which lead to the formation of product molecules).

17. According to **collision theory**, rate collisions which lead to the formation of product molecules

$= Z_{AB}\, e^{-E_a/RT}$ where, Z_{AB} = collision frequency of the reactants A and B.

$e^{-E_a/RT}$ = fraction of molecules with energies equal to or greater than E_a.

Practice Questions

1. Rate of which of the following reactions can be determined easily?

(a) Rusting of iron in the presence of air and moisture
(b) Hydrolysis of starch
(c) Reaction of silver nitrate with sodium chloride
(d) All of the above

2. For the reaction,

$$2X + Y \longrightarrow X_2Y$$

What will be the expression for instantaneous rate of the reaction?

(a) $\frac{-d[X]}{2dt}$ *(b)* $+\frac{1}{2}\frac{d[Y]}{dt}$
(c) $-\frac{1}{2}\frac{d[X_2Y]}{dt}$ *(d)* None of these

3. Choose the correct value of $\frac{d[\mathrm{NH_3}]}{dt}$ for the reaction,

$$\mathrm{N_2 + 3H_2 \longrightarrow 2NH_3}$$

(a) $-\frac{2}{3}\frac{d[\mathrm{H_2}]}{dt}$ *(b)* $\frac{2}{3}\frac{d[\mathrm{H_2}]}{dt}$
(c) $\frac{3}{2}\frac{d[\mathrm{N_2}]}{dt}$ *(d)* $-\frac{3}{2}\frac{d[\mathrm{N_2}]}{dt}$

4. In a reaction, $2x \rightarrow y$, the concentration of x decreases from 3.0 M to 1.5 M in 4 min.

The rate of the reaction is

(a) 0.187 M $\mathrm{min^{-1}}$ *(b)* 1.87 M $\mathrm{min^{-1}}$
(c) 3.75×10^{-1} M $\mathrm{min^{-1}}$ *(d)* 0.75 M $\mathrm{min^{-1}}$

5. Rate law cannot be determined from balanced chemical equation, if ....

(a) reverse reaction is involved
(b) it is an elementary reaction
(c) it is a sequence of elementary reactions
(d) Both *(a)* and (c)

6. On mixing $1\,\mathrm{dm^3}$ of 3M ethanol with $1\,\mathrm{dm^3}$ of 2 M ethanoic acid, an ester is formed.

$$\mathrm{C_2H_5OH + CH_3COOH \longrightarrow CH_3COOC_2H_5 + H_2O}$$

If each solution is diluted with an equal volume of water, the decrease in the initial rate would be

(a) 0.5 times *(b)* 3 times
(c) 0.25 times *(d)* 2 times

7. Which of the following rate expression is correct against its reaction?

(a) $\mathrm{2NO}(g) + \mathrm{O_2}(g) \longrightarrow \mathrm{2NO_2}(g)$; Rate = $k[\mathrm{NO}]^2\,[\mathrm{O_2}]$

(b) $\mathrm{CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl}$;
Rate = $k[\mathrm{CHCl_3}]\,[\mathrm{Cl_2}]^{1/2}$

(c) $\mathrm{CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH}$;
Rate = $k[\mathrm{CH_3COOC_2H_5}]^1\,[\mathrm{H_2O}]^0$.

(d) All of the above

8. Consider the following reactions,

$$\mathrm{O_3 \rightleftharpoons O_2 + O} \quad \text{(fast)} \qquad \ldots\text{(i)}$$
$$\mathrm{O + O_3 \longrightarrow 2O_2} \quad \text{(slow)} \qquad \ldots\text{(ii)}$$

The rate law expression should be

(a) $r = k\,[O_3]^2\,[O_2]^{-1}$ *(b)* $r = k\,[O_3][O_2]$

(c) $r = k\,[O_3]^2$ *(d)* $r = k\,[O_2]^{-1}$

9. Reaction of chloroform with chlorine is an example of fraction order reaction.

Its rate law expression is rate $= k[CHCl_3][Cl_2]^{1/2}$. If both are assumed in gaseous state and pressure is measured in bar, then units of rate and rate constant respectively are

(a) bar min^{-1}, $\text{bar}^2\ \text{min}^{-1}$

(b) bar min^{-1}, $\text{bar}^{-1/2}$, min^{-1}

(c) $\text{bar}^{-1/2}$, min^{-1}, $\text{bar}^2\ \text{min}^{-1}$

(d) bar min^{-1}, $\text{bar}^{-1/2}\ \text{min}^{-1}$

10. The rate constant is numerically equal for three reactions of first, second and third order respectively. Which of the following is true?

(a) If $[A] > 1;\ r_3 > r_2 > r_1$ *(b)* If $[A] = 1;\ r_1 = r_2 = r_3$

(c) If $[A] < 1;\ r_1 > r_2 > r_3$ *(d)* All of the above

11. For the reaction, $I^- + OCl^- \longrightarrow IO^- + Cl^-$

in aqueous medium, the rate of a reaction is given by $\frac{d[IO^-]}{dt} = k\frac{[I^-][OCl^-]}{[OH^-]}$ the overall order of the reaction is

(a) −1 *(b)* 1 *(c)* 0 *(d)* 2

12. The reaction, $2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$ is

(a) bimolecular and first order

(b) unimolecular and second order

(c) bimolecular and second order

(d) unimolecular and first order

13. Four reactions are given below. Which one of them is of zero order?

(a) $PCl_5 \longrightarrow PCl_3 + Cl_2$

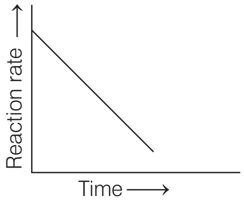
(b) $2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$

(c) $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

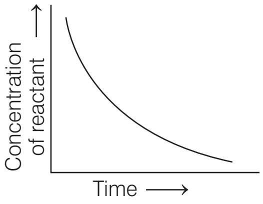
(d) $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

14. Which of the following graph is correct for a zero order reaction?

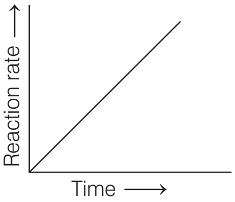
(a)



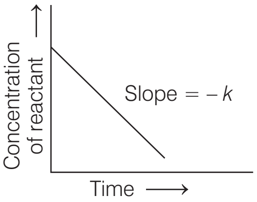
(b)



(c)



(d)



15. For a zero order reaction, a graph of concentration (along y-axis) and time (along x-axis) is linear with

(a) a zero intercept and a +ve slope

(b) a zero intercept and a –ve slope

(c) a non-zero intercept and a –ve slope

(d) a non-zero intercept and a +ve slope

16. The rate constant of the reaction, $A \rightarrow B$ is 0.6×10^{-3} mole per litre per second. If the concentration of A is 5 M then, concentration of B after 20 min is

(a) 1.08 M *(b)* 3.60 M

(c) 0.36 M *(d)* 0.72 M

17. A first order reaction has a rate constant of $2.303 \times 10^{-3}\ s^{-1}$. The time required for 40 g of this reactant to reduce to 10 g will be [Given that $\log_{10} 2 = 0.3010$]

(a) 230.3 s *(b)* 301 s

(c) 2000 s *(d)* 602 s

18. For a first order reaction,

(a) $t_{1/2} = \frac{k}{a}$ *(b)* $t_{3/4} = 2t_{1/2}$

(c) $t_{1/2} = \frac{0.693}{2k}$ *(d)* $t_{1/2} = k \times 0.693$

19. If half-life of a substance is 36 minutes. The amount left after 2 hrs will be [Given $(A_0) = 10\,\text{g}$]

(a) 1 g *(b)* 2 g

(c) 3 g *(d)* 4 g

20. 99% completion of a first order reaction takes place in 32 min. The time taken in 99.9% completion of the reaction will be

(a) 48 min *(b)* 52 min

(c) 56 min *(d)* 44 min

21. The temperature coefficient of a reaction is

(a) the ratio of rate constant at two temperatures

(b) the ratio of rate constant differing by 10° preferably 25°C and 35°C

(c) the rate constant at a fixed temperature

(d) None of the above

22. A chemical reaction was carried out at 300 K and 280 K. The rate constant were found to be k_1 and k_2 respectively, then

(a) $k_2 = 4k_1$ *(b)* $k_2 = 0.25k_1$

(c) $k_2 = 2k_1$ *(d)* $k_1 = 0.5k_1$

23. What is the activation energy (kJ/mol) for a reaction if its rate constant doubles when the temperature is raised from 300 K to 400 K ?

(R = 8.314 $\text{Jmol}^{-1}\text{K}^{-1}$).

(a) 69.1 *(b)* 6.91

(c) 34.4 *(d)* 3.44

24. In order to produce the effective collisions, the colliding molecules must have

(a) a certain minimum amount of energy

(b) proper orientation

(c) Both threshold energy and proper orientation

(d) energy equal to or greater than threshold energy

25 Higher order (>3) reactions are rare due to

(a) low probability of simultaneous collision of all the reacting species

(b) increase in entropy and activation energy as more molecules are involved

(c) shifting of equilibrium towards reactants due to elastic collisions

(d) loss of active species on collision

ANSWERS

1. (b)	**2.** (a)	**3.** (a)	**4.** (a)	**5.** (b)	**6.** (c)	**7.** (d)	**8.** (a)	**9.** (d)	**10.** (d)
11. (b)	**12.** (a)	**13.** (c)	**14.** (d)	**15.** (c)	**16.** (d)	**17.** (d)	**18.** (b)	**19.** (a)	**20.** (a)
21. (b)	**22.** (b)	**23.** (b)	**24.** (d)	**25.** (a)					

Hints & Solutions

1. (*b*) Rate of only those chemical reactions can be determined easily which occurs at moderate speed, e.g. hydrolysis of starch, inversion of cane sugar etc.

2. (*a*) For the reaction,

$$2X + Y \longrightarrow X_2Y$$

The instantaneous rate of the reaction is given as,

$$-\frac{d[X]}{2dt} = \frac{-d[Y]}{dt} = +\frac{d[X_2Y]}{dt}$$

3. (*a*) For the reaction,

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

The instantaneous rate of reaction is given as

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

$$\therefore \quad \frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$$

4. (*a*) Rate of reaction $= -\frac{1}{2}\frac{d[x]}{dt} = -\frac{1}{2}\frac{[1.5-3.0]}{4}$

$$= \frac{1.5}{8} = 0.187 \text{ M min}^{-1}$$

6. (*c*) For the given reaction,

$$C_2H_5OH + CH_3COOH \longrightarrow CH_3COOC_2H_5 + H_2O$$

$$r = k[CH_3COOH][C_2H_5OH] \text{ or } r = k\left[\frac{n}{V}\right]\left[\frac{n}{V}\right]$$

Increasing volume (V) by twice (due to dilution) will reduce the rate by 4 times.

i.e. $r = 0.25\,k\,[CH_3COOH][C_2H_5OH]$

8. (*a*) Given, $O_3 \rightleftharpoons O_2 + O$ (fast) ...(i)

$O + O_3 \longrightarrow 2O_2$ (Slow) ...(ii)

From Eq. (i) $K_{eq} = \frac{[O_2][O]}{[O_3]}$

or $[O] = \frac{K_{eq}[O_3]}{[O_2]}$

From Eq. (ii)

rate law = $k[O_3][O]$

or $r = \frac{k[O_3][O_3]}{[O_2]}K_{eq}$

or $r = k'\,[O_3]^2[O_2]^{-1}\,[k' = k \times K_{eq}]$

9. (*d*) Given, rate = $k[CHCl_3]\,[Cl_2]^{1/2}$

$$\because \quad \text{Order} = 1 + \frac{1}{2} = \frac{3}{2}$$

$$\therefore \text{Units of rate constant} = \frac{\text{Units of rate}}{[CHCl_3]\,[Cl_2]^{1/2}}$$

$$= \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2}\text{min}^{-1}$$

and units of rate is bar min^{-1}.

10. (*d*) Consider a reaction $A \longrightarrow$ Products

Let r_1, r_2 and r_3 are the rate for first, second and third order respectively.

$\therefore$ $r_1 = k[A]^1$ for 1st order ...(i)

$r_2 = k[A]^2$ for 2nd order ...(ii)

$r_3 = k[A]^3$ for 3rd order ...(iii)

$\because$ k is same in all the three cases.

Therefore, If $[A] = 1$, $r_1 = r_2 = r_3$

If $[A] < 1$, $r_1 > r_2 > r_3$

If $[A] > 1$, $r_3 > r_2 > r_1$

11. (b) $\because$ The rate of reaction is given by,

$$\frac{d[\mathrm{IO}^-]}{dt}=\frac{k[\mathrm{I}^-][\mathrm{OCl}^-]}{[\mathrm{OH}^-]}.$$

Therefore, overall order of reaction $= 1 + 1 - 1 = 1$

12. (a) The given reaction,

i.e. $$2N_2O_5 \rightleftharpoons 2N_2O_4 + O_2$$

occurs in two steps and, hence biomolecular reaction and the rate determining step is the slowest step which is of first order.

13. (c) Among the given reactions, reaction between hydrogen and chlorine under influence of UV-light is an example of zero order reaction,

i.e. $$H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$$

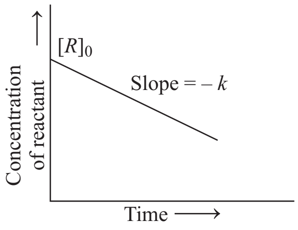
14. (d) For a zero order reaction,

$$[R] = (-k)\,t + [R]_0 \qquad \text{...(i)}$$

On comparing with equation of straight line;

$$y = mx + c$$
$$y = [R]\,\text{concentration}$$
$$x = t\,\text{(time)}$$
$$\text{Slope } (m) = -k \text{ (rate constant)}$$
$$\text{Intercept } (c) = [R]_0 \text{ (initial concentration)}$$

Thus, the graph between conc. of reactant and time is given as,



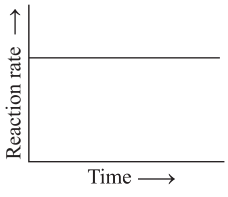
Moreover, on rearranging Eq. (i)

$$\frac{[R]-[R]_0}{t} = -k$$

$$\frac{[R]-[R]_0}{t} = -kt^0$$

$$\text{Rate} \propto t^0$$

Therefore, the graph between reaction rate and time is given as,



15. (c) For a zero order reaction, a graph of concentration and time is linear with a non-zero intercept, $[R]_0$ and a (–)ve slope, $-k$.

16. (d) For a zero order reaction, unit of rate constant is (mol $L^{-1}\,s^{-1}$).

Hence, we can easily calculate the concentration of B after 20 min by the following formula,

$$X = kt = 0.6 \times 10^{-3} \times 20 \times 60 = 0.72\ \text{M}$$

17. (d) For first order reaction,

$$t = \frac{2.303}{k}\log\frac{a}{a-x} \qquad \text{...(i)}$$

Given : $k = 2.303 \times 10^{-3}\ s^{-1}$,

$a = 40$ g, $a - x = 10$ g

On substituting the given values in Eq. (i), we get

$$t = \frac{2.303}{2.303 \times 10^{-3}}\log\frac{40}{10}$$
$$= 10^3 \log 2^2 = 2 \times 10^3 \times \log 2$$
$$= 2 \times 10^3 \times 0.3010 = 602\ \text{s}$$

Alternative method

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} \Rightarrow t_{1/2}(t_{50\%}) = \frac{0.693}{2.303 \times 10^{-3}} = 301\text{s}$$

Also, $t_{75\%} = 2t_{50\%}$

$\therefore$ $t_{75\%} = 2 \times 301 = 602$ s

18. (b) Decomposition of benzene diazonium chloride occur the following manner.

$$C_6H_5\overset{+}{N}\equiv N\overset{-}{Cl} \longrightarrow C_6H_5Cl + N_2 \uparrow$$

The volume of nitrogen obtained shows the extent of decomposition of benzene diazonium chloride, so

$$a \propto V_\infty = 162\ \text{mL}$$
$$(a - x) \propto (V_\infty - V_t)\ \text{mL}$$

For first order reaction,

$$k = \frac{2.303}{t}\log_{10}\frac{V_\infty - V_0}{V_\infty - V_t}$$

or $$k = \frac{2.303}{t}\log_{10}\frac{V_\infty}{V_\infty - V_t} \qquad (\because V_0 = 0)$$

At 20 min,

$$k = \frac{2.303}{20}\log_{10}\frac{162}{162-10} = \frac{2.303}{20}\log_{10}\frac{162}{152}$$
$$= 3.18 \times 10^{-3}\ \text{min}^{-1} \approx 3.2 \times 10^{-3}\ \text{min}^{-1}$$

19. (a) Given,

$t_{1/2} = 36$ min, $t = 2$ hrs $= 120$ min, $[A]_0 = 10$ g

For first order reaction,

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

$\therefore$ $$k = \frac{0.693}{36} = 0.01925$$

As, we know that, $t = \dfrac{2.303}{k}\log\dfrac{[A]_0}{[A]}$

where, $[A]_0$ = initial amount

$[A]$ = final amount

$\therefore$ $$120 = \frac{2.303}{0.019}\log\frac{[A]_0}{[A]}$$

$$\log 10 - \log[A] = 1 \Rightarrow 1 - \log[A] = 1$$
$$\log[A] = 0$$

Thus, $[A] = 1\,\text{g}$

20. (*a*) For first order reaction,

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

$$\therefore\ k = \frac{2.303}{32\ \text{min}}\log\frac{a}{a-0.99a} = 0.1439\ \text{min}^{-1}$$

$$\Rightarrow\ t = \frac{2.303}{0.1439}\log\frac{a}{a-0.999a} = 48\ \text{min}$$

21. (*b*) The temperature coefficient of a reaction is the ratio of rate constant differing by 10° preferably 25°C and 35°C.

22. (*b*) For every 10°C rise, rate constant gets doubled. Hence, for every 20° C rise, rate constant will be 4 times.

Therefore, according to the given statement,

Temperature	280K	300K
Rate constant	k_2	$k_1(4k_2)$

Thus, $k_1 = 4k_2$

$\Rightarrow$ $k_2 = 0.25k_1$

23. (*b*) Given, $T_1 = 300\ \text{K},\ T_2 = 400\ \text{K}$

$R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$

$$\Rightarrow\quad \frac{k_2}{k_1} = \frac{2}{1} \Rightarrow \log\frac{k_2}{k_1} = \frac{E_a}{2.303\times R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Thus, $$\log\frac{2}{1} = \frac{E_a}{2.303\times 8.314}\left[\frac{1}{300} - \frac{1}{400}\right]$$

$$E_a = 0.3010\times 2.303\times 8.314\times 3\times 400$$

$$E_a = 6.91\ \text{kJ mol}^{-1}$$

24. (*d*) Energy ≥ threshold energy and proper orientation both results in effective collisions.

25. (*a*) The main conditions for the occurrence of a reaction are proper orientation and effective collision of the reactants.

Since, the chances of simultaneous collision with proper orientation between two species in high order reactions are very rare, so reaction with order greater than 3 are rare.