

### 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:-**  $A + B \rightarrow AB$

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

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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**Q4:-**

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

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

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'

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

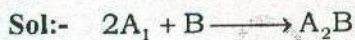
$$\therefore (1) \Rightarrow \frac{[A']^2}{10^{-6}} R_1 = \frac{[A']}{10^{-3}} R_2 = R_3$$

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

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

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

**Q5:-**



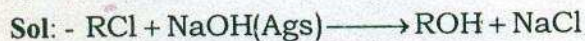
$$\text{Rate}_1 = K[A]^2[B]$$

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

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

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

**Q 6:**

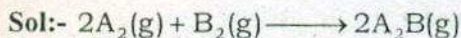


$$\text{Rate} = K_1[\text{RCl}]$$

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:-**



$$\text{At } t = 0 \quad 200 \quad 0 \quad 0$$

$$\text{At } t \rightarrow \infty \quad 200 - P \quad P \quad P$$

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:-**

<b>Sol:-</b> In zero order	In first order	In 2 <sup>nd</sup> order
$C_t = C_o - Kt$	$\log C_t = \frac{-K}{2.303} t + \log C_o$	$\frac{1}{C_t} = \frac{1}{C_o} + K_t$

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

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

$$C_o = 1 \text{ M}$$

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

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

$$1.2 = -2.303 \log C_t$$

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

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

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

**Q13:-**



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

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

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

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

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

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  $\text{H}^+$ , rate doesn't depend & so there will be no change in rate as conc of  $\text{H}^+$  changes

**Q15**



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

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



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

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

$$\frac{(A_o)^{1-n}}{1-n} - \frac{|A_t|^{1-n}}{1-n} = Kt$$

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

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

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

**Q16:-**

**Sol:-**  $A_o$  = initial count rate = 16.1 counts / min

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

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

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

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

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

**Q17:-**

<b>Sol:-</b>	<b>t(s)</b>	<b>P(mm of Hg)</b>	<b><math>\frac{1}{P}</math></b>	<b>Log P</b>
	0	348	$2.87 \times 10^{-3}$	2.54
	600	247	$2.87 \times 10^{-3}$	2.39
	1200	185	$5.41 \times 10^{-3}$	2.267
	2400	105	$9.524 \times 10^{-3}$	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

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

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

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

Q18:-

Sol:- For 2<sup>nd</sup> order reaction:-

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

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

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

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

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

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

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

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

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

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



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

**Q20:-**

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

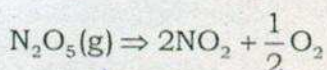
$$t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$$

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

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

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

$\therefore$  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  $\text{N}_2\text{O}_5$ .

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

$$0.10 = K(0.34)$$

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

**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 2<sup>nd</sup> 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 1<sup>st</sup> vessel

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

In 2<sup>nd</sup> 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 <sup>3</sup> R	(T+30)K

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

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

**Q3:-**

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            C<sup>2</sup>R

(T + 30) K           C<sup>3</sup>R

If T is increased by 20 K, Rate<sub>1</sub> = (2.3)<sup>2</sup>R

If T is increased by 30 K, Rate<sub>2</sub> = (2.3)<sup>3</sup>R

At intermediate temperature, temperature is increased by 25 K.

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

∴ Rate will be increased by 8.72 times

Q31:-

Sol:- For 2<sup>nd</sup> 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

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

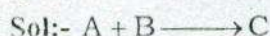
$$\frac{1}{40} = \frac{1}{100} + \frac{1}{400 \times 500} \times t$$



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

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

**Q32:-**



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

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

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

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

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

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

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

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

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

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

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

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

**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:-**



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

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

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

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

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

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

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

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

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

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



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

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

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

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

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

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

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

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

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

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

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

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

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

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

**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 2<sup>nd</sup> 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 = 6 hr

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

For time = 2 days =  $2 \times 24 \text{ hrs} = 48 \text{ hrs}$

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

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

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

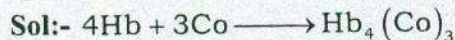
$$\therefore \% \text{ remained} = \frac{A_t}{A_o} \times 100 = 63.4\% \quad \text{Ans}$$

Q43:-

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

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

Q44:-



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

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

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



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

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

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

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

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

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

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

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

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

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

**Q45:-**

**Sol:-** 50% completed in 30 min at 27°C

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

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

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

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

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

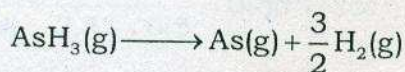
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$$E_a = 4800 \times 2.303R \log 3 = 43.85 \text{ KJ} \quad \text{Ans}$$



**Q46:-**

**Sol:-**



Initially  $P_o$                       0                      0

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

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

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

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

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

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

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

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

**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  $P_o$                       0                      0                      0

At (t)  $P_o - x$                       x                      x                      x

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



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

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

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

### 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

$$\therefore \text{Rate}_f = K[PNO]_f^2 [PO_2]_f$$

$$\text{Rate}_f = K[PNO]_f^2 [PO_2]_f$$

$$= K \frac{[PNO]_i^2}{4} \frac{[PO_2]_i}{2} = \frac{1}{8} K[PNO]_i^2 [PO_2]_i = \frac{1}{8} \text{Rate}_i$$

**Q7:Ans:(a)** Rate of any reaction increases with temp, its equilibrium constant depends as  $\Delta H$

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

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

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

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

**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):  $t_{1/2} = 69.3 \text{ sec} \& K = 10^{-2} = \frac{0.693}{0.693} = \frac{0.693}{t_{1/2}}$

$\therefore$  So it is a first order reaction

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

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 =  $0.5 \text{ M}$

$A_t = A_0 - Kt$

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

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% compete in  $-t \text{ min}$

$\therefore$  75% compete 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)  $K = 3 \times 10^{-4} \text{ s}^{-1}$

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



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

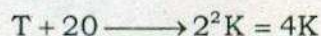
$$\text{as } T \rightarrow \infty; \log K = \log A - \frac{2a}{2.303 RT}$$

$$\log K = \log A$$

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

**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  $T \longrightarrow K$



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 =  $K \text{ mol/lit} - \text{min}$

Unit of K order of reaction = 0.

For zero order reaction

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

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

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

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

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

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

Implies that order of reaction = 2

For 2<sup>nd</sup> 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)**  $\text{Rate}_f = K[A]^n$

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

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

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

**Q37:Ans (d)** order  $\leq 3$

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

So final rate will be maximum 8 times.

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

(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:

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

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

Now for 100% completion  $A_t = 0$

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

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

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



**Q42:Ans (a), (b)**

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

$$a - x = a - Kt$$

**Q 43: Ans (a)**

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

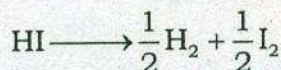
$$-\frac{1}{2} \frac{dA}{dt} = -\frac{1}{\beta} \frac{dB}{dt} = \frac{1}{\gamma} \frac{dC}{dt} = \frac{1}{\delta} \frac{dD}{dt}$$

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)**