Chapter 17: Chemical Kinetics

Q1:-

Sol: For 50% completion time required = 69.3 min

$$\therefore t_{1/2} = 69.\text{min}$$

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

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

For first order reaction –

$$Kt = 2.303\log\frac{Co}{Ct}$$

$$\Rightarrow t = \frac{2.303}{10^{-2}}\log\frac{10}{2} = 2.303\times10^{2}\log 5 \quad = 160.9\ \text{minutes}$$ **Ans**

Q2:-

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

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

$$A/q; \frac{Co}{Ct} = \frac{4}{1}$$

$$Kt = 2.303\log\frac{Co}{Ct}$$

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

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

Q3:-

Sol:- $A + B \rightarrow AB$

Rate of reaction $= 5\times10^{-5}\ \text{mole}/\text{lit}-\text{min}$

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

$$5\times10^{-5} = K[A][B] = K[0.05][0.01]$$

$$K = \frac{5\times10^{-5}\ \text{mol}/\text{L}-\text{min}}{5\times10^{-4}(\text{mol}/\text{l})^{2}} = 0.1(\text{mol}/\text{l})^{-1}\ \text{min}^{-1}$$

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For first order reaction –

$$Kt = 2.303 \log \frac{Co}{Ct}$$

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

Q2:-

Sol :- $t\tfrac{1}{2} = 500\,\text{sec}$

$$K = \frac{0.693}{t\tfrac{1}{2}} = \frac{0.693}{500} S^{-1}$$

$$A/q; \frac{Co}{Ct} = \frac{4}{1}$$

$$Kt = 2.303 \log \frac{Co}{Ct}$$

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

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

Q3:-

Sol:- $A + B \rightarrow AB$

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

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

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

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

Q4:-

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

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

Given: $K_1 = K_2 = K_3$

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

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

Now if conc are in mole/mL = A'

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

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

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

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

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

Q5:-

Sol:- $2A_1 + B \longrightarrow A_2B$

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

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

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

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

Q 6:

Sol: - $RCl + NaOH(Ags) \longrightarrow ROH + NaCl$

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

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:

Sol:- $2A_2(g) + B_2(g) \longrightarrow 2A_2B(g)$

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

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

$\therefore \text{Rate} = K\left[4\,{}^{A_2}\!/_{4}\right]^2 [B_2] = K[A_2]^2[B_2]$

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

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

So concentration of B_2 should be increased by 16 time.

Q8:-

Sol:- $2A + B + C \longrightarrow \text{Product}$

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:-

Sol:- $C_2H_5Br \xrightarrow{\Delta} C_2H_4 + HBr$

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 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

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

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

Fraction reaction unchanged $= \dfrac{190-100}{190} = \dfrac{90}{190} = 0.47$ **Ans**

Because only 190 mm of Hg press is present for decomposition

Q10:-

Sol:- In zero order | In firs order | In 2nd order

$C_t = Co - Kt$ | $\log Ct = \dfrac{-K}{2.303}t + \log Co$ | $\dfrac{1}{C_t} = \dfrac{1}{Co} + K_t$

At, t = 53 minutes

$C_t = 50 \,\&\, C_O = 100$

At t = 100 min

$C_t = (100-73) = 27 \,\&\, Co = 100$

Plotting logC 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, $\dfrac{C_O}{C_t} = \dfrac{100}{32.5}$

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

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

(ii) For 25 % decomposed, Co/Ct = 100/75

K.t = 2.303 log (100/75)

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

Q12:-

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

Time = 2 min = 2 × 60 sec

$C_O = 1M$

$$K.t = 2.303 \log \frac{Co}{Ct}$$

$$1 \times 10^{-2} \times 2 \times 60 = 2.303 \text{loh} \frac{C_O}{C_t}$$

$1.2 = -2.303 \log C_t$

$Ct = 10^{-0.52} = 0.3\ M$

$\therefore Ri = K[C_o] = 1\times10^{-2} mol/lit.sec$

$Rf = K[C_t] = 1\times10^{-2}\times0.3 = 3\times10^{-3}\ mole/lit.sec$ **Ans**

Q13:-

Sol:- $A + B \longrightarrow P$

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

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

When $[A] = [B] = 1$, $Rate = 1\times10^{-2} mole/lit-s$

$1\times10^{-2}\ {}^{mol}\!/_{lit-s} = K\times1\times1^2$

$K = 1\times10^{-1}\ {}^{mol}\!/_{lit-sec/(mol/lit)^3}$

When half of the reactant converts into product, then

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

$Rate = K[A][B]^2 = 1\times10^{-2}\times\frac{1}{20}\times\left(\frac{1}{2}\right)^2$

$= \frac{1}{80}\times10^{-2} mol/lit-sec = 1.25\times10^{-3} mol/lit.sec$ **Ans**

Q14:-

Sol:- $CH_3COOC_2H_5 + H_2O \xrightarrow{[H^+]} CH_3COOH + C_2H_5OH$

$$\frac{dx}{dt} = K[CH_3COOC_2H_5][H_2O]^o$$

(i) Rate is directly proportional to concentration of $[CH_3COOC_2H_5]$ & hence Rate doubles when concentration of easter doubles.

(ii) On concentration of H^+, rate doesn't depend & so there will no change in rate as conc of H^+ changes

Q15

Sol : $A \longrightarrow Product$

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

$$\int_{A=Ao}^{At}\frac{d[A]}{[A]^n} = \int_{t=O}^{t} -Kdl \quad \Rightarrow \quad \frac{A^{1-n}}{1-n}\Big|_{Ao}^{At} = -K(t-O)$$

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

For $t=t\frac{1}{2},\quad [A_t]=\frac{Ao}{2}$

$$\frac{(Ao)^{1-n}}{1-n}-\frac{|At|^{1-n}}{1-n}=Kt$$

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

$$t\frac{1}{2}=(Ao)^{1-n}\left\{\frac{1}{1-n}-\frac{1}{(1-n)(2)^{1-n}}\right\} \quad => t\frac{1}{2}=\frac{1}{[Ao]^{n-1}}\left\{\frac{1}{(1-n)}-\frac{1}{(1-n)(2)^{1-n}}\right\}$$

$t\frac{1}{2}\,\alpha\,\frac{1}{[Ao]^{n-1}}$ **Proved**

Q16:-

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

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

$t\frac{1}{2} = 5770\,\text{years}$

$$\therefore k=\frac{0.693}{t\frac{1}{2}}=\frac{0.693}{5770}Y^{-1}$$

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

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

$$Kt = 2.303 \log \frac{Po}{Pt}$$

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

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

Q18:-

Sol:- For 2nd order reaction:-

$$\frac{-d[A]}{dt} = K[A]^2 \qquad => \qquad \int_{[A_O]}^{[A]} \frac{d[A]}{[A]^2} = -\int_{t=O}^{t} Kdt$$

$$\left[\frac{-1}{A}\right]_{[Ao]}^{[At]} = -Kt \qquad => \qquad \frac{1}{[A_O]} - \frac{1}{A_t} = -Kt$$

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

$$\text{For } t = t\tfrac{1}{2}, \qquad [A_t] = \frac{[A_O]}{2}$$

$$\therefore (1) \Rightarrow \frac{2}{[A_O]} = \frac{1}{[A_O]} + Kt_{1/2} \qquad => \qquad t_{1/2} = \frac{1}{K[A_O]}$$

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

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

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

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

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

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

Q20:-

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

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

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

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

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

$\therefore$ order of reaction = 2.

$$N_2O_5(g) \Rightarrow 2NO_2 + \frac{1}{2}O_2$$

At $t = 1$ hr 24 ml

At $t \to \infty$ 35 ml

$\therefore$Fraction of $N_2O_5(g)$ decomposed in 1 hr $= \frac{24}{35} = 0.686$ **Ans**

Q22:-

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

$$\frac{-d[N_2O_5]}{dt} = K[N_2O_5]$$

$$0.10 = K(0.34)$$

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

Q23:-

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

From the give date,

Rate remain constant it [A] changes

$\therefore m = 0 \Rightarrow$ order w.r.t $A = 0$ **Ans**

Rate becomes half as the conc of [B] doubles

$n = -1$ order w.r.t $B = -1$ **Ans**

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

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

$P = {}^3\!/_2 \Rightarrow$ order w.r.t C $= {}^3\!/_2$ **Ans**

Q24:-

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

Rate $= K[A]^1[B]^2$

If [A] is doubled, Rate doubles

$\therefore R_2 = 2 \times 0.10 = 0.20M$ **Ans**

Q25:-

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

$\therefore Ea > +25KJ/mole$ Ans (c)

Q26:-

Sol:- $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

$t{}^1\!/_2 = 2.4\,hr$

$$K = \frac{0.693}{t{}^1\!/_2} = \frac{0.693}{2.4}$$

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

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

Q27:-

Sol:-

In first vessel	In 2nd vessel
$[A] = \frac{1}{V}$	$[A]\frac{2}{V}$
$[B] = \frac{2}{V}$	$[B] = \frac{1}{V}$

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

$$\text{Rate1} = K\left(\frac{1}{V}\right)\left(\frac{2}{V}\right) = \frac{2K}{V^2} \quad \therefore R_1 = R_2$$

$\text{Rate}_2 = K\left(2/_V\right)\left(1/_V\right) = 2K/_{V^2}$ ∴ 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:-

Sol:- $2A \longrightarrow A_2B$

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

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

$$[Bf] = \frac{[Bi]}{2}$$

$\therefore \text{Rate}_1 = K[Ai]^2[Bi]$

$$\text{Rate}_f = K\{[Af]\}^2[Bf] = K\{3[At]\}^2\frac{[Bi]}{2}$$

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

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^3R	**(T+30)K**

A/q, $C^3 = 15.6$

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

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	C^2R
(T + 30) K	C^3R

If T is increased by 20 K, $\text{Rate}_1 = (2.3)^2R$

If T is increased by 30 K, $\text{Rate}_2 = (2.3)^3R$

At intermediate temperature, temperature is increased by 25 K

$$\text{Rate} = \frac{\text{Rate}_1 + \text{Rate}_2}{2} = \frac{(2.3)^3R + (2.3)^2R}{2}$$

$$= \frac{5.29R + 12.167R}{2} = 8.72R$$

∴ Rate will be increased by 8.72 times

Q31:-

Sol:- For 2^{nd} order reaction

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

According to reaction ; [A] = [B]

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

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

A/q, $[A_t] = 100 - 20 = 80$ in t = 500 sec

(20% completion)

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

$$K \times 500 = \frac{1}{80} - \frac{1}{120} = \frac{10-8}{800} = \frac{1}{400}$$

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

If 60% completion

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

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

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

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

Q32:-

Sol:- $A + B \longrightarrow C$

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

n = order w.r.t B

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

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

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

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

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

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

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

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

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

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

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

Q33:-

Sol:- $A \longrightarrow B + C$

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

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

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

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:-

Sol:- $2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$

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

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

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

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

$\therefore$ Rate $= K[NOCl]^2$

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

Overall order of reaction = 2

Q36:-

Sol:- $2NOCl \longrightarrow 2NO + Cl_2$

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

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

Q36:-

Sol:- $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$$\text{Rate of reaction} = \frac{-1d[N_2O_5]}{2dt} = K[N_2O_5],\ K = 3.1 \times 10^{-4}\ \text{min}^{-1} \text{ at } 45^{\circ}C$$

(a) when $[N_2O_5] = 0.40M$

$\therefore$ Rate of decomposition =

$$\frac{-d[N_2O_5]}{dt} = 2K[N_2O_5] = 2 \times 3.1 \times 10^{-4} \times 0.40$$

$$= 2.48 \times 10^{-4} \text{ mole}/1-\text{min} \quad \textbf{Ans}$$

(b) $\dfrac{d[NO_2]}{dt}$ = Rate of formation of NO_2

We know that $\dfrac{-1}{2}\dfrac{d[N_2O_5]}{dt} = \dfrac{1}{4}\dfrac{d[NO_2]}{dt} = \dfrac{1}{1}\dfrac{d10}{dt}$

$$\frac{d[NO_2]}{dt} = \frac{-4}{2}\frac{d[N_2O_5]}{dt} = 2\left\{\frac{-d[N_2O_5]}{dt}\right\}$$

$$= 4K[N_2O_5]$$

$$= 4\times3.1\times10^{-4}\times0.40 = 4.96\times10^{-4}\ \text{M/min}$$

$$\frac{d[O_2]}{dt} = \frac{-1}{2}\frac{d[N_2O_5]}{dt} = K[N_2O_5]$$

$$= 3.1\times10^{-4}\times0.40 = 1.24\times10^{-4}\ \text{mole/lit}-\text{min}$$

(c) Rate of reaction $= \dfrac{-1}{2}\dfrac{d[N_2O_5]}{dt} = K[N_2O_5]$

$$= 3.1\times10^{-4}\times0.40 = 1.24\times10^{-4}\ \text{mole/lit}-\text{min}$$ **Ans**

Q37:-

Sol:- $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$

Since plot of in $[SO_2Cl_2]$ V& time is linear, so order of reaction is 1. Now for first order Reaction

$$Kt = 2.303\log\frac{[SO_2Cl_2]_o}{[SO_2Cl_2]_t}$$

$$K\times240 = 2.303\log\frac{0.4}{0.28}$$

$$K = \frac{0.35674}{240} = 1.487\times10^{-3}\ s^{-1}$$ **Ans**

Q38:-

Sol:- Ea = 45.0 KJ/mole

K = Rate constant without catalyst = $5.0\times10^{-4}\ s^{-1}$

K'= rate constant with catalyst = $2.0\times10^{-2}\ s^{-1}$

$$K = Ae^{-Ea/RT} \quad \& \quad K' = Ae^{-Ea'/RT}$$

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

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

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

$$Ea - Ea' = 2.303\times8.314\times10^{3}\times310\log\frac{2\times10}{5\times10^{-4}}$$

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

Q39:-

Sol:- Rate constant of disappearance of $H^+ = 1.0\times10^7 \text{ mol/l.s}$

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

For Zero order reaction

$$At = A_o - Kt$$

$$O = \frac{3\times10^{-6}}{0.05\times10^{-3}} - 1\times10^7 t$$

$$t = \frac{3\times10^{-6}}{0.5\times10^{-4}} / 1\times10^7 = \frac{6\times10^{-2}}{10^7}$$

$t = 6\times10^{-9}$ sec **Ans**

Q40:-

Sol:- For 2^{nd} order reaction

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

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

Integerating (1) we have

$$\frac{1}{At} = \frac{1}{Ao} + 2Kt$$

$$Ao = 4\times10^{-3}M$$

$$At = Ao - x = 4\times10^{-3} - 1.5\times10^{-3} = 2.5\times10^{-3}M$$

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

$$\frac{1}{2.5\times10^{-3}} = \frac{1}{4\times10^{-3}} + 2(0.81)\times t$$

$$t = \frac{10^3}{2\times0.81}\left(\frac{1}{2.5} - \frac{1}{4}\right) = \frac{1.5\times10^2}{2\times0.81} = \frac{185.2\,\text{sec}}{2} = 92.6\text{Sec}$$ **Ans**

Q41:-

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

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

$K = 2.42 \,{}^{L}\!/_{mol.s}$ & $[Ao] = 0.5\,{}^{mole}\!/_{L}$

At $t = t^1\!/_2$, $[At] = \frac{[Ao]}{2}$

$$t\tfrac{1}{2} = \frac{1}{K[Ao]} = \frac{1}{2.42 \times 0.5} = 0.8264\,\text{sec} \qquad \textbf{Ans}$$

Q42:-

Sol:- $t\tfrac{1}{2}$ for $Tc-99 = 6hr$

$t\tfrac{1}{2}$ for $Th-201 = 73\,hr$

For time $= 2$ days $= 2 \times 24$ hrs $= 48$ hrs

For Tc-99

$$At = Ao\left(\frac{1}{2}\right)^{t/t\frac{1}{2}}$$

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

$$\therefore \%\,\text{remained} = \frac{At}{Ao} \times 100 = \frac{2}{256} \times 100 = 0.39\% \qquad \textbf{Ans}$$

For Th -201

$$At = Ao\left(\frac{1}{2}\right)^{t/t\frac{1}{2}}$$

$$\frac{A't}{A'o} = \left(\frac{1}{2}\right)^{\frac{48}{73}} = 0.634$$

$$\therefore \%\,\text{remained} = \frac{A't}{A'o} \times 100 = 63.4\% \qquad \textbf{Ans}$$

Q43:-

Sol:- $K = Ae^{-Fo/RT}$

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

Q44:-

Sol:- $4Hb + 3Co \longrightarrow Hb_4(Co)_3$

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

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

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

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

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

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

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

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

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

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

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

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

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

Q45:-

Sol:- 50% completed in 30 min at 27^0C

$$t\tfrac{1}{2} = 30\,\text{min} \Rightarrow K_1 = \frac{0.693}{30}\,\text{min}^{-1} = 0.0231\,\text{min}^{-1}$$

$$t\tfrac{1}{2} = 10\,\text{min at } 47^0C \Rightarrow K_2 = \frac{0.693}{10} = 0.0693\,\text{min}^{-1}$$

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

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

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

$$16$$

$$Ea = 4800 \times 2.303R\log 3 = 43.85\ \text{KJ}$$ **Ans**

Q46:-

Sol:- $AsH_3(g) \longrightarrow As(g) + \frac{3}{2}H_2(g)$

Initially **Po** **o** **o**

At t = 5.5 h **Po – x** **o** $\frac{3}{2}x$

$Po = 0.9654$ atm

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

$x/2 = 1.06 - 0.9654 = 0.0946$ atm

$X = 0.1892$ atm

$\therefore Po - x = 0.9654 - 0.1892 = 0.7762$ atm

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

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

Q47:-

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

Companing with

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

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

(a) $Ea = 239.34$ KJ **Ans**

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

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

Q48:-

Sol:- $A \longrightarrow B + C + D$

Initially **Po** **0** **0** **0**

At (t) **Po – x** **x** **x** **x**

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

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

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

$$\Rightarrow \quad K = \frac{2.303}{t} \log \frac{2Po}{3Po - P} \qquad \textbf{Ans}$$

Objective problems

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

Molecularity = order

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

$$Rate = K[A]^2[B]$$

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

$$\therefore Rate_f = K[PNo]^2{}_f[Po_2]_f$$

$$Rate_f = K[PNo]_f{}^2[Po_2]_f$$

$$= K\frac{[P_{NO}]_i^2}{4}\frac{[Po_2]_i}{2} = \frac{1}{8}K[P_{NO}]^2[Po_2] = \frac{1}{8}Rate_i$$

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) $K = 1.6\times10^{-3}\ {}^{mol}\!/_{1-min}$

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

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

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

Q11:Ans (b), (d)

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

Q12:Ans (b): $t\tfrac{1}{2} = 69.3\,\text{sec} \;\&\; K = 10^{-2} = \dfrac{0.693}{09.3} = \dfrac{0.693}{t\tfrac{1}{2}}$

$\therefore$ So it is a first order reaction

Q13:Ans (a): $K = 1\times10^{-3}\,s^{-1}$ (first order reaction, since unit is s^{-1})

$\text{Rate} = K[A] = 1\times10^{3}\times0.1 = 10^{-4}$

Q14:Ans (d)

$K = 2\times10^{-2}\,\text{mole}/\text{lit}-\text{sec}$

At t = 25 sec, concentration = 0.5 M

$At = Ao - Kt$

$0.5 = Ao - 2\times10^{-2}\times25 \;\Rightarrow Ao = 1M$

Q15:Ans (b)

$a_O = 10\,M$

80% changed into product

$\therefore\; a_t = 10 - \dfrac{10\times80}{100} = 2\,M$

If $a_O{}' = 5M$, 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): $\therefore\; t\tfrac{1}{2}$ is independent from a.

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

Q18:Ans (b) $\therefore$ 50% compete in – t min

$\therefore$ 75% compete in – 2t min (for next 25%, it is just another $t\tfrac{1}{2}$)

$\therefore 2t = 32 \quad t = 16$ min **Ans**

Q19:Ans (d) $t\tfrac{1}{2}\times\dfrac{1}{(A)^{n-1}}$

A/q, $t\tfrac{1}{2}\times[A] \;\Rightarrow 1-n=1 \;\Rightarrow n=O$

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

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

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

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

Q23: Ans (c) $K = 8\times10^{-5}\ M^{-1}\ min^{-1}$

$a_o = 1M,\ a_t = 0.5M$

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

$\frac{1}{0.5} = \frac{1}{1} + 8\times10^{-5}t$

$t = \frac{2}{8\times10^{-5}} = \frac{1}{4}\times10^{5}$ min **Ans**

Q24: Ans (c) Rate $= 0.6932\times10^{-2}$ mole/lit − min = Kao (1)

$a_o = 0.1M,\quad t/\tfrac{1}{2} = \frac{0.693}{K} = \frac{0.693}{\frac{0.693\times10^{2}}{10^{-1}}}$

= 10 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

$t\frac{1}{2}\times(A)^{1-n}\times(A)$ (According to question)

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

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

According to question, n–1 = 1 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, Ea backward can be less the or greater than 50 kcal

Q30:Ans(b) $K = 3\times10^{-4}\ s^{-1}$

$Ea = 104.4\ KJ/mole$

$$A = 6\times10^{15}\ s^{-1}$$

as $T\to\infty$; $\log K = \log A - \dfrac{2a}{2.303RT}$

log K= log A

$K = A = 6\times10^{14}\ s^{-1}$ **Ans**

Q31: Ans(b) order can be anything –ve fractional, O 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 $T\xrightarrow{\quad}K$

$T+10\xrightarrow{\quad}2K$

$T+20\xrightarrow{\quad}2^2K = 4K$

$T+30\xrightarrow{\quad}2^3K = 8K$

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

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

Q33:Ans (d) Rate constant = K $\text{mol}/_{\text{lit}-\text{min}}$

Unit of K order of reaction = O.

For zero order reaction

$$-\frac{1}{2}\frac{d[A]}{dt} = K[A]^O \quad => \int_{[A_O]}^{[A_t]} d[A] = -2K\int_{t=O}^{t} dt$$

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

For $t = t^1/_2,\ Aq = Ao/_2$

$$\frac{A_O}{2} = A_O - 2K\,t^1/_2 \Rightarrow t^1/_2 = \frac{a_O}{4K} = \frac{a}{4K}$$

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

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

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

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

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

$(2)^n = 7$, So n will be bet 2 to 3

Q37:Ans (d) order ≤ 3

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

So final rate will be maximum 8 times.

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

Integating by taking (1), we have

$$\frac{-da}{d} = 2K_2a_t^{\,2} \quad => \int\left(\frac{da_1}{at^2}\right) = \int -2K_2dt$$

$$\frac{1}{a_t} = \frac{1}{a_O} + 2K_2t$$

$$t = \frac{1}{2k_2}\left(\frac{1}{a_t} - \frac{1}{a_O}\right) = \frac{1}{2K_2}\left\{\frac{1}{a-x} - \frac{1}{a}\right\} \quad => t = \frac{1}{2K_2} - \left\{\frac{x}{a(a-x)}\right\} \quad \textbf{Ans}$$

Q39:Ans (c) For zeroth order reaction:

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

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

Now for 100% completion At = O

$$O = Ao - \frac{Ao}{20} \times t \quad \Rightarrow t = 20 \min$$

Q40:Ans (c) $\dfrac{t\,{}^{3}\!/\!{}_{4}}{t\,{}^{1}\!/\!{}_{2}} = \dfrac{\frac{1}{2}\left\{\dfrac{{}^{3}\!/\!{}_{4}\ a}{a \times {}^{1}\!/\!{}_{4}\ a}\right\}}{\frac{1}{K} \times \dfrac{{}^{a}\!/\!{}_{2}}{a \times {}^{a}\!/\!{}_{2}}} = \dfrac{{}^{3}\!/\!{}_{a}}{{}^{1}\!/\!{}_{a}} = 3 : 1$

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 $\times A + \beta B \longrightarrow \gamma C + \delta D$

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

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

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

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

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

$$HI \longrightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2$$

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

$$\downarrow$$

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

Mol/lit-sec

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

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

Q 50: Ans (c)