Short Answer Questions-II

Short Answer Questions-II (PYQ)

Q. Define half-life of a reaction. Write the expression of half-life for

[CBSE (F) 2014]

i. **zero order reaction and**
ii. **first order reaction.**

Ans. The half life ($t_{1/2}$) of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration.

i. $t_{1/2}$ for a zero order reaction $= \dfrac{[R]_0}{2k}$ where $[R]_0$ = initial concentration, k = rate constant

ii. $t_{1/2}$ for a first order reaction $= \dfrac{0.693}{k}$

Q.5. The reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ contributes to air pollution whenever a fuel is burnt in air at a high temperature. At 1500 K, equilibrium constant K for it is 1.0 × 10⁻⁵. Suppose in a case [N₂] = 0.80 mol L⁻¹ and [O₂] = 0.20 mol L⁻¹ before any reaction occurs. Calculate the equilibrium concentrations of the reactants and the product after the mixture has been heated to 1500 K.

[CBSE (AI) 2012] [HOTS]

Ans.

	N₂	+ O₂	→ 2NO
Initial conc. in mol L⁻¹	0.8	0.2	0
Change in conc. in mol L⁻¹	−x	−x	+2x
Equilibrium conc. in mol L⁻¹	0.8−x	0.2−x	2x

$$K_C = \frac{[NO]^2}{[N_2][O_2]} \qquad \therefore \quad 1 \times 10^{-5} = \frac{(2x)^2}{(0.8 - x)(0.2 - x)}$$

As $x \ll 0.2$, therefore $0.8 - x \approx 0.8$ and $0.2 - x \approx 0.2$

$$\therefore \quad 1 \times 10^{-5} = \frac{4x^2}{0.16} \quad \Rightarrow \quad 4x^2 = 16 \times 10^{-7}$$

$$x = 6.324 \times 10^{-4} \text{ mol L}^{-1}$$

Thus at equilibrium,

$$[NO] = 2x = 2 \times 6.324 \times 10^{-4}$$

$$= 12.648 \times 10^{-4} \text{ mol L}^{-1}$$

$$[N_2] = 0.8 - 6.324 \times 10^{-4} \text{ mol L}^{-1}$$

$$= 0.799 \text{ mol L}^{-1}$$

$$[O_2] = 0.2 - 6.324 \times 10^{-4} \text{ mol L}^{-1}$$

$$= 0.199 \text{ mol L}^{-1}$$

Q.3. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{ K}$$

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})

[CBSE Delhi 2016]

Ans.

Comparing the equation, $\log k = 14.2 - \frac{1.0 \times 10^4}{T}$ K with the equation, $\log k = \log A - \frac{E_a}{2.303 \text{ } RT}$, we get

$$\frac{E_a}{2.303 \text{ } RT} = \frac{1.0 \times 10^4 K}{T} \text{ or } E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times R$$

$$E_a = 1.0 \times 10^4 \text{ K} \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$
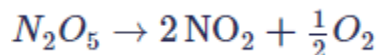
$$= 19.1471 \times 10^4 \text{ J mol}^{-1}$$

$$= 191.47 \text{ kJ mol}^{-1}$$

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

$$\therefore \quad k = \frac{0.693}{200 \text{ min}} = 3.465 \times 10^{-3} \text{ min}^{-1}$$

Q.4. Following data are obtained for the reaction:

$$N_2O_5 \rightarrow 2\,NO_2 + \tfrac{1}{2}O_2$$

t/s	0	300	600
[N₂O₅]/mol L⁻¹	1.6×10⁻²	0.8×10⁻²	0.4×10⁻²

  i.   Show that it follows first order reaction.
  ii.   Calculate the half-life.

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

Ans.

i. At 300 s,

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

$$= \frac{2.303}{300}\log\frac{1.6\times10^{-2}}{0.8\times10^{-2}} = \frac{2.303}{300}\log 2$$

$$k = \frac{2.303}{300} \times 0.3010 = 2.31 \times 10^{-3}s^{-1}$$

At 600 s

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

$$= \frac{2.303}{600}\log\frac{1.6\times10^{-2}}{0.4\times10^{-2}} = \frac{2.303}{600}\log 4$$

$$k = \frac{2.303}{600} \times 0.6021 = 2.31 \times 10^{-3}s^{-1}$$

k is constant and is equal to 2.31 × 10⁻³ s⁻¹ when we use first order equation. Hence, it follows first order reaction.

ii. $t_{1/2} = \dfrac{0.693}{k}$

$$= \frac{0.693}{2.31 \times 10^{-3}s^{-1}} = 300s$$

Q.5. The rate constant of a first order reaction increases from 2 × 10⁻² to 4 × 10⁻² **when the temperature changes from 300 K to 310 K. Calculate the energy of activation (E_a).**

(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

Ans.

Substituting $k_1 = 2 \times 10^{-2}$, $k_2 = 4 \times 10^{-2}$, $T_1 = 300\ K$, $T_2 = 310\ K$, $R = 8.314\ J\ K^{-1} mol^{-1}$ in the expression

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left(\frac{T_2 - T_1}{T_1 T_2} \right), \text{ we get}$$

$$\log \frac{4 \times 10^{-2}}{2 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314} \left(\frac{310 - 300}{300 \times 310} \right)$$

$$\log 2 = \frac{E_a}{19.147} \times \frac{10}{300 \times 310}$$

$$E_a = 0.3010 \times 19.147 \times 300 \times 31 = 53598\ J\ mol^{-1}$$

$$E_a = 53.598\ kJ\ mol^{-1}$$

Short Answer Questions-II (OIQ)

Q.1. $A + 2B \rightarrow 3C + 2D$. The rate of disappearance of B is 1 × 10⁻² mol L⁻¹ s⁻¹. What will be

   i. **Rate of the reaction**
   ii. **Rate of change in concentration of A and C?**

Ans.

i. As $\dfrac{-d\,[B]}{dt} = 1 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$

$\therefore$ Rate $= -\dfrac{1}{2} \dfrac{d\,[B]}{dt} = \dfrac{1}{2} \times 1 \times 10^{-2} = 0.5 \times 10^{-2}\ mol\ L^{-1}\ s^{-1}$

ii. $\quad$ Rate $= -\dfrac{d\,[A]}{dt} = -\dfrac{1}{2} \dfrac{d\,[B]}{dt} = +\dfrac{1}{3} \dfrac{d\,[C]}{dt}$

Rate of change in concentration of A

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

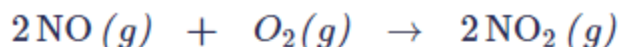$$= 0.5 \times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

Rate of change in concentration of C

$$= +\frac{d\,[C]}{dt} = -\frac{3}{2}\frac{d\,[B]}{dt} = \frac{3}{2} \times 1 \times 10^{-2}$$

$$= 1.5 \times 10^{-2}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

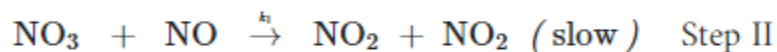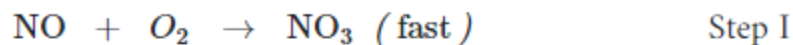**Q.2. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide.**

[HOTS]

$$2\,\text{NO}\,(g) + O_2(g) \rightarrow 2\,\text{NO}_2\,(g)$$

The rate law for this reaction is:

$$\text{Rate} = k\,[\text{NO}]^2\,[O_2]$$

Propose a mechanism for the reaction.

Ans.

The probable proposed mechanism may be,

$$\text{NO} + O_2 \rightarrow \text{NO}_3\ (\text{fast})\qquad\qquad \text{Step I}$$

$$\text{NO}_3 + \text{NO} \xrightarrow{k_1} \text{NO}_2 + \text{NO}_2\ (\text{slow})\quad \text{Step II}$$

Since slowest reaction is the rate determining step, therefore

$$\text{Rate} = k_1\,[\text{NO}_3]\,[\text{NO}]$$

$$K = \frac{[\text{NO}_3]}{[\text{NO}]\,[O_2]}$$

$$[NO_3] = K[NO][O_2]$$

$$\text{Rate} = k_1 K[NO][O_2][NO] = K'[NO]^2[O_2], \text{ where } K' = k_1.K$$

Q.3. The rate of reaction, $2NO+Cl_2 \rightarrow 2NOCl$ is doubled when concentration of Cl_2 is doubled and it becomes eight times when concentration of both NO and Cl_2 are doubled. Deduce the order of the reaction.

[*HOTS*]

Ans. Let $\qquad r = k[NO]^x[Cl_2]^y \qquad\qquad\qquad ...(i)$

$\qquad\qquad\qquad 2r = k[NO]^x[2Cl_2]^y \qquad\qquad\qquad ...(ii)$

$\qquad\qquad\qquad 8r = k[2NO]^x[2Cl_2]^y \qquad\qquad\qquad ...(iii)$

Dividing (iii) by (ii), we get

$$\frac{8r}{2r} = \frac{k\,[2\,NO\,]^x\,[2\,Cl_2\,]^y}{k\,[\,NO\,]^x\,[2\,Cl_2\,]^y}$$

$$2^2 = [2]^x$$

$$x = 2$$

Putting the value of x in (i) and (ii), we get

$$r = k[NO]^2[Cl_2]^y$$

$$2r = k[NO]^2[2Cl_2]^y$$

$$\frac{2r}{r} = \frac{[2\,Cl_2\,]^y}{[\,Cl_2\,]^y}$$

$$2 = [2]^y$$

$$y = 1$$

$$\text{Rate} = k[NO]^2[Cl_2]^1$$

Overall order of reaction $= x + y = 2 + 1 = \mathbf{3}$

Q.4. A solution of H_2O_2 when titrated against $KMnO_4$ solution at different intervals of time gave the following results:

Time (minutes)	0	10	20
Volume of $KMnO_4$ (mL)	23.8	14.7	9.1

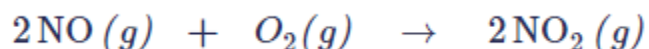**Show that decomposition of H_2O_2 is first order reaction.**

Ans.

i. $k = \dfrac{2.303}{10} \log \dfrac{23.8}{14.7} = \dfrac{2.303}{10} \times 0.2093 = 0.048 \ \text{min}^{-1}$

ii. $k = \dfrac{2.303}{20} \log \dfrac{23.8}{9.1} = \dfrac{2.303}{20} \times 0.4176 = 0.048 \ \text{min}^{-1}$

Since the value of k comes out to be constant in both the cases, therefore the reaction is of first order.

Q.5. Following reaction takes place in one step:

$$2\,NO\,(g) \ + \ O_2(g) \ \rightarrow \ 2\,NO_2\,(g)$$

How will the rate of the above reaction change if the volume of the reaction vessel is reduced to one-third of its original volume? Will there be any change in the order of the reaction with reduced volume?

[HOTS]

Ans.

$$\text{Rate} = k\,[NO]^2\,[O_2]$$

Let initially, moles of NO = a, moles of O_2 = b, volume of the vessel = V. Then

$$[NO] = \tfrac{a}{V}\,M, \ [O_2] = \tfrac{b}{V}\,M$$

$$\therefore \qquad \text{Rate } (r_1) = k\left(\tfrac{a}{V}\right)^2\left(\tfrac{b}{V}\right) = k\dfrac{a^2b}{V^3} \qquad\qquad ...(i)$$

Now, new volume = $\dfrac{V}{3}$

∴ New concentrations: $[NO] = \dfrac{a}{V/3} = \dfrac{3a}{V}$

$$[O_2] = \dfrac{b}{V/3} = \dfrac{3b}{V}$$

∴ New rate $(r_2) = k \left(\dfrac{3a}{V}\right)^2 \left(\dfrac{3b}{V}\right) = \dfrac{27\,ka^2\,b}{V^3}$ ...(ii)

∴ $\dfrac{r_2}{r_1} = 27$ or $r_2 = 27r_1$, i.e., rate becomes **27 times.**

Thus, there is no effect on the order of reaction.

Q.6. The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at a constant volume:

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

S. No.	Time/s	Total Pressure/atm
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

[HOTS]

Ans. Let the pressure of $N_2O_5(g)$ decrease by $2x$ atm. As two moles of N_2O_5 decompose to give two moles of $N_2O_4(g)$ and one mole of $O_2(g)$, the pressure of $N_2O_4(g)$ increases by $2x$ atm and that of $O_2(g)$ increases by x atm.

	$2N_2O_5(g)$	$\longrightarrow$ $2N_2O_4(g)$	$+$ $O_2(g)$
At $t = 0$	0.5 atm	0 atm	0 atm
At time t	$(0.5 - 2x)$ atm	$2x$ atm	x atm

$p_t = p_{N_2O_5} + p_{N_2O_4} + p_{O_2}$

$= (0.5 - 2x) + 2x + x = 0.5 + x$

$x = p_t - 0.5$

$p_{N_2O_5} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$

$= (0.5 - 2x) + 2x + x = 0.5 + x$

$x = p_t - 0.5$

$p_{N_2O_5} = 0.5 - 2x = 0.5 - 2(p_t - 0.5) = 1.5 - 2p_t$

At $t = 100$ s; $p_t = 0.512$ atm,

$p_{N_2O_5} = 1.5 - 2 \times 0.512 = 0.476$ atm

Thus, $k = \frac{2.303}{t} \log \frac{p_i}{p_A}$

$= \frac{2.303}{100 \ s} \log \frac{0.5 \ atm}{0.476 \ atm}$

$= \frac{2.303}{100 \ s} \times 0.0216 = 4.98 \times 10^{-4} \ s^{-1}$

Q.7. For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K, if $k = 1.6 \times 10^6$ s⁻¹ at 280 K? [$R = 8.31$ J K⁻¹ mol⁻¹]

Ans.

Given $T_1 = 280$ K, $k_1 = 1.6 \times 10^6$ s⁻¹, $k_2 = ?$, $E_a = 0$, $T_2 = 300$ K.

By Arrhenius equation,

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

As, $E_a = 0$

$\therefore$ $\log \frac{k_2}{k_1} = 0$

or $\frac{k_2}{k_1} = 1$ or $k_2 = k_1$

Thus, the rate constant at 300 K is **1.6×10^6 s⁻¹**.

Q.8. The rate constant for the decomposition of ethyl iodide

$$C_2H_5I(g) \rightarrow C_2H_4(g) + HI(g)$$

at 600 K is 1.60×10^{-5} s⁻¹. Its energy of activation is 209 kJ/mol. Calculate the rate constant of the reaction at 700 K.

Ans. We know that,

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

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

$$\log k_2 = \log\left(1.60 \times 10^{-5}\ s\right) + \frac{209000\ J\ mol^{-1}}{2.303 \times 8.314\ J\ mol^{-1}\ K^{-1}}\left[\frac{1}{600\ K} - \frac{1}{700\ K}\right]$$

$$\log k_2 = -4.796 + 2.599 = -2.197 \text{ or } k_2 = \text{Antilog}\ (\overline{3}.803)$$

$$k_2 = 6.36 \times 10^{-3}\ s^{-1}$$

Q.9. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is again 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction.

[R = 8.314 J K⁻¹ mol⁻¹; log 4 = 0.602]

[*HOTS*]

Ans.

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

$T_1 = 300\ K,$ $\qquad\qquad k_1 = \dfrac{0.693}{20} = 3.456 \times 10^{-2}\ min^{-1}$

$T_2 = 350\ K,$ $\qquad\qquad k_2 = \dfrac{0.693}{5} = 1.386 \times 10^{-1}\ min^{-1}$

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

$$\log \frac{1.386 \times 10^{-1}}{3.465 \times 10^{-2}} = \frac{E_a}{2.303 \times 8.314}\left(\frac{350 - 300}{350 \times 300}\right)$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314}\left(\frac{50}{350 \times 300}\right)$$

$$0.602 = \frac{E_a}{19.147} \left(\frac{50}{350 \times 300} \right)$$

$$E_a = \frac{0.602 \times 19.147 \times 350 \times 300}{50}$$

$$= 24205.63 \text{ J mol}^{-1} = \textbf{24.206 kJ mol}^{-1}$$

Q.10.

$^{238}_{92}U$ changes to $^{206}_{92}Pb$ by successive radioactive decay. A sample of uranium ore was analysed and found to contain 1.0 g of ^{238}U and 0.1 g of ^{206}Pb had accumulated due to decay of ^{238}U, find out the age of the ore. (Half-life of ^{238}U = 4.5 × 10^9 years)

[HOTS]

Ans.

$[A]_0$ = Initial amount of ^{238}U = amount of ^{238}U left at time t + amount of ^{238}U decayed

$[A]_0$ = 1.0 + amount of ^{238}U decayed

Now, amount of ^{238}U decayed = $\frac{0.1 \times 238}{206}$ g = 0.1155 g

∴ $[A]_0$ = 1.0 g + 0.1155 g = 1.1155 g

Determination of k: $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9} = 0.154 \times 10^{-9}$ year^{-1}

Determination of time: $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$

Substituting the values of $[A]_0$ = 1.1155 g and k = 0.154 × 10^{-9} year^{-1}

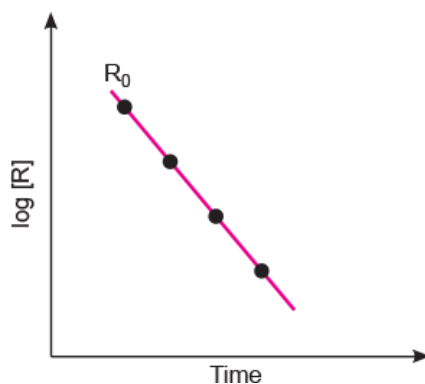$$t = \frac{2.303}{0.154 \times 10^9} \log \frac{1.1155}{1}$$

$$= 0.7099 \times 10^9 \text{ year}$$

$$= 7.099 \times 10^8 \text{ year}$$

Q.11. Observe the graph in diagram and answer the following questions.

i.   If slope is equal to -2.0×10^{-6} sec^{-1}, what will be the value of rate constant?
ii.   How does the half-life of zero order reaction relate to its rate constant?

Ans.

i. Slope $= -\dfrac{k}{2.303}$ or $k = -2.303 \times$ Slope

∴ $k = -2.303 \times \left(-2.0 \times 10^{-6} \text{ s}^{-1}\right)$

   $k = 4.606 \times 10^{-6} \text{ s}^{-1}$

ii. For a zero order reaction

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

$$\text{At } t = t_{1/2}, [R] = \frac{[R]_0}{2}$$

∴ $t_{1/2} = \dfrac{[R]_0 - \frac{[R]_0}{2}}{k}$ or $t_{1/2} = \dfrac{[R]_0}{2k}$