Chemical Kinetics

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.

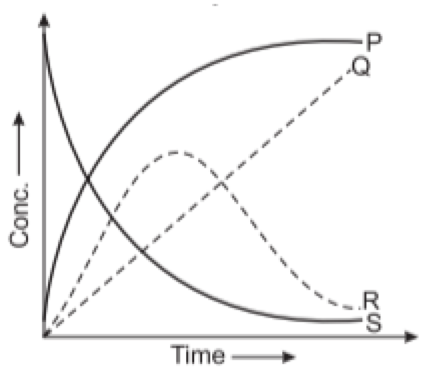
The integrated rate equation are different for the reactions of different reaction orders. We shall determine these equations only for zero and first order chemical reactions. Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants. Consider the reaction,
RP → 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,

$$R \longrightarrow P,\ \text{Rate} = \frac{d[R]}{dt} = k[R] \text{ and the integrating}$$

rate equation is k = (1/t) In [R]/[R] where, [R] is final concentration and [R], is initial concentration of reactant, respectively.
Read the given passage carefully and give the answer of the following questions:

Q1. For a hypothetical reaction,
R→ 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→ R+S The curve which depicts the variation of the concentration of products is:



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

Q3. For the reaction,
Hg() + Cl2(g) → $HgCl_2$(s)
The rate of reaction is given as:

a. $\frac{\Delta[HgCl_2]}{\Delta t}$
b. $-\frac{\Delta[Hg]}{\Delta t}$
c. $-\frac{\Delta[Cl_2]}{\Delta t}$
d. All of these

Q4. Contact process is used in the formation of sulphur trioxide, W
250$_2$(g) + O2(g) = 250$_3$(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 x 10^{-5} mol L-1 s-1
b. 3.75 x 10^{-4} mol L-1s-1
c. 2.5 x 10^{-4} mol L-1s-1
d. 4.12 x 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 x 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 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] [B], 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:

Q1. Calculate the overall order of a reaction which has the following rate expression:
Rate = k $[A]^1$/2[B]3/2

Q2. What is the effect of temperature on rate of reaction?

Q3. 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 1×10-3 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:

Q1. What is average rate of reaction?

Q2. Write two factors that affect the rate of reaction.

Q3. (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 → 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 $L^{-1}5^{-1}$

OR

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

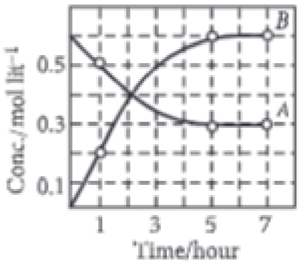
(ii) Pseudo first order reaction is defined as the reac- tion which is bimolecular but order is one. For example: acidic hydrolysis of ester (ethyl acetate).

Solutions for Questions 4 to 13 are Given Below

Case Study 4

Read the passage given below and answer the following questions :

The progress of the reaction, $A \rightleftharpoons nB$ with time is represented in the following figure :



The following questions are multiple choice questions. Choose the most appropriate answer :

(i) What is the value of n?

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

(ii) Find the value of the equilibrium constant.

(a) 0.6 M (b) 1.2 M (c) 0.3 M (d) 2.4 M

(iii) The initial rate of conversion of A will be

(a) 0.1 mol L^{-1} hr^{-1} (b) 0.2 mol L^{-1} hr^{-1}

(c) 0.4 mol L^{-1} hr^{-1} (d) 0.8 mol L^{-1} hr^{-1}

(iv) For the reaction, if $\frac{d[B]}{dt}=2\times10^{-4}$, value of $-\frac{d[A]}{dt}$ will be

(a) 2×10^{-4} (b) 10^{-4} (c) 4×10^{-4} (d) 0.5×10^{-4}

OR

Which factor has no effect on rate of reaction?

(a) Temperature (b) Nature of reactant

(c) Concentration of reactant (d) Molecularity

Case Study 5

Read the passage given below and answer the following questions :

For the reaction : $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$, the following data were collected. All the measurements were taken at 263 K.

Experiment No.	Initial [NO] (M)	Initial $[Cl_2]$ (M)	Initial rate of disapp. 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	?

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The molecularity of the reaction is

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

(ii) The expression for rate law is

(a) $r = k[NO][Cl_2]$ (b) $r = k[NO]^2[Cl_2]$ (c) $r = k[NO][Cl_2]^2$ (d) $r = k[NO]^2[Cl_2]^2$

(iii) The overall order of the reaction is

(a) 2 (b) 0 (c) 1 (d) 3

(iv) The value of rate constant is

(a) 150.32 M^{-2} min^{-1} (b) 200.08 M^{-1} min^{-1} (c) 177.77 M^{-2} min^{-1} (d) 155.75 M^{-1} min^{-1}

OR

The initial rate of disappearance of Cl_2 in experiment 4 is

(a) 1.75 M min^{-1} (b) 3.23 M min^{-1} (c) 2.25 M min^{-1} (d) 2.77 M min^{-1}

Case Study 6

Read the passage given below and answer the following questions :

A reaction is said to be of the first order if the rate of the reaction depends upon one concentration term only. For a first order reaction of the type $A \rightarrow$ Products, the rate of the reaction is given as : rate = $k[A]$. The differential rate law is given as : $\frac{dA}{dt} = -k[A]$. The integrated rate law is : $\ln \frac{[A]}{[A]_0} = -kt$, where $[A]$ is the concentration of reactant left at time t and $[A]_0$ is the initial concentration of the reactant, k is the rate constant.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The unit of rate constant for a first order reaction is

(a) s^{-1} (b) mol L^{-1} s^{-1} (c) L mol^{-1} s^{-1} (d) L^2 mol^{-2} s^{-1}

(ii) Half-life period of a first order reaction is 10 min. Starting with initial concentration 12 M, the rate after 20 min is

(a) 0.693 × 3 M min^{-1} (b) 0.0693 × 4 M min^{-1} (c) 0.0693 M min^{-1} (d) 0.0693 × 3 M min^{-1}

OR

50% of a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction.

(a) 70.4 minutes (b) 76.4 minutes (c) 38.7 minutes (d) 35.2 minutes

(iii) For a first order reaction, $(A) \rightarrow$ products, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M, is

(a) 3.47×10^{-4} M/min (b) 3.47×10^{-5} M/min (c) 1.73×10^{-4} M/min (d) 1.73×10^{-5} M/min

(iv) The half-life period of a 1st order reaction is 60 minutes. What percentage will be left over after 240 minutes?

(a) 6.25% (b) 4.25% (c) 5% (d) 6%

Case Study 7

Read the passage given below and answer the following questions :

Number of molecules which must collide simultaneously to give product is called molecularity. It is equal to sum of coefficients of reactants present in stoichiometric chemical equation.

For reaction, $m_1A + m_2B \rightarrow$ Product

Molecularity = $[m_1 + m_2]$

In complex reaction each step has its own molecularity which is equal to the sum of coefficients of reactants present in a particular step. Molecularity is a theoretical property. Its value is any whole number. Number of concentration terms on which rate of reaction depends is called order of reaction or sum of powers of concentration terms present in the rate equation is called order of reaction.

If rate equation of reaction is : Rate $= k \cdot C_A^{m_1} \cdot C_B^{m_2}$

Then order of reaction $= m_1 + m_2$.

In simple reaction, order and molecularity are same.

In complex reaction, order of slowest step is the order of over all reaction. This step is known as rate determining step. Order is an experimental property. Its value may be zero, fractional or negative.

The following questions are multiple choice questions. Choose the most appropriate answer :

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

(a) shifting of equilibrium towards reactants due to elastic collisions
(b) loss of active species on collision
(c) low probability of simultaneous collision of all the reacting species
(d) increase in entropy and activation energy as more molecules are involved.

(ii) The molecularity of the reaction :
$6FeSO_4 + 3H_2SO_4 + KClO_3 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$ is

(a) 6 (b) 3
(c) 10 (d) 7

(iii) Which of the following statements is false in the following?

(a) Order of a reaction may be even zero.
(b) Molecularity of a reaction is always a whole number.
(c) Molecularity and order always have same values for a reaction.
(d) Order of a reaction depends upon the mechanism of the reaction.

OR

The rate of reaction, $A + 2B \rightarrow$ products, is given by the following equation:

$$-\frac{d[A]}{dt} = k[A][B]^2$$

If B is present in large excess, the order of the reaction is

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

(iv) The rate of the reaction, $A + B + C \rightarrow$ products, is given by $r = -\frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/3}[C]^{1/4}$. The order of the reaction is

(a) $\frac{1}{3}$ (b) $\frac{1}{4}$ (c) $\frac{1}{2}$ (d) $\frac{13}{12}$

Case Study 8

Read the passage given below and answer the following questions :

In a reaction, the rates of disappearance of different reactants or rates of formation of different products may not be equal but rate of reaction at any instant of time has the same value expressed in terms of any reactant or product. Further, the rate of reaction may not depend upon the stoichiometric coefficients of the balanced chemical equation. The exact powers of molar concentrations of reactants on which rate depends are found experimentally and expressed in terms of 'order of reaction.' Each reaction has a characteristic rate constant depends upon temperature. The units of the rate constant depend upon the order of reaction.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The rate constant of a reaction is found to be 3×10^{-3} $\text{mol}^{-2}\,\text{L}^2\,\text{sec}^{-1}$. The order of the reaction is

(a) 0.5 (b) 2 (c) 3 (d) 1

(ii) In the reaction, $A + 3B \rightarrow 2C$, the rate of formation of C is

(a) the same as rate of consumption of A

(b) the same as the rate of consumption of B

(c) twice the rate of consumption of A

(d) 3/2 times the rate of consumption of B.

(iii) Rate of a reaction can be expressed by following rate expression, Rate = $k[A]^2\,[B]$, if concentration of A is increased by 3 times and concentration of B is increased by 2 times, how many times rate of reaction increases?

(a) 9 times (b) 27 times (c) 18 times (d) 8 times

(iv) The rate of a certain reaction is given by, rate = $k[\text{H}^+]^n$. The rate increases 100 times when the pH changes from 3 to 1. The order (n) of the reaction is

(a) 2 (b) 0 (c) 1 (d) 1.5

OR

In a chemical reaction $A + 2B \rightarrow$ products, when concentration of A is doubled, rate of the reaction increases 4 times and when concentration of B alone is doubled rate continues to be the same. The order of the reaction is

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

Case Study 9

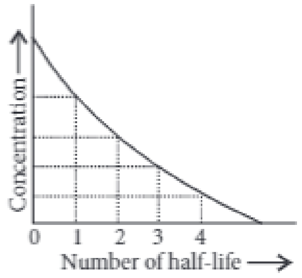
Read the passage given below and answer the following questions :

The half-life of a reaction is the time required for the concentration of reactant to decrease by half, *i.e.*,

$$[A]_t = \frac{1}{2}[A]$$

For first order reaction,

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



this means $t_{1/2}$ is independent of initial concentration. Figure shows that typical variation of concentration of reactant exhibiting first order kinetics. It may be noted that though the major portion of the first order kinetics may be over in a finite time, but the reaction will never cease as the concentration of reactant will be zero only at infinite time.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) A first order reaction has a rate constant $k = 3.01 \times 10^{-3}$ /s. How long it will take to decompose half of the reactant?

(a) 2.303 s (b) 23.03 s (c) 230.3 s (d) 2303 s

(ii) The rate constant for a first order reaction is $7.0 \times 10^{-4}\ s^{-1}$. If initial concentration of reactant is 0.080 M, what is the half life of reaction?

(a) 990 s (b) 79.2 s (c) 12375 s (d) 10.10×10^{-4} s

(iii) For the half-life period of a first order reaction, which one of the following statements is generally false?

(a) It is independent of initial concentration. (b) It is independent of temperature.

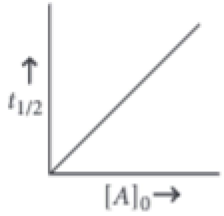
(c) It decreases with the introduction of a catalyst. (d) None of these.

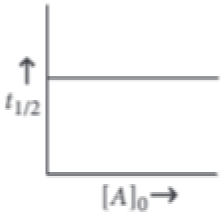
(iv) The rate of a first order reaction is 0.04 mol $L^{-1}\ s^{-1}$ at 10 minutes and 0.03 mol $L^{-1}\ s^{-1}$ at 20 minutes after initiation. The half-life of the reaction is

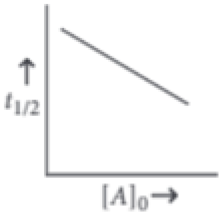
(a) 4.408 min (b) 44.086 min (c) 24.086 min (d) 2.408 min

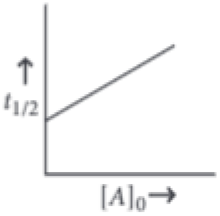
OR

The plot of $t_{1/2}$ *vs* initial concentration $[A]_0$ for a first order reaction is given by

(a)


(b)


(c)


(d)


Case Study 10

Read the passage given below and answer the following questions :

The following reaction, $A_{(g)} \xrightarrow{\Delta} P_{(g)} + Q_{(g)} + R_{(g)}$, follows first order kinetics. The half-life period of this reaction is 69.3 s at 500°C. The gas A is enclosed in a container at 500°C and at a pressure of 0.4 atm.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The rate constant for the reaction is

(a) $0.4\ s^{-1}$ (b) $0.02\ s^{-1}$ (c) $0.01\ s^{-1}$ (d) $0.3\ s^{-1}$

OR

The pressure of the gas A after 230 s will be

(a) 0.04 atm (b) 0.36 atm (c) 0.4 atm (d) 0.036 atm

(ii) The total pressure of the system after 230 s will be

(a) 2.15 atm (b) 1.12 atm (c) 0.4 atm (d) 3.08 atm

(iii) The plot of $\ln[A]$ *vs* t will be

(a) linear with slope = k (b) linear with intercept = $\ln[A]_0$

(c) linear with slope = $\ln[A]_0$ (d) linear with intercept = $[A]_0$

(iv) Which of the following is not an example of first order reaction?

(a) $C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$ (b) $2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$

(c) $2NH_{3(g)} \xrightarrow[\Delta]{Pt} N_{2(g)} + 3H_{2(g)}$ (d) $2N_2O_{(g)} \xrightarrow{\Delta} 2N_{2(g)} + O_{2(g)}$

Case Study 11

Read the passage given below and answer the following questions :

A reaction in which rate of reaction is independent of concentration of the reactants is called zero order reaction. Photochemical combination of hydrogen and chlorine to give hydrogen chloride is an example of zero order reaction. The rate constant of a zero order reaction is equal to the rate of reaction. The half life period of a zero order reaction is directly proportional to initial concentration of the reactant. For a zero order reaction, $k = \frac{1}{t}\{[A]_0 - [A]\}$

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** For a zero order reaction, plot of rate *vs* concentration will be a straight line parallel to concentration axis.
Reason : For a zero order reaction, rate is independent of concentration.

(ii) **Assertion :** Photochemical combination of hydrogen and chlorine to give hydrogen chloride is an example of zero order reaction.
Reason : The rate of reaction depends on the concentration of hydrogen and independent of concentration of chlorine.

(iii) **Assertion :** If in a zero order reaction, the concentration of the reactant is doubled, the half-life period is also doubled.
Reason : For a zero order reaction, the rate of reaction is independent of initial concentration.

(iv) **Assertion :** In a reaction $A \longrightarrow$ products, the concentration of the reactant is reduced to zero after a finite time.
Reason : The order of reaction is zero.

Assertion : Rate constant of a zero order reaction has same units as the rate of reaction.
Reason : Rate constant of a zero order reaction does not depend on the unit of concentration.

Case Study 12

Read the passage given below and answer the following questions :

Decrease in concentration of reactant or increase in concentration of product per unit time is called rate of reaction. It is of two types :

(i) **Instantaneous rate of reaction :** Rate of change of concentration of reactant or product at a particular time is called instantaneous rate of reaction.

$$r_{inst.} = \frac{dC}{dt}$$

where, dC = infinitely small change in concentration
dt = infinitely small change in time.

(ii) **Average rate of reaction :** Ratio of change in concentration and time required for the change is average rate of reaction.

$$r_{av} = \frac{\Delta x}{\Delta t} = \frac{\text{Change in concentration}}{\text{Time required for the change}}$$

For a reaction of the type, $m_1A + m_2B \rightarrow n_1C + n_2D$

Rate of reaction is given as

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

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** The kinetics of the reaction, $mA + nB + pC \rightarrow m'X + n'Y + p'Z$ obey the rate expression as $\frac{dx}{dt} = k[A]^m[B]^n$.

Reason : The rate of the reaction does not depend upon the concentration of C.

(ii) **Assertion :** Instantaneous rate of reaction is equal to dx/dt.

Reason : It is the rate of reaction at any particular instant of time.

(iii) **Assertion :** For the reaction, $RCl + NaOH \rightarrow ROH + NaCl$, the rate of reaction is reduced to half on reducing the concentration of RCl to half.

Reason : The rate of reaction is represented by $k[RCl]$.

(iv) **Assertion :** In rate law, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match the stoichiometric coefficients.

Reason : It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate.

OR

Assertion : In a reaction, $2A + B \rightarrow A_2B$, the reactant B will disappear at twice the rate as A will decrease.

Reason : The rate of disappearance of reactant will be $-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt}$

Case Study 13

Read the passage given below and answer the following questions :

For a first order reaction, $A \rightarrow$ Products, $k = \frac{2.303}{t}\log\frac{a}{a-x}$, where a is the initial concentration of A and $(a-x)$ is the concentration of A after time t. k is rate constant. Its value is constant at constant temperature for a reaction. The time in which half of the reactant is consumed is called half-life period. Half-life period of a first order reaction is constant. Its value is independent of initial concentration or any other external conditions.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Rate of reaction doubles when concentration of reactant is doubled if it is a first order reaction.
Reason : Rate constant also doubles.

OR

Assertion : For the first order reaction, half-life period is expressed as $t_{1/2} = \frac{2.303}{k}\log 2$.

Reason : The half-life time of a first order reaction is not always constant and it depends upon the initial concentration of reactants.

(ii) **Assertion :** Hydrolysis of ethyl acetate in presence of acid is a reaction of first order whereas in presence of alkali, it is a reaction of second order.
Reason : Acid only acts as a catalyst whereas alkali acts as one of the reactants.

(iii) **Assertion :** For a first order reaction, the concentration of the reactant decreases exponentially with time.
Reason : Rate of reaction at any time depends upon the concentration of the reactant at that time.

(iv) **Assertion :** Half-life period for a first order reaction is independent of initial concentration of the reactant.

Reason : For a first order reaction, $t_{1/2} = \frac{0.693}{k}$, where k is rate constant.

HINTS & EXPLANATIONS

4. **(i) (b):** According to the figure, in the given time of 4 hours (1 to 5) concentration of A falls from 0.5 to 0.3 M, while in the same time concentration of B increases from 0.2 to 0.6 M.
Decrease in concentration of A in 4 hours
$= 0.5 - 0.3 = 0.2$ M
Increase in concentration of B in 4 hours
$= 0.6 - 0.2 = 0.4$ M
Thus, increase in concentration of B in a given time is twice the decrease in concentration of A. Thus, $n = 2$.

(ii) (b): $K = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{0.3} = 1.2 \text{ M}$

(iii) (a): From $t = 0$ to $t = 1$ hr,
For A, $dx = 0.6 - 0.5 = 0.1 \text{ mol L}^{-1}$

$\therefore$ Initial rate of conversion of $A = \frac{dx}{dt}$

$= \frac{0.1 \text{ mol L}^{-1}}{1 \text{ hr}} = 0.1 \text{ mol L}^{-1}\text{ hr}^{-1}$

(iv) (b): $A \rightleftharpoons 2B$

$$-\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{2} \times 2 \times 10^{-4} = 10^{-4}$$

OR

(d) : The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction is called molecularity and it has no influence on the rate of reaction.

5. **(i) (c) :** $2NO_{(g)} + Cl_{2(g)} \rightarrow 2NOCl_{(g)}$
Molecularity = 3

(ii) (b): Let rate of this reaction, $r = k[NO]^m[Cl_2]^n$

then $\frac{r_1}{r_2} = \frac{0.60}{1.20} = \frac{k(0.15)^m(0.15)^n}{k(0.15)^m(0.30)^n}$

or, $\frac{1}{2} = \left(\frac{1}{2}\right)^n \Rightarrow n = 1$

Again from $\frac{r_2}{r_3} = \frac{1.20}{2.40} = \frac{k(0.15)^m(0.30)^n}{k(0.30)^m(0.15)^n}$

or $\frac{1}{2} = \left(\frac{1}{2}\right)^m \cdot \frac{2}{1}$ or $\frac{1}{4} = \left(\frac{1}{2}\right)^m \Rightarrow m = 2$

Hence, expression for rate law is
$r = k[NO]^2\,[Cl_2]^1$

(iii) (d): As the order *w.r.t.* NO is 2 and order *w.r.t.* Cl_2 is 1, hence the overall order is 3.

(iv) (c): Substituting the values of experiment 1 in rate law expression

$0.60\ M\ min^{-1} = k(0.15\ M)^2\ (0.15\ M)^1$

$$\text{or}\quad k = \frac{0.60\ M\ min^{-1}}{0.0225 \times 0.15\ M^3} = 177.77\ M^{-2}\ min^{-1}$$

OR

(d) : $r = 177.7\ M^{-2}\ min^{-1} \times (0.25\ M)^2\ (0.25\ M)$

$= 2.77\ M\ min^{-1}$

6. **(i) (a):** Unit of rate constant for a reaction of n^{th} order = $(conc.)^{1-n}\ time^{-1}$

For a first order reaction, $n = 1$

Unit of rate constant = $(mol\ L^{-1})^{1-1}\ s^{-1} = s^{-1}$

(ii) (d): $\underset{\text{Initial conc.}}{12\ M} \xrightarrow{t_{1/2}} 6\ M \xrightarrow{t_{1/2}} 3\ M$

$t_{1/2} = 10$ min

$$k = \frac{0.693}{10} = 0.0693\ min^{-1}$$

As $t_{1/2}$ is 10 min, after 20 minutes the concentration will be 3 M.

Hence, Rate = $0.0693 \times 3\ M\ min^{-1}$

OR

(b) : $t_{1/2} = 23$ minutes

$$t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{t_{1/2}} \Rightarrow k = \frac{0.693}{23}\ min^{-1}$$

For 90% completion,

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

$$t = \frac{2.303 \times 23}{0.693}\log\left(\frac{100}{100-90}\right)$$

$t = 76.4$ minutes

(iii) (a): For the first order reaction,

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

$a = 0.1\ M,\ a - x = 0.025\ M,\ t = 40$ min

$$k = \frac{2.303}{40}\log\frac{0.1}{0.025} = \frac{2.303}{40}\log 4 = 0.0347\ min^{-1}$$

$[A] \rightarrow$ product

Thus, rate = $k[A]$

rate = $0.0347 \times 0.01\ M\ min^{-1} = 3.47 \times 10^{-4}\ M\ min^{-1}$

(iv) (a): $t_{1/2} = \dfrac{0.693}{k} \Rightarrow \dfrac{0.693}{t_{1/2}} = k \Rightarrow \dfrac{0.693}{60} = k$

$k = 0.01155\ min^{-1}$

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

Let the initial amount (a) be 100.

$$0.01155\ min^{-1} = \frac{2.303}{240\ min}\log\left(\frac{100}{a-x}\right)$$

$$\frac{0.01155\ min^{-1} \times 240\ min}{2.303} = \log\left(\frac{100}{a-x}\right)$$

$1.204 = \log 100 - \log (a - x)$

$1.204 = 2 - \log (a - x)$

$\log (a - x) = 2 - 1.204 = 0.796$

$(a - x) = 6.25\%$

7. **(i) (c):** The reactions of higher order are very rare because of the less chances of the molecules to come together simultaneously and collide.

(ii) (c): The total number of reactant molecules participating in a chemical reaction is known as its molecularity, hence the molecularity = 6 + 3 + 1 = 10.

(iii) (c) : Molecularity may or may not be equal to the order of a reaction.

OR

(b) : From the expression

$$-\frac{d[A]}{dt} = k[A][B]^2$$

when B is present in large excess, rate will be independent upon the change in conc. of B, therefore order of reaction will be one.

(iv) (d): Order of reaction $= \dfrac{1}{2} + \dfrac{1}{3} + \dfrac{1}{4} = \dfrac{6+4+3}{12} = \dfrac{13}{12}$

8. **(i)(c):** Unit of k for n^{th} order = $(mol\ L^{-1})^{1-n}\ sec^{-1}$ ...(i)

Here, $k = 3 \times 10^{-3}\ mol^{-2}\ L^2\ sec^{-1}$

Unit of $k = mol^{-2}\ L^2\ sec^{-1} \Rightarrow (mol\ L^{-1})^{-2} sec^{-1}$ ...(ii)

Comparing (i) and (ii) we get, $1 - n = -2 \Rightarrow n = 3$

(ii) (c) : Rate $= -\dfrac{d[A]}{dt} = -\dfrac{1}{3}\dfrac{d[B]}{dt} = \dfrac{1}{2}\dfrac{d[C]}{dt}$

(iii) (c) : Given, $R_1 = k[A]^2\ [B]$

According to question, $R_2 = k[3A]^2\ [2B]$

$= k \times 9\ [A]^2 \times 2\ [B] = 18 \times k\ [A]^2\ [B] = 18\ R_1$

(iv) (c) : Rate $(r) = k[H^+]^n$

When pH = 3 ; $[H^+] = 10^{-3}$

and when pH = 1 ; $[H^+] = 10^{-1}$

$$\therefore\quad \frac{r_1}{r_2} = \frac{k(10^{-3})^n}{k(10^{-1})^n} \Rightarrow \frac{1}{100} = \left(\frac{10^{-3}}{10^{-1}}\right)^n \quad (\because r_2 = 100\, r_1)$$

$\Rightarrow\ (10^{-2})^1 = (10^{-2})^n \ \Rightarrow\ n = 1$

OR

(b) : Let the order of reaction w.r.t. A is x and w.r.t. B is y.

$$r_1 = k[A]^x[B]^y \quad \text{...(i)}$$
$$r_2 = k[2A]^x[B]^y \quad \text{...(ii)}$$
$$r_3 = k[A]^x[2B]^y \quad \text{...(iii)}$$

$$\frac{r_1}{r_2} = \frac{k[A]^x[B]^y}{k[2A]^x[B]^y}$$

$$\Rightarrow \frac{1}{4} = \left(\frac{1}{2}\right)^x \Rightarrow \left(\frac{1}{2}\right)^2 = \left(\frac{1}{2}\right)^x \Rightarrow x = 2$$

Similarly, $\frac{r_1}{r_3} = \frac{k[A]^x[B]^y}{k[A]^x[2B]^y}$

$$\Rightarrow 1 = \left(\frac{1}{2}\right)^y \Rightarrow \left(\frac{1}{2}\right)^0 = \left(\frac{1}{2}\right)^y \Rightarrow y = 0$$

Hence the rate law equation is

Rate $= k[A]^2[B]^0 \Rightarrow$ Order of reaction = 2

9. **(i) (c) :** For a first order reaction :

$$t_{1/2} = \frac{0.693}{k}, \ k = 3.01 \times 10^{-3}\ \text{s}^{-1}$$

$$\therefore \quad t_{1/2} = \frac{0.693}{3.01 \times 10^{-3}} = 230.3\ \text{s}$$

(ii) (a) : Half life ($t_{1/2}$) of a first order reaction is given as :

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{7.0 \times 10^{-4}} = 990\ \text{s}$$

(iii) (b): For a first order reaction $t_{1/2} = \frac{0.693}{k}$ therefore $t_{1/2}$ depends upon k and hence depends on temperature because rate constant k is a function of temperature.

(iv) (c) : Let the concentrations of the reactant after 10 min and 20 min be C_1 and C_2 respectively.

$\therefore$ Rate after 10 min $= k.C_1$
$= 0.04 \times 60$ mol L^{-1}min^{-1}

and rate after 20 min $= k.C_2$
$= 0.03 \times 60$ mol L^{-1}min^{-1}

$$\therefore \quad \frac{C_1}{C_2} = \frac{4}{3}$$

Let the reaction starts after 10 minutes.

$$k = \frac{2.303}{10}\log\frac{C_1}{C_2} = \frac{2.303}{10}\log\frac{4}{3} = 0.02878$$

$$\therefore \quad t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{0.02878} = 24.086\ \text{min}$$

OR

(b) : For a first order reactions, $t_{1/2} = k[A]_0^0 = k$. Thus $t_{1/2}$ is independent of initial concentration. Hence plot of $t_{1/2}$ *vs* $[A]_0$ will be a horizontal line.

10. **(i) (c) :** $t_{1/2} = 69.3$ s

For first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 0.01\ \text{s}^{-1}$$

OR

$$\textbf{(a)}: k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{230}\log\frac{0.4}{0.4-x}$$

$$0.01 = \frac{2.303}{230}\log\frac{0.4}{0.4-x} = 0.01\log\frac{0.4}{0.4-x}$$

$$\frac{0.01}{0.01} = \log\frac{0.4}{0.4-x} \Rightarrow 1 = \log\frac{0.4}{0.4-x}$$

$$\text{Antilog of } 1 = \frac{0.4}{0.4-x} \Rightarrow 10 = \frac{0.4}{0.4-x} \Rightarrow x = 0.36$$

$\therefore \quad a - x = 0.4 - 0.36 = 0.04$ atm

(ii) (b): For the given reaction,

	$A_{(g)} \xrightarrow{\Delta}$	$P_{(g)}$ +	$Q_{(g)}$ +	$R_{(g)}$
Initial pressure	0.4	0	0	0
Final pressure	0.4 – 0.36	0.36	0.36	0.36

Total pressure = (0.4 – 0.36) + (3 × 0.36) = 1.12 atm

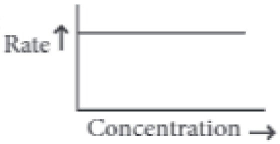
(iii) (b): Expression that relates concentration of reactant and time for first order reaction is

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

So, the plot of ln $[A]$ *vs* t will be linear with slope = $-k$ and intercept = ln $[A]_0$

(iv) (c) : Decomposition of ammonia on a hot platinum surface at high pressure is a zero order reaction.

11. **(i) (a) :**



(zero order reaction)

(ii) (c) : The reaction proceeds with a constant rate which is independent of concentration of hydrogen and chlorine. That is why, this reaction is a zero order reaction.

(iii) (b): For a zero order reaction, $t_{1/2} = [a]/2k$.

(iv) (a)

OR

(c) : For a zero order reaction, units of k is mol L^{-1} s^{-1}, *i.e.*, it depends upon units of concentration.

12. **(i) (a) :** Rate expression $\frac{dx}{dt} = k[A]^m[B]^n$

shows that the total order of reactions is $m + n + 0 = m + n$, as the rate of reaction is independent of concentration of C, *i.e.*, the order with respect to C is zero. This is the reason that C does not figure in the rate expression.

(ii) (b): Instantaneous rate of a reaction is equal to small change in concentration (dx) during a small interval of time (dt) at that particular instant of time divided by the time interval.

(iii) (a): For the given reaction, rate of reaction (r) = k[RCl] (where k is rate constant). Therefore if the concentration of [RCl] is reduced to half, then new rate $(r') = \frac{k}{2}[\text{RCl}]$.

(iv) (a)

OR

(d) : $2A + B \rightarrow A_2B$

The rate of disappearance of reactant will be

$$-\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[A_2B]}{dt}$$

Therefore, the reactant B will disappear at half the rate as A will decrease.

13. **(i) (c) :** For first order reaction, $\text{Rate}_1 = k[A_1]$

According to question,

$[A_2] = [2A_1]$

$\therefore$ $\text{Rate}_2 = k[2A_1]$

$\Rightarrow$ $\text{Rate}_2 = 2\ \text{Rate}_1$

For a given reaction, rate constant is constant and independent of the concentration of reactant.

OR

(c) : For a first order reaction $k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$k = \frac{2.303}{t_{1/2}}\log\frac{a}{a-a/2} = \frac{2.303}{t_{1/2}}\log\frac{a}{a/2} = \frac{2.303}{t_{1/2}}\log 2$$

Therefore half-life period $t_{1/2} = \frac{2.303}{k}\log 2$.

Thus $t_{1/2}$ is independent of initial concentration of reactant for first order reaction.

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

Rate $\propto [CH_3COOC_2H_5]$

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

Rate $\propto [CH_3COOC_2H_5]\,[NaOH]$

(iii) (b): For a first order reaction, $[A] = [A]_0 e^{-kt}$

or $\log[A] = -\frac{kt}{2.303} + \log[A]_0$

(iv) (a): For a first order reaction, $t_{1/2}$ is inversely proportional to k, it does not depend on the initial concentration of the reactant.