

Chapter 17: Chemical Kinetics

Q1:-

Sol: For 50% completion time required = 69.3 min

$$\therefore t_{1/2} = 69.3 \text{ min}$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 10^{-2} \text{ min}^{-1}$$

For 80% completion, $\frac{C_o}{C_t} = \frac{100}{100 - 80} = \frac{100}{20} = \frac{10}{2}$

For first order reaction -

$$Kt = 2.303 \log \frac{C_o}{C_t}$$

$$\Rightarrow t = \frac{2.303}{10^{-2}} \log \frac{10}{2} = 2.303 \times 10^2 \log 5 = 160.9 \text{ minutes} \quad \text{Ans}$$

Q2:-

Sol :- $t_{1/2} = 500 \text{ sec}$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{500} \text{ S}^{-1}$$

A/q; $\frac{C_o}{C_t} = \frac{4}{1}$

$$Kt = 2.303 \log \frac{C_o}{C_t}$$

$$\frac{0.693}{500} \cdot t = 2.303 \log 4$$

$$\Rightarrow t = \frac{500 \times 2.303}{0.693} \log 4 = 1661 \text{ sec} \quad \text{Ans}$$

Q3:-

Sol:- $A + B \rightarrow AB$

Rate of reaction = $5 \times 10^{-5} \text{ mole/lit} - \text{min}$

Assuming the reaction is first order w.r.t. A & B

$$5 \times 10^{-5} = K[A][B] = K[0.05][0.01]$$

$$K = \frac{5 \times 10^{-5} \text{ mol/L} - \text{min}}{5 \times 10^{-4} (\text{mol/l})^2} = 0.1 (\text{mol/l})^{-1} \text{ min}^{-1}$$

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Q2:-

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$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{500} \text{ S}^{-1}$$

A/q; $\frac{C_0}{C_t} = \frac{4}{1}$

$$Kt = 2.303 \log \frac{C_0}{C_t}$$

$$\frac{0.693}{500} \cdot t = 2.303 \log 4$$

$$\Rightarrow t = \frac{500 \times 2.303}{0.693} \log 4 = 1661 \text{ sec} \quad \text{Ans}$$

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Q4:-

Sol:- $R_1 = K_1[A] \Rightarrow K_1 = \frac{R_1}{[A]}$ [A] is in mol/lit

$R_2 = K_2[A]^2 \Rightarrow K_2 = \frac{R_2}{[A]^2}$ & $R_3 = K_3[A]^3 \Rightarrow K_3 = \frac{R_3}{[A]^3}$

Given: $K_1 = K_2 = K_3$

$$\frac{R_1}{[A]} = \frac{R_2}{[A]^2} = \frac{R_3}{[A]^3}$$

$$[A]^2 R_1 = [A] R_2 = R_3 \text{ ----- (1)}$$

Now if conc are in mole/mL = A'

Then $[A] = \frac{[A']}{10^{-3}}$

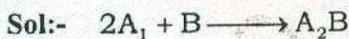
$\therefore (1) \Rightarrow \frac{[A']^2}{10^{-6}} R_1 = \frac{[A']}{10^{-3}} R_2 = R_3$

$$\frac{1}{10^{-6}} \frac{R_1}{[A']} = \frac{1}{10^{-3}} \frac{R_2}{[A']^2} = \frac{R_3}{[A']^3}$$

$$\frac{K_1}{10^{-6}} = \frac{K_2}{10^{-3}} = K_3 \begin{bmatrix} \because R_1 = K_1[A'] \\ \because R_2 = K_2[A']^2 \\ \because R_3 = K_3[A']^3 \end{bmatrix}$$

$K_1 = K_2 \times 10^{-3} = K_3 \times 10^{-6}$ **Ans**

Q5:-



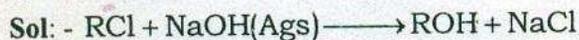
$\text{Rate}_1 = K[A]^2[B]$

If concentration of A is doubled & that of B is halved

Then $\text{Rate}_2 = K(2A)^2 \cdot \frac{B}{2} = 2K[A]^2 \cdot B$

$\text{Rate} = 2 \cdot \text{Rate}_1$

Q 6:

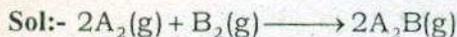


$\text{Rate} = K_1[RCl]$

So, Rate is directly proportional to concentration of RCl. hence Rate of reaction becomes half as the concentration of RCl decreases to one-half.

Ans(b)

Q7:



$$\text{Rate} = K[A_2]^2[B_2]$$

If A_2 is decreased four times & rate remain same, then let the conc of $B_2 = B_2'$

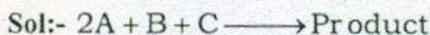
$$\therefore \text{Rate} = K \left[4 \frac{A_2}{4} \right]^2 [B_2'] = K[A_2]^2[B_2']$$

$$\frac{K[A_2]^2}{16} [B_2'] = K[A_2]^2[B_2]$$

$$\Rightarrow [B_2'] = [B_2] \times 16 = 16 [B_2]$$

So concentration of B_2 should be increased by 16 time.

Q8:-



Order w.r.t A = 1

Order w.r.t B = 2

Order w.r.t C = 0

$$\text{Rate}_1 = K[A]^1[B]^2[C]^0 = K[A][B]^2$$

If A, B & C are all increased two times, then

$$\text{Rate}_2 = K[2A][2B]^2 = K \times 2 \times 4[A][B]^2 = 8 K [A][B]^2 = 8 \text{Rate}_1$$

$$\therefore \text{Rate}_2 = 8 \text{Rate}_1$$

Q9:-



At $t = 0$ 200 0 0

At $t \rightarrow \infty$ 200 - P P P

Total pressure initial = 200 mm of Hg

Total pressure final = 390 mm of Hg

$$200 - P + P + P = 390$$

$$P = 390 - 200 = 190 \text{ mm of Hg}$$

So there is only 190 mm of Hg present for decomposition.

If the total pressure at any time $t = 300$ mm of Hg

$$200 - P' + P' + P' = 300$$

$$200 - P' = 300 \Rightarrow P' = 300 - 200 = 100 \text{ mm of Hg}$$

$$\text{Fraction reaction unchanged} = \frac{190 - 100}{190} = \frac{90}{190} = 0.47 \quad \text{Ans}$$

Because only 190 mm of Hg press is present for decomposition

Q10:-

Sol:- In zero order $C_t = C_o - Kt$	In first order $\log C_t = \frac{-K}{2.303} t + \log C_o$	In 2 nd order $\frac{1}{C_t} = \frac{1}{C_o} + K_t$
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At, $t = 53$ minutes

$$C_t = 50 \text{ \& } C_o = 100$$

At $t = 100$ min

$$C_t = (100 - 73) = 27 \text{ \& } C_o = 100$$

Plotting $\log C$ vs time, it gives a straight line & hence it is first order reaction.

Now in first order reaction, doesn't depend as the concentration & so the rate constant, so in 100 min same amount of completion will occur as previously.

Q11:-

Sol:- (i) At $t = 540$ sec, $\frac{C_o}{C_t} = \frac{100}{32.5}$

$$Kt = 2.303 \log \frac{C_o}{C_t}$$

$$K \times 540 = 2.303 \log \frac{100}{32.5} \Rightarrow K = \frac{1.124}{540} = 2.08 \times 10^{-3} \text{ s}^{-1} \quad \text{Ans}$$

(ii) For 25 % decomposed, $C_o/C_t = 100/75$

$$K.t = 2.303 \log (100/75)$$

$$t = 2.303 \log \frac{100}{75} = 138.83 \text{ sec} \quad \text{Ans}$$

Q12:-

Sol:- $K = 1 \times 10^{-2} \text{ s}^{-1}$

$$\text{Time} = 2 \text{ min} = 2 \times 60 \text{ sec}$$

$$C_o = 1M$$

$$K.t = 2.303 \log \frac{C_o}{C_t}$$

$$1 \times 10^{-2} \times 2 \times 60 = 2.303 \log \frac{C_o}{C_t}$$

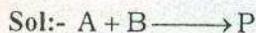
$$1.2 = -2.303 \log C_t$$

$$C_t = 10^{-0.52} = 0.3 \text{ M}$$

$$\therefore R_i = K[C_0] = 1 \times 10^{-2} \text{ mol/lit. sec}$$

$$R_f = K[C_t] = 1 \times 10^{-2} \times 0.3 = 3 \times 10^{-3} \text{ mole/lit. sec} \quad \text{Ans}$$

Q13:-



Reaction is first order w.r.t. A & second order w.r.t. B

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

When $[A] = [B] = 1$, Rate = 1×10^{-2} mole/lit - s

$$1 \times 10^{-2} \text{ mol/lit - s} = K \times 1 \times 1^2$$

$$K = 1 \times 10^{-1} \text{ mol/lit - sec / (mol/lit)}^3$$

When half of the reactant converts into product, then

$$[A] = [B] = \frac{1}{2} \text{ M}$$

$$\begin{aligned} \text{Rate} &= K[A][B]^2 = 1 \times 10^{-2} \times \frac{1}{20} \times \left(\frac{1}{2}\right)^2 \\ &= \frac{1}{80} \times 10^{-2} \text{ mol/lit - sec} = 1.25 \times 10^{-3} \text{ mol/lit. sec} \quad \text{Ans} \end{aligned}$$

Q14:-



$$\frac{dx}{dt} = K[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]^0$$

- (i) Rate is directly proportional to concentration of $[\text{CH}_3\text{COOC}_2\text{H}_5]$ & hence Rate doubles when concentration of ester doubles.
- (ii) On concentration of H^+ , rate doesn't depend & so there will be no change in rate as conc of H^+ changes

Q15



$$\frac{-dA}{dt} = K[A]^n$$

$$\int_{A=A_0}^{A_t} \frac{d[A]}{[A]^n} = \int_{t=0}^t -K dt \quad \Rightarrow \quad \frac{A^{1-n}}{1-n} \Big|_{A_0}^{A_t} = -K(t-0)$$

$$\frac{(A_t)^{1-n}}{1-n} - \frac{[A_0]^{1-n}}{1-n} = -Kt$$

For $t = t_{1/2}$, $[A_t] = \frac{A_0}{2}$

$$\frac{(A_0)^{1-n}}{1-n} - \frac{|\frac{A_0}{2}|^{1-n}}{1-n} = Kt$$

$$\frac{(A_0)^{1-n}}{1-n} - \frac{|A_0|^{1-n}}{(1-n)(2)^{1-n}} = Kt \frac{1}{2}$$

$$t_{1/2} = (A_0)^{1-n} \left\{ \frac{1}{1-n} - \frac{1}{(1-n)(2)^{1-n}} \right\} \Rightarrow t_{1/2} = \frac{1}{[A_0]^{n-1}} \left\{ \frac{1}{(1-n)} - \frac{1}{(1-n)(2)^{1-n}} \right\}$$

$$t_{1/2} \propto \frac{1}{[A_0]^{n-1}} \quad \text{Proved}$$

Q16:-

Sol:- A_0 = initial count rate = 16.1 counts / min

$$A_t = 9.6 \text{ count / min}$$

$$t_{1/2} = 5770 \text{ years}$$

$$\therefore k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} \text{ Y}^{-1}$$

$$\therefore K_t = 2.303 \log \frac{A_0}{A_t}$$

$$t = \frac{2.303}{0.693} \times 5770 \log \frac{16.1}{9.6} = 4304 \text{ years} \quad \text{Ans}$$

Q17:-

Sol:-	t(s)	P(mm of Hg)	$\frac{1}{P}$	Log P
	0	348	2.87×10^{-3}	2.54
	600	247	2.87×10^{-3}	2.39
	1200	185	5.41×10^{-3}	2.267
	2400	105	9.524×10^{-3}	2.0212
	3600	58	0.01724	1.7632
	4800	33	0.03030	1.5185
	6000	18	0.05556	1.2553
	7200	10	0.1	1

Since LogP vs time curve is linear, so it is a first order reaction.

Now

$$Kt = 2.303 \log \frac{P_0}{P_t}$$

$$K \times 7200 \text{ sec} = 2.303 \log \frac{348}{10} = 2.303 \log 34.8$$

$$K = \frac{2.303 \times \log 34.8}{7200} = \frac{3.55}{7200} = 4.93 \times 10^{-4} \text{ sec}^{-1} \quad \text{Ans}$$

Q18:-

Sol:- For 2nd order reaction:-

$$\frac{-d[A]}{dt} = K[A]^2 \quad \Rightarrow \quad \int_{[A_0]}^{[A]} \frac{d[A]}{[A]^2} = - \int_{t=0}^t K dt$$

$$\left[\frac{-1}{A} \right]_{[A_0]}^{[A]} = -Kt \quad \Rightarrow \quad \frac{1}{[A_0]} - \frac{1}{A_t} = -Kt$$

$$\frac{1}{[A_t]} = \frac{1}{[A_0]} + Kt \quad \text{-----(1)}$$

For $t = t_{1/2}$, $[A_t] = \frac{[A_0]}{2}$

$$\therefore (1) \Rightarrow \frac{2}{[A_0]} = \frac{1}{[A_0]} + Kt_{1/2} \quad \Rightarrow \quad t_{1/2} = \frac{1}{K[A_0]}$$

$$\therefore t_{1/2} = \frac{1}{6.8 \times 10^{-4} \times 0.05} = 2.94 \times 10^4 \text{ sec} \quad \text{Ans}$$

$$t_{1/2} = \frac{1}{6.8 \times 10^{-4} \times 0.01} = 1.47 \times 10^4 \text{ sec} \quad \text{Ans}$$

Q19:-

Sol:- In $\Delta t = 5 \text{ min}$, concentration becomes half from 0.5 mole/lit to 0.25 mole/lit

In another $\Delta t = 5 \text{ min}$; concentration becomes half from 0.25 mole/lit to 0.125 mole/lit

Since $t_{1/2} = 5 \text{ min}$, which doesn't depend on the concentration of the substance, so it is a first order reaction because

$$t_{1/2} \propto \frac{1}{[A_0]^{n-1}} \text{ for } n = 1 \text{ only, } t_{1/2} \text{ is independent from initial concentration.}$$

$$\text{Also } t_{1/2} = 5 \text{ min} = \frac{\ln 2}{K}$$

$$K = \frac{0.693}{5} = 0.138 \text{ min}^{-1} \quad \text{Ans}$$

Q20:-

Sol:- P(mm)	250	300	400	450
$t_{1/2}$ (min)	136	112.5	85	75.5
		(1)	(2)	

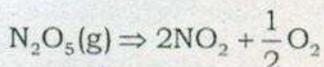
$$t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$$

$$\frac{t_{1/2}(1)}{t_{1/2}(2)} = \frac{[A_0]_2^{n-1}}{[A_0]_1^{n-1}}$$

$$\frac{112.5}{85} = \left(\frac{400}{300}\right)^{n-1} = \left(\frac{4}{3}\right)^{n-1}$$

$$1.323 = (1.333)^{n-1} \Rightarrow n-1 = 1 \Rightarrow n = 2$$

\therefore order of reaction = 2.



At $t = 1 \text{ hr}$ 24 ml

At $t \rightarrow \infty$ 35 ml

$$\therefore \text{Fraction of } \text{N}_2\text{O}_5(\text{g}) \text{ decomposed in 1 hr} = \frac{24}{35} = 0.686 \quad \text{Ans}$$

Q22:-

Sol:- Rate of reaction is directly proportional to the concentration of N_2O_5 .

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = K[\text{N}_2\text{O}_5]$$

$$0.10 = K(0.34)$$

$$K = \frac{10}{34} \text{ hr}^{-1} = 0.29 \text{ hr}^{-1} \quad \text{Ans}$$

Q23:-

Sol:- Let Rate = $K[A]^m[B]^n[O]^p$

From the give date,

Rate remain constant it [A] changes

$$\therefore m = 0 \Rightarrow \text{order w.r.t A} = 0 \quad \text{Ans}$$

Rate becomes half as the conc of [B] doubles

$$n = -1 \text{ order w.r.t B} = -1 \quad \text{Ans}$$

Rate becomes $\frac{14.1}{5}$ times as the conc of [C] increases two times.

$$\frac{14.1}{5} = (2)^p$$

$$P = \frac{3}{2} \Rightarrow \text{order w.r.t C} = \frac{3}{2} \quad \text{Ans}$$

Q24:-

Sol:- For $A + B \longrightarrow P$

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

If [A] is doubled, Rate doubles

$$\therefore R_2 = 2 \times 0.10 = 0.20 \text{ M} \quad \text{Ans}$$

Q25:-

Sol:- $E_a > \Delta H$ for endothermic reaction.

$$\therefore E_a > +25 \text{ KJ/mole} \quad \text{Ans (c)}$$

Q26:-



$$t_{1/2} = 2.4 \text{ hr}$$

$$K = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.4}$$

$$Kt = 2.303 \log \frac{5 \times 10^{10}}{10^8}$$

$$t = \frac{2.303}{0.693/2.4} \log 500 = \frac{2.303 \times 2.4}{0.693} \log 500 = 21.52 \text{ hr} \quad \text{Ans}$$

Q27:-

Sol:- In first vessel

$$[A] = \frac{1}{V}$$

$$[B] = \frac{2}{V}$$

In 2nd vessel

$$[A] = \frac{2}{V}$$

$$[B] = \frac{1}{V}$$

(i) If Rate = K [A] [B]

$$\text{Rate}_1 = K \left(\frac{1}{V} \right) \left(\frac{2}{V} \right) = \frac{2K}{V^2} \therefore R_1 = R_2$$

$$\text{Rate}_2 = K \left(\frac{2}{V} \right) \left(\frac{1}{V} \right) = \frac{2K}{V^2} \therefore \text{Rate are same in two vessel}$$

$$(ii) \text{Rate} = K[A]^2[B],$$

In 1st vessel

$$\text{Rate}_1 = K \left(\frac{1}{V} \right)^2 \left(\frac{2}{V} \right) = \frac{2K}{V^3}$$

In 2nd vessel

$$\text{Rate}_2 K \left(\frac{2}{V} \right)^2 \left(\frac{1}{V} \right) = \frac{4K}{V^3}$$

So, $\text{Rate}_1 \neq \text{Rate}_2$

Hence in this case rate is not equal

Q28:-



$$\text{Rate} = K[A]^2[B] \text{ (Assuming single step reaction)}$$

$$\text{If } [A_f] = 3[A_i]$$

$$[B_f] = \frac{[B_i]}{2}$$

$$\therefore \text{Rate}_1 = K[A_i]^2[B_i]$$

$$\text{Rate}_f = K \{ [A_f] \}^2 [B_f] = K \{ 3[A_i] \}^2 \frac{[B_i]}{2}$$

$$\text{Rate}_f = K \frac{9}{2} [A_i]^2 [B_i] = \frac{9}{2} \text{Rate}_1$$

So Rate increases by 4.5 times.

Q29:-

Sol:- Let at T K rate is R, If C is the temp coefficient then

Rate	Temp
R	T
CR	(T+10)K
C.CR	(T+20)K
C ³ R	(T+30)K

$$A/q, C^3 = 15.6$$

$$C = (15.6)^{1/3} = 2.5 \quad \text{Ans}$$

O3:-

Sol:- C = temperature coefficient = 2.3

If Temperature is T, let the rate is R.

Temp Rate

T K R

(T + 10)K CR

(T + 20)K C²R

(T + 30) K C³R

If T is increased by 20 K, Rate₁ = (2.3)²R

If T is increased by 30 K, Rate₂ = (2.3)³R

At intermediate temperature, temperature is increased by 25 K.

$$\begin{aligned} \text{Rate} &= \frac{\text{Rate}_1 + \text{Rate}_2}{2} = \frac{(2.3)^2 R + (2.3)^3 R}{2} \\ &= \frac{5.29R + 12.167R}{2} = 8.72R \end{aligned}$$

∴ Rate will be increased by 8.72 times

Q31:-

Sol:- For 2nd order reaction

$$\text{Rate} = K [A] [B]$$

According to reaction ; [A] = [B]

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

$$\therefore \frac{1}{[At]} = \frac{1}{[A_0]} + Kt$$

A/q, [At] = 100 - 20 = 80 in t = 500 sec
(20% completion)

$$\frac{1}{80} = \frac{1}{100} + K \times 500$$

$$K \times 500 = \frac{1}{80} - \frac{1}{100} = \frac{10-8}{800} = \frac{1}{400}$$

$$K = \frac{1}{400 \times 500}$$

If 60% completion

$$[At] = 100 - 60 = 40$$

$$\frac{1}{40} = \frac{1}{100} + \frac{1}{400 \times 500} \times t$$

$$\frac{1}{40} = \frac{1}{100} + \frac{t}{400 \times 500}$$

$$\frac{10-4}{400} = \frac{t}{400 \times 500} \Rightarrow t = 6 \times 500 \text{ sec} = 3000 \text{ sec} \quad \text{Ans}$$

Q32:-



Let Rate = $K[A]^m[B]^n$; where $m = \text{order w.r.t. A}$
 $n = \text{order w.r.t B}$

A/q, when $[A] = [B] = 0.1 \text{ M}$, Rate = 1×10^{-4}

$$1 \times 10^{-4} = K(0.1)^m(0.1)^n \text{ -----(1)}$$

$$9 \times 10^{-4} = K(0.1)^m(0.3)^n \text{ -----(2)}$$

$$2.7 \times 10^{-3} = K(0.3)^m(0.3)^n \text{ -----(3)}$$

$$(2) \div (1): \frac{9 \times 10^{-4}}{1 \times 10^{-4}} = \frac{K(0.3)^n}{K(0.1)^n}$$

$$9 = (3)^n \Rightarrow n = 2$$

$$(3) \div (2) \Rightarrow \frac{2.7 \times 10^{-3}}{9 \times 10^{-4}} = \frac{\cancel{K}(0.3)^m}{\cancel{K}(0.1)^m} = 3^m$$

$$3 = 3^m \Rightarrow m = 1$$

Now (1) $\Rightarrow 1 \times 10^{-4} = K(0.1)^1(0.1)^2$

$$K = \frac{10^{-4}}{10^{-3}} = 10^{-1} = 0.1$$

\therefore Rate = $K[A]^1[B]^2$ where $K = 0.1$

Q33:-



t (s)	0	900	1800
[A]	50.8	19.7	7.62
log [A]	1.7058	1.29446	0.882

\therefore slope of log [A] vs t

$$= \frac{1.7058 - 1.26446}{900 - 0} = 4.57 \times 10^{-4}$$

$$\& \frac{1.29446 - 0.882}{1800 - 900} = 4.58 \times 10^{-4}$$

Slope of log P vs t is same, & hence graph of log P vs t is linear, which is the case of first

order reaction.

Q34:-



$$8 \times 10^{-10} = R_1 = K(0.10)^n \text{ -----(1)}$$

$$3.2 \times 10^{-9} = R_2 = K(0.20)^n \text{ -----(2)}$$

$$(2) \div (1) 1^n = 4 \Rightarrow n = 2$$

$$8 \times 10^{-10} K(0.1)^2 \Rightarrow K = 8 \times 10^{-8} \text{ K/mole-sec}$$

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

$$\text{where } K = 8 \times 10^{-8} \text{ L/mol-s}$$

Overall order of reaction = 2

Q36:-



$$\frac{-d[\text{NOCl}]}{dt} = (8.0 \times 10^{-8} \text{ L/mol.s}) [\text{NOCl}]^2$$

$$t_{1/2} \text{ for 2nd order reaction} = \frac{1}{K[\text{NOCl}]} = \frac{1}{8.0 \times 10^{-8} \times 0.15} = 8.34 \times 10^7 \text{ sec Ans}$$

Q36:-



$$\text{Rate of reaction} = \frac{-1d[\text{N}_2\text{O}_5]}{2dt} = K[\text{N}_2\text{O}_5], K = 3.1 \times 10^{-4} \text{ min}^{-1} \text{ at } 45^\circ\text{C}$$

(a) when $[\text{N}_2\text{O}_5] = 0.40\text{M}$

\therefore Rate of decomposition =

$$\frac{-d[\text{N}_2\text{O}_5]}{dt} = 2K[\text{N}_2\text{O}_5] = 2 \times 3.1 \times 10^{-4} \times 0.40$$

$$= 2.48 \times 10^{-4} \text{ mole/l-min Ans}$$

(b) $\frac{d[\text{NO}_2]}{dt}$ = Rate of formation of NO_2

$$\text{We know that } \frac{-1d[\text{N}_2\text{O}_5]}{2dt} = \frac{1d[\text{NO}_2]}{4dt} = \frac{1d\text{O}}{1dt}$$

$$\frac{d[\text{NO}_2]}{dt} = \frac{-4}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = 2 \left\{ \frac{-d[\text{N}_2\text{O}_5]}{dt} \right\}$$

$$= 4K[\text{N}_2\text{O}_5]$$

$$= 4 \times 3.1 \times 10^{-4} \times 0.40 = 4.96 \times 10^{-4} \text{ M/min}$$

$$\frac{d[\text{O}_2]}{dt} = \frac{-1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = K[\text{N}_2\text{O}_5]$$

$$= 3.1 \times 10^{-4} \times 0.40 = 1.24 \times 10^{-4} \text{ mole/lit - min}$$

$$(c) \text{ Rate of reaction} = \frac{-1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = K[\text{N}_2\text{O}_5]$$

$$= 3.1 \times 10^{-4} \times 0.40 = 1.24 \times 10^{-4} \text{ mole/lit - min} \quad \text{Ans}$$

Q37:-



Since plot of $\ln [\text{SO}_2\text{Cl}_2]$ V & time is linear, so order of reaction is 1. Now for first order Reaction

$$Kt = 2.303 \log \frac{[\text{SO}_2\text{Cl}_2]_0}{[\text{SO}_2\text{Cl}_2]_t}$$

$$K \times 240 = 2.303 \log \frac{0.4}{0.28}$$

$$K = \frac{0.35674}{240} = 1.487 \times 10^{-3} \text{ s}^{-1} \quad \text{Ans}$$

Q38:-

Sol:- $E_a = 45.0 \text{ KJ/mole}$

$$K = \text{Rate constant without catalyst} = 5.0 \times 10^{-4} \text{ s}^{-1}$$

$$K' = \text{rate constant with catalyst} = 2.0 \times 10^{-2} \text{ s}^{-1}$$

$$K = A e^{-E_a/RT} \quad \& \quad K' = A e^{-E_a'/RT}$$

$$\frac{K'}{K} = e^{-E_a'/RT + E_a/RT}$$

$$2.303 \times \log \left(\frac{K'}{K} \right) = \frac{1}{RT} (E_a - E_a')$$

$$(E_a - E_a') = 2.303 RT \log \left(\frac{K'}{K} \right)$$

$$E_a - E_a' = 2.303 \times 8.314 \times 10^3 \times 310 \log \frac{2 \times 10^{-2}}{5 \times 10^{-4}}$$

$$= 5.9356 \times \log \frac{200}{5} \times 40 = 9.81 \text{ KJ} \quad \text{Ans}$$

Q39:-

Sol:- Rate constant of disappearance of $H^+ = 1.0 \times 10^7 \text{ mol/l.s}$

Unit of Rate constant is same as rate of reaction so order of reaction = 0

For Zero order reaction

$$A_t = A_o - Kt$$

$$0 = \frac{3 \times 10^{-6}}{0.05 \times 10^{-3}} - 1 \times 10^7 t$$

$$t = \frac{3 \times 10^{-6}}{0.5 \times 10^{-4}} / 1 \times 10^7 = \frac{6 \times 10^{-2}}{10^7}$$

$$t = 6 \times 10^{-9} \text{ sec} \quad \text{Ans}$$

Q40:-

Sol:- For 2nd order reaction

$$\therefore \frac{-1}{2} \frac{d[\text{NOBr}]}{dt} = K[\text{NOBr}]$$

$$\Rightarrow \frac{-d[\text{NOBr}]}{dt} = 2K[\text{NOBr}] \quad (1)$$

Integrating (1) we have

$$\frac{1}{A_t} = \frac{1}{A_o} + 2Kt$$

$$A_o = 4 \times 10^{-3} \text{ M}$$

$$A_t = A_o - x = 4 \times 10^{-3} - 1.5 \times 10^{-3} = 2.5 \times 10^{-3} \text{ M}$$

$$K = 0.81 \text{ M}^{-1} \text{ s}^{-1}$$

$$\frac{1}{2.5 \times 10^{-3}} = \frac{1}{4 \times 10^{-3}} + 2(0.81) \times t$$

$$t = \frac{10^3}{2 \times 0.81} \left(\frac{1}{2.5} - \frac{1}{4} \right) = \frac{1.5 \times 10^2}{2 \times 0.81} = \frac{185.2 \text{ sec}}{2} = 92.6 \text{ Sec} \quad \text{Ans}$$

Q41:-

Sol:- $\frac{-d[A]}{dt} = K[A]^2$

$$\frac{1}{[A_t]} = \frac{1}{[A_o]} + Kt$$

$$K = 2.42 \text{ L/mol.s} \quad \& \quad [A_o] = 0.5 \text{ mole/L}$$

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

$$t_{1/2} = \frac{1}{K[A_0]} = \frac{1}{2.42 \times 0.5} = 0.8264 \text{ sec} \quad \text{Ans}$$

Q42:-

Sol:- $t_{1/2}$ for Tc-99 = 6hr

$t_{1/2}$ for Th-201 = 73hr

For time = 2 days = 2×24 hrs = 48 hrs

For Tc-99

$$A_t = A_o \left(\frac{1}{2} \right)^{t/t_{1/2}}$$

$$\frac{A_t}{A_o} = \left(\frac{1}{2} \right)^{\frac{48}{6}} = \left(\frac{1}{2} \right)^8 = \frac{1}{256}$$

$$\therefore \% \text{ remained} = \frac{A_t}{A_o} \times 100 = \frac{1}{256} \times 100 = 0.39\% \quad \text{Ans}$$

For Th-201

$$A_t = A_o \left(\frac{1}{2} \right)^{t/t_{1/2}}$$

$$\frac{A_t}{A_o} = \left(\frac{1}{2} \right)^{\frac{48}{73}} = 0.634$$

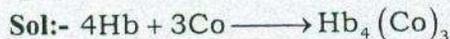
$$\therefore \% \text{ remained} = \frac{A_t}{A_o} \times 100 = 63.4\% \quad \text{Ans}$$

Q43:-

Sol:- $K = A e^{-E_a/RT}$

If E_a are same then at same temperature, value of $\frac{E_a}{RT}$ is same, but A can be different so, K can be different.

Q44:-



$$\text{Rate of reaction} = \frac{-1}{4} \frac{d[\text{Hb}]}{dt} = \frac{1}{4} \{ \text{Rate of diassfera of Hb} \}$$

$$\text{Let } -\frac{d(\text{Hb})}{at} = K'[\text{Hb}]^m[\text{Co}]^n$$

$$0.941 = K(3.36)^m(1.00)^n \longrightarrow (1)$$

$$1.88 = K'(6.72)^m(1.00)^n \longrightarrow (2)$$

$$(2) \div (1) \rightarrow 2 = (2)^m \rightarrow m = 1$$

$$5.65 = K'(6.75)^m(3.00)^n \longrightarrow (3)$$

$$(3) \div (2) \rightarrow \frac{5.64}{1.88} = 3 = 3^n \rightarrow n = 1$$

$$\therefore \frac{-d[\text{Hb}]}{dt} = K'[\text{Hb}][\text{Co}]$$

$$\therefore \text{Rate of reaction} = -\frac{1}{4} \frac{d[\text{Hb}]}{dt} = \frac{K'}{4} [\text{Hb}][\text{Co}] = K[\text{Hb}][\text{CO}]$$

$$(a) \therefore (1) \Rightarrow \frac{0.942}{4} = K(3.36)(1.00)$$

$$\Rightarrow K = 7 \times 10^{-2} \text{ } \frac{1}{\mu\text{mol. sec}} \quad \text{Ans}$$

$$(b) \text{Rate of reaction} = \frac{1}{4} \left\{ \frac{-d[\text{Hb}]}{dt} \right\} = K[\text{Hb}][\text{CO}]$$

$$= 7 \times 10^{-2} (1.5)(0.6) = 6.3 \times 10^{-2} \mu\text{mol/l. sec} \quad \text{Ans}$$

Q45:-

Sol:- 50% completed in 30 min at 27°C

$$t_{1/2} = 30 \text{ min} \Rightarrow K_1 = \frac{0.693}{30} \text{ min}^{-1} = 0.0231 \text{ min}^{-1}$$

$$t_{1/2} = 10 \text{ min at } 47^\circ\text{C} \Rightarrow K_2 = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$$

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

$$\log \left(\frac{0.0231}{0.0693} \right) = \frac{-E_a}{2.303R} \left(\frac{1}{300} - \frac{1}{320} \right)$$

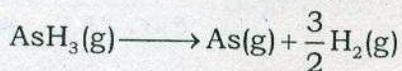
$$\log 3 \times 2.303R = E_a \left(\frac{20}{300 \times 620} \right)$$

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$$E_a = 4800 \times 2.303R \log 3 = 43.85 \text{ KJ} \quad \text{Ans}$$

Q46:-

Sol:-



Initially P_0 0 0

At $t = 5.5 \text{ h}$ $P_0 - x$ 0 $\frac{3}{2}x$

$$P_0 = 0.9654 \text{ atm}$$

$$\text{Also } P_0 - x + \frac{3}{2}x = P_0 + \frac{x}{2} = 1.06 \text{ atm}$$

$$\frac{x}{2} = 1.06 - 0.9654 = 0.0946 \text{ atm}$$

$$x = 0.1892 \text{ atm}$$

$$\therefore P_0 - x = 0.9654 - 0.1892 = 0.7762 \text{ atm}$$

$$\text{Now, } Kt = 2.303 \log \frac{P_0}{P_0 - x}$$

$$K = \frac{2.303}{5.5 \text{ hr}} \log \frac{0.9654}{0.7762} = 4 \times 10^{-2} \text{ hr}^{-1} \quad \text{Ans}$$

Q47:-

$$\text{Sol:- } \log K(\text{S}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T} K \quad (1)$$

Comparing with

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

$$\frac{E_a}{2.303R} = 1.25 \times 10^4$$

$$(a) E_a = 239.34 \text{ KJ} \quad \text{Ans}$$

$$(1) \log K = 14.34 - \frac{1.25 \times 10^4}{670} = 14.34 - 18.65 = -4.3167$$

$$K = 4.8 \times 10^{-5} \text{ s}^{-1} \quad \text{Ans}$$

Q48:-

Sol:-



Initially P_0 0 0 0

At (t) $P_0 - x$ x x x

$$A/q, P_0 - x + x + x + x = P \Rightarrow x = \frac{P - P_0}{2}$$

$$\therefore P_0 - x = \frac{P_0 - P_0 - P_0}{2} = \frac{3P_0 - P}{2}$$

$$\therefore Kt = 2.303 \log \frac{P_0}{P_0 - x} = 2.303 \log \frac{P_0}{\frac{3P_0 - P}{2}}$$

$$\Rightarrow K = \frac{2.303}{t} \log \frac{2P_0}{3P_0 - P} \quad \text{Ans}$$

Objective problems

Q1:Ans (b):- For single step process

Molecularity = order

\therefore For reaction $2A + B \rightarrow 2C$

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

Q2:Ans (c) overall order = sum of order w.r.t. individual reactants.

Q3: Ans (b) If is taken in excess constant, concentration of A doesn't change much as concentration of B changes & hence we can assume that by changing B, A remain almost same so rate of the reaction will be simply assumed to be of order 1 w.r.t. B.

Q4:Ans(d) molecularity is equal to no. of molecules taking part in single step reaction.

Q5: Ans(b) when volume is halved, pressure doubles, so rate of forward reaction becomes double to that of reverse one which are equal at the equilibrium.

Q6:Ans (b) When volume is doubled, pressure becomes half

$$\therefore \text{Rate}_f = K[\text{PNO}]_f^2 [\text{PO}_2]_f$$

$$\text{Rate}_f = K[\text{PNO}]_f^2 [\text{PO}_2]_f$$

$$= K \frac{[\text{PNO}]_i^2}{4} \frac{[\text{PO}_2]_i}{2} = \frac{1}{8} K[\text{PNO}]^2 [\text{PO}_2] = \frac{1}{8} \text{Rate}_i$$

Q7:Ans:(a) Rate of any reaction increases with temp, its equilibrium constant depends as ΔH

Q8:Ans: (d) On temp, K, depends only.

Q9:Ans: (a) $K = 1.6 \times 10^{-3} \text{ mol/lit} \cdot \text{min}$

$$\text{Unit of } K = \left(\frac{\text{mol}}{\text{lit}} \right)^{1-n} \text{ min}^{-1} = \left(\frac{\text{mole}}{\text{lit}} \right) \text{ min}^{-1}$$

$$1 - n = 0 \quad \Rightarrow n = 0$$

Q10:Ans(c) Rate K ; when concentration of all species is equal to 1

Q11:Ans (b), (d)

K depends on temp & E_a which is affected by a catalyst

Q12:Ans (b): $t_{1/2} = 69.3 \text{ sec}$ & $K = 10^{-2} = \frac{0.693}{09.3} = \frac{0.693}{t_{1/2}}$

\therefore So it is a first order reaction

Q13:Ans (a): $K = 1 \times 10^{-3} \text{ s}^{-1}$ (first order reaction, since unit is s^{-1})

Rate = $K[A] = 1 \times 10^3 \times 0.1 = 10^{-4}$

Q14:Ans (d)

$K = 2 \times 10^{-2} \text{ mole/lit-sec}$

At $t = 25 \text{ sec}$, concentration = 0.5 M

$A_t = A_0 - Kt$

$0.5 = A_0 - 2 \times 10^{-2} \times 25 \Rightarrow A_0 = 1\text{M}$

Q15:Ans (b)

$a_0 = 10\text{M}$

80% changed into product

$\therefore a_t = 10 - \frac{10 \times 80}{100} = 2\text{M}$

If $a_0' = 5\text{M}$, In the same time duration same percentage of initial concentration changes into products because in first order reaction is independent from initial concentration.

Q16:Ans(b): $\therefore t_{1/2}$ is independent from a.

Q17:Ans (a) For zeroth order reaction ; $x = x_0 - Kt$

Q18:Ans (b) \therefore 50% complete in $-t \text{ min}$

\therefore 75% complete in $-2t \text{ min}$ (for next 25%, it is just another $t_{1/2}$)

$\therefore 2t = 32 \quad t = 16 \text{ min} \quad \text{Ans}$

Q19:Ans (d) $t_{1/2} \times \frac{1}{(A)^{n-1}}$

A/q, $t_{1/2} \times [A] \Rightarrow 1 - n = 1 \Rightarrow n = 0$

Q20:Ans(c) $\log C_t = \log C_0 - \frac{Kt}{2.303}$ (for first order reac)

Q21:Ans (b) Because for first order $t_{1/2}$ is independent from initial concentration.

Q22: Ans (c) $A/q, t_{1/2} \propto \frac{1}{A}$ Also $t_{1/2} \propto \frac{1}{(A)^{n-1}}$

$$n-1=1 \Rightarrow n=2$$

Q23: Ans (c) $K = 8 \times 10^{-5} \text{ M}^{-1} \text{ min}^{-1}$

$$a_0 = 1\text{M}, a_t = 0.5\text{M}$$

$$\frac{1}{a_t} = \frac{1}{a_0} + Kt \text{ (for 2nd order reaction)}$$

$$\frac{1}{0.5} = \frac{1}{1} + 8 \times 10^{-5} t$$

$$t = \frac{2}{8 \times 10^{-5}} = \frac{1}{4} \times 10^5 \text{ min Ans}$$

Q24: Ans (c) Rate = $0.6932 \times 10^{-2} \text{ mole/lit} - \text{min} = K a_0 \text{ (1)}$

$$a_0 = 0.1\text{M}, t_{1/2} = \frac{0.693}{K} = \frac{0.693}{\frac{0.693 \times 10^2}{10^{-1}}}$$

$$= 10 \text{ min Ans}$$

Q25: Ans(a) In 20 min $-\frac{1}{2}$

after, 40 min - next 20 min $-\frac{1}{2} \times \frac{1}{2} = \frac{1}{4}$

Q26: Ans (a) As done before

$$t_{1/2} \times (A)^{1-n} \times (A) \text{ (According to question)}$$

$$\text{So } 1-n=1 \quad n=0$$

Q27: Ans (c) $t_{1/2} \times \frac{1}{a^{n-1}} \Rightarrow t_{1/2} a^{n-1} = \text{constant}$

According to question, $n-1=1 \quad n=2$.

Q28: Ans(b)

Q29: Ans (d) For endothermic reaction, Backward activation energy < 50 Kcal for exothermic reaction, forward activation energy > 50 Kcal so for a general reaction, E_a backward can be less the or greater than 50 kcal

Q30: Ans(b) $K = 3 \times 10^{-4} \text{ s}^{-1}$

$$E_a = 104.4 \text{ KJ/mole}$$

$$A = 6 \times 10^{15} \text{ s}^{-1}$$

$$\text{as } T \rightarrow \infty; \log K = \log A - \frac{2a}{2.303RT}$$

$$\log K = \log A$$

$$K = A = 6 \times 10^{14} \text{ s}^{-1} \quad \text{Ans}$$

Q31: Ans(b) order can be anything -ve fractional, 0 or +ve. Its maximum value is 3 But as we know between any two real no. infinite no are possible & since order can be fractional / any real no. so it has infinite values.

Q32: Ans (c) At $T \longrightarrow K$

$$T + 10 \longrightarrow 2K$$

$$T + 20 \longrightarrow 2^2 K = 4K$$

$$T + 30 \longrightarrow 2^3 K = 8K$$

At mid Temp ($T + 25$) it can be only mid way between 4 K & 8 K

If option C will not be there, we say (d), but it is not

Q33: Ans (d) Rate constant = $K \frac{\text{mol}}{\text{lit} \cdot \text{min}}$

Unit of K order of reaction = 0.

For zero order reaction

$$-\frac{1}{2} \frac{d[A]}{dt} = K[A]^0 \Rightarrow \int_{[A_0]}^{[A_t]} d[A] = -2K \int_0^t dt$$

$$[A_t] = [A_0] - 2Kt$$

$$\text{For } t = t_{1/2}, A_q = \frac{A_0}{2}$$

$$\frac{A_0}{2} = A_0 - 2K t_{1/2} \Rightarrow t_{1/2} = \frac{a_0}{4K} = \frac{a}{4K}$$

Q34:- Ans (b) $A \longrightarrow \text{Products}$

In this case again unit of $K = L/\text{mol} \cdot \text{min}$

Implies that order of reaction = 2

For 2nd order reac

$$\frac{1}{a_t} = \frac{1}{a} + Kt$$

$$\frac{2}{a} - \frac{1}{a} = K t_{1/2} \Rightarrow t_{1/2} = \frac{1}{ak}$$

Q35:-Ans (a) Clearly order should be half so that rate will increase two times as concentration will be increased by 4 time.

Q36:Ans (c) $\text{Rate}_f = K[A]^n$

$$\text{Rate}_f = K(2[A])^n = (2)^n K[A]^n = (2)^n \text{Rate}_i$$

$$7 \text{Rate}_i = (2)^n \text{Rate}_i$$

$$(2)^n = 7, \text{ So } n \text{ will be bet } 2 \text{ to } 3$$

Q37:Ans (d) order ≤ 3

$$\text{So } \text{Rate}_f \leq K(2[A])^3 \leq 8K[A]^3 = 8 \text{Rate}_i$$

So final rate will be maximum 8 times.

Q38:- Ans (b) $\text{Rate} = -\frac{1}{2} \frac{d(a-x)}{df} = -\frac{d\left(\frac{x}{2}\right)}{df} = K_2(a-x)^2$

(I) (II)

Integrating by taking (1), we have

$$\frac{-da}{d} = 2K_2 a_t^2 \Rightarrow \int \left(\frac{da_t}{a_t^2} \right) = \int -2K_2 dt$$

$$\frac{1}{a_t} = \frac{1}{a_o} + 2K_2 t$$

$$t = \frac{1}{2K_2} \left(\frac{1}{a_t} - \frac{1}{a_o} \right) = \frac{1}{2K_2} \left\{ \frac{1}{a-x} - \frac{1}{a} \right\} \Rightarrow t = \frac{1}{2K_2} - \left\{ \frac{x}{a(a-x)} \right\} \quad \text{Ans}$$

Q39:Ans (c) For zeroth order reaction:

$$At = A_o - Kt; \text{ After } 50\% \text{ completion, } At = \frac{A_o}{2}$$

$$A/q, \frac{A_o}{2} = A_o - K \times 10 \Rightarrow K = \frac{A_o}{20}$$

Now for 100% completion $At = 0$

$$0 = A_o - \frac{A_o}{20} \times t \Rightarrow t = 20 \text{ min}$$

Q40:Ans (c) $\frac{t_{3/4}}{t_{1/2}} = \frac{\frac{1}{2} \left\{ \frac{3/4 a}{a \times 1/4 a} \right\}}{\frac{1}{K} \times \frac{a/2}{a \times a/2}} = \frac{3/a}{1/a} = 3 : 1$

Q41:Ans (a) Since molecularity can never be zero, It is always 1, 2, 3, 4- - - (+ve integer)

Q42: Ans (a), (b)

$$a_t = a_0 - Kt \Rightarrow (a - x) = a - Kt$$

$$a - x = a - Kt$$

Q 43: Ans (a)

Q44: Ans (a) For $\alpha A + \beta B \longrightarrow \gamma C + \delta D$

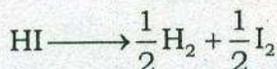
$$-\frac{1}{2} \frac{dA}{dt} = -\frac{1}{\beta} \frac{dB}{dt} = \frac{1}{\gamma} \frac{dC}{dt} = \frac{1}{\delta} \frac{dD}{dt}$$

hence similarly for $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$\frac{-d[N_2]}{dt} = \frac{-1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

Q45: Ans (b) For $2HI \longrightarrow H_2 + I_2$

$$\frac{-1}{2} \frac{d[HI]}{dt} = K[HI]^n \Rightarrow \frac{d[HI]}{dt} = 2K[HI]^n \quad (1)$$



$$\frac{-d[HI]}{dt} = 2K[HI]^n \text{ (from 1)}$$

↓

rate constant

Q46: Ans (c) $2A \longrightarrow \frac{1}{2} B$

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

Q47: Ans(a) In law of mass action, molecularity becomes equal to order, which is not possible in case of zeroth order reaction because molecularity can never be zero

Q48: -Ans(d) Rate = $K[A]^x$

Mol/lit-sec

$$\text{unit of } K = \frac{\text{mol/L} \cdot \text{sec}}{(\text{mol/L})^x} = (\text{mol/L})^{1-x} \text{ sec}^{-1}$$

Q49: -Ans (b) Catalyst decreases the activation energy but it remain +ve. So it can be only (2).

Q 50: Ans (c)