# 3
## CHAPTER
# Chemical Kinetics

## Level - 1 CORE SUBJECTIVE QUESTIONS

## MULTIPLE CHOICE QUESTIONS (MCQs) (1 Mark)

1. **Option (C) is correct.**
**Explanation:** The order of reaction is zero as the unit of $k$ is mol $L^{-1}s^{-1}$.

$$\text{Thus, half life} = \frac{[R]_o}{2k}$$

$$= \frac{4.62\times10^{-2}}{2\times2.31\times10^{-2}} = 1\text{ s}$$

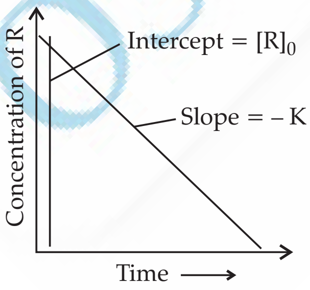
2. **Option (D) is correct.**
**Explanation:** First order reaction $[R] = [R_0]\ e^{-kt}$ If $[R]=0$ then $e^{-kt} = 0$, which is not possible for any finite value of $t$. Here, $t$ is $\infty$.

3. **Option (A) is correct.**
**Explanation:**

$$\text{Rate} = K\,[P]^n \quad \text{...(i)}$$
$$8 \times \text{Rate} = K\,[2P]^n \quad \text{...(ii)}$$
$$\frac{\text{Rate}}{8\times\text{Rate}} = \frac{K[P]^n}{K[2P]^n}$$
$$\frac{1}{\rho} = \frac{1}{[2]^n}$$
$$[2]^n = 8$$
$$[2]^3 = 8$$
$$n = 3$$

4. **Option (C) is correct.**
**Explanation:** In the presence of catalyst activation energy decreases which lead to increase the rate constant.

5. **Option (B) is correct.**
**Explanation:**



6. **Option (A) is correct.**
**Explanation:**

$$\text{rate} = \frac{-d[X]}{dt} = -\frac{1}{2}\frac{d[Y]}{dt} = +\frac{d[P]}{dt}$$

$$-\frac{1}{2}\frac{d[Y]}{dt} = +\frac{d[P]}{dt}$$

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

7. **Option (D) is correct.**
**Explanation:**

$$\log K = \log A - \frac{E_a}{2.303RT}$$
$$\text{Slope} = -\frac{E_a}{2.303R}$$
$$\text{Intercept} = \log A$$

8. **Option (B) is correct.**
**Explanation:**

$$\text{Rate} = K[A]^n \quad \text{...(i)}$$
$$n = \text{order of the reaction}$$
$$16\,r = K[4A]^n \quad \text{...(ii)}$$

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

$$16 = 4n$$
$$n = 2$$

Order of the reaction = 2

9. **Option (C) is correct.**
**Explanation:** The Arrhenius equation describes how the rate constant (k) depends on Temperature (T) and activation energy (e).
According to Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

Where, $k$ = rate constant;
A = frequency factor (pre-exponential factor)
$E_a$ = activation energy
R = gas constant
T = Temperature in kelvin

10. **Option (B) is correct.**
**Explanation:** A catalyst creates a new reaction pathway which has different activation energy.

11. **Option (C) is correct.**
**Explanation:**

$$r = K[A]^n \quad \text{...(i)}$$
$$2r = K[4A]^n \quad \text{...(ii)}$$

From eq. (i)

$$2 \times K[A]^n = K[4[A])^n$$
$$2 = 4^n$$
$$2 = 2^{2n}$$
$$1 = 2n$$
$$n = \frac{1}{2}$$

**12. Option (C) is correct.**

**Explanation:** Rate = $K[A]^2[B]^0$

**13. Option (B) is correct.**

**Explanation:**

$$\text{rate} = -\frac{1}{3}\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$$
$$-\frac{2}{3}\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

**14. Option (C) is correct.**

**Explanation:** This is because the rate of reaction is independent of the concentration of the reactants.

**15. Option (B) is correct.**

**Explanation:**

$$\text{Unit of K} = (\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$$

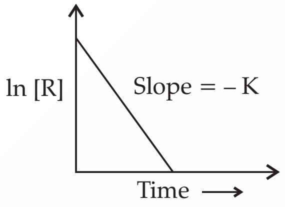
If $n = 0$

$$K = \text{mol L}^{-1}\ s^{-1}$$

The above unit of $K$ is similar to the unit of rate of reaction.

**16. Option (B) is correct.**

**Explanation:** For first order reaction



**17. Option (D) is correct.**

**Explanation:** $t_{1/2} = \frac{[R]}{2K}$

**18. Option (A) is correct.**

**Explanation:**

$$\text{Rate} = KC^n$$
$$r = KC^n \quad \text{...(i)}$$
$$16r = K(4C)^n \quad \text{...(ii)}$$

Dividing equation (ii) by (i), we get

$$(2)^4 = 2^{2n}$$
$$2n = 4$$
$$n = \frac{4}{2} = 2$$

**19. Option (C) is correct.**

**Explanation:** Activation energy ($E_a$) is affected by the catalyst. A catalyst lowers the activation energy ($E_a$) of a reaction.

**20. Option (A) is correct.**

**21. Option (C) is correct.**

**Explanation:** $r = K[A]^2$

If $A = \frac{A}{2},$

then $r = K\left[\frac{A}{2}\right]^2$

$$r = \frac{1}{4}K[A]^2$$

**22. Option (D) is correct.**

**Explanation:**

$$\text{Unit of K} = (\text{mol L}^{-1})^{1-n}\ s^{-1}$$

If $n = 0$, $k = \text{Mol L}^{-1}\ s^{-1}$

## ASSERTION-REASON QUESTIONS (1 Mark)

1. **Option (A) is correct.**

**Explanation:** Rate = $K[A]^{\circ}$

Unit of K is mol $L^{-1}$ s–1 is same that of rate of reaction.

2. **Option (D) is correct.**
3. **Option (A) is correct.**

**Explanation:** The rate constant increases for an increases in temperature and as activation energy increase the rate constant decreases.

4. **Option (A) is correct.**

**Explanation:** For zero order reaction

$$\text{Rate} = K[A]^{\circ}$$

5. **Option (D) is correct.**

**Explanation:** Order and molecularity may or not be same as order of reaction of reaction is sum of power of reactant which can be determined experimentally.

6. **Option (A) is correct.**

**Explanation:** $H_2 + Br_2 \rightarrow 2HBr$

$$\text{molecularity} = 1 + 1 = 2$$

## VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. (1) $r = k[A]^n$ ...(i)

After changing concentration to its triple value A = 3A, $r$ becomes $27r$

$$27r = K[3A]^n \quad \text{...(ii)}$$

Dividing eq. (i) by (ii)

$$\frac{r}{27r} = \frac{K[A]^n}{K[3A]^n}$$
$$\frac{1}{27} = \left(\frac{1}{3}\right)^n$$

$$\left(\frac{1}{3}\right)^3 = \left(\frac{1}{3}\right)^n$$

$$n = 3$$

Hence, the order of reaction is three.

(ii) A bimolecular reaction may become kinetically of first order if one of the reactants is in excess.

$CH_3COOCH_3 + H_2O \text{ (excess)} \rightarrow CH_3COOH + CH_3OH$

**2.** $[A_0] = 5g, [A] = 2.5g, K = 1.25 \times 10^{-3}\ s^{-1}$

$$t = \frac{1}{K}\log\left(\frac{[A_0]}{[A]}\right)$$

$$t = \frac{1}{1.25\times10^{-3}}\log\left(\frac{5}{2.5}\right)$$

$$t = \frac{1}{1.25\times10^{-3}}\log 2$$

$$t = \frac{1}{1.25\times10^{-3}}\times 0.301 \times 2.303$$

$$t \approx 554.56\ s$$

**3.** Case 1

If A = 100, A – X = 100–99 = 1

For 99%, $t_{99\%} = \frac{2.303}{K}\log\frac{100}{1}$

$$t_{99\%} = \frac{2.303\times2}{K} \quad \text{...(i)}$$

Case 2

If A = 100, A – X = 10

For 90%, $t_{90\%} = \frac{2.303}{K}\log\frac{100}{10}$

$$t_{90\%} = \frac{2.303}{K}\times1 \quad \text{...(ii)}$$

On dividing eq. (i) by eq. (ii), we get

$$\frac{t_{99\%}}{t_{90\%}} = \frac{4.603}{K}\times\frac{K}{2.303} = 2$$

$$t_{99\%} = 2 \times t_{90\%}$$

**4.** Molecularity of a reaction is defined as the number of reacting molecule that collide simultaneously to bring about a chemical reaction.

A bimolecular reaction may appear to be of first order when one of the reactants is present in large excess so that its concentration remains practically constant during the reaction.

**5.** (i) The order of reaction is defined as the sum of the exponents to which the concentration terms in the rate law are raised.

(ii) Activation energy ($E_a$) is the minimum amount of energy required for reactants to undergo chemical reaction and produce product.

**6.**

$$t = \frac{2.303}{K}\log_{10}\frac{[A]_o}{[A]}$$

$$t = \frac{2.303}{K}\log_{10}\frac{[A]_o}{\frac{1}{4}[A]_o}$$

$$t = \frac{2.303}{2.3\times10^{-3}}\log_{10}4$$

$$t = \frac{2.303}{2.3\times10^{-3}}\times0.6021$$

$$t = 602.88\ s$$

**7.** $$-\frac{1}{2}\frac{\Delta(N_2O_5)}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = +\frac{\Delta[O_2]}{\Delta t}$$

(i) Rate of formation of $NO_2$

$$= \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$$

$$= \frac{1}{4}\times\frac{5\times10^{-3}}{10}\ mol\ L^{-1}$$

$= 1.25 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$

(ii) Rate of consumption of $N_2O_5$

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{2}{4}\frac{\Delta[N_2O_5]}{\Delta t}$$

$= 0.5 \times 1.25 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$

$= 0.625 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}$

or $6.25 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$

**8.** (i) A → B follow second order kinetics

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

$$\text{Rate}_1 = KA^2$$

If concentration of A is increased to three times then

$$A = 3A$$

$$\text{Rate}_2 = K[3A]^2 = 9K\,A^2$$

Hence, the rate of formation of B will increase by 9 times.

(ii) A psuedo first order neaction is a chemical reaction that has a molecularity of two but an order of readtion in one.

Hydrolysis of an ester is an example of pseudo first order reaction.

**9.** As the temperature of a chemical reaction is increased, the rate constant (*k*) also increases. This is because *k* is proportional to the rate of reaction or temperature of reaction.

The activation energy ($E_a$) remains unchanged as the temperature of reaction increases. This is because activation energy ($E_a$) only depends on the nature of reactants. It depends m the difference between the energy of activated complex and reactants.

**10.** $T_1 = 293\ K, T_2 = 313\ K$

According to Arrhenius equation

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

$$E_a = 2.303\ R\left[\frac{T_2T_1}{T_2-T_1}\right]\log\frac{K_2}{K_1}$$

$$\left[\frac{T_2T_1}{T_2-T_1}\right] = \frac{293\times 313}{313-293} = 4585.45\text{K}$$

$$\log\frac{K_2}{K_1} = \log 4 = 0.6021$$

$$\begin{aligned} Ea &= 2.303\ \times\ 8.314\ \times\ 4585.45 \\ &\quad \times 0.6021 \\ &= 52863\ \text{J mol}^{-1} \\ &= 52.8\ \text{KJ mol}^{-1} \end{aligned}$$

## SHORT ANSWER TYPE QUESTIONS (3 Marks)

**1.** (i) General rate law:

$$\text{Rate} = K[NO]^P\,[Br_2]^q$$

For experiment 1

$$1.0\times 10^{-3} = K[0.05]^P[0.05]^q$$

For experiment 2

$$3\times 10^{-3} = K[0.05]^P\,[0.15]^q$$

For experiment 3

$$9\times 10^{-3} = K[0.15]^P\,[0.05]^q$$

Divide Exp. 2 by Exp. 1

$$\frac{3\times 10^{-3}}{1\times 10^{-3}} = \frac{K[0.05]^P[0.15]^q}{K[0.05]^P[0.05]^q}$$

$$\begin{aligned} 3 &= 3^q \\ q &= 1 \end{aligned}$$

Divide Exp. 3 by Exp. 1

$$\frac{9\times 10^{-3}}{1\times 10^{-3}} = \frac{K[0.15]^P[0.05]^q}{K[0.05]^P[0.05]^q}$$

$$\begin{aligned} 9 &= 3^p \\ p &= 2 \end{aligned}$$

Order of reaction w.r.t to NO. = 2 and w.r.t $Br_2$ = 1

(ii) By using Experiment 1

$$\begin{aligned} 1\times 10^{-3} &= K[0.05]^2[0.05]^1 \\ K &= 8\ L^2\ \text{mol}^{-2}\ s^{-1} \end{aligned}$$

(iii) Determine the rate of reaction for given concentration [NO] = 0.4 M and $Br_2$ = 0.2 M

$$\begin{aligned} \text{Rate} &= K[NO]^2\,[Br_2] \\ &= 8\times(0.4)^2\times 0.2 \\ &= 0.256\ \text{mol}^{-1}\ L^{-1}\ s^{-1} \end{aligned}$$

**2.**

$$\begin{aligned} T_1 &= 17+273 = 290\ K \\ T_2 &= 27+273 = 300\ K \end{aligned}$$

According to Arrhenius equation

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

$$\log 3 = \frac{E_a}{2.303\ R}\times\frac{10}{87000}$$

$$0.48 = \frac{E_a}{2.303\times 8.31}\times\frac{10}{87000}$$

$$\begin{aligned} Ea &= 0.48\times 2.303\times 8.314 \\ &\quad \times 8700 \\ Ea &\approx 79958.46\ \text{J/mol} \\ &= 79.958\ \text{KJ/mol} \end{aligned}$$

**3.** We know,

$$K = \frac{2.303}{t}\log\frac{[A]_o}{[A]}$$

For 25%,

$$\begin{aligned} K &= \frac{2.303}{40}\log\frac{100}{75} \\ K &= \frac{2.303}{40}(\log 4\ -\log 3) \\ K &= \frac{2.303}{40}(0.60-0.48) \\ K &= \frac{2.303}{40}\times 0.12 \\ K &= 0.006909\ m^{-1} \end{aligned}$$

For 80% completion,

$$\begin{aligned} K &= \frac{2.303}{t}\log\frac{[A]_o}{[A]} \\ 0.006909 &= \frac{2.303}{t}\log\frac{100}{20} \\ t &= \frac{2.303}{0.006909}\times\log 5 \\ &= \frac{2.303}{0.006909}\times 0.69 \\ t &= 230\ \text{minutes} \end{aligned}$$

**4.**

$$\frac{\log K_2}{\log K_1} = \frac{E_a}{2.303\ R}\left(\frac{T_2-T_1}{T_1T_2}\right)$$

Given $K_2 = 4K_1$

$$\therefore\ \log\frac{4K_1}{K_1} = \frac{E_a}{2.303\times R}\left(\frac{320-300}{320\times 300}\right)$$

$$0.60 = \frac{20\times E_a}{19.15\times 320\times 300}$$

$$E_a = \frac{0.60\times 19.15\times 320\times 300}{20}$$

$$= 55152\ \text{J mol}^{-1}\ \text{or} = 55.152\ \text{kJ mol}^{-1}$$

**5.** Given

Let $[A]_o = 100$

At time $t = t_{99.9\%}$ $[A] = 100 - 99.9 = 0.1$

$$K = \frac{2.303}{t}\log\frac{[A]_o}{[A]}$$

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

For $t_{99.9\%}$

$$t_{99.9\%} = \frac{2.303}{K}\log 1000$$

$$t_{99.9\%} = \frac{2.303}{K}\times 3$$

$$t_{99.9} = \frac{6.909}{K} \quad \text{...(i)}$$

$$t_{1/2} = \frac{0.693}{K} \quad \text{...(ii)}$$

On comparting both equation

$$t_{99.9\%} = 10 \times t_{1/2} \text{ or } 10 \times t_{50\%}$$

**6.** (i) Rate = $K\,[C_{12}H_{22}O_{11}]$

(ii) Molecularity = 2

Order = 1

(iii) Psuedo first order reaction

**7.** $C_2H_5Cl_{(g)} \rightarrow C_2H_{4(g)} + HCl_{(g)}$

At t = 0 $P^\circ$ O O

At t = t $P^\circ - P$ P P

$$P_t = P_o - P + P + P$$

$$P_t = P_o + P$$

$$P = P_t - P_o$$

$$K = \frac{2.303}{t}\log\frac{P^o}{P^o - P}$$

$$K = \frac{2.303}{t}\log\left(\frac{P}{2P_o - P_t}\right)$$

$t$ = 100 S Pt = 0.6

$P_o = 0.4$

$$K = \frac{2.303}{t}\log\left(\frac{0.4}{0.2}\right)^2$$

$$K = \frac{2.303}{100}\times 0.3010$$

$$K = 0.0069\ s^{-1}$$

$$K = 6.9 \times 10^{-3}\ s^{-1}$$

**8.** $T_1 = 27 + 273 = 300$ K

$T_2 = 37 + 273 = 310$ K

$K_1 = K$

$K_2 = 2K$

According to Arrhenius equation

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

$$\log\frac{2K}{K} = \frac{E_a}{2.303\ R}\left[\frac{310 - 300}{300\times 310}\right]$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\times\frac{10}{300\times 310}$$

$$E_a = 53598.6\ J\ mol^{-1}$$

$$E_a = 53.6\ kJ\ mol^{-1}$$

**9.** (i) $2N_2O_5 \rightarrow 4NO_2 + O_2$

$$-\frac{d[N_2O_5]}{dt} = 1.4 \times 10^{-3}\ ms^{-1}$$

Rate of reaction

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{2}\times 1.4\times 10^{-3}$$

$$= 0.7 \times 10^{-3}\ ms^{-1}$$

$$\text{or } 7 \times 10^{-4}\ ms^{-1}$$

(ii)

$$K = \frac{2.303}{t}\log\frac{[A]_o}{[A]}$$

$$t_{99\%} = \frac{2.303}{K}\log\frac{100}{1} \quad \text{...(i)}$$

$$t_{90\%} = \frac{2.303}{K}\log\frac{100}{10} \quad \text{...(ii)}$$

Divide eq. (i) by (ii)

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\frac{2.303}{K}\log\frac{100}{1}}{\frac{2.303}{K}\log\frac{100}{10}}$$

$$\frac{t_{99\%}}{t_{90\%}} = 2$$

$$t_{99\%} = 2 \times t_{90\%}$$

**10.** Given $t_{1/2} = 30$ min, $T_1 = 300$ K

$t_{1/2} = 10$ min $T_2 = 320$ K

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

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

$$K_1 \text{ at } 300\text{ K} = \frac{0.693}{30}\,\text{min}^{-1}$$

$$K_2 \text{ at } 320\text{ K} = \frac{0.693}{10}\,\text{min}^{-1}$$

$$\log\frac{K_2}{K_1} = \frac{E_a}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\left(\frac{\frac{0.693}{10}}{\frac{0.693}{30}}\right) = \frac{Ea}{2.303\ R}\left[\frac{1}{300} - \frac{1}{320}\right]$$

$$\log(3) = \frac{Ea}{2.303\ R}\left[\frac{20}{300\times 320}\right]$$

$$Ea = 0.4771 \times 2.303 \times 8.314 \times 300 \times 16$$

$$Ea = 43.8\ kJ\ mol^{-1}$$

## LONG ANSWER TYPE QUESTIONS (5 Marks)

**1.** (i) The rate law for a first-order reaction is:

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

Where: $k$ = rate constant, and [A] = concentration of reactant A

Half-life ($t_{1/2}$) for a First Order Reaction:

The half-life is the time required for the concentration of a reactant to reduce to half of its initial value.

For a first-order reaction:

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

This expression does not contain $[\text{A}]_0$ (initial concentration).

**Justification:**

Since $t_{1/2}$ is independent of the initial concentration, it means no matter what $[\text{A}]_0$ is, the time it takes to reach half of it is the same. First-order reactions have constant half-lives, useful in drug dosing and radioactive decay.

(ii) Time for 99% and 90% Completion – First Order Derivation

The integrated rate law for a first-order reaction is:

$$kt = 2.303 \log\left(\frac{[\text{A}]_0}{[\text{A}]}\right)$$

Time for 90% Completion:

For 90% completion: $[\text{A}] = 10\% = 0.1[\text{A}]_0$

$$t_{90\%} = \frac{2.303}{k}\log\left(\frac{[\text{A}]_0}{0.1[\text{A}]_0}\right)$$

$$= \frac{2.303}{k}\log(10) = \frac{2.303}{k}\times 1$$

$$= \frac{2.303}{k}$$

Time for 99% Completion:

For 99% completion: $[\text{A}] = 1\% = 0.01[\text{A}]_0$

$$t_{90\%} = \frac{2.303}{k}\log\left(\frac{[\text{A}]_0}{0.01[\text{A}]_0}\right)$$

$$= \frac{2.303}{k}\log(100)$$

$$= \frac{2.303}{k}\times 2 = \frac{4.606}{k}$$

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\frac{4.606}{k}}{\frac{2.303}{k}} = 2$$

Hence, time required for 99% completion is exactly twice the time required for 90% completion of a first-order reaction.

**2.** (i) Using the two-temperature Arrhenius equation:

$$\log\left(\frac{k_2}{k_1}\right) = \frac{\text{E}_a}{2.303\text{R}}\left(\frac{\text{T}_2 - \text{T}_1}{\text{T}_1\text{T}_2}\right)$$

Given:

$$\text{T}_1 = 300\,\text{K},\ \text{T}_2 = 330\,\text{K}$$
$$t_1 = 45\,\text{min},\ t_2 = 15\,\text{min}$$

For first-order reaction $\frac{k \propto 1}{t}$, so:

$$\log(3) = \frac{\text{E}_a}{2.303\times 8.314}\left(\frac{330-300}{300\times 330}\right)$$

$$0.4771 = \frac{\text{E}_a}{19.14742}\times\left(\frac{30}{99000}\right)$$

$$\frac{\text{E}_a\times 30}{1895,687.8}$$

$$\text{E}_a = \approx \frac{0.4771\times 1895687.8}{30}$$

$$= 30{,}136\ \text{J/mol} = 31.14\ \text{kJ/mol}$$

(ii) The conditions for effective collisions are:

(1) **Proper Orientation:** Reacting species must collide in an orientation that allows bond-breaking and bond-forming to occur.

(2) **Sufficient Energy:** Colliding particles must possess energy equal to or greater than the activation energy ($\text{E}_a$).

(iii)

| Order of Reaction | Molecularity |
|---|---|
| Sum of powers of concentration terms in rate law | Number of molecules colliding in elementary step |
| Experimental data only | Reaction mechanism |
| Can be fractional or zero | Always a whole number (1, 2, or 3) |
| Macroscopic (overall reaction) | Microscopic (elementary step only) |
| Overall and complex reactions | Elementary (single-step) reactions only |

## Level - 2 ADVANCED COMPETENCY FOCUSED QUESTIONS

## MULTIPLE CHOICE QUESTIONS (MCQs) (1 Mark)

**1. Option (C) is correct.**

**Explanation:** The organisim's age can also be found by measuring how much potassium-40 or beryllium –10 is present in relation to potassium –39 and beryllium –9.

**2. Option (C) is correct.**

**Explanation:** It is because rate of reaction is independent on concentration of A.

## ASSERTION-REASON QUESTIONS (1 Mark)

1. Option (A) is correct

   **Explanation:** Assertion is true. According to the Arrhenius equation, $k = Ae^{-E_a/RT}$, an increase in temperature T increases the rate constant $k$, thereby increasing the reaction rate.

   Reason is also true. At higher temperatures, more molecules have kinetic energy ≥ activation energy ($E_a$), leading to more effective collisions and a faster reaction.

2. Option (A) is correct

   **Explanation:** Assertion is true. In a zero-order reaction, the rate law is expressed as: Rate = $k$

   This means the reaction rate is constant and does not change with the change in concentration of the reactant. This behaviour is typically observed in reactions occurring on surfaces or when a catalyst becomes saturated.

   Reason is also true. Since the rate law is Rate = $k$, it directly implies that the rate is equal to the rate constant ($k$) for zero-order reactions. It remains unchanged as the reaction proceeds, regardless of how much reactant is present.

3. Option (A) is correct

   **Explanation:** Assertion is true. For a first-order reaction, the half-life $t_{\frac{1}{2}}$ is given by:

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

   This expression shows that the half-life depends only on the rate constant $k$ and not on the initial concentration $[R]_0$.

   Reason is also true. The integrated rate law for a first-order reaction is

   $$k = \frac{2.303}{t}\log\left(\frac{[R]_0}{[R]}\right)$$

   This is indeed the correct integrated form of the rate law for a first-order reaction, where:

   $[R]_0$ = initial concentration

   $[R]$ = concentration at time t

4. Option (A) is correct

   **Explanation:** Assertion is true. For a second-order reaction ($n = 2$), the unit of the rate constant $k$ is derived from the rate law:

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

   $$\Rightarrow k = \frac{\text{Rate}}{[A]^2} = \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{ Ls}^{-1}$$

   Reason is also true. This is the general formula for the unit of rate constant k for a reaction of order $n$.

5. Option (A) is correct

   **Explanation:** Assertion is true. For a first-order reaction, the integrated rate law is:

   $$\log[R]_0 = \log[R]_0 - \frac{k}{2.303}t$$

   This is in the form of a straight-line equation:

   $y = mx + c$

   where: $y = \log[R]$, $x = t$, and $m = -\frac{k}{2.303}$ (constant slope).

   Reason is also true. The integrated rate law for a first-order reaction shows that the graph of log[R] vs time is a straight line with negative slope $= -\frac{k}{2.303}$

## VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. Since the concentration of $^{14}C$ decays with time at a particular rate (which depends on initial concentration), the kinetics for first-order could be used to identify the time required to change in the concentration of $^{14}C$.

   $$\Rightarrow \quad K = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}$$

   $$\Rightarrow \quad t = \left(\frac{2.303}{K}\right)\log\left(\frac{A_0}{A}\right)$$

   $$\Rightarrow \quad t = \left(\frac{2.303 \times 5730}{0.693}\right) \times \log\frac{100}{10}$$

   $$\Rightarrow \quad t = 19042 \text{ years (approx)}$$

2. The expiry date of food.

   Average rate of reaction

   $$= \frac{\text{Average change in concentration}}{\Delta t}$$

   $$\Delta t = \frac{40}{4} \text{ per day} = 10 \text{ days.}$$

   Expiry date = 10th April 2022

## SHORT ANSWER TYPE QUESTIONS (3 Marks)

1. (i) Order of reaction:

   Based on the table, the decrease in partial pressure of ethane is constant over time that is $t_{1/2}$ is constant. So it's a first order reaction.

   (ii) Rate constant:

   For first order reaction, rate constant ($k$) is given by $0.693/t_{1/2}$

   $$\Rightarrow \quad k = \frac{0.693}{100} = 0.00693 \text{ min}^{-1}$$

   Or

   $$\Rightarrow \quad k = 0.00011 \text{ s}^{-1}$$

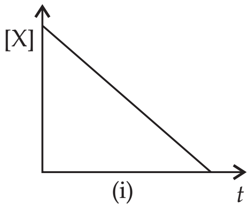
(iii) Ratio

Time required for the completion of 50% of the reaction = 1 × $t_{1/2}$

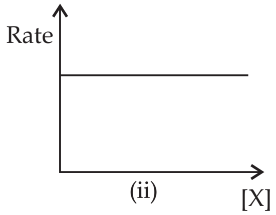
Time required for the completion of 75% of the reaction = 2 × $t_{1/2}$

So the ratio = 1/2 or 1 : 2

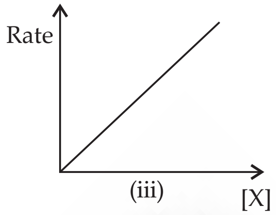
**2.** (i)



(ii)



(iii)



## CASE BASED QUESTIONS (4 Mark)

**1.** (i)

$$\text{Rate} = k\,[H_2]\,[Br_2]^{1/2}$$

$$\text{Order} = \frac{3}{2}$$

$$\text{units of } k = \frac{mol\,L^{-1}s^{-1}}{mol^{3/2}L^{-3/2}} = mol^{-1/2}L^{1/2}S^{-1}$$

(ii) (a)

$$\text{Rate} = k\,[H_2]\,[Br_2]^{1/2}$$

If concentration of $Br_2$ is tripled

$$\text{Rate}' = k\,[H_2]\,[3Br_2]^{1/2}$$

$$\text{Rate}' = \sqrt{3}\;k\,[H_2]\,[Br_2]^{1/2}$$

$$\text{Rate}' = \sqrt{3}\;\text{Rate}$$

**OR**

(b)

$$\text{Rate} = k\,[H_2]\,[Br_2]^{1/2}$$

If concentration of $Br_2$ is tripled

$$\text{Rate}' = 3$$

$$\text{Rate} = k\,[xH_2]\,[Br_2]^{1/2}$$

$$3\,\text{Rate} = k\,[xH_2]\,[Br_2]^{1/2}$$

$x = 3$, the concentration of $H_2$ is tripled.

(iii) The slowest step is the rate-determining step.

From mechanism 2, Rate = $k$ [A] [B]

while from mechanism 1 Rate = $k$ [A]

Therefore, mechanism 2, is consistent with the experimental finding.

**2.** (i) The average rate of reaction is the rate of change in concentration of a reactant or product over a specific time period.

(ii) The two factors on which the rate of reaction depend upon are concentration and temperature.

(iii) (a) (1) For a zero order reaction, the rate of reaction remains constant.

(2) Unit of K for zero order is mol $L^{-1}s^{-1}$

**OR**

(b) (1)

$$\text{Rate} = K[P]^{1/2}[Q]^{1}$$

$$\text{order} = \frac{1}{2}+1=1\frac{1}{2}$$

(2) **Psuedo first order reaction:** The reaction which is bimolecular but order is one is called psuedo first order reaction. This happens when one of the reactant is in excess. e.g. acidic hydrolysis of ester.

**3.** (i) (1) **Experimentally determined rate law:** Order is obtained only by experiment, not from the balanced equation.

(2) **Dependence of rate on concentration:** It depends on the powers of concentration terms in the experimentally determined rate law.

(ii) Order of reaction = 1

(iii) (a) (1) The rate of reaction is the change in concentration of reactants or products per unit time.

Mathematically:

$$\text{Rate} = -\frac{d[\text{Reactant}]}{dt} + \frac{d[\text{Product}]}{dt}$$

(2) **Reaction:**

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

**Rate expressioin:**

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

$$= \frac{1}{2}\frac{d[NH_3]}{dt}$$

**OR**

(b) (i) **Given:** Reaction is first order w.r.t. A, second order w.r.t. B.

$$A + B \longrightarrow \text{Product}$$

(1) Differential rate equation:

$$\text{Rate} = k\,[A]^1\,[B]^2$$

(2) If[B] → 2[B],.

Rate new = $k[A](2[B])^2 = k[A].4[B]^2$ = 4 × Rate old Rate becomes 4 times.

## LONG ANSWER TYPE QUESTIONS (5 Marks)

**1.** (i) The half-life of a drug is the time it takes for the concentration of the drug in the bloodstream to reduce to half its initial value.

Doctors use the half-life to schedule drug dosages so that the drug remains effective within the therapeutic range (not too low to be ineffective, and not too high to be toxic).

Drugs with short half-lives need to be taken more frequently, while drugs with long half-lives can be taken less often.

(ii) The order of reaction determines how the concentration of the drug affects its rate of metabolism. For a first-order reaction, the rate depends on the concentration of the drug. As the concentration decreases, the rate slows down. For a zero-order reaction, the drug is eliminated at a constant rate, regardless of its concentration (common in high doses where enzymes are saturated). Understanding the order helps in predicting how long the drug will act and designing sustained-release formulations.

(iii) Drug Remaining After 24 Hours (First-Order Kinetics):

Given:

Half-life, $t_{\frac{1}{2}}$ =6 hours

Time elapsed = 24 hours

Number of half-lives = $\frac{24}{6}$ =4

For first-order reactions, the amount remaining after n half-lives is:

$$\text{Remaining fraction} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

So, only $\frac{1}{16}$th (or 6.25%) of the original drug amount remains after 24 hours.

**2.** **(i)** The Arrhenius equation is:

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

Where : $k$ = rate constant

$Ea$ = activation energy

$R$ = gas constant

$T$ = temperature in Kelvin

$A$ = frequency factor

According to this equation, As temperature increases, the rate constant ($k$) increases exponentially. This means chemical reactions causing spoilage (e.g., oxidation, microbial action) occur faster at higher temperatures, leading to faster spoilage of food.

(ii) Chemical kinetics helps in:

(1) Predicting reaction rates of spoilage processes (like enzymatic browning or microbial growth).

(2) Designing preservatives or packaging that slows down these reactions (e.g., vacuum packing to reduce oxygen, use of antioxidants). Example: Modified Atmosphere Packaging (MAP) uses low oxygen levels to reduce the rate of oxidation and microbial growth based on kinetic studies.

(iii) Refrigeration lowers the temperature, and thus reduces the kinetic energy of molecules.

Fewer molecules have energy ≥ activation energy, so the reaction rate (k) decreases, as per Arrhenius equation.