Long Answer Questions

Long Answer Questions (PYQ)

Q.1. For the reaction,

$$2\,\mathrm{NO}\,(g) \;+\; \mathrm{Cl_2}\,(g) \;\rightarrow\; 2\,\mathrm{NOCl}\,(g),$$

the following data were collected. All the measurements were taken at 263 K:

Experiment	**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 units.**
- **iii. What is the initial rate of disappearance of Cl_2 in experiment 4?**

[*CBSE Delhi 2012*]

Ans. Suppose order w.r.t. NO is *m* and order w.r.t. Cl_2 is *n*. Then the rate will be

$$\text{Rate} = k\,[\mathrm{NO}]^m\,[\mathrm{Cl_2}]^n$$

Substituting the values of experiment 1 to 3 in the rate expression, we get

$$0.60 = k(0.15)^m\,(0.15)^n \qquad \text{...(i)}$$

$$1.20 = k(0.15)^m\,(0.30)^n \qquad \text{...(ii)}$$

$$2.40 = k(0.30)^m\,(0.15)^n \qquad \text{...(iii)}$$

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

$$\frac{2.40}{0.60} = \frac{k\,(0.30)^m\,(0.15)^n}{k\,(0.15)^m(0.15)^n}$$

$$4 = 2^m \text{ or } 22 = 2^m \text{ or } m = 2$$

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

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

$$2 = 2^n \text{ or } n = 1$$

i. Rate law expression is, Rate = $k[\text{NO}]^2\ [\text{Cl}_2]$

ii. $0.60 \text{ mol L}^{-1} \text{ min}^{-1} = k(0.15 \text{ mol L}^{-1})^2\ (0.15 \text{ mol L}^{-1})$

$$k = \mathbf{177.77\ mol^{-2}\ L^2\ min^{-1}}$$

iii. Rate $= 177.77 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1} \times (0.25 \text{ mol L}^{-1})^2\ (0.25 \text{ mol L}^{-1})$

$$= \mathbf{2.778\ mol\ L^{-1}\ min^{-1}}$$

Q.2. Answer the following questions:

Q. For a reaction *A* + *B* → *P*, the rate is given by

Rate = $k[A]\ [B]^2$

- **a. How is the rate of reaction affected if the concentration of B is doubled?**
- **b. What is the overall order of reaction if A is present in large excess?**

Ans. (a) Rate, $r = k\ [A]\ [B]^2$

If concentration of *B* is doubled, then

$r' = k\ [A]\ [2B]^2$

$r' = 4k\ [A]\ [B]^2$, *i.e.*, **the rate will increase by 4 times.**

(b) As *A* is present in large excess therefore, order of the reaction w.r.t. A will be zero.

Rate = $k\ [A]^0\ [B]^2 = k\ [B]^2$

∴ Order of reaction = **2**

Q. A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction. (log 2 = 0.3010)

[*CBSE Delhi 2015*]

Ans.

$$t_{1/2} = 30 \text{ min.}$$

$$[R] = [R]_0 - 90\% \text{ of } [R]_0 = [R]_0 - \frac{90\ [R]_0}{100}$$

$$[R] = \frac{[R]_0}{10}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

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

$$t = \frac{2.303}{0.0231} \log \frac{[R]_0}{\frac{[R]_0}{10}} = \frac{2.303}{0.0231} \log 10$$

$$t = 99.7 \text{ min.}$$

Q.3. Nitrogen pentoxide decomposes according to equation:

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

This first order reaction was allowed to proceed at 40°C and the data below were collected:

$[N_2O_5]$ (M)	**Time (min)**
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

- i. **Calculate the rate constant. Include units with your answer.**
- ii. **What will be the concentration of N_2O_5 after 100 minutes?**
- iii. **Calculate the initial rate of reaction.**

[*CBSE Delhi 2011*]

Ans. i. When $t = 20$ min, $[R] = 0.289 \text{ mol L}^{-1}$

Also, $[R]0 = 0.400 \text{ mol L}^{-1}$

For a first order reaction

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

$$\therefore \qquad k = \frac{2.303}{20} \log \frac{0.400}{0.289}$$

$$\Rightarrow \qquad k = \frac{2.303}{20} \log \frac{4.00}{2.89}$$

$$\Rightarrow \qquad k = \frac{2.303}{20} [\log 4.00 - \log 2.89]$$

$$\Rightarrow \qquad k = \frac{2.303}{20} [0.6021 - 0.4609]$$

$$\Rightarrow \qquad k = \frac{2.303}{20} \times 0.1412$$

$$\Rightarrow \qquad k = 2.303 \times 0.00706 = 0.016259 \text{ min}^{-1}$$

$$\Rightarrow \qquad k = \mathbf{1.6259 \times 10^{-2} \text{ min}^{-1}}$$

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

Here, $[R]_0 = 0.400 \text{ mol}^{-1}$, $t = 100$ min, $k = 1.626 \times 10^{-2} \text{ min}^{-1}$

$$100 = \frac{2.303}{1.626 \times 10^{-2}} \log \frac{0.400}{[R]}$$

$$\frac{100 \times 1.626 \times 10^{-2}}{2.303} = \log \frac{0.4}{[R]} \qquad \Rightarrow \qquad 0.7060 = \log \frac{0.4}{[R]}$$

$$\text{Antilog } (0.7060) = \frac{0.4}{[R]}$$

$$5.082 = \frac{0.4}{[R]} \qquad \Rightarrow \qquad [R] = \frac{0.4}{5.082} = 0.0787\ M$$

iii. Initial rate, *i.e.*, rate of reaction when $t = 0$

When, $\qquad t = 0.00$ min, $[R] = 0.400 \text{ mol L}^{-1}$

Also, $k = 1.626 \times 10^{-2}\ \text{min}^{-1}$

$\therefore$ $\text{Initial rate} = k\,[R]$

$= 1.626 \times 10^{-2}\ \text{min}^{-1} \times 0.400\ \text{mol L}^{-1}$

$= \mathbf{6.504 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}}$

Q.4. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	**0**	**30**	**60**
[CH_3COOCH_3]/mol L^{-1}	**0.60**	**0.30**	**0.15**

- **i.** **Show that it follows pseudo first order reaction, as the concentration of water remains constant.**
- **ii.** **Calculate the average rate of reaction between the time interval 30 to 60 seconds.**

(Given log 2 = 0.3010, log 4 = 0.6021)

[*CBSE Delhi 2015*]

Ans.

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

Substituting $[R]_0 = 0.60$ mol L^{-1}, $[R] = 0.30$ mol L^{-1} and $t = 30$ s in equation (i), we get

$$k = \frac{2.303}{30} \log \frac{0.60}{0.30}$$

$$k = \frac{2.303}{30} \log 2 = \frac{2.303}{30} \times 0.3010 \qquad k = 0.0231\ \text{s}^{-1}$$

Again substituting, $[R]_0 = 0.60$ mol L^{-1}, $[R] = 0.15$ mol L^{-1} and $t = 60$ in equation (i), we get

$$k = \frac{2.303}{60} \log \frac{0.60}{0.15}$$

$$k = \frac{2.303}{60} \times \log 4 = \frac{2.303}{60} \times 0.6021 \qquad k = 0.0231\ \text{s}^{-1}$$

As the value of *k* is same in both the cases, therefore, hydrolysis of methylacetate in aqueous solution follows pseudo first order reaction.

ii. $$\text{Average rate} = -\frac{\Delta / CH_3\,COOCH_3 /}{\Delta t}$$

$$= \frac{-/0.15 - 0.30/}{60 - 30} = \frac{0.15}{30}$$

Average rate = **0.005 mol L^{-1} s^{-1}**

Q.5. Answer the following questions:

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

[*CBSE (F) 2017*]

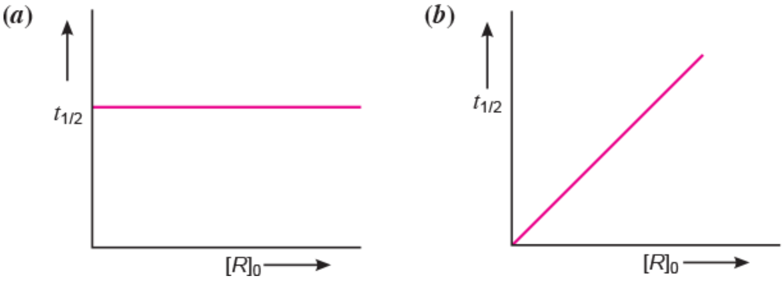
Ans.

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

$$\therefore \quad \frac{t_{3/4}}{t_{1/2}} = \frac{\frac{2.303}{k}\log\frac{100}{25}}{\frac{2.303}{k}\log\frac{100}{50}} = \frac{\log 4}{\log 2} = \frac{0.6021}{0.3010}$$

$$\frac{40\text{ min}}{t_{1/2}} = 2 \qquad \text{or} \qquad t_{1/2} = 20\text{ min}\,.$$

Q.



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

(Given: log 2 = 0.3010, log 4 = 0.6021)

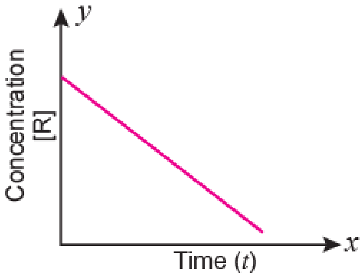
Ans. (*a*) First order **(*b*)** Zero order

Long Answer Questions (OIQ)

Q.1. Consider the reaction $R \xrightarrow{k} P$. The change in concentration of *R* with time is shown in the following plot:

[*HOTS*]

i. **Predict the order of the reaction.**
ii. **Derive the expression for the time required for the completion of the reaction.**
iii. **What does the slope of the above line indicate?**



Ans.

i. The reaction $R \rightarrow P$ is a zero order reaction.

ii. For the reaction $R \xrightarrow{k} P$

$$\text{rate} = \frac{-d[R]}{dt} = k$$

$$d[R] = -k\,dt$$

Integrating both sides,

$$[R] = -kt + C, \text{ where } C = \text{constant of integration} \qquad \ldots(i)$$

At $t = 0$, $[R] = [R]_0$

Substituting this in equation (i)

$C = [R]_0$

Substituting the value of C in equation (i)

$[R] = -kt + [R]_0 \qquad ...(ii)$

$kt = [R]_0 - [R]$

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

On completion of reactions, $[R] = 0$

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

iii. From equation (ii), we have slope of curve

$\text{Slope} = \frac{d\,[R]}{dt} = -k$

Q.2. Answer the following questions:

Q. For an elementary reaction

$$2A + B \rightarrow 3C$$

the rate of appearance of C at time '*t*' is 1.3×10^{-4} mol L^{-1} s^{-1}.

Calculate at this time

- **a. rate of the reaction.**
- **b. rate of disappearance of A.**

Ans.

a. $\text{Rate} = \frac{1}{3}\frac{d\,[C]}{dt}$

$= \frac{1}{3} \times 1.3 \times 10^{-4} \text{ mol L}^{-1}\text{ s}^{-1} = \mathbf{0.43 \times 10^{-4} \text{ mol L}^{-1}\text{ s}^{-1}}$

b. $\text{Rate} = \frac{-d\,[A]}{dt} = \frac{2}{3} \times \frac{d\,[C]}{dt}$

$= \frac{2}{3} \times 1.3 \times 10^{-4} \text{ mol L}^{-1}\text{ s}^{-1} = \mathbf{0.86 \times 10^{-4} \text{ mol L}^{-1}\text{ s}^{-1}}$

Q. The decomposition of $N_2O_5(g)$ is a first order reaction with a rate constant of 5 × 10^{-4} s^{-1} at 45°C, *i.e.*, $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. If initial concentration of N_2O_5 is 0.25 M, calculate its concentration after 2 min. Also, calculate half-life for decomposition of $N_2O_5(g)$.

Ans.

$[R]_0 = 0.25$ M, $t = 2$ min $= 2 \times 60$ s $= 120$ s, $k = 5.0 \times 10^{-4}$ s^{-1}

For a first order reaction,

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

$$5.0 \times 10^{-4} = \frac{2.303}{120} \log \frac{0.25}{[R]} \text{ or } \log \frac{0.25}{[R]} = 0.026$$

$$\log \frac{[R]}{0.25} = -\ 0.026 \text{ or } \frac{[R]}{0.25} = \text{Antilog } (\bar{1}.974)$$

$$\frac{[R]}{0.25} = 0.9419 \text{ or } [R] = 0.235 \text{ m}$$

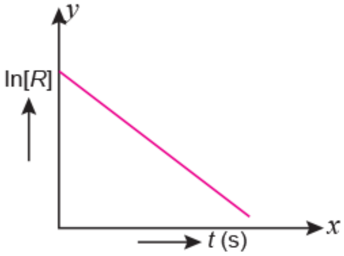
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5 \times 10^{-4} s^{-1}} = 1386 \text{ s}$$

Q.3. For a certain chemical reaction variation in the concentration ln [R] vs. time plot is given alongside.

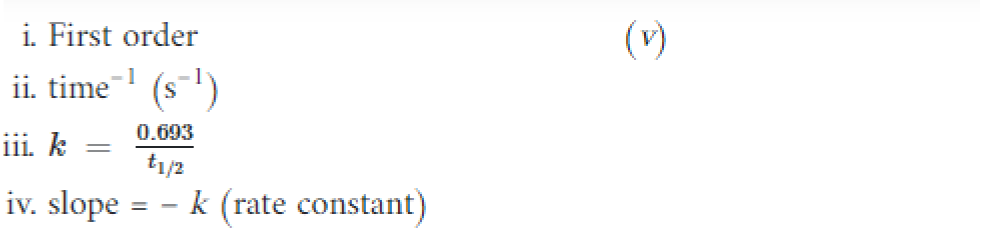
[*HOTS*]

For this reaction

- **i. what is the order of the reaction?**
- **ii. what are the units of rate constant *k*?**
- **iii. give the relationship between *k* and $t_{1/2}$ (half-life period).**
- **iv. what is the slope of the curve?**
- **v. draw the plot log $[R]_0$ /$[R]$ vs time *t*(s).**



Ans.

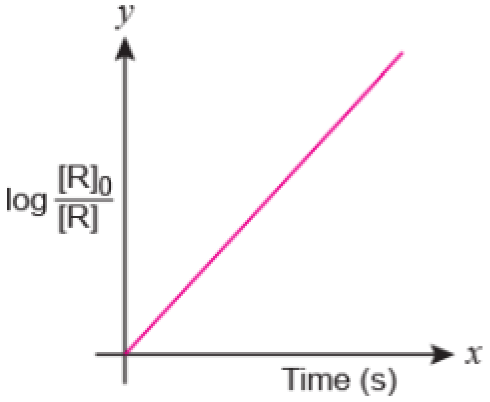


i. First order (v)

ii. time^{-1} (s^{-1})

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

iv. slope = − k (rate constant)



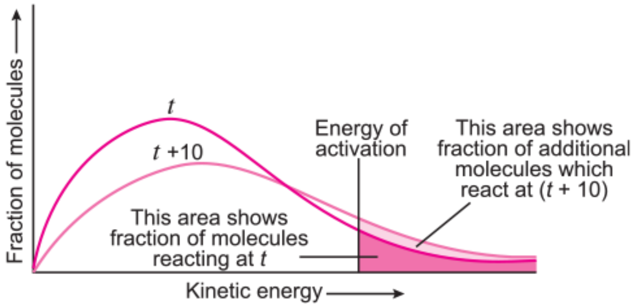
Q.4. Answer the following questions:

Q. Graphically explain the effect of temperature on the rate constant of reaction. How can this temperature effect on rate constant be represented quantitatively?

Ans. Increasing the temperature of a reaction mixture increased the fraction of molecules which colloide with energies greater than E_a. It is clear from the graph below that with 10°C rise in temperature the area showing the fraction of molecules having energy equal to or greater than activation energy gets almost double leading to almost to doubling the rate constant. Quantitatively the effect of temperature on rate constant (k) is given by Arrhenius equation.

$$k = A\, e^{-E_a/RT} \text{ or } k = A\, \frac{1}{e^{E_a/RT}}$$

where A is the frequency factor, R is the gas constant and E_a is the activation energy.



Thus, from Arrhenius equation we find that increasing the temperature or decreasing the activation energy will result in an exponential increase in rate constant.

Q.The decomposition of a hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} s^{-1}) e^{-28000\ K/T}$$

Calculate *E_a*.

Ans.

Comparing with Arrhenius equation $k = \mathrm{A}e^{-E_a/\mathrm{RT}}$, we get

$$-\frac{E_a}{\mathrm{RT}} = -\frac{28000\ K}{T} \text{ or } E_a = 28000 \text{ K} \times R$$

$$E_a = 28000 \text{ K} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 232792 \text{ J mol}^{-1}$$

$$E_a = 232.79 \text{ kJ mol}^{-1}$$

Q.5. Answer the following questions:

Q. Write the rate law for a first order reaction. Justify the statement that half life for a first order reaction is independent of the initial concentration of the reactant.

Ans. Consider the first order reaction,

$$R \rightarrow P$$

For this reaction, rate law which relates the rate of reaction to the concentration of reactants can be given as

$$\text{Rate} = \frac{-d[R]}{\mathrm{dt}} = k[R]$$

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}, \text{ where } [R]_0 = \text{initial concentration, } [R] = \text{concentration at time } t.$$

At $t_{1/2}$, $[R] = [R]_0 /2$

So, the above equation becomes

$$t_{1/2} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0/2}$$

$$t_{1/2} = \frac{2.303}{k}\log 2 \quad \text{or} \quad t_{1/2} = \frac{2.303}{k} \times 0.3010$$

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

Q. The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and it lowers to 50.14 kJ $mol^{-1}$with a catalyst. How many times will the rate of reaction grow in the presence of a catalyst if the reaction proceeds at 25°C?

Ans. According to Arrhenius equation,

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

For uncatalysed reaction,

$$\log k_1 = \log A - \frac{E_{a_1}}{2.303\ \text{RT}} \quad ...(i)$$

For catalysed reaction,

$$\log k_2 = \log A - \frac{E_{a_2}}{2.303\ \text{RT}} ...(ii)$$

A is equal for both reactions.

Subtracting equation (i) from equation (ii),

$$\log\frac{k_2}{k_1} = \frac{E_{a_1} - E_{a_2}}{2.303\ \text{RT}} = \frac{(75.2 - 50.14)\ \text{kJ}\ \text{mol}^{-1}}{2.303\times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}\times 298\ K} = 4.39$$

$$\frac{k_2}{k_1} = \text{anti}\log\ (4.39) = 2.45 \times 10^4$$

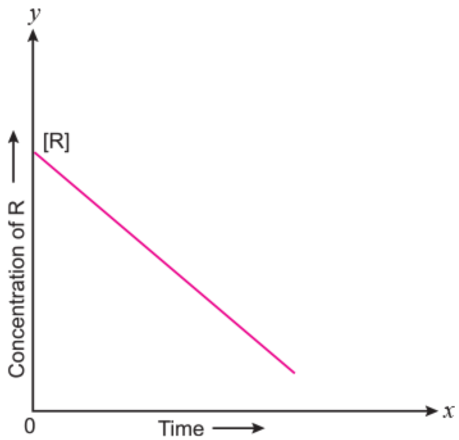
Rate of reaction increases by 2.45×10^4 times.

Q.6. Answer the following questions:

Q. In the reaction

Q + R → Products

The time taken for 99% reaction of Q is twice the time taken for 90% reaction of *R*. The concentration of *R* varies with time as shown in the figure given alongside.



What is the overall order of the reaction? Give the units of the rate constant for the same. Write the rate expression for the above reaction.

Ans. For reactant Q, $t_{99\%} = 2 \times t_{90\%}$

Therefore, order of reaction w.r.t. reactant $Q = 1$.

From the graph, order of reaction w.r.t. reactant, $R = 0$.

So, overall order of reaction = 1 + 0 = 1

Unit of rate constant, $k = \text{time}^{-1}$

Rate = $k[Q][R]^0$

Rate = $k[Q]$

Q. Rate constant for a first order reaction has been found to be $2.54 \times 10^{-3} s^{-1}$.

Calculate its three-fourth life.

Ans.

$$[R] = [R]_0 - \frac{3}{4}[R]_0 = \frac{[R]_0}{4}$$

Substituting $[R] = \frac{[R]_0}{4}$, $k = 2.54 \times 10^{-3}\ s^{-1}$ in the expression $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$, we get

$$t = \frac{2.303}{2.54 \times 10^{-3}} \log \frac{[R]_0}{[R]_0/4} = \frac{2.303 \times 10^3}{2.54} \log 4$$

$$t = \frac{2.303 \times 10^3}{2.54} \times 0.6021 = 545.92\ s$$

Alternative Method:

For a first order reaction, $t_{3/4} = 2 \times t_{1/2}$

$$\therefore \quad t_{3/4} = 2 \times \frac{0.693}{k}$$

$$t_{3/4} = \frac{2 \times 0.693}{2.54 \times 10^{-3} s} = 545.67\ s$$