# 3

# Chemical Kinetics

## Fastrack Revision

- Chemical kinetics is the branch of chemistry which deals with the study of reaction rates and their mechanisms.
- **Rate of a Chemical Reaction:** Rate of a reaction is the change in concentration of a reactant or product in unit time.
- For the reaction, $R \longrightarrow P$

  Rate of reaction $= -\dfrac{\Delta[R]}{\Delta t} = +\dfrac{\Delta[P]}{\Delta t}$

  where, Rate of disappearance of reactant $R = -\dfrac{\Delta[R]}{\Delta t}$,

  and Rate of formation of product $P = +\dfrac{\Delta[P]}{\Delta t}$
- Unit of rate of a reaction is mol $L^{-1}\,s^{-1}$ or mol $L^{-1}\,min^{-1}$ (in liquid form) and atm $s^{-1}$ or atm $min^{-1}$ (in gaseous form).
- **Instantaneous Rate:** For the reaction,

$n_1 A + n_2 B \longrightarrow m_1 C + m_2 D$, the instantaneous rates can be represented in the following manner:

$$-\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = +\frac{1}{m_1}\frac{d[C]}{dt} = +\frac{1}{m_2}\frac{d[D]}{dt}$$

- **Factors Affecting the Rate of Reaction**
  - Concentration of reactants
  - Temperature of reaction
  - Pressure of reaction
  - Presence of catalyst
  - Nature of reactants
  - Surface area of reactants
  - Effect of radiations
- **Rate Law**
  - It is the representation of rate of reaction in terms of concentration of the reactants. It is also called as rate expression or rate equation.
  - For a general reaction, $aA + bB \longrightarrow cC + dD$

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

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

  where, $k$ = proportionality constant or rate constant, $a$ and $b$ are exponents.
- **Order of a Reaction**
  - It is the sum of powers of the concentration of the reactants in the rate law expression.
  - Order of a reaction can be 0, 1, 2, 3 and even a fraction.
  - Reactions taking place in one step are called elementary reactions.
  - When a sequence of elementary reactions gives us the products, the reactions are called complex reactions.
- **Molecularity of a Reaction**
  - It is 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.
  - For a complex reaction, molecularity of the slowest step is same as the order of the overall reaction.
  - The slowest step in a reaction mechanism is called the **rate determining step**.
- **Integrated Rate Equations**
  - These are different for the reactions of different reaction orders.
  - **Half-life** of a reaction is the time in which the concentration of a reactant is reduced to one half (½) of its initial concentration and is represented as $t_{1/2}$.
  - **Life time** is the time in which 98% of the reaction is completed.
- **For a Zero Order Reaction**
  - Rate $= k[A]^0$
  - Integrated rate law, $[A]_t = -kt + [A]_0$

    or $\quad k = \dfrac{[A]_0 - [A]_t}{t}$

    where, $[A]_0$ = initial concentration,

    $[A]_t$ = final concentration after time '$t$',
  - Unit of the rate constant '$k$' is mol $L^{-1}\,s^{-1}$.
  - Half-life period, $t_{1/2} = \dfrac{[A]_0}{2k} \qquad (t_{1/2} \propto [A]_0)$
- **For a First Order Reaction**
  - Rate $= k[A]$
  - Integrated rate law,

    $$\ln[A]_t = -kt + \ln[A]_0$$

    or $\quad k = \dfrac{2.303}{t}\log_{10}\dfrac{[A]_0}{[A]_t}$

    or $\quad k = \dfrac{2.303}{t}\log_{10}\dfrac{a}{(a-x)}$

    where, $a$ = initial concentration,

    $(a - x)$ = concentration after time '$t$'.
  - Unit of '$k$' is $s^{-1}$ or $min^{-1}$.
  - Half-life period, $t_{1/2} = \dfrac{0.693}{k}$

    (Thus, half-life is independent of $[R]_0$.)
- **For a Second Order Reaction**
  - Rate $= k[A]^2$
  - Integrated rate law, $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$

or $$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

- Unit of '$k$' is $\text{mol}^{-1}\,\text{L}\,\text{s}^{-1}$ or $\text{M}^{-1}\,\text{s}^{-1}$ where, M is molarity.
- Half-life period, $t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k \times a}$

- **For $n$th Order Reaction**
  - Rate $= k[A]^n$
  - Integrated rate law, $(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}$
  - Half-life period, $t_{1/2} = \frac{2^{(n-1)}-1}{k(n-1)[A]_0^{n-1}}$
- **Pseudo First Order Reaction:** This reaction is not truly of the first order but under certain conditions become reaction of first order.

  For example, acidic hydrolysis of ester (ethyl acetate).
- **Arrhenius Equation:** The temperature dependence of rate of a chemical reaction is expressed by Arrhenius equation.

  $$k = A \cdot e^{-E_a/RT}$$

  where, $A$ = Arrhenius factor or frequency factor, $E_a$ = activation energy (in J $\text{mol}^{-1}$), $R$ = gas constant and $T$ = temperature.
- **Activation Energy:** It is given by the energy difference between activated complex and the reactant molecules. It is the energy needed to form the intermediate called activated complex or it is the extra energy contained by the reactant molecules that results into effective collisions between them to form the products.
- If $k_2$ and $k_1$ are rate constants at temperature $T_2$ and $T_1$ respectively, then

  $$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 . T_2}\right]$$
- **Catalyst:** A catalyst is a substance which increases the rate of reaction without itself undergoing any permanent chemical change.
- **Characteristics of Catalyst:**
  - It does alter Gibbs energy ($\Delta G$) of a reaction.
  - It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.
  - It does not change the equilibrium constant.
  - It catalyse forward as well as backward reactions.
- **Collision Theory:** According to this theory, rate of reaction depends on the collision frequency and effective collisions. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency ($z$). Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

## Practice Exercise

### Multiple Choice Questions

Q 1. The unit of rate constant for a first order reaction is:

a. $\text{mol L}^{-1}\text{ s}^{-1}$　　b. $\text{L mol}^{1}\text{ s}^{-1}$
c. $\text{s}^{-1}$　　d. $\text{mol L}^{-1}$

Q 2. The velocity (rate) for a zero order reaction:

$$A + B \longrightarrow C$$

a. rate = $k(A)^0(B)^0$　　b. rate = $k(A)^1(B)^0$
c. rate = $k(A)^0(B)^1$　　d. None of these

Q 3. For a zero order reaction of the type $A \longrightarrow$ products, the rate equation may be expressed as: *(CBSE 2023)*

a. $k = \frac{[A]_0 - [A]}{t}$　　b. $k = \frac{[A] - [A]_0}{t}$
c. $k = \frac{[A]_0 - [A]}{2t}$　　d. $k = \frac{[A]_0 - [A]}{2} . t$

Q 4. The rate constant for the reaction, $A + 2B \longrightarrow$ product is expressed by $R = [A][B]^2$. The order of reaction will be:

a. 2　　b. 3
c. 5　　d. 6

Q 5. The order of the reaction

$\text{H}_2(g) + \text{Cl}_2(g) \xrightarrow{h\nu} 2\text{HCl}(g)$ is: *(CBSE 2023)*

a. 2　　b. 1
c. 0　　d. 3

Q 6. A first order reaction takes 30 minutes for 50% completion. The value of rate constant $k$ would be: *(CBSE 2023)*

a. $2.5 \times 10^{-3}\ \text{min}^{-1}$　　b. $2.75 \times 10^{-4}\ \text{min}^{-1}$
c. $1.25 \times 10^{-3}\ \text{min}^{-1}$　　d. $2.31 \times 10^{-2}\ \text{min}^{-1}$

Q 7. The slope in the plot of $\log\frac{[R]_0}{[R]}$ *vs* time for a first order reaction is: *(CBSE 2023)*

a. $\frac{+k}{2.303}$　　b. $+k$
c. $\frac{-k}{2.303}$　　d. $-k$

Q 8. In a reaction, the initial concentration of the reactants increases four fold and the rate becomes sixteen times its initial value. The order of the reaction is: *(CBSE 2023)*

a. 2.0　　b. 3.5　　c. 1.5　　d. 2.5

Q 9. Which of the following statement is true? *(CBSE SQP 2023-24)*

a. Molecularity of reaction can be zero or a fraction.
b. Molecularity has no meaning for complex reactions.
c. Molecularity of a reaction is an experimental quantity
d. Reactions with the molecularity three are very rare but are fast.

**Q 10.** **The time required for the half-completion ($t_{1/2}$) of a first order reaction is:**

a. dependent on its initial concentration
b. inversely proportional to its initial concentration
c. independent of its initial concentration
d. dependent on square root of its initial concentration

**Q 11.** **The half-life period of a first order reaction is 400s. Its rate constant will be:**

a. $1.73 \times 10^{-3}\ s^{-1}$ b. $1.44 \times 10^{-3}\ s^{-1}$
c. $2.72 \times 10^{-3}\ s^{-1}$ d. $2.88 \times 10^{-3}\ s^{-1}$

**Q 12.** **If a reaction obeys the following equation:**

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

**The order of reaction will be:**

a. zero b. first c. second d. third

**Q 13.** **The half-life of a reaction is doubled when the initial concentration is doubled. The order of the reaction is:** *(CBSE 2023)*

a. 1 b. 2 c. 4 d. 0

**Q 14.** **For the reaction, $A + 2B \rightarrow AB_2$, the order w.r.t. reactant $A$ is 2 and w.r.t. reactant $B$. What will be change in rate of reaction if the concentration of $A$ is doubled and $B$ is halved?** *(CBSE SQP 2022-23)*

a. increases four times
b. decreases four times
c. increases two times
d. no change

**Q 15.** **For the reaction $3A \rightarrow 2B$, rate of reaction $-\frac{d[A]}{dt}$ is equal to:** *(CBSE 2023)*

a. $\frac{+3}{2}\frac{d[B]}{dt}$ b. $\frac{+2}{3}\frac{d[B]}{dt}$
c. $\frac{+1}{3}\frac{d[B]}{dt}$ d. $\frac{+1}{2}\frac{d[B]}{dt}$

**Q 16.** **The number of molecules that react with each other in an elementary reaction is a measure of the:** *(CBSE 2023)*

a. activation energy of the reaction
b. order of the reaction
c. stoichiometry of the reaction
d. molecularity of the reaction

**Q 17.** **The value of rate constant for a first order reaction is $2.303 \times 10^{-2}s^{-1}$. What will be the time required to reduce the concentration to 1/10th of its initial concentration?**

a. 100 s b. 10 s c. 2303 s d. 23.03 s

**Q 18.** **The half-life for a first order reaction is 4 minutes. The time after which 99.9% reaction gets completed is:**

a. 16 minutes b. 8 minutes
c. 32 minutes d. 40 minutes

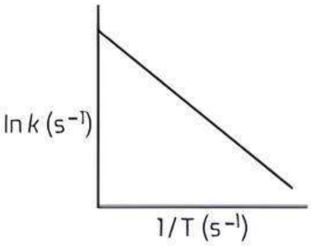
**Q 19.** **If the initial concentration of substance $A$ is 1.5 M and after 120 seconds the concentration of substance $A$ is 0.75 M, the rate constant for the reaction if it follows zero order kinetics is:** *(CBSE SQP 2023-24)*

a. 0.00625 mol $L^{-1}s^{-1}$
b. 0.00625 $s^{-1}$
c. 0.00578 mol $L^{-1}s^{-1}$
d. 0.00578 $s^{-1}$

**Q 20.** **Which radioactive isotope would have the longer half life $^{15}O$ or $^{19}O$? (Given rate constants for $^{15}O$ and $^{19}O$ are $5.63 \times 10^{-3}\ s^{-1}$ and k = $2.38 \times 10^{-2}s^{-1}$ respectively):** *(CBSE SQP 2022-23)*

a. $^{15}O$
b. $^{19}O$
c. Both will have the same half life
d. None of the above information given is insufficient

**Q 21.** **Arrhenius equation can be represented graphically as follows:**



**The (i) intercept and (ii) slope of the graph are :** *(CBSE SQP 2022-23)*

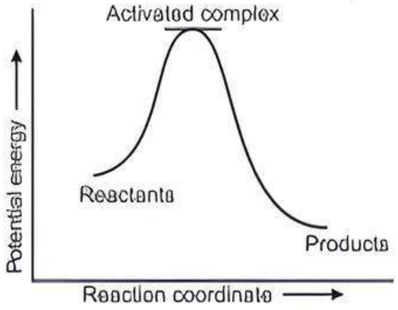
a. (i) ln $A$ (ii) $E_a/R$
b. (i) $A$ (ii) $-E_a$
c. (i) ln $A$ (ii) $-E_a/R$
d. (i) $A$ (ii) $-Ea$

**Q 22.** **Activation energy of a chemical reaction can be calculated by:** *(NCERT EXEMPLAR)*

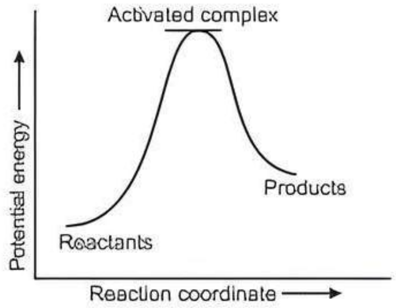
a. determining the rate constant at standard temperature
b. determining the rate constant at two temperatures
c. determining the probability of collision
d. using catalyst

**Q 23.** **Which of the following graphs represents exothermic reaction?** *(NCERT EXEMPLAR)*

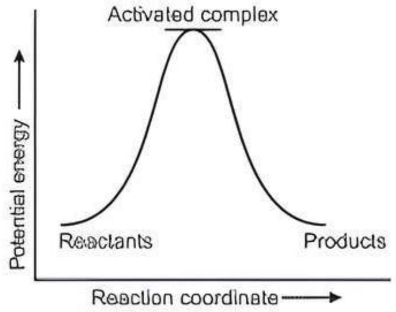
(I)



(ii)



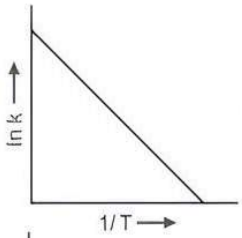
(iii)



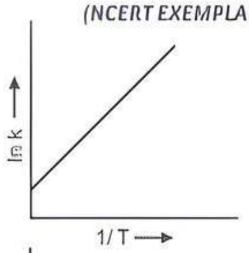
a. (i) only
b. (ii) only
c. (iii) only
d. (i) and (ii)

**Q 24. According to Arrhenius equation rate constant $k$ is equal to $Ae^{-E_a/RT}$. Which of the following options represents the graph of $\ln k$ vs $\frac{1}{T}$?** *(NCERT EXEMPLAR)*

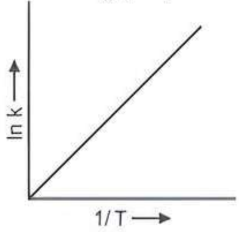
a.



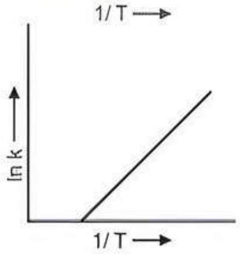
b.



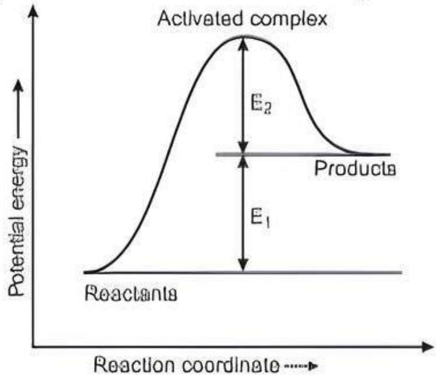
c.



d.



**Q 25. Consider the given figure and mark the correct option.** *(NCERT EXEMPLAR)*



a. Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.
b. Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.
c. Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.
d. Activation energy of backward reaction is $E_1$ and product is more stable than reactant.

**Q 26. The role of a catalyst is to change:** *(NCERT EXEMPLAR)*
a. Gibbs' energy of reaction
b. enthalpy of reaction
c. activation energy of reaction
d. equilibrium constant

**Q 27. Which of the following is affected by catalyst?** *(CBSE 2023)*
a. $\Delta H$ b. $\Delta G$ c. $E_a$ d. $\Delta S$

## Assertion & Reason Type Questions

**Directions (Q. Nos. 28-34):** *Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:*
a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
c. Assertion (A) is true but Reason (R) is false.
d. Assertion (A) is false but Reason (R) is true.

**Q 28. Assertion (A):** Order of the reaction can be zero or fractional.
**Reason (R):** We cannot determine order from balanced chemical equation. *(NCERT EXEMPLAR)*

**Q 29. Assertion (A):** Order and molecularity of a reaction are always same.
**Reason (R):** Complex reactions involve a sequence of elementary reactions and the slowest step is rate determining. *(CBSE 2023)*

**Q 30. Assertion (A):** Order and molecularity are same.
**Reason (R):** Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step. *(NCERT EXEMPLAR)*

**Q 31. Assertion (A):** The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ appears to be 2.
**Reason (R):** Two molecules of the reactants are involved in the given elementary reaction. *(CBSE 2023)*

**Q 32. Assertion (A):** The enthalpy of reaction remains constant in the presence of a catalyst.
**Reason (R):** A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactants and products remains the same. *(NCERT EXEMPLAR)*

**Q 33. Assertion (A):** All collisions of reactant molecules lead to product formation.
**Reason (R):** Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation. *(NCERT EXEMPLAR)*

**Q 34.** **Assertion (A):** Rate constant determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.

**Reason (R):** Reactant molecules undergo chemical change irrespective of their orientation during collision.

*(NCERT EXEMPLAR)*

## Answers

**1.** (c) Unit $= \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{molL}^{-1})^1} = \text{s}^{-1}$

**2.** (a) rate $= k\,(\text{A})^0\,(\text{B})^0$

**3.** (a) $k = \frac{(\text{A})_0 - (\text{A})}{t}$

**4.** (b) 3

**5.** (c) Given reaction is a photochemical reaction and the order of all such reactions is zero as it does not depend upon the concentration of reactants.

**6.** (d) For a first order reaction, the relation between $t_{1/2}$ and rate constant is $t_{1/2} = \frac{0.693}{k}$

$$\Rightarrow \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 2.31 \times 10^{-2}\,\text{min}^{-1}$$

**7.** (a) $\frac{+k}{2.303}$

**8.** (a) According to the rate law,

$$r = k(A)^n \qquad \text{...(1)}$$

where $k$ = rate constant

Now, on increasing the concentration four fold and rate sixteen times its initial value,

$$16r = k\,(4A)^n \qquad \text{...(2)}$$

Combining eqs. (1) and (2), we get

$16 = 4^n$

or, $4^2 = 4^n$

or, $n = 2.0$

Hence, the order of the reaction is 2.0.

**9.** (b) Molecularity has no meaning for complex reactions.

**10.** (c) Independent of its initial concentration

**11.** (a) Given, $t_{1/2} = 400\text{s}$

For first order reaction, $t_{1/2} = \frac{0.693}{k}$

$$\Rightarrow \quad k = \frac{0.693}{t_{1/2}} \quad \Rightarrow \quad k = \frac{0.693}{400}$$

$$= 0.0017325$$

$$= 1.73 \times 10^{-3}\ \text{s}^{-1}$$

**12.** (b) first

**13.** (d) We know that half life is related to concentration as:

$$t_{1/2} = (A)^{1-n} \text{ where } n = \text{order of the reaction}$$

Here, $\quad n = 2$

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

For $n = 0$, $t_{1/2} = (A)$

If $t_{1/2}$ is doubled, $(A)$ is also doubled, so the reaction is of zero order.

**14.** (a) increases four times

**Given:** order w.r.t. reactant A = 2

So, for the given reaction, Rate = $(A)^2$

If (A) is doubled, then Rate = $(2A)^2 = 4\,(A)^2 = 4$ Rate

**15.** (a) Given reaction is $3A \rightarrow 2B$

For this reaction,

rate of reaction: $\frac{-1}{3}\frac{d(A)}{dt} = \frac{1}{2}\frac{d(B)}{dt}$

$$\Rightarrow \quad \frac{-d(A)}{dt} = \frac{3}{2}\frac{d(B)}{dt}$$

**16.** (d) molecularity of the reaction

**17.** (a) Let initial concentration be $a$

Then, final concentration $(a - x) = \frac{1}{10}$ of $a = \frac{a}{10}$

For first order reaction,

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

$$= \frac{2.303}{2.303 \times 10^{-2}}\log\frac{a}{a/10}$$

$$= 100 \log 10$$

$$t = 100\text{s}.$$

**18.** (d) For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} \quad \Rightarrow \quad 4 = \frac{0.693}{k}$$

$$\Rightarrow \quad k = \frac{0.693}{4} \qquad \text{...(1)}$$

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

$$t = \frac{2.303 \times 4}{0.693}\log\frac{100}{(100 - 99.9)} \qquad \text{[from eq. (1)]}$$

$$= \frac{2.303 \times 4}{0.693}\log 1000$$

$$= \frac{2.303 \times 4 \times 3}{0.693} = 39.9 \approx 40\ \text{minutes}$$

**19.** (a) For zero order kinetics, the rate constant,

$$k = \frac{[R_0] - [R]}{t}$$

or, $$k = \frac{1.5 - 0.75}{120}$$

$$= 0.00625\ \text{mol L}^{-1}\text{s}^{-1}$$

**20.** (a) $^{15}O$

The rate constant for the decay of $^{15}O$ is less than that for $^{19}O$. therefore, the rate of decay of $^{15}O$ will be slower and will have a longer half-life as compared to $^{19}O$.

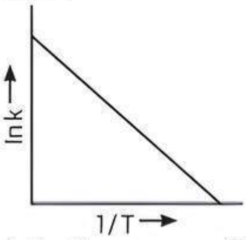
**21.** (c) (i) ln A. (ii) $-E_a/R$

In Arrhenius equation, a plot of ln $k$ with $1/T$ gives a straight line with slope $= -E_a/R$ and intercept $=$ ln $A$.

**22.** (b) determining the rate constant at two temperatures

**23.** (a) (i) only

**24.** (a)



**25.** (a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.

**26.** (c) activation energy of reaction

**27.** (c) $E_a$

**28.** (b) Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).

**29.** (d) Order and molecularity are same for an elementary reaction because such reactions proceed in a single step but they are not same for all reactions. So, assertion is false.

**30.** (d) Order and molecularity may or may not be same as order can be zero and even a fraction but molecularity cannot be zero or a non-integer.

**31.** (a) In the given reaction, two moles of reactants *i.e.*, $H_2$ and $Br_2$ are in the elementary step of the reaction and hence, the molecularity appears to be 2. It is clear that both assertion and reasons are true and reason is the correct explanation of assertion.

**32.** (a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).

**33.** (d) Only effective collisions lead to the formation of product so assertion is false but reason is true as it defines the correct meaning of effective collision.

**34.** (c) Assertion (A) is true but Reason (R) is false.

## Case Study Based Questions

### Case Study 1

The instantaneous rate can be measured by determination of slope of the tangent at point '$t$' in concentration vs time plot. This makes it difficult to determine the rate law and hence the order of the reaction. In order to avoid this difficulty, we can integrate the differential rate equation to give a relation between directly measured experimental data, *i.e.*, concentrations at different times and rate constant. The integrated rate equation are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions.

Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,

$$R \longrightarrow P, \text{ Rate} = d[R]/dt = k[R]^0$$

First order reaction means that, the rate of the reaction is proportional to the first power of the concentration of reactants, $R$. For the reaction, $R \longrightarrow P$, Rate $= \dfrac{d[R]}{dt} = k[R]$ and the integrating rate equation is $k = (1/t)$ ln $[R]_0/[R]$ where, $[R]$ is final concentration and $[R]_0$ is initial concentration of reactant, respectively.

***Read the given passage carefully and give the answer of the following questions:***

**Q 1. For a hypothetical reaction,**

**$R \longrightarrow$ products; rate $= -k[R]$. The negative sign used in the rate expression indicates:**

a. decrease in the concentration of reactants with time

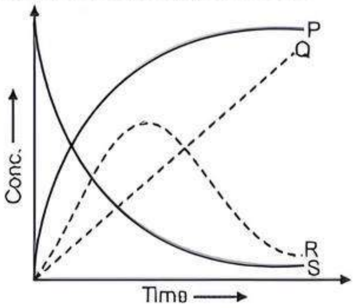
b. decrease in the rate with time

c. reaction is reversible

d. None of the above

**Q 2. For a reaction, $P + Q \longrightarrow R + S$**

**The curve which depicts the variation of the concentration of products is:**



a. P b. Q c. R d. S

**Q 3. For the reaction,**

**$Hg(l) + Cl_2(g) \longrightarrow HgCl_2(s)$**

**The rate of reaction is given as:**

a. $\dfrac{\Delta(HgCl_2)}{\Delta t}$

b. $-\dfrac{\Delta(Hg)}{\Delta t}$

c. $-\dfrac{\Delta(Cl_2)}{\Delta t}$

d. All of these

**Q 4. Contact process is used in the formation of sulphur trioxide,W**

**$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$**

**The rate of reaction can be expressed as**

$$\frac{-\Delta[O_2]}{\Delta t} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

**Then rate of disappearance of [$SO_2$] will be:**

a. $50.0 \times 10^{-5}$ mol $L^{-1}$ $s^{-1}$
b. $3.75 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$
c. $2.5 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$
d. $4.12 \times 10^{-4}$ mol $L^{-1}$ $s^{-1}$

### Answers

1. (a) decrease in the concentration of reactants with time
2. (a) P
3. (d) All of these
4. (a) $50.0 \times 10^{-5}$ mol $L^{-1}$ $s^{-1}$

## Case Study 2

The rate law for a chemical reaction relates the reaction rate with the concentrations or partial pressures of the reactants. For a general reaction $aA + bB \longrightarrow C$ with no intermediate steps in its reaction mechanism, meaning that it is an elementary reaction, the rate law is given by $r = k[A]^x [B]^y$, where $[A]$ and $[B]$ express the concentrations of $A$ and $B$ in moles per litre. Exponents $x$ and $y$ vary for each reaction and are determined experimentally. The value of $k$ varies with conditions that affect reaction rate, such as temperature, pressure, surface area, etc. The sum of these exponents is known as overall reaction order. A zero order reaction has a constant rate that is independent of the concentration of the reactants. A first order reaction depends on the concentration of only one reactant. A reaction is said to be second order when the overall order is two. Once we have determined the order of the reaction, we can go back and plug in one set of our initial values and solve for $k$. *(CBSE 2022 Term-2)*

***Read the given passage carefully and give the answer of the following questions:***

**Q 1. Calculate the overall order of a reaction which has the following rate expression:**

**Rate = $k\,[A]^{1/2}[B]^{3/2}$**

**Q 2. What is the effect of temperature on rate of reaction?**

**Q 3. A first order reaction takes 77.78 minutes for 50% completion. Calculate the time required for 30% completion of this reaction (log 10 = 1, log 7 = 0.8450).**

***OR***

**A first order reaction has a rate constant $1 \times 10^{-3}$ per sec. How long will 5g of this reactant take to reduce to 3 g?**

**(log 3 = 0.4771; log 5 = 0.6990)**

### Answers

1. Overall order of reaction $= \frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$
2. The rate of reaction increases on increasing the temperature.
3. For first order reaction,

$$t_{50\%} = t_{1/2} = \frac{0.693}{k}$$

$$\Rightarrow \quad 77.78 = \frac{0.693}{k}$$

$$\Rightarrow \quad k = \frac{0.693}{77.78} = 0.009$$

$$\text{and} \quad t_{30\%} = \frac{2.303}{k}\log\frac{a}{(a-x)}$$

$$= \frac{2.303}{0.009}\log\frac{100}{(100-30)}$$

$$= 255.89\,(\log 10 - \log 7)$$

$$= 255.89\,(1 - 0.8450)$$

$$= 39.66 \text{ minutes}$$

*OR*

Given $(A)_0 = 5g$, $(A) = 3g$

and $k = 1 \times 10^{-3}$ per sec

Using,

$$t = \frac{2.303}{k}\log\frac{(A)_0}{(A)}$$

$$= \frac{2.303}{1 \times 10^{-3}}\log\frac{5}{3}$$

$$= 2.303 \times 10^{3}\,(\log 5 - \log 3)$$

$$= 2.303\,(0.6990 - 0.4771)$$

$$\simeq 511 \text{ sec.}$$

## Case Study 3

The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. Mathematical representation of rate of reaction is given by rate law. Rate constant and order of a reaction can be determined from rate law or its integrated rate equation. *(CBSE 2023)*

***Read the given passage carefully and give the answer of the following questions:***

**Q 1. What is average rate of reaction?**

**Q 2. Write two factors that affect the rate of reaction.**

**Q 3. (i) What happens to rate of reaction for zero order reaction?**

**(ii) What is the unit of $k$ for zero order reaction?**

***OR***

**(i) For a reaction $P + 2Q \rightarrow$ Products.**
**Rate = $k\,[P]^{1/2}[Q]^{1}$. What is the order of the reaction?**

**(ii) Define pseudo first order reaction with an example.**

## Answers

1. Average rate of reaction is defined as the ratio of change in concentration of reactants or products to the change in time interval of a chemical reaction. It is denoted by '$r$' and is represented as:

$$\text{Average rate of reaction} = \frac{\text{change in concentration}}{\text{time}}$$

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

2. The two factors that affect the rate of reaction are:
   (i) concentration of the reactants.
   (ii) temperature of the reactants.

3. (i) For zero order reaction, the rate of reaction is independent of the reactant concentration. Hence, increasing or decreasing the concentration of the reacting species has no effect on the reaction rate.
   (ii) For zero order reaction, the unit of '$K$' is mol $L^{-1}s^{-1}$.

*OR*

(i) Order of the reaction $= \frac{1}{2} + 1 = \frac{3}{2} = 1.5$

(ii) Pseudo first order reaction is defined as the reaction which is bimolecular but order is one.
For example: acidic hydrolysis of ester (ethyl acetate).

## Very Short Answer Type Questions

**Q 1. What do you mean by velocity of a reaction? Explain.**

**Ans.** The rate at which concentration of reactants changes in unit time is called velocity of the reaction.

If the change in mole product (concentration) of reactant during infinitesimally small time $dt$ is $dx$, then

$$\text{Velocity of reaction} = \frac{dx}{dt}$$

If during the period $dt$, the remaining mole of reactant are $dC$, then

$$\text{Velocity of reaction} = -\frac{d[C]}{dt}.$$

**Q 2. What is instantaneous velocity? How could you predict it?**

**Ans.** The actual velocity of a reaction at a particular moment is called its instantaneous velocity. It can be determined by plotting a graph between time and concentration. The slope of tangent drawn at a point of time *vs* concentration plot at some specific time and specific concentration show the instantaneous velocity of the reaction.

**Q 3. For the following reaction, write the average velocity of the reaction.**

$$n_1A + n_2B \longrightarrow m_1C + m_2D$$

**Ans.** For the reaction, $n_1A + n_2B \longrightarrow m_1C + m_2D$

$$\text{Average velocity} = -\frac{1}{n_1}\frac{d(A)}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt}$$

$$= +\frac{1}{m_1}\frac{d|C|}{dt} = +\frac{1}{m_2}\frac{d|D|}{dt}$$

**Q 4. For which type of reactions, order and molecularity have the same value?** *(NCERT EXEMPLAR)*

**Ans.** Reactions completing in only one step *i.e.*, the first order reactions have same value of order and molecularity.

**Q 5. State a condition under which a bimolecular reaction is kinetically first order reaction.** *(NCERT EXEMPLAR)*

**Ans.** The given condition is possible only when one of the reactant is in excess and there occurs a very small change in its concentration during the course of the reaction. This happens in pseudo first order reaction (kinetically bimolecular reaction) *e.g.*, hydrolysis of ester in acidic medium.

**Q 6. The specific rate of a reaction is $6.2 \times 10^{-3}$ mol $L^{-1}s^{-1}$. What is the order of the reaction?**

**Ans.** The reaction is of zero order.

**Q 7. Give one example of a fractional order reaction.**

**Ans.** $H_2 + Br_2 \longrightarrow 2HBr$ ; Rate $= k(H_2)(Br_2)^{1/2}$ ; Order $= 1\frac{1}{2}$.

**Q 8. Rate of reaction is given by the equation : Rate $= k[A]^2[B]$. What are the units for the rate and rate constant for the reaction?**

**Ans.** Unit of rate = Mol $L^{-1}s^{-1}$; Unit of rate constant $(k) = L^2\,mol^{-2}\,s^{-1}$.

**Q 9. What is the rate determining step in a multi-step reaction?**

**Ans.** The slowest step in the reaction is the rate determining step.

**Q 10. State one condition in which a bimolecular reaction may be kinetically of the first order.**

**Ans.** By taking one of the reactants in large excess so that it may not contribute towards the order.

**Q 11. Give an example of pseudo first order reaction.**

**Ans.** $CH_3COOC_2H_5 + \underset{\text{(Excess)}}{H_2O} \longrightarrow CH_3COOH + C_2H_5OH$

$$\text{Rate} = k(CH_3COOC_2H_5)\,(H_2O)^0$$

**Q 12. For a reaction $R \longrightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction?** *(CBSE 2017)*

**Ans.** For the reaction, $R \longrightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants, thus it follows first order reaction.

**Q 13. What is an elementary reaction?**

**Ans.** The reaction taking place in a single step is an elementary reaction. For example,

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

**Q 14. In some chemical reactions, it is found that a large number of colliding molecules have energy more than threshold energy value, yet the reactions are quite slow. Explain.**

**Ans.** The reactant molecules may not be properly oriented at the time of collisions.

**Q 15. Express the relation between the half-life period of a reaction and initial concentration for the reaction of the *n*th order.**

**Ans.** For *n*th order reaction, $t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$.

**Q 16. For a reaction, $A + B \longrightarrow$ Product, the rate law is given by $(r) = k[A]^{1/2}[B]^2$. What is the order of reaction?**

**Ans.** Order of reaction = 1/2 + 2 = 2.5

**Q 17. For a reaction $A \longrightarrow B$, the rate of reaction becomes twenty seven times when the concentration of *A* is increased three times. What is the order of the reaction?**

**Ans.** For the reaction, let $r = k(A)^n$

According to the data, $27r = k(3A)^n$

$$\frac{27r}{r} = \frac{k(3A)^n}{k(A)^n} \text{ or } (3)^3 = 3^n$$

$\therefore$ Order of reaction $(n) = 3$.

**Q 18. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of reaction?**

**Ans.** Since the amount left after one-half period (2 hrs) is one-half (50%) of the original amount and the amount left after two-half periods (4 hrs) is one-fourth (25%), this suggests that the reaction is of first order.

**Q 19. What is meant by elementary step in a reaction?**

**Ans.** A complex reaction occurs through a sequence of steps known as elementary steps. Each elementary step has its own molecularity.

**Q 20. Derive an expression to calculate time required for completion of zero order reaction.** *(NCERT EXEMPLAR)*

**Ans.** For a zero order reaction, $[A] = [A]_0 - kt$

When the reaction is completed, $[A] = 0$

$$\therefore \qquad t = \frac{[A]_0}{k}$$

**Q 21. Write the order and units of velocity constant for the following reaction:**

$$H_2 + Cl_2 \longrightarrow 2HCl$$

**Ans.** For the reaction, $H_2 + Cl_2 \xrightarrow{\text{Sunlight}} 2HCl$

The order of reaction = 0.

(This is because concentration of none of the reactant changes with time.)

For a zero order reaction, $k = \frac{x}{t}$

On substituting the units,

$$\text{Unit of } k = \frac{\text{mol/L}}{\text{s}} = \text{mol L}^{-1}\text{ s}^{-1}$$

**Q 22. Will the rate constant of the reaction depend upon *T* if the $E_{act}$ (activation energy) of the reaction is zero?** *(CBSE 2020)*

**Ans.** No, when $E_{act} = 0$, $k = Ae^{-0/RT} = A$. Thus, *k* becomes independent of *T*.

**Q 23. If the concentration is expressed in mol $L^{-1}$ units and time in seconds, what would be the units of *k*: (i) for a zero order reaction, (ii) for a first order reaction?**

**Ans.** (i) For zero order reaction ; *k* has unit ; mol $L^{-1}s^{-1}$.

(ii) For first order reaction ; *k* has unit ; $s^{-1}$.

**Q 24. Why does the rate of a reaction not remain constant throughout the reaction?**

**Ans.** The rate of reaction represents the change in molar concentration of reacting species taking part in the reaction per unit time. Since the change in molar concentration is not uniform, the rate of reaction does not remain constant.

**Q 25. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalysed by iodide ions.**

$$2H_2O_2 \xrightarrow{OH^-} 2H_2O + O_2$$

**This reaction takes place in two steps as given below:**

**Step-I:** $H_2O_2 + I^- \longrightarrow H_2O + IO^-$**(slow)**

**Step-II:** $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ **(fast)**

**(i) Write the rate law expression and determine the order of reaction w.r.t. $H_2O_2$.**

**(ii) What is the molecularity of each individual step?**

**Ans.** (i) For a complex reaction, the rate of overall reaction depends upon the rate of reaction slowest step.

Hence, Rate law expression: Rate = k $(H_2O_2)$ $(I^-)$

Order of reaction w.r.t. $H_2O_2$ = 1

(ii) Molecularity of both Step-I and Step-II is two.

**Q 26. A first order reaction is found to have rate constant $k = 5.5 \times 10^{-14} s^{-1}$. Find the half-life of the reaction.**

**Ans.** For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{(5.5 \times 10^{-14}\,s^{-1})} = 1.26 \times 10^{13}\,s.$$

**Q 27. Give an example of second order reaction.**

**Ans.** $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

**Q 28. What is activation energy? How is rate constant related to activation energy?**

**Ans.** Activation energy is given by the energy difference between activated complex and the reactant molecules or it is the extra energy contained by the reactant molecules that results into effective collision between them to form the products.

Rate constant (*k*) for a reaction is related to activation energy as:

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

**Q 29. On increasing temperature, activation energy for a reaction decreases. Why?**

**Ans.** Activation energy and temperature are inversely proportional to each other.

**Q 30. What is the effect of adding a catalyst on:**

**(i) Activation energy ($E_a$), and**

**(ii) Gibbs energy ($\Delta G$) of a reaction?** *(CBSE 2017)*

**Ans.** (i) Activation energy ($E_a$) of the reaction decreases on adding catalyst.

(ii) Addition of catalyst does not change the value of Gibbs energy ($\Delta G$) of a reaction.

## Short Answer Type-I Questions

**Q 1. What do you mean by rate of a reaction? For the reaction $NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$, the proposed mechanism is as follows:**

**(i) $NO_2 + NO_2 \longrightarrow NO + NO_3$ (slow)**

**(ii) $NO_3 + CO \longrightarrow CO_2 + NO_2$ (fast)**

**What is the velocity (rate) of reaction?**

**Ans.** The rate of change in concentration of reactant with time is called velocity (rate) of reaction.

**For reaction:** $NO_2(g) + CO(g) \rightarrow NO(g)$.

The rate of the reaction is decided by slow reaction (step (i)) of the proposed mechanism. Thus,

Velocity (rate) of reaction $= k\,[NO_2]\,[NO_2] = k[NO_2]^2$

**Q 2. Explain how and why will the rate of reaction for a given reaction be affected when:**

**(i) a catalyst is added**

**(ii) the temperature at which the reaction was taking place is decreased.**

**Ans.** (i) When a catalyst is added, the rate of reaction will increase. The catalyst decreases the activation energy of the reaction therefore, the reaction becomes faster.

(ii) When the temperature at which the reaction was taking place is decreased, the rate of reaction will decrease. At lower temperatures, the kinetic energy of molecules decreases thereby, the collisions decrease resulting in a lowering of rate of reaction.

**Q 3. Write the order of following reactions with reason:**

**(i) $N_2 + 3H_2 \underset{Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3^-$**

**(ii) $CH_3COOC_2H_5 + NaOH \rightleftharpoons CH_3COONa + C_2H_5OH$**

**Ans.** (i) $N_2 + 3H_2 \underset{Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$

The velocity of this reaction does not depend upon the concentration of $N_2$ and $H_2$. So it is a **zero order reaction**.

(ii) $CH_3COOC_2H_5 + NaOH \rightleftharpoons CH_3COONa + C_2H_5OH$

Since concentration of one mole of each reactant is changing, so it is a **second order reaction**.

**Q 4. For the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$, the rate of formation of $NO_2(g)$ is $2.8 \times 10^{-3}$ M s$^{-1}$. Calculate the rate of disappearance of $N_2O_5(g)$.** *(CBSE 2018)*

**Ans.** For the reaction,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Overall rate of reaction can be given as under:

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

Given,

$$\frac{d[NO_2]}{dt} = 2.8 \times 10^{-3}\,\text{M s}^{-1}$$

$$-\frac{d[N_2O_5]}{dt} = ?$$

**TiP**

*Do not forget to put correct sign against products and reactants while writing rate law for a reaction.*

$$\therefore \quad -\frac{1}{2}\frac{d[N_2O_5]}{dt} = +\frac{1}{4}\frac{d[NO_2]}{dt}$$

or

$$-\frac{d[N_2O_5]}{dt} = \frac{1}{4} \times 2 \times 2.8 \times 10^{-3}\,\text{M s}^{-1}$$

$$= 1.4 \times 10^{-3}\,\text{M s}^{-1}$$

**Q 5. What are pseudo unimolecular reactions? Explain with an example.**

**Ans. Pseudo Unimolecular Reactions:** The reactions for which the values of order and molecularity are not same are called pseudo unimolecular reactions.

*e.g.* **(i) Hydrolysis of sugar:**

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

**(ii) Hydrolysis of ethyl acetate:**

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{H^+} CH_3COOH(l) + C_2H_5OH(l)$$

For both the above reactions, order is one because concentration of $H_2O$ remains unchanged but molecularity is two. So these reactions are pseudo unimolecular or pseudo molecular reactions.

For these reactions, rates can be given as:

Rate $= k\,[C_{12}H_{22}O_{11}]$.

Rate $= k\,[CH_3COOC_2H_5]\,[H_2O]^0$

**Q 6. (i) The conversion of molecule A to B followed second order kinetics. If concentration of A increased to three times, how will it affect the rate of formation of B?**

**(ii) Define Pseudo first order reaction with an example.**

**Ans.** (i) The given reaction is $A \longrightarrow B$

Since, it follows second order kinetics so,

Rate$_1 = k[A]^2$ ...(1)

where $k$ = rate constant

$[A]$ = concentration of $A$.

If the concentration of $[A]$ is made to increase 3 times, then rate will increase by 9 times as:

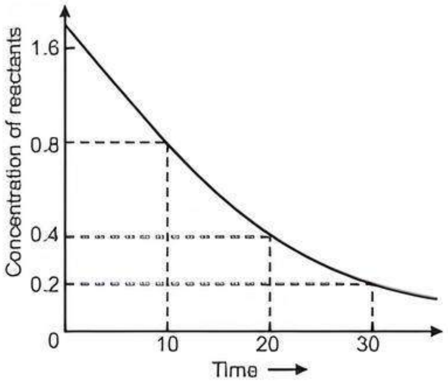
Rate$_2 = k(3A)^2 = 9k(A)^2$ ...(2)

From eqs. (1) and (2), we have $(\text{Rate})_2 = 9 \times (\text{Rate})_1$

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

(ii) Pseudo first order reaction is defined as the reaction which is bimolecular but order is one. For example: acidic hydrolysis of ester (ethyl acetate).

**Q 7. Analyse the given graph drawn between concentration of reactant *vs* time**



**(i) Predict the order of reaction.**

**(ii) Theoretically, can the concentration of the reactant reduce to zero after infinite time? Explain.** *(CBSE 2020)*

**Ans.** (i) It can be seen that, the concentration of the reactant decreases exponentially with time which is a characteristic of the 'first order reaction' and the rate of the reaction here is proportional to the first power of the concentration of the reactants.

(ii) The first order rate equation, $A = A_0 e^{-kt}$

where, $A$ is the concentration of the reactant at time $t$ and $A_0$ is the initial concentration of the reactant.

Putting the value $A = 0$, we get

$$A_0 e^{-kt} = 0, \text{ therefore } e^{-kt} = 0$$

Hence, $t = \infty$, since $k$ cannot be zero. So, theoretically, the concentration of the reactant will become zero at infinite time.

**Q 8. In a reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$, the concentration of $N_2O_5$ decreases from 0.5mol $L^{-1}$ to 0.4 mol $L^{-1}$ in 10 minutes. Calculate the average rate of this reaction and rate of production of $NO_2$ during this period.** *(CBSE 2022 Term-2)*

**Sol.** Average rate of this reaction $= -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$

$$= -\frac{1}{2}\frac{(0.4-0.5)}{(10 \text{ minutes})} \text{mol L}^{-1}$$

$$= \frac{0.1}{20} \text{mol L}^{-1} \text{min}^{-1} = 0.005 \text{ mol L}^{-1} \text{min}^{-1}$$

For the given equation,

$$\frac{1}{2} \times \text{Rate of disappearance of } N_2O_5$$

$$= \frac{1}{4} \times \text{Rate of formation of } NO_2$$

$$\Rightarrow \text{Rate of formation of } NO_2 = 4 \times \left[-\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}\right]$$

$$= 4 \times 0.005 = 0.02 \times \text{mol L}^{-1} \text{min}^{-1}.$$

**Q 9. In a first order reaction, the concentration of substance reduces to half of the initial concentration in 40 seconds. Calculate velocity constant for the reaction.**

**Sol.** Concentration of the substance reduces to half of its initial value in 40 seconds, so this is the half-life period ($t_{1/2}$) of the substance.

For a first order reaction,

$$\text{Velocity constant } (k) = \frac{0.693}{t_{1/2}} = \frac{0.693}{40\text{s}}$$

$$= 1.73 \times 10^{-2} \text{ s}^{-1}$$

**Q 10. A first order reaction is completed 50% in 100 seconds. Find out the rate constant of the reaction.**

**Ans.** Time required for 50% (half) completion of a reaction is called its half-life period ($t_{1/2}$).

So here $t_{1/2} = 100$ s.

For a first order reaction,

$$\text{Rate constant, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} \text{s}^{-1}$$

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

**Q 11. A first-order reaction takes 69.3 min for 50% completion. What is the time needed for 80% of the reaction to get completed?**

**(Given: log 5 = 0.6990, log 8 = 0.9030, log 2 = 0.3010)** *(CBSE SQP 2022-23)*

**Sol.** Given: $t_{1/2} = 69.3$ min

We know that, Half-life $t_{1/2} = 0.693/k$

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

$$k = 0.693/69.3 = 1/100 = 0.01 \text{ min}^{-1}$$

$$\text{For first order reaction, } k = \frac{2.303}{t}\log\frac{[R_0]}{[R]}$$

where, $[R_0] = 100$, $[R] = 100 - 80 = 20$

or, $t = \frac{2.303}{0.01}\log\frac{100}{20}$

or, $t = 230.3 \log 5$

or, $t = 160.9$ min $\quad (\because \log 5 = 0.6990)$

So, the time needed for 80% of the reaction to get completed is 160.9 min.

**Q 12. Time required to decompose $SO_2Cl_2$ to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.** *(NCERT INTEXT)*

**Sol.** Time required to decompose half of a substance is called its half-life ($t_{1/2}$). So here $t_{1/2} = 60$ minutes.

For a first order reaction,

$$\text{Rate constant, } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60 \text{ minutes}}$$

$$= 1.15 \times 10^{-2} \text{ minute}^{-1}$$

**Q 13. The half-life of a first order reaction is 60 minutes. How long will it take to consume 90% of the reactant?**

**[Given: log 2 = 0.3010, log 3 = 0.4771, log 10 = 1]** *(CBSE 2023)*

**Ans.** For a first order reaction.

Velocity constant, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60}\text{min}^{-1}$

Let the first order reaction takes $t_1$ minutes to consume 90% of the reactant, then,

Initial amount of the reactant $(a) = 100$ and remaining amount of the reactant $(a-x)$

$$= (100 - 90) = 10$$

For a first order reaction,

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

or, $$\frac{0.693}{60} = \frac{2.303}{t}\log_{10}\frac{100}{10}$$

or, $$t = \frac{2.303 \times 60}{0.693} \text{ minutes}$$

$$= 199.39 \text{ min.}$$

Hence, the time required will be 199.39 minutes.

**Q 14. Show that for a first order reaction, time required for completion of 99% of reaction is twice the time required for completion of 90% of reaction.**

*(CBSE 2019)*

**Sol.** For first order reaction,

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

Given: $[R]_0 = 100$ (suppose)

then $[R] = 100 - 99$

(for 99% completion of reaction)

$t = t_{99\%}$

Putting the values, we get

$$t_{99\%} = \frac{2.303}{k}\log\frac{100}{1}$$

or $$t_{99\%} = \frac{2.303}{k}\log 100$$

or $$t_{99\%} = \frac{2.303 \times 2}{k} \quad ...(1)$$

For 90% completion of reaction,

$$t_{90\%} = \frac{2.303}{k}\log\frac{100}{10}$$

or $$t_{90\%} = \frac{2.303}{k} \quad ...(2)$$

On comparing eqs. (1) and (2), we find

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

**Q 15. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half ?** *(NCERT EXERCISE)*

**Ans.** Let the reaction be: A $\xrightarrow{\quad}$ Products

Reaction rate $(r) = k[A]^2$ (for second order reaction)

(i) When concentration is doubled, the rate of reaction may be expressed as:

Reaction rate $(r') = k(2A)^2$

$$\therefore \frac{r'}{r} = \frac{k(2A)^2}{k(A)^2} = 4 \text{ or } r' = 4r$$

Hence, reaction rate becomes four times.

(ii) When concentration is reduced to half, the rate of reaction may be expressed as:

Reaction rate $(r'') = k(1/2\ A)^2$

$$\frac{r''}{r} = \frac{k(A/2)^2}{k(A)^2} = 1/4 \text{ or } r'' = 1/4$$

Hence, reaction rate will be reduced to 1/4.

**Q 16. Velocity (rate) constant for a first order reaction is $7 \times 10^{-4}\ s^{-1}$. Calculate the time taken by the reactant to reduce to 1/4 of its initial concentration.**

**Sol.** Given, $k = 7 \times 10^{-4}\ s^{-1}$.

Suppose initial concentration of the reactant = $a$

$\therefore$ Remaining amount of reactant $(a - x) = \frac{a}{4}$

For a first order reaction,

Velocity (rate) constant, $\frac{2.303}{t}\log_{10}\frac{}{(a-x)}$

On substituting the values, we have

$$k = \frac{2.303}{t}\log_{10}\frac{a}{a/4}$$

$$= \frac{2.303}{7 \times 10^{-4}}\log_{10} 4 = \frac{2.303 \times 2 \times 0.3010}{7 \times 10^{-4}}$$

$$= 0.198 \times 10^4 = 1.98 \times 10^3 \text{ seconds}$$

**Q 17. The rate constant for the first order reaction is $60\ s^{-1}$. How much time will it take to reduce the initial concentration of the reactant to its 1/16th value?** *(NCERT EXERCISE)*

**Sol.** For the first order reaction,

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

Let the initial concentration be $a$.

Final concentration $(a - x) = a/16$; $k = 60\ s^{-1}$

$$t = \frac{2.303}{(60s^{-1})}\log\frac{a}{a/16}$$

$$= \frac{2.303}{(60s^{-1})}\log 16 = \frac{2.303 \times 1.2041}{(60s^{-1})} = 0.0462\,s$$

$$= 4.62 \times 10^{-2}\,s$$

**Q 18. The half-life for radioactive decay of 14C is 5730 years. An archaeological artifact contained wood had only 80% of the 14C found in a living tree. Estimate age of the sample.** *(NCERT EXERCISE)*

**Sol.** Decay constant $(k) = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730}\text{yr}^{-1}$

Radioactive decays follow first order kinetics

$$t = \frac{2.303}{k}\log\frac{[A_0]}{[A]},$$

$$k = \frac{0.693}{5730}\ \text{yr}^{-1}$$

$[A_0] = 100\% ; [A] = 80\%$

$$\therefore \quad t = \left(\frac{2.303 \times 5730}{0.693} \text{yr}\right) \times \log\frac{100}{80}$$

$$= \left(\frac{2.303 \times 5730 \times 0.0969}{0.693}\right) \text{yr}$$

$$= 1845 \text{ years.}$$

**Q 19. The rate constant for the first order decomposition of $N_2O_5$ is given by the following equation:**

$$\log k = 23.6 - \frac{2 \times 10^4 k}{T}$$

**Calculate $E_a$ for the reaction.**

**$[R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}]$** *(CBSE 2023)*

**Sol.** Given, $\log k = 23.6 - \frac{2 \times 10^4 k}{T}$

According to Arrhenius equation,

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

Equating similar terms in the equations, we get

$$\frac{-E_a}{RT} = \frac{-2 \times 10^4 k}{T}$$

or, $E_a = 2 \times 10^4 \times R$

$= 2 \times 10^4 K \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

$= 16.628 \times 10^4 \text{ J mol}^{-1}$

Hence, $E_a$ for the reaction will be $166.28 \text{ KJ mol}^{-1}$.

**Q 20. (i) Radioactive decay follows first-order kinetics. The initial amount of two radioactive elements *X* and *Y* is 1 gm each. What will be the ratio of *X* and *Y* after two days if their half-lives are 12 hours and 16 hours respectively?**

**(ii) The hypothetical reaction $P + Q \rightarrow R$ is half order w.r.t. '*P*' and zero order w.r.t. '*Q*'. What is the unit of rate constant for this reaction?**

*(CBSE SQP 2023-24)*

**Sol.** (i) For first order reaction, half-life of $X = 12$ hours

Two days = 48 hours which means 4 half lives

Amount of $X$ left $= \frac{1}{16}$ of initial value

Now, half-life of $Y = 16$ hours

Two days = 48 hours which means 3 half lives

Amount of $X$ left $= \frac{1}{8}$ of initial value

Ratio of $X : Y = \frac{1}{16} : \frac{1}{8} = 1 : 2$

(ii) Rate for the given reaction $= k[P]^{1/2}$

So, the unit of rate constant for this reaction is $\text{mol}^{-1/2} \text{ L}^{-1/2} \text{ s}^{-1}$.

## Short Answer Type-II Questions

**Q 1. What do you mean by average velocity and instantaneous velocity of a chemical reaction? Describe briefly the effect of temperature on velocity of reaction.**

**Ans. Average Velocity:** The change in concentration of reactant or product present in a reaction per unit time is called the average velocity of the reaction.

Average velocity

$$= -\frac{\text{change in concentration of reactant}}{\text{time taken for the change}}$$

$$= +\frac{\text{change in concentration of product}}{\text{time taken for the change}}$$

**Instantaneous Velocity:** The actual velocity of a reaction at a particular moment is called its instantaneous velocity. If change in concentration of reactant or product of a reaction is represented by $\Delta C$ and time taken is represented by $\Delta t$, then instantaneous velocity of the reaction $= \pm\frac{\Delta C}{\Delta t}$.

**Effect of Temperature on Velocity of Reaction:** On increasing the temperature of a reaction, the number of activated molecules of reactants increases. Consequently, the number of effective collisions between them increases. The number of effective collision between reactant molecules in unit time is called velocity of reaction. Thus, on increasing temperature of a reaction, its velocity increases. The value of rate constant also increases on increasing temperature. 10°C rise in temperature makes the value of rate constant double or triple. This is also the reason for increasing the velocity of reaction on increasing temperature.

**Q 2. Define molecularity and order of reaction.**

**Ans. Molecularity of Reaction:** The number of reactant molecules taking part in a chemical reaction is called the molecularity of the reaction. If the number of reactant molecules taking part in a chemical reaction, is 1, 2, 3, etc., then the reaction is called unimolecular, bimolecular, trimolecular, etc. respectively.

**Example:** When ammonium nitrite is heated, its one molecule takes part in the reaction, so molecularity of this reaction is one.

$$NH_4NO_2 \xrightarrow{\Delta} 2H_2O + N_2 \uparrow$$

Molecularity of reaction is always a whole number *i.e.*, it is not in fraction.

**Order of Reaction:** The number of the reactant molecules taking part in a chemical reaction, concentration of which changes during the course of the reaction is called order of the reaction.

**Example:**

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

In this reaction, concentration of one molecule of each reactant changes during the course of the reaction. So it is a second order reaction.

**Q 3. Answer the following questions:**

**(i) Identify the order of reaction from the following unit for its rate constant:**

**$[\text{mol}^{-1} \text{ s}^{-1}]$**

**(ii)** **The conversion of molecules from *A* to *B* follow second order kinetics. If concentration of *A* is increased to three times, how will it affect the rate of formation of *B*?**

**(iii)** **Write the expression of integrated rate equation for zero order reaction.**

**Ans.** (i) The order of the reaction is 2.

(ii) The given reaction is $A \longrightarrow B$

Thus, Rate $(r) = K[A]^2$ ....(1)

(it follows second order kinetics)

If concentration of A is increased three times,

New rate $(r^1) = k[3A]^2 = 9\,k[A]^2 = 9r$ (from eq. (1))

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

(iii) Integrated rate equation for zero order reaction: $kt = [R]_0 - [R]$, where $k$ = rate constant, $[R]^0$ = initial concentration of reactant and $[R]$ is the concentration of reactant at time $t$.

**Q 4. The decomposition of $NH_3$ on platinum surface is a zero order reaction. What are the rates of production of $N_2$ and $H_2$, if $k = 2.5 \times 10^{-4}$ mol$^{-1}$ L s$^{-1}$?**

*(NCERT EXERCISE)*

**Sol.** Decomposition of $NH_3$ on platinum surface can be represented as

$$2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$$

Here rate of decomposition of $NH_3$ and rates of formation of $N_2$ and $H_2$ are related in the following manner:

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

Since, the reaction is of zero order.

$$\therefore \quad -\frac{1}{2}\frac{\partial[NH_{\delta}]}{dt} = \frac{[N\ \ ]}{dt} = \frac{1}{3}\frac{[H\ \ ]}{dt} = k$$

$$= \underline{2.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{g}^{-1}}$$

$$\therefore \text{ Rate of formation of } N_2 = \frac{d[N_2]}{dt} = k$$

$$= \underline{2.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}$$

and rate of formation of

$$H_2 = \frac{d[H_2]}{dt} = 3k$$

$$= 3 \times 2.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$= \underline{7.5 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}$$

**Q 5. How the rate of the reaction will be affected when:**

**(i) surface area of the reactant is increased?**

**(ii) temperature of the reaction is decreased?**

**(iii) catalyst is added in a reversible reaction?**

*(CBSE 2020)*

**Ans.** (i) The rate of the reaction increases when surface area of the reactant is increased.

(ii) The rate of the reaction decreases when temperature of the reaction is decreased.

(iii) The rate of the reaction increases when catalyst is added in a reversible reaction.

**Q 6. A reaction is first order in *A* and second order in *B*:**

**(i) Write differential rate equation.**

**(ii) How is rate affected when the concentration of B is tripled?**

**(iii) How is rate affected when the concentration of both A and B are doubled?**

*(NCERT EXERCISE; CBSE 2022 Term 2)*

**Ans.** (i) Differential rate equation for the reaction is:

rate $(r) = k[A]^1[B]^2$.

(ii) Differential rate equation for the reaction is:

rate $(r') = k[A]^1[3B]^2$

$$\frac{r'}{r} = \frac{k[A]^1[3B]^2}{k[A]^1[B]^2} = 9 \text{ or } r' = \underline{9r}$$

The reaction rate will increase 9 times.

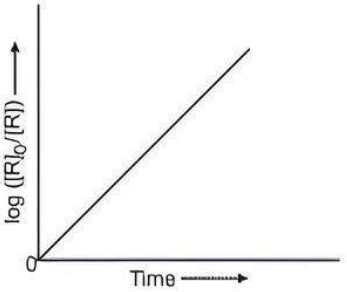
(iii) Differential rate equation for the reaction is:

$$\text{Rate } (r'') = k[2A]^1[2B]^2;\ \frac{r''}{r} = \frac{k[2A]^1[2B]^2}{k[A]^1[B]^2} = 8$$

or $r' = 8r$

The reaction rate will increase 8 times.

**Q 7. Observe the graph shown in figure and answer the following questions.**



**(i) What is the order of the reaction?**

**(ii) What is the slope of the curve?**

**(iii) Write the relationship between *k* and $t_{1/2}$ (half-life period).**

**Ans.** (i) The reaction is of first order.

(ii) For first order reaction,

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

$$\text{or} \quad \log\frac{[R]_0}{[R]} = \frac{kt}{2.303}$$

$$\text{Thus, slope} = \underline{\frac{k}{2.303}}$$

(iii) For first order reaction,

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

**Q 8. The reaction between *A* and *B* is first order with respect to *A* and zero order with respect to *B*. For this reaction, fill in the blanks in the following table.**

| Experiment | [A] mol/L | [B] mol/L | Initial Rate mol/L/min |
|---|---|---|---|
| I | 0.1 | 0.1 | $2.0 \times 10^{-2}$ |
| II | – | 0.2 | $4.0 \times 10^{-2}$ |
| III | 0.4 | 0.4 | – |
| IV | – | 0.2 | $2.0 \times 10^{-2}$ |

*(CBSE 2019)*

**Sol.**

**TiP**

*Do not forget to check units as they must be in same system of units.*

According to the given data.

Rate law expression can be given as below:

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

or Rate $= k[A]$

Now, from experiment I,

$2.0 \times 10^{-2}$ mol L$^{-1}$ min$^{-1}$ $= k(0.1)$ mol L$^{-1}$

$$k = \frac{2.0 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}}{0.1\ \text{mol L}^{-1}}$$

$$= \underline{0.2\ \text{min}^{-1}}$$

Again, from experiment II

$4.0 \times 10^{-2} = 0.2[A]$ $\qquad$ $(\because\ r = k(A))$

$[A] = \underline{0.2\ \text{mol L}^{-1}}$

From experiment III,

Rate $= 0.2 \times 0.4$

$= \underline{8.0 \times 10^{-2}\ \text{mol L}^{-1}\ \text{min}^{-1}}$

From experiment IV,

$2.0 \times 10^{-2} = 0.2\ [A]$ $\qquad$ $(\because\ r = k(A))$

$[A] = \underline{0.1\ \text{mol L}^{-1}}$

**Q 9. The initial concentration of $N_2O_5$ at 318 K was $0.60 \times 10^{-2}$ mol L$^{-1}$ in the first order reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2$, which became $0.20 \times 10^{-2}$ mol L$^{-1}$ after 60 minutes. Calculate the rate constant at 318 K. (log 3 = 0.4771)**

**Sol.** Given, initial concentration,

$a = 0.60 \times 10^{-2}$ mol L$^{-1}$

Remaining concentration $(a - x) = 0.20 \times 10^{-2}$ mol L$^{-1}$

Time taken, $t = 60$ minutes.

For a first order reaction,

Rate constant, $\underline{k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}}$

On substituting the values, we have

$$k = \frac{2.303}{60\ \text{minutes}}\log_{10}\frac{(0.60 \times 10^{-2}\ \text{mol L}^{-1})}{(0.20 \times 10^{-2}\ \text{mol L}^{-1})}$$

$$= \frac{2.303}{60\ \text{minutes}}\log_{10}3 = \frac{2.303 \times 0.4771}{60}\text{minutes}^{-1}$$

$$= \underline{1.83 \times 10^{-2}\ \text{minute}^{-1}}$$

**Q 10. A first order reaction is 20% completed in 10 minutes. How much time it takes for 75% completion? ($\log_{10}2 = 0.3010$)**

**Sol.** For a first order reaction,

velocity constant, $\underline{k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}}$

where $a$ = initial concentration of reactant = 100

$(a - x)$ = amount (concentration) of reactant after time $t$.

$\because$ The reaction takes 10 minutes for 20% completion.

$\therefore$ After 10 minutes, $(a - x) = (100 - 20) = 80$

$$\therefore \quad k = \frac{2.303}{10}\log_{10}\frac{100}{80} = \frac{2.303}{10} \times 0.097$$

$$= 0.022\ \text{minutes}$$

Suppose the reaction takes $t_1$ minutes for 75% completion.

*i.e.*, $t = t_1$ and $(a - x) = 100 - 75 = 25$

$$\therefore \quad k = \frac{2.303}{t_1}\log_{10}\frac{100}{25} = \frac{2.303}{t_1} \times \log_{10}4$$

$$\text{or} \quad 0.022 = \frac{2.303}{t_1} \times 2 \times 0.3010$$

$$\therefore \quad t_1 = \frac{2.303 \times 0.6020}{0.022}$$

$$= \underline{63.02\ \text{minutes}}$$

**Q 11. A first order reaction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.**

**Given:**

**[log 2 = 0.3, log 3 = 0.48, log 4 = 0.6, log 5 = 0.7]**

**Sol.** Let initial concentration be $(A)_0$.

Then, concentration after 30 minutes

$$(A) = \frac{25}{100} \times (A)_0 = \frac{(A)_0}{4}$$

For first order reaction,

$$\underline{k = \frac{2.303}{t} = \log_{10}\frac{[A_0]}{(A)}}$$

$$k = \frac{2.303}{30}\log\frac{(A)_0}{(A_0)/4} = 0.077\log 4$$

$$= 0.077 \times 0.6$$

$$= 0.046 \times \text{m}^{-1}$$

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.046} = \underline{15.07\ \text{minutes}}$$

**Q 12. In a first order reaction, a substance remains half of its initial amount in 100 minutes, then predict, in how much time, it will remain one-fourth of its initial amount?**

**Sol.** For a first order reaction,

Velocity constant, $\underline{k = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}}$

when $t = 100$ minutes, $(a - x) = a/2$.

$$\therefore \quad k = \frac{2.303}{100}\log_{10}\frac{a}{a/2}$$

$$= \frac{2.303}{100}\log_{10}2 = \frac{2.303}{100} \times 0.3010$$

$$= 6.93 \times 10^{-3}\ \text{minute}^{-1}$$

Suppose, the substance remains one fourth of its initial amount $(a)$ in $t_1$ minutes, then $(a - x) = a/4$.

$$\therefore\ 6.93\times10^{-3}=\frac{2.303}{t_1}\log_{10}\frac{a}{a/4}=\frac{2.303}{t_1}\log_{10}4$$

$$\text{or } 6.93\times10^{-3}=\frac{2.303\times2\times0.3010}{t_1}$$

$$\text{or}\qquad t_1=\frac{2.303\times2\times0.3010}{6.93\times10^{-3}}=\underline{200\text{ minutes}}$$

**Q 13. Rate constant for the first order reaction has been found to be $k = 2.54\times10^{-3}\ s^{-1}$. Calculate its $\frac{3}{4}$th life. (log2 = 0.3010).**

**Sol.** For a first order reaction,

$$\text{Rate constant, } \underline{k=\frac{2.303}{t}\log_{10}\frac{a}{(a-x)}}$$

where, $k = 2.54\times10^{-3}\ s^{-1}$ (given)

$a$ = initial concentration of the reactant.

$(a-x)$ = concentration after completion of 3/4th part of the reaction.

$$=a-\frac{3}{4}a=\frac{4a-3a}{4}=\frac{a}{4}$$

On substituting the values in above equation of rate constant, we have

$$k=\frac{2.303}{t}\log_{10}\frac{a}{a/4}=2.54\times10^{-3}\ s^{-1}$$

$$t=\frac{2.303}{2.54\times10^{-3}s^{-1}}\log_{10}4$$

$$=\frac{2.303\times2\times\log_{10}2}{2.54\times10^{-3}s^{-1}}$$

$$=\frac{2.303\times2\times0.3010}{2.54\times10^{-3}}s$$

$$=\frac{1.386}{2.54\times10^{-3}}s=\underline{545.67\ s}$$

**Q 14. A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed.** *(CBSE 2017)*
**(Given: log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021)**

**Sol.** For a first order reaction, $\underline{k=\frac{2.303}{t}\log\frac{a}{a-x}}$

where, $k$ = rate constant, $a$ = initial concentration

$(a-x)$ = concentration after time '$t$'

It is given that the first order reaction is 25% completed in 20 min.

$a = 100,\ a-x = 100-25 = 75,\ t = 20$ min.

$$\therefore\qquad k=\frac{2.303}{20}\log\frac{100}{75}$$

$$=\frac{2.303}{20}(\log4-\log3)$$

$$=\frac{2.303}{20}(2\times0.3010-0.4771)$$

$$=\underline{0.0143\ \text{min}^{-1}}$$

For 75% completion of reaction,

$a = 100,\ a-x = 100-75 = 25,\ k = 0.0143\ \text{min}^{-1}$

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

$$=\frac{2.303}{0.0143}\log\frac{100}{25}$$

$$=\frac{2.303}{0.0143}\log4=\underline{96.968\text{ min}}$$

**COMMON ERROR**

*Students often make mistakes in doing calculations or forget to write units.*

**Q 15. Prove that half-life of a first order reaction does not depend upon the initial concentration of the reactant.**

**Sol.** For a first order reaction,

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

When half of the reactant is used,

changed concentration $(x) = 0.5a$ and $t = t_{1/2}$ (half-life)

$$k=\frac{2.303}{t_{1/2}}\log_{10}\frac{a}{a-0.5a}$$

$$=\frac{2.303}{t_{1/2}}\log_{10}\frac{a}{0.5a}$$

$$=\frac{2.303}{t_{1/2}}\log_{10}2$$

$$\text{or}\qquad t_{1/2}=\frac{2.303}{k}\log_{10}2$$

$$=\frac{2.303\times0.3010}{k}$$

$$[\because \log_{10}2=0.3010]$$

$$\text{or}\qquad \underline{t_{1/2}=\frac{0.693}{k}}$$

There is no concentration term in the above equation, so time required for the half-completion of a first order reaction (i.e., half-life) does not depend upon the concentration of the reactant. Proved

**Q 16. Following data are obtained for the reaction:**

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

| t/s | 0 | 300 | 600 |
|---|---|---|---|
| $[N_2O_5]$/mol $L^{-1}$ | $1.6\times10^{-2}$ | $0.8\times10^{-2}$ | $0.4\times10^{-2}$ |

**(i) Show that it follows first order reaction.**
**(ii) Calculate the half-life.**
**(Given: log 2 = 0.3010, log 4 = 0.6021)** *(CBSE 2017)*

**Sol.** (i) Given data,

| t/s | 0 | 300 | 600 |
|---|---|---|---|
| $[N_2O_5]$/mol $L^{-1}$ | $1.6\times10^{-2}$ | $0.8\times10^{-2}$ | $0.4\times10^{-2}$ |

Using hit and trial method,

For first order reaction, $\underline{k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}}$

From the above data, $t = 300$ s, $[R]_0 = 1.6\times10^{-2}$ mol $L^{-1}$ and $[R] = 0.8\times10^{-2}$.

Putting the values in the expression, we get

$$k = \frac{2.303}{300}\log\frac{(1.6\times10^{-2})\text{ mol L}^{-1}}{(0.8\times10^{-2})\text{ mol L}^{-1}}$$

$$= \frac{2.303}{300}\log 2 = \frac{2.303}{300}\times 0.3010$$

$$\underline{k = 2.31\times10^{-3}\text{ s}^{-1}}$$

Thus, it is proved that reaction proceed through first order kinetics as the rate constant remains same.

(ii) $\underline{\text{Half-life } (t_{1/2}) = \frac{0.693}{k}}$

$$t_{1/2} = \frac{0.693}{2.31\times10^{-3}\text{ s}^{-1}} = \underline{300\text{ s}}$$

**Q 17. Prove that the time required is 10 times of the half-life period for the completion of 99.9% of a first order reaction.**

**Sol.** Suppose for the given first order reaction, half-life period is $t_{1/2}$ then:

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

(where, $k$ = velocity or rate constant)

or $$\underline{k = \frac{0.693}{t_{1/2}}} \qquad ...(1)$$

Suppose the reaction takes time $t$ for 99.9% completion, then:

$$\begin{array}{lccc} & A & \longrightarrow & B \\ \text{Initially} & 100 & & 0 \\ \text{After time } t & (100-99.9) & & 99.9 \\ & = 0.1 & & \end{array}$$

For a first order reaction,

Velocity constant,

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

where, $a = 100$ and $(a-x) = 0.1$

$$\therefore \quad k = \frac{2.303}{t}\log_{10}\frac{100}{0.1} = \frac{2.303}{t}\times\log_{10}1000$$

$$k = \frac{2.303}{t}\log_{10}10^3 = \frac{2.303}{t}\times 3\log_{10}10$$

$$= \frac{2.303\times3}{t} \qquad ...(2)$$

From eqs. (1) and (2),

$$\frac{0.693}{t_{1/2}} = \frac{2.303\times3}{t} \quad \text{or} \quad \underline{t = \frac{2.303\times3}{0.693}t_{1/2} = 10t_{1/2}}$$

Thus, the time required for the completion of 99.9% of a first order reaction is 10 times of its half-life period ($t_{1/2}$). **Proved.**

**Q 18. Prove that time required for the completion of three-fourth of a first order reaction is twice the time required for the completion of half reaction.**

**Sol.** For a first order reaction,

Velocity constant, $$\underline{k = \frac{2.303}{t}\log\frac{a}{(a-x)}} \qquad ...(1)$$

When half of the reaction is completed,

$$t = t_{1/2} \quad \text{and} \quad x = \frac{a}{2}$$

On substituting the values in eq. (1), we have

$$k = \frac{2.303}{t_{1/2}}\log\frac{a}{\left(a-\frac{a}{2}\right)} = \frac{2.303}{t_{1/2}}\log\frac{a}{a/2}$$

$$k = \frac{2.303}{t_{1/2}}\log 2 \qquad ...(2)$$

When $\frac{3}{4}$ th part of the reaction is completed,

$$t = t_{3/4} \quad \text{and} \quad x = a\times\frac{3}{4}$$

$$k = \frac{2.303}{t_{3/4}}\log\frac{a}{\left(a-\frac{3a}{4}\right)} = \frac{2.303}{t_{3/4}}\log\frac{a}{\frac{a}{4}}$$

$$k = \frac{2.303}{t_{3/4}}\log 4 = \frac{2.303}{t_{3/4}}\times 2\log 2$$

or $$t_{3/4} = \frac{2.303}{k}\times 2\log 2 \qquad ...(3)$$

On substituting the value of $k$ from eq. (2) in eq. (3), we have

$$t_{3/4} = \frac{2\times2.303\times\log2\times t_{1/2}}{2.303\times\log 2} = 2\times t_{1/2}$$

$$\therefore \quad \underline{t_{3/4} = 2\times t_{1/2}}$$

Thus, the time required for the completion of three-fourth of a first order reaction is twice the time required for the completion of half reaction.

**Q 19. Write short note on the following:**

**(i) specific velocity constant**

**(ii) activation energy**

**Ans.** (i) **Specific Velocity Constant:** Suppose in a chemical reaction, the molar concentration of the reactant at any moment is $C$, then at that moment, velocity of the reaction ($dx/dt$) is directly proportional to the concentration of the reactant, *i.e.*,

$$\frac{dx}{dt} \propto C \quad \text{or} \quad \frac{dx}{dt} = kC$$

where $k$ is a constant called **velocity constant**.

If $C = 1$ mol/L, then $\frac{dx}{dt} = k$.

Thus, at constant temperature and unit concentration of the reactant, the velocity of a reaction is called the specific velocity constant of the reaction. Its value is different for different reactions and its units depend upon the nature of the reaction. Its value raises with rise in temperature.

**(ii) Activation Energy:** The extra amount of energy obtained from the collision of reactant molecules, which is enough to carry out a reaction and form products is called **activation energy.** Thus, the minimum energy other than the average potential energy of the reactions, which is obtained by the collisions of reactant molecules and converts reactant molecules into products is called activation energy.

Activation energy = Threshold energy – Average potential energy of reactant molecules.

Arrhenius proposed an equation to explain the effect of temperature, on velocity of reaction, called the Arrhenius equation.

According to this equation $k = Ae^{-E_a/RT}$ ...(1)

where, $A$ = pre-exponential coefficient or frequency factor

$E_a$ = activation energy

$k$ = velocity constant of the reaction

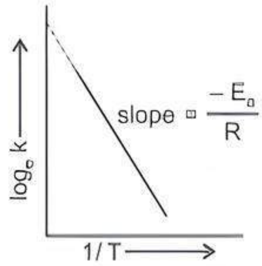
$R$ = gas constant

and $T$ = absolute temperature

**Q 20. Give Arrhenius equation. How would you calculate the activation energy of a reaction by graphical method?**

**Ans. Arrhenius Equation:**

$$k = Ae^{-E_a/RT} \qquad ...(1)$$



**Plot of $\log_e k$ vs 1 / T**

where, $k$ = velocity constant of a reaction, $E_a$ = activation energy of a reaction, $R$ = gas constant, $T$ = absolute temperature, and $A$ = pre-exponential constant or frequency factor.

On taking logarithm eq. (1), we have

$$\log_e k = \log_e A - E_a/RT \qquad ...(2)$$

On the basis of eq. (2), following graph is obtained, when $\log_e k$ is plotted with $1/T$.

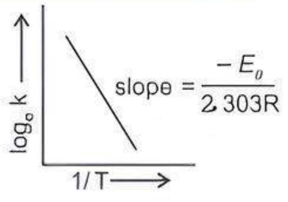
From the slope of this plot, value of $E_a$ can be calculated. Unit of $E_a$ depends upon the units of $R$. This is because slope is $-E_a/R$. By substituting the value of $R$, we get the value of $E_a$.

Above eq. (2) can also be written as

$$2.303\log_{10} k = 2.303\log_{10} A - \frac{E_a}{RT}$$

or
$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT} \qquad ...(3)$$

On the basis of this equation, when $\log_{10} k$ is plotted with $1/T$, slope of the plot is equal to $-E_a/2.303$. From it value of $E_a$ is calculated.



**Plot of $\log_{10}$ k vs 1 / T**

**Q 21. The following data were obtained during the first order thermal decomposition of $C_2H_5Cl$ at a constant volume: $C_2H_5Cl\,(g) \rightarrow C_2H_4(g) + HCl\,(g)$**

| Experiment | Time ($s^{-1}$) | Total pressure (atm) |
|---|---|---|
| 1 | 0 | 0.4 |
| 2 | 100 | 0.6 |

**Calculate the rate constant.**

**(Given: log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021)** *(CBSE 2023)*

**Sol.** The given reaction is:

$C_2H_5Cl(g) \longrightarrow C_2 \quad H_4\,(s^{-1}) + HCl\,(g)$

At $t = 0$ $\quad P_0 \quad 0 \quad 0$

At $t = 100$ $\quad P_0 - P \quad P \quad P$

After time $t$, total pressure = $(P_0 - P) + P + P$

or, $P_t = P_0 + P$

or, $P_0 - P = 2P - P_t$

For a first order reaction, we have

$$k = \frac{2.303}{t}\log\left(\frac{P_0}{P_0 - P}\right)$$

$$= \frac{2.303}{t}\log\left(\frac{P_0}{2P_0 - P_t}\right)$$

At $t = 100$, $P_t = 0.6$, $P_0 = 0.4$

$$k = \frac{2.303}{100}\log\left(\frac{0.4}{2 \times 0.4 - 0.6}\right)$$

$$= 2.303 \times 0.3010 \times 10^{-2}\ \text{sec}^{-1}$$

$$= 6.932 \times 10^{-3}\ \text{sec}^{-1}$$

Hence, the rate constant is $6.932 \times 10^{-3}$ sec$^{-1}$.

**Q 22. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5}$ s$^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor?** *(NCERT EXERCISE)*

**Sol.** Given, $k = 2.418 \times 10^{-5}$ s$^{-1}$, $E_a = 179.9$ kJ mol$^{-1}$, $T = 546$ K

According to Arrhenius equation, $k = Ae^{-E_a/RT}$

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

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

$$\text{or} \quad \log A = \log k + \frac{E_a}{2.303RT} = \log(2.418 \times 10^{-5}) + \frac{179.9}{2.303 \times 8.314 \times 10^{-3} \times 546\ \text{K}}$$

$$= (-5 + 0.3834) + 17.2081 = 12.5915\ \text{s}^{-1}$$

$$\text{or} \quad A = \text{Antilog}\ (12.5915)\ \text{s}^{-1} = \underline{3.9 \times 10^{12}\ \text{s}^{-1}}$$

**Q 23. In general, it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If the generalisation holds for a reaction in the temperature range 295 K to 305 K, what would be the value of activation energy for the reaction?** *(NCERT INTEXT)*

**Sol.** According to Arrhenius equation,

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

$k_2/k_1 = 2$ ; $T_1 = 295$ K; $T_2 = 305$ K; $R = 8.314\ \text{J}\ K^{-1}\ \text{mol}^{-1}$

$$\therefore \quad \log 2 = \frac{E_a}{2.303 \times (8.314\ \text{JK}^{-1}\ \text{mol}^{-1})}\left[\frac{1}{295\text{K}} - \frac{1}{305\text{K}}\right]$$

$$\text{or } 0.3010 = \frac{E_a}{2.303 \times (8.314\ \text{J mol}^{-1})} \times \frac{(10)}{295 \times 305}$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 295 \times 305}{10}\ (\text{Jmol}^{-1})$$

$$= 51855\ \text{J mol}^{-1} = \underline{51.855\ \text{kJ mol}^{-1}}$$

**Q 24. A first order reaction is 50% complete in 80 minutes at 300 K and in 10 minutes at 320 K. Calculate activation energy ($E_a$) for the reaction.**

**($R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$)**

**(Given: $\log 2 = 0.3010, \log 3 = 0.4771, \log 4 = 0.6021$)**

*(CBSE 2023)*

**Sol.** Given, $t_{1/2} = 80$ min at 300 $K$

$\therefore$ For first order,

$$k_1 = \frac{0.693}{(t_{1/2})_1} = \frac{0.693}{80\ \text{min}}$$

$$= \frac{0.693}{80}\text{min}^{-1}$$

Similarly, at $T_2 = 320K$

$$k_2 = \frac{0.693}{(t_{1/2})_2} = \frac{0.693}{10}\text{min}^{-1}$$

For calculation of activation energy, we know

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303\ R}\left(\frac{T_2 - T_1}{T_1\ T_2}\right)$$

Putting the values in above equation, we get

$$\log\left(\frac{0.693}{10} \times \frac{80}{0.693}\right) = \frac{E_a}{2.303 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}}\left(\frac{320 - 300}{300 \times 320}\right)$$

$$\text{or.} \quad \log 8 = \frac{E_a}{19.147\ \text{JK}^{-1}\ \text{mol}^{-1}}\left(\frac{20}{96000\ \text{K}}\right)$$

$$\text{or.} \quad E_a = \frac{19.147 \times 96000}{20 \times 3 \log 2}$$

$$= \frac{19.147 \times 1600}{0.3010}$$

$$= \underline{101778.073\ \text{J mol}^{-1}}$$

Hence, activation energy ($E_a$) for the reaction is 101.778 kJ $\text{mol}^{-1}$.

**Q 25. The rate of a reaction doubles when temperature changes from 27°C to 37°C. Calculate energy of activation for the reaction.** *(CBSE 2023)*

**Sol.** We know that

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

$$E_a = 2.303\ \text{R} \log\left(\frac{k_2}{k_1}\right)\left[\frac{T_1 T_2}{T_2 - T_1}\right]$$

$T_1 = 27°\ \text{C} = 273 + 27 = 300\ \text{K}$

$T_2 = 37°\ \text{C} = 273 + 37 = 310\ \text{K}$

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

$$\therefore\ E_a = 2.303 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times \log\left(\frac{2}{1}\right)\left[\frac{300 \times 310}{10}\right]$$

$$= 2.303 \times 8.314 \times 0.3010 \times 9300\ \text{J mol}^{-1}$$

$$= \underline{53,598.595\ \text{Jmol}^{-1}}$$

Hence, energy of activation for the reaction is 53.599 kJ $\text{mol}^{-1}$.

**Q 26. The rate constants of a reaction at 200K and 500K are 0.02 $\text{s}^{-1}$ and 0.20 $\text{s}^{-1}$ respectively. Calculate the value of $E_a$. (Given $2.303R = 19.15\ \text{JK}^{-1}\ \text{mol}^{-1}$).** *(CBSE SQP 2023-24)*

**Sol.** We know that

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303\ \text{R}}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where, $k_2 = 0.20\ \text{s}^{-1}$, $k_1 = 0.02\ \text{s}^{-1}$

$T_1 = 200\text{K}$, $T_2 = 500\text{K}$ and $2.303R = 19.15\ \text{JK}^{-1}\ \text{mol}^{-1}$

$$\therefore \quad \log\left(\frac{0.20}{0.02}\right) = \frac{E_a}{2.303\ R}\left[\frac{1}{200} - \frac{1}{500}\right]$$

$$\log 10 = \frac{E_a}{19.15}\left(\frac{300}{200 \times 500}\right)$$

$$\text{or.} \quad E_a = \frac{19.15 \times 200 \times 500}{300} = \underline{6383\ \text{J mol}^{-1}}$$

Hence, the value of $E_a$ is 6.383 kJ $\text{mol}^{-1}$.

## **Long Answer** Type Questions

**Q 1. What is the difference between molecularity and order of a reaction? Explain by giving an example.**

**Ans. Difference between molecularity and order of a reaction:**

(i) Molecularity of a reaction is always a whole number while order of a reaction can be in fractions.

(ii) Molecularity of a reaction can never be zero whereas order of reaction can be zero.

(iii) Molecularity and order of a reaction can be same or different.

(iv) Molecularity shows the number of molecules taking part in a step of a reaction whereas order of reaction shows a relationship between the velocity of reaction and concentration of reactants.

(v) The number of molecules taking part in the velocity (rate) determining step of a reaction, is called the molecularity of the reaction. Order of a reaction shows the number of molecules, concentration of which determines the velocity of the reaction.

(vi) Molecularity of a reaction is obtained from its mechanism whereas order of reaction is obtained from experiments.

**Example:** Following examples clearly show difference between molecularity and order of the reactions.

(i) $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$

(ii) $CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$

Reactions (i) and (ii) both are bimolecular. Reaction (i) is of second order because velocity of the reaction depends upon the concentrations of $CH_3COOC_2H_5$ and NaOH both. However reaction (ii) is of first order. This is because velocity of this reaction depends only upon the concentration of $CH_3COOC_2H_5$.

**Q 2. What do you mean by order of a reaction? Find the expression of velocity constant of a first order reaction.**

**Ans. Order of a reaction:** The number of the reactant molecules taking part in a chemical reaction, concentration of which changes during the course of the reaction is called order of the reaction.

**Expression of Velocity Constant of First Order Reaction:** Suppose a first order reaction is as follows:

| | A $\longrightarrow$ | Product |
|---|---|---|
| Initial concentration | $a$ mol/L | 0 mol/L |
| Concentration after time $t$ | $(a-x)$ mol/L | $x$ mol/L |

For a first order reaction,

Velocity of the reaction, $\frac{dx}{dt} \propto [A]^0$

Velocity of the reaction after time $t$, $\frac{dx}{dt} = k(a-x)$

or $$\frac{dx}{(a-x)} = k.dt \qquad ...(1)$$

Here, $k$ is a constant, called the velocity constant of first order reaction.

On integrating both sides, $\int \frac{dx}{(a-x)} = \int k.dt$

or $$-\log_e (a-x) = kt + I \qquad ...(2)$$

where $I$ = integration constant.

When $t = 0$, $x = 0$ then $-\log_e a = I$

On substituting the value of $I$ in eq. (2), we have

$$-\log_e (a-x) = kt - \log_e a$$

$$kt = \log_e a - \log_e (a-x)$$

$$kt = \log_e \frac{a}{a-x} \quad \text{or} \quad k = \frac{1}{t}\log_e \frac{a}{a-x}$$

$$k = \frac{2.303}{t}\log_{10}\frac{a}{a-x} \qquad ...(3)$$

Eq. (3) is called **kinetic equation of first order reaction.**

With the help of this equation, value of $k$ can be calculated. Value of $k$ remains constant at constant temperature.

**Q 3. The following data were obtained for the reaction:**

$$2\,NO + O_2 \longrightarrow 2NO_2$$

| **Experiment** | **[NO]/M** | **$[O_2]$/M** | **Initial rate of formation of $NO_2$ / M $min^{-1}$** |
|---|---|---|---|
| 1 | 0.3 | 0.2 | $7.2 \times 10^{-2}$ |
| 2 | 0.1 | 0.1 | $6.0 \times 10^{-3}$ |
| 3 | 0.3 | 0.4 | $2.88 \times 10^{-1}$ |
| 4 | 0.4 | 0.1 | $2.40 \times 10^{-2}$ |

**(i) Find the order of reaction with respect to NO and $O_2$.**

**(ii) Write the rate law and overall order of reaction.**

**(iii) Calculate the rate constant ($k$).**

**Sol.** (i) For the given reaction: $2NO + O_2 \longrightarrow 2NO_2$

The rate law can be expressed as:

Rate law = $k\,[NO]^x\,[O_2]^y$

Now, with the given data, we can determine the values of $x$ and $y$ as:

$$7.2 \times 10^{-2} = k\,[0.3]^x\,[0.2]^y \qquad ...(1)$$

$$6.0 \times 10^{-3} = k\,[0.1]^x\,[0.1]^y \qquad ...(2)$$

$$2.88 \times 10^{-1} = k\,[0.3]^x\,[0.4]^y \qquad ...(3)$$

$$2.40 \times 10^{-2} = k\,[0.4]^x\,[0.1]^y \qquad ...(4)$$

Dividing eq. (4) by eq. (2), we get

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^x\,[0.1]^y}{k[0.1]^x\,[0.1]^y}$$

$$4.0 = (4)^x \quad \text{or} \quad x = 1$$

Next, dividing eq. (3) by eq. (1), we get

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k[0.3]^x\,[0.4]^y}{k[0.3]^x\,[0.2]^y}$$

$$4 = (2)^y \quad \text{or} \quad (2)^2 = (2)^y \text{ or, } y = 2$$

So, order w.r.t. NO is 1 and order w.r.t. $O_2$ is 2.

(ii) Rate law = $k\,[NO]^1\,[O_2]^2$

Overall order of reaction is 3.

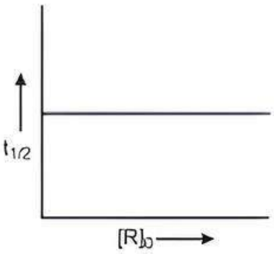
(iii) Rate constant, $k = \frac{\text{Rate}}{[NO]^1\,[O_2]^2} = \frac{7.2 \times 10^{-2}}{[0.3]^1\,[0.2]^2}$

$$= \frac{7.2 \times 10^{-2}}{1.2 \times 10^{-2}} = 6 \text{ mol}^{-2}\,\text{L}^{-2}\,\text{min}^{-1}$$

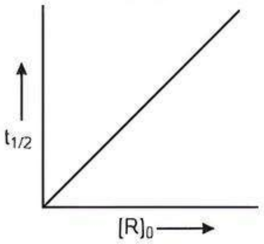
**Q 4.** **(i) A first order reaction is 75% completed in 40 minutes. Calculate its $t_{1/2}$.**

**(ii) Predict the order of the reaction in the given plots:**

**(a)**



**(b)**



**where $[R]_0$ is the initial concentration of reactant.**

**[Given : log 2 = 0.3010, log 4 = 0.6021]**

*(CBSE 2017)*

**Sol.** (i) For a first order reaction, $k = \frac{2.303}{t}\log\frac{a}{a-x}$

where, $k$ = rate constant, $a$ = initial concentration

$(a-x)$ = concentration after time '$t$'

It is given that the first order reaction is 75% completed in 40 min.

$a = 100$, $a - x = 100 - 75 = 25$, $t = 40$ min

$$k = \frac{2.303}{40}\log\frac{100}{25}$$

$$= \frac{2.303}{40}\log 4$$

$$= \frac{2.303}{40}\times 0.6021$$

$$k = 0.0347\ \text{min}^{-1}$$

Now, half-life $(t_{1/2}) = \frac{0.693}{k}$

$$t_{1/2} = \frac{0.693}{0.0347}$$

$$= 19.98 \equiv \underline{20\ \text{min}}.$$

(ii) (a) First order reaction

(b) Zero order reaction.

# Chapter Test

## Multiple Choice Questions

**Q 1.** **The activation energy for a reaction at a given temperature is found to be 2.303 RT J mol$^{-1}$. The ratio of rate constant to the Arrhenius factor is:**

a. 0.01 b. 0.1 c. 0.02 d. 0.001

**Q 2.** **Which of the following expression is correct for rate of reaction given below?**

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

a. $\frac{\Delta(Br^-)}{\Delta t} = 5\frac{\Delta(H^+)}{\Delta t}$ b. $\frac{\Delta(Br^-)}{\Delta t} = \frac{6}{5}\frac{\Delta(H^+)}{\Delta t}$

c. $\frac{\Delta(Br^-)}{\Delta t} = \frac{5}{6}\frac{\Delta(H^+)}{\Delta t}$ d. $\frac{\Delta(Br^-)}{\Delta t} = 6\frac{\Delta(H^+)}{\Delta t}$

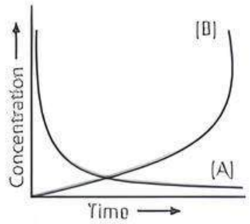
**Q 3.** **The decomposition of a substance follows first order kinetics. If its concentration is reduced to 1/8 of its initial value in 12 minutes, the rate constant of the decomposition system is:**

a. $\left(\frac{2.303}{12}\log\frac{1}{8}\right)\text{min}^{-1}$ b. $\left(\frac{2.303}{12}\log 8\right)\text{min}^{-1}$

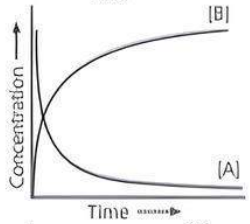
c. $\left(\frac{0.693}{12}\right)\text{min}^{-1}$ d. $\left(\frac{1}{12}\log 8\right)\text{min}^{-1}$

**Q 4.** **Consider the reaction, $A \rightleftharpoons B$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?**

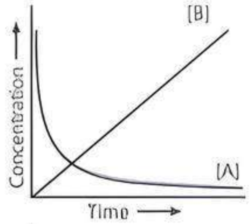
a.



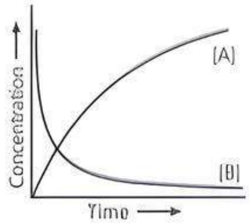
b.



c.



d.



**Directions (Q. Nos. 5-6):** *Each of the following questions consists of two statements, one is Assertion (A) and the other is Reason (R). Give answer:*

a. Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of Assertion (A).
b. Both Assertion (A) and Reason (R) are true but Reason (R) is not the correct explanation of Assertion (A).
c. Assertion (A) is true but Reason (R) is false.
d. Assertion (A) is false but Reason (R) is true.

**Q 5.** **Assertion (A):** For the reaction

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

$$\text{Rate} = k[CHCl_3][Cl_2]^{1/2}$$

**Reason (R):** Rate of reaction is always equal to the sum of the stoichiometric coefficient of the reaction species in a balanced chemical equation.

**Q 6.** **Assertion (A):** 50% of zero order reaction is completed in 100 sec, therefore, 75% reaction will be complete in 150 sec .

**Reason (R):** The rate constant of a zero order reaction depends upon time.

## Case Study Based Question

**Q 7.** The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst affect the rate of reaction. Mathematical representation of rate of a reaction is given by rate law:

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

$x$ and $y$ indicate how sensitive the rate is to the change in concentration of $A$ and $B$. Sum of $x + y$ gives the overall order of a reaction.

When a sequence of elementary reactions gives us the products, the reactions are called complex reactions. Molecularity and order of an elementary reaction are same. Zero order reactions are relatively uncommon but they occur under special conditions. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics.

***Read the given passage carefully and give the answer of the following questions:***

(i) What is the effect of temperature on the rate constant of a reaction?

(ii) How order and molecularity are different for complex reactions?

(iii) A first order reaction has a rate constant $2 \times 10^{-3}\ s^{-1}$. How long will 6g of this reactant take to reduce to 2g?

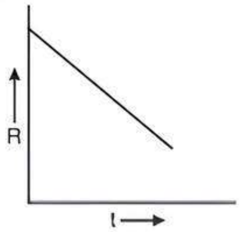
*OR*

The half-life for radioactive decay of $^{14}C$ is 6930 years. An archaeological artifact containing wood had only 75% of the $^{14}C$ found in a living tree. Find the age of the sample.

[log 4 = 0.6021 log 3 = 0.4771 log 2 = 0.3010 log 10 = 1]

## Very Short Answer Type Questions

**Q 8.** For a chemical reaction $R \longrightarrow P$, the variation in the concentration ($R$) *vs* time ($t$) plot is given as:



(i) Predict the order of the reaction.

(ii) What is the slope Wof the curve?

**Q 9.** In some cases, it is found that a large number of colliding molecules have energy more than threshold energy yet the reaction is slow, why?

## Short Answer Type-I Questions

**Q 10.** With the help of a diagram, explain the role of activated complex in a reaction.

**Q 11.** For a reaction: $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$

(i) Write the order and molecularity of this reaction

(ii) Write the unit of $k$.

**Q 12.** The rate of most reactions become double when their temperature is raised from $298K$ to $308K$. Calculate their activation energy.

(Given, $R = 8.314\ J\ mol^{-1}K^{-1}$)

## Short Answer Type-II Questions

**Q 13.** The rate constant for the first order decomposition of $H_2O_2$ is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T}$$

Calculate $E_a$ for this reaction and rate constant $k$ if its half-life period be 200 minutes.

(Given $R = 8.314\ JK^{-1}\ mol^{-1}$)

**Q 14.** A first order gas phase reaction:

$A_2B_2(g) \longrightarrow 2A(g) + 2B(g)$

at the temperature 400°C has the rate constant $k = 2.0 \times 10^{-4}\ s^{-1}$. What percentage of $A_2B_2$ is decomposed on heating for 900 seconds?

[Antilog 0.0781 = 1.197]

Q 15. For the reaction,

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

The following data were collected. All the measurements were taken at 263K.

| Exp. No. | Initial [NO] (M) | Initial [$Cl_2$] (M) | Initial rate of disappearance of $Cl_2$ (M/min) |
|---|---|---|---|
| 1 | 0.15 | 0.15 | 0.60 |
| 2 | 0.15 | 0.30 | 1.20 |
| 3 | 0.30 | 0.15 | 2.40 |
| 4 | 0.25 | 0.25 | ? |

(i) Write the expression for rate law.

(ii) Calculate the value of rate constant and specify its unit.

(iii) What is the initial rate of disappearance of $Cl_2$ in experiment 4?

## Long Answer Type Questions

Q 16. (i) Rate constant '$k$' of a reaction varies with temperature '$T$' according to the equation

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

where $E_a$ is the activation energy. When a graph is plotted for log $k$ vs $\frac{1}{T}$, a straight line with a slope of $-4250K$ is obtained. Calculate '$E_a$' for the reaction. (Given $R = 8.314\ JK^{-1}\ mol^{-1}$)

(ii) Draw the plot of ln $k$ vs $1/T$ for a chemical reaction. What does the intercept represent? What is the relation between slope and $E_a$?

Q 17. (i) Explain the following terms:

(a) Order of reaction

(b) Rate determining step of a reaction

(c) Molecularity of a reaction

(ii) A reactant has a half-life of 10 min.

(a) Calculate the rate constant for the first order reaction.

(b) What fraction of the reactant will be left after an hour of the reaction has occurred?