TOPIC : CHEMICAL KINETICS

EXERCISE # 1

Section (A)

1. $x A + yB \longrightarrow z C$

$$\frac{-d}{dt}[A] = \frac{-d}{dt}[B] = 1.5\frac{-d}{dt} \longrightarrow [C]$$

$$\Rightarrow \quad \frac{-1}{3}\frac{-d}{dt}[A] = \frac{-1}{3}\frac{-d}{dt}[B] = \frac{1}{2}\frac{-d}{dt}[C]$$

$x = 3$ $y = 3$ $z = 2$

2. $$\frac{1}{2}\frac{d[c]}{dt} = -\frac{1}{3}\frac{d[D]}{dt} = \frac{1}{A}\frac{d[A]}{dt} = \frac{-d[B]}{dt}$$

B & Dwill be same side and A & C will be same state ratio of stoichiometric coefficient
B:D: A : C = 1 : 3 : 4 : 2.

5. $3A \rightarrow 2B,\ \frac{-1}{2}\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

6. $A + 2B \longrightarrow 3C + D$

$$\frac{-d[A]}{dt} = \frac{-1}{2}\frac{d[B]}{dt} = \frac{+1}{3}\frac{d[c]}{dt} = \frac{+d[D]}{dt}$$

7. $x A \longrightarrow Y B$

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

$$\Rightarrow \quad \frac{-d}{dt}[A] = \frac{x}{y}\frac{d}{dt}[B]$$

$$\log\left(\frac{-\ d[A]}{dt}\right) = \log\left(\frac{x}{y}\right)\left(\frac{+\ d[B]}{dt}\right)$$

$$\Rightarrow \quad \log[A]\frac{-d}{dt} = \log\frac{d}{dt}[B] + \log\left(\frac{x}{y}\right)$$

$$\log\left(\frac{x}{y}\right) = \log 2$$

$$\Rightarrow \quad \frac{x}{y} = \frac{2}{1}$$

$\Rightarrow \quad x : y \quad 2 : 1$

10. $$\frac{d[P]}{dt} = \frac{15-5}{20-0} = 0.5\ MS^{-1}$$

11. $\frac{d}{dt}[SO_3]$ = 100 gram / min = $\frac{100}{80}$ mole / min = 1.25 mole/min.

$$\frac{-1}{2}\frac{d}{dt}[SO_2] = \frac{-d}{dt}[O_2] = \frac{1}{2}\frac{d}{dt}[SO_3]$$

$\frac{-d}{dt}[O_2] = \frac{1.25}{2}$ mole/min = $\frac{1.25}{2} \times 32$ gram/min = 20 gram/min

12.

Rate law for :	Ist order	IInd order	IIIrd order
	Rate = $K[A]^1$	$R_2 = K[A]^2$	$R_3 = K[A]^3$

than we can say [A] = 1 $r_1 = r_2 = r_3$ [A] < 1 then $r_1 > r_2 > r_3$

[A] > 1 then $r_3 > r_2 > r_1$

Section (B)

1. R k $[A]^a [B]^b$

acc. to data, a = 2 , $b = \frac{1}{2}$

$2A + \frac{1}{2} B \rightarrow$ Product $-\frac{1}{4}\frac{d[A]}{dt} = \frac{-d[B]}{dt}$

2. Order of reaction is experimentally determined.

3. Overall order = sum of individual orders.

4.✍ Overall order = $\frac{1}{2} + \frac{1}{3} + \frac{1}{4} = \frac{13}{12}$.

5. Rate of reaction is independent of concentration of reactant for zero order reaction.

6. R K [A] [B]

Order wrt. A = 1 & above wr.t B = 1

K depends an temperature

7.✍ $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$

$$\frac{-1}{2}\frac{d[\times 10]}{dt} = -\frac{1}{2}\frac{d[H_2]}{dt} = \frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt} = \text{Rate}$$

$$k_1 = \frac{k}{2} = \frac{k_1'}{2} = \frac{k_1''}{2}.$$

9. A + B Products

$R = k [A]^2 [B]^3$

$R' = R.2^2 [A]^2 2^3 [B]^3 = 2^5 R = 32R$

10. $R = k [A]^m [B]^n$

$2R = k\, 2^m [A]^m [B]^n$ $2R = k\, 2 [A]^m 2^n [B]^n$

m = 1 n = 0.

Section (C)

1. Unit of k is L $mol^{-1} sec^{-1}$

so order is 2.

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

$\Rightarrow$ $t = \frac{2.303}{K} [\log C_O - \log C_t]$

$\frac{K\ \ t}{2.303} = \log C_O - \log C_t$

$\Rightarrow$ $C_t = \left(\frac{-\ K}{2.303}\right) t + \log C_O$

So, slope = $\left(\frac{-\ K}{2.303}\right)$

3. Amount decayed = a – (a / 8) = 7a / 8

4.✍ According to graph given it would be zero order reaction so rate independent of time.

5.✍ $N_2O_5 \rightarrow 2NO_2 + \frac{1}{2} O_2$

$R = K [N_2O_5]$

$R = 6.2 \times 10^{-4}\ S^{-1} \times 1.25$ mole $L^{-1} = 7.75 \times 10^{-4}$ mole 2^{-1} Se^{-1}

6. As per unit, zero orde reaction

Co – Ct = KT

Co– 0.5 = 2× 10^{-2} × 25

Co = 1.0 m

7. log(a–x) vs time t is straight line

log(a –x) = kt (k & k' are some constants)

ln(a –x) = K't

$\frac{1}{a-x} \times -\frac{-dx}{dt} = K.$ (on defferenciating) $\frac{-dx}{dt} = K\,(a-x)'$ shows a first order reaction.

8. Equal amount of Rxn completed in equal time property as zero order Rxn, and unit as Rate constant mole $Litre^{-1}$ sec^{-1}

9. $t_1 = 2 \times t_{1/2}$; $t_2 = t_{1/2}$

10. Unit of rate constant is $(time)^{-1}$. Hence first order reaction.

Time required to change concentration 1 M to 0.25 M = $2 \times t_{1/2} = 2 \times \frac{\ln 2}{k}$ = 20 min.

11. $C_t = Co\ kt \Rightarrow \underline{kt = co.ct}$

$\underline{kt\ \ 75\% = 0.75co}$. f $\underline{kt\ \ 50\% = 0.5co}$

$\Rightarrow \quad \frac{t75\%}{t50\%} = \frac{75}{50} = 1.5.$

12.✍ A + B $\longrightarrow$ product

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

$r_1 = K [1]^1 [1]^2 = 1 \times 10^{-2}$ $(K = 1 \times 10^{-2})$

$r_1 = K \left[\frac{1}{2}\right] \left[\frac{1}{2}\right]^2 = 1 \times 10^{-2} \times \frac{1}{8} = 1.25 \times 10^{-3}$

13. Reaction is zero order (unit of k)

[B] = 2 × moles of A reacted

[B] = 2 × kt = 0.2 mol lit^{-1}.

14.✍ $C_t = C_0\, e^{-Kt}$

According to question

$C_{A,\,t} = C_{B,\,t}$

$C_A\, e^{-K_A t} = C_B\, e^{-K_B t}$

$\frac{C_A}{C_B} = \frac{e^{-K_B t}}{e^{-K_A t}}$

$\Rightarrow \quad \frac{C_A}{C_B} = e^{(K_A - K_B)t}$

$\Rightarrow \quad 4 = e^{\left[\frac{\ln 2}{5} - \frac{\ln 2}{15}\right] \times t}$

$\ln 4 = \left[\frac{\ln 2}{5} - \frac{\ln 2}{15}\right] t$

$$\Rightarrow \quad \ln(2)^2 = \left[\frac{\ln 2}{5} - \frac{\ln 2}{15}\right] t$$

$$2\ln 2 = \left[\frac{\ln 2}{5} - \frac{\ln 2}{15}\right] t$$

$$\Rightarrow \quad 2 = \left[\frac{1}{5} - \frac{1}{15}\right] t$$

$$2 = \frac{2}{15} \times t$$

$\Rightarrow$ t = 15 minute.

15.✍ $t_{1/2}$ = 10No. of Half life = $\frac{60}{10}$ = 6 half life $\quad C_t = \frac{C_O}{(2)^n} = \frac{C_O}{(2)^6} = \left(\frac{C_O}{64}\right)$

16. $\frac{1}{C_t} = \frac{1}{C_0} + Kt.$

$\frac{1}{0.04} = \frac{1}{0.2} + 0.002 \times t. \quad \Rightarrow \quad 25 = 5 + 0.002 \times t \quad \Rightarrow \quad t = \frac{20}{2\times10^{-3}} = 10{,}000$ sec.

17.✍ It is properties of Ist order Rxn and other all are properties of IInd order.

Section (D)

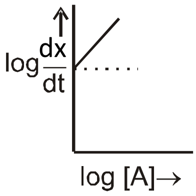
1.✍ $A + B \rightarrow C$

$R = k\,[A]^m[B]^n$

compere exp. (1) & (2)

$\frac{0.1}{0.8} = \left(\frac{1}{2}\right)^n \Rightarrow m = 3$ compere exp. (2) & (4) $\Rightarrow \quad \frac{0.8}{0.8} = \left(\frac{1}{2}\right)^n$ n = 0 so. $R = K[A]^3$

3. $\frac{dx}{dt} = K[A]^2$



$\log \frac{dx}{dt} = 2\log[A] + \log k$. Compare with y = m × + c graph obtained

4. $A \xrightarrow{\quad} \text{Product}$

a

a – x

Since equal interval of time equal conc. decreased then reaction zero order

$$\text{Rate} = \frac{\Delta A}{\Delta t} = \frac{20-12}{20} = \frac{8}{20} = 0.4$$

7.✍ $A(s) \xrightarrow{\quad} 2B(g) + C(g)$

$K = \frac{1}{t}\ln\left(\frac{P_\infty - P_0}{P_\infty - P_t}\right) \quad P_0 = 0 \quad P_t = 150 \quad P_\infty = 225$

$$\frac{1}{20}\ln\left[\frac{225}{225-150}\right]$$

$$\Rightarrow \quad \frac{1}{20}\ln\left(\frac{225}{75}\right) = 0.05 \ln 3$$

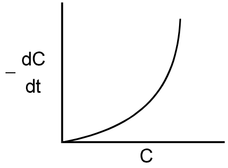
$$\frac{1}{20}\ln\left(\frac{225}{75}\right) = \frac{1}{20}\ln\left(\frac{225}{225\times P_{40}}\right)$$

$\Rightarrow \quad \left(\frac{225}{75}\right)^2 = \frac{225}{225 \times P_{40}}$

$\frac{225}{75 \times 75} = \frac{1}{225 - P_{40}}$

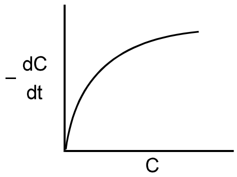
$\Rightarrow \quad P_{40} = 200$

8. dt is parb parabolic graph of $y = x^2$



So This the graph of second order

$y^2 = x \qquad y = (x)\ \frac{1}{2}$



$\frac{-dc}{dt} = K\ [C]^{\frac{1}{2}}$ So reaction is $\left(\frac{1}{2}\right)$ order.

Section (E)

1. $2\,A\,(g) \longrightarrow 3\,B\,(g) + C\,(g)$

t = 0 $\quad P^0 \quad 0 \quad 0$

t = 3 hour $\quad (P^0 - x) \quad \frac{3\ x}{2} \quad \left(\frac{x}{2}\right)$

$(P^0 + x) = 2\,P^0$

$x = P^0$

Reaction is completed in limited time so reaction is zero order reaction.

2. $A \longrightarrow 2\,B + C$

t = 0 $\quad P_0 \quad 0 \quad 0 \qquad P_0$

t = t $\quad (P_O - x) \quad 2x \quad x \qquad P_0 + 2x = 176$

$0 \quad 2\,P_0 \quad P_0 \qquad 3\,P_0 = 270 \qquad P_0 = 90$

$2\,x = 176 - 90 = 86$

$x = 43$

Pressure of A after 10 minute = 90 – 43 = 47

3. $A \rightarrow B + C +$

t = 0 $\quad$ Po

$t = t_1 \quad P_0 - x$

4.

Initial pressure	65	105	y	185
Half life	290	x	670	820

Initial pressure of gas a Initial moles of gas in above question.
Half life a Initial pressure
So, it must be zero order reaction

$$t_{1/2} = \frac{C_O}{2k} = \frac{P_O}{2k} \quad 290 = \frac{65}{2\,k} \quad \Rightarrow \quad x = \frac{105\times2\times290}{2\times65} = 468 \text{ sec}$$

5. $NH_4NO_2\,(aq) \xrightarrow{\quad} N_2\,(g) + 2H_2O\,(\ell)$

$$K = \frac{2.303}{t}\log\left(\frac{V_\infty - V_O}{V_\infty - V_t}\right) \quad \Rightarrow \quad V_0 = 0 \quad \Rightarrow \quad K = \frac{2.303}{20}\log\left(\frac{70-0}{70-40}\right)$$

$$= \frac{2.303}{20}\log\left(\frac{70}{30}\right) \quad \Rightarrow \quad K = \frac{2.303}{1200}\log\frac{7}{3}\,.$$

Section (F)

1. Rate of reaction increases as temp increases.

2. Rate increases as temperature increases.

4. $K = A \times e^{-\,Ea/RT} = A \times e^{-\,Ea/R\,\times\,\infty} = A = 6.0 \times 10^{14}\ s^{-1.}$

7. $\Delta H = Ea_t - Ea_b \quad -20 = 60 - Ea_b$ so Ea_b = so .

9. $k = \frac{1}{t}\ln\left(\frac{a}{a-x}\right) \quad \Rightarrow V_\infty \propto a \quad \Rightarrow V_t \propto x \quad \Rightarrow \left(\frac{a}{a-x}\right) = \left(\frac{V_\infty}{V_\infty - V_t}\right)$

10. $\log k = 15.0 - \frac{10^6}{T}$

compair this relation with $\log k = \log A - \frac{E}{2.303RT}$

we find $A = 10^{15}$. $E = 1.9 \times 10^4$ KJ

11. $\Delta H = E_f - E_b \qquad -40 = 80 - E_b \qquad E_b = 120$ kJ/mole,
catalyst lower the E_f To 20 kJ/ mole for forward Rxn then $E_f' = 20$ kJ/mol
we know catalyst decreases the Activation energy equal amount in both direction
$E_b' = (120 - 60) = 60$ kj/mol

$$\frac{E_b}{E'_b} = \frac{120}{60} = 2.0$$

12. Now $\ln k = \ln A - \frac{E_a}{R} \times \frac{1}{T} \quad \Rightarrow \quad \text{Slope} = -\frac{E_a}{R} = \frac{-8.3\times10^3}{8.3} = \mathbf{1000}$

Section (G)

1. Maleculerity defined for one step reactions only.

2. Slowesr step is rate determining step.

3. $A + B \xrightarrow{\text{Slow}} C + D$

$A + B \xrightarrow{\text{fast}}$
R = k [A] [B] (slow step rate is determining step)

4. Slow step is
$A + B \rightarrow C + D$ (slow). Hence $r = k[A][B]$

5.✍ Since (A) is the intermediate reactive species whose concentration is determined from equilibrium step.
Slow step is :

$A + B_2 \longrightarrow AB + B$ (slow)

$r = k[A][B_2]$

From equilibrium step

$A_2 \rightleftharpoons A + A$ (fast)

$$k_{eq} = \frac{[A]^2}{[A_2]} \qquad \therefore\ [A] = (k_{eq}[A_2])^{1/2}$$

Substitute the value of [A] in equation (i),

$$r = k.k_{eq}{}^{1/2}[A_2]^{1/2}[B_2] \qquad \text{Thus, order of reaction} = \frac{1}{2} + 1 = 1\frac{1}{2}$$

7. For Rxn rate determining step is slowest step
Then in 1st mechanism

$$\text{Rate} = k\,[NO_2]\,[O_3] \qquad .....(i)$$

But in 2nd mechanism

$$O_3 \underset{k_b}{\overset{k_a\ \text{fast}}{\rightleftharpoons}} O_2 + [O] \qquad ....(1)$$

$$NO_2 + O \xrightarrow{\text{slow}} NO_3 \qquad ....(2)$$

$$NO_3 + NO_2 \xrightarrow{\text{fast}} N_2O_5 \qquad ....(3)$$

Then for Rxn (1)

$$\frac{k_a}{k_b} = \frac{[O_2]\ [O]}{[O_3]} = k_{eq} \qquad ....(4)$$

by Rxn (2)

$$\text{Rate} = k\,[NO_2]\,[O] \qquad ....(ii)$$

put value of [O] from (4) to (ii)

$$\text{Rate} = k\,\frac{k_{eq}[O_3]}{[O_2]} \times [NO_2] \qquad \Rightarrow \qquad \text{Rate} = \frac{k_1\ [NO_2]\ [O_3]}{[O_2]}$$

Section (H)

1.✍ $$\%\text{ of B} = \frac{k_1 \times 100}{k_1 + k_2} = \frac{1.26 \times 10^{-4} \times 100}{12.6 \times 10^{-5} + 3 \times 10^{-5}} = 76.83\%.$$

$$\%\text{ of C} = \frac{k_2 \times 100}{k_1 + k_2} = \frac{3 \times 10^{-5} \times 100}{12.6 \times 10^{-5} + 3 \times 10^{-5}} = 23.18\%.$$

Exercise # 2

1.✍ Total time for drop to dissapear $(a_o - a_t) = kt$ $a_t = 0$

$$\frac{3.0 \times 10^{-6}}{(0.05 \times 10^{-3}) \times 1.0 \times 10^{7}} = t_{100\%} \quad \Rightarrow \quad t_{100\%} = 6 \times 10^{-9}\ \text{sec}$$

2. $$K = \frac{2.303}{10} \log\left(\frac{50}{50 - 10}\right) = \frac{2.303}{10} \log 1.25\ \text{min}^{-1}$$

3. Rate constant depends on temperature.

4. Unit of K is mole L^{-1} Sc^{-1}
So order is 0.

5. $A + B \longrightarrow$ product

$r = K\,[A]^1\,[B]^2$

$r_1 = K\,[1]^1\ [1]^2 = 1 \times 10^{-2} \qquad (K = 1 \times 10^{-2})$

$$r_1 = K\left[\frac{1}{2}\right]\left[\frac{1}{2}\right] = 1 \times 10^{-2} \times \frac{1}{8} = 1.25 \times 10^{-3}$$

6. Suppose A_t

We know $(A_0 - A_t) = kt$ for zeroth order

$(0.50 - A_t) = 0.025 \times t$

$0.50 - A_t = 0.025 \times 15$

$A_t = 0.125$ M

7.✍ As given, it is an elementary reaction.

8. As $t_{50\%}$ is constant. Hence order of reaction is 1.

$t_{50\%} = \frac{0.693}{K} \Rightarrow n = 1,\ t_{1/2} = \frac{0.693}{K}$

9. $K = \frac{1}{t}\left[\ln\frac{a}{a-x}\right) = \frac{2.303}{t}\log\frac{a}{a-x}$

$K = \frac{2.303}{20}\log\frac{1}{0.25} = \frac{2.303}{20}\log\frac{4}{1} = 0.0693\ \text{min}^{-1}$

10.✍ by graph we can say $\log t_{1/2} = \log a$ $t_{1/2} = a$ .....(1)

$t_{1/2} \propto a$ for zero order Rxn $k \times t_{1/2} = \frac{a}{2}$ .....(2)

then $k = \frac{1}{2}$

11. $k = \frac{1}{t}\ \text{en}\ \frac{a}{a-x} = \frac{1}{1.308 \times 5600}\ \text{en}\ \frac{9}{0.25a} = 2.77 \times 10^{-4}\ \text{sec}^{-1}$.

12.

	A (g)	$\longrightarrow$ B (g)	+ C(g)	+ D(g)
Initially	P_i	0	0	0
At time t	$(P_i - P_x)$	P_x	P_x	P_x

total pressure at time t = $(P_i + 2P_x) = P_t$

So $P_x =$

K = log = log.

13. $K = Ae^{-E/RT}$

14. $K_1 = A_1e^{-E_1/RT}$ and $K_2 = A_2e^{-E_2/RT}$

$\frac{K_1}{K_2} = \frac{A_1}{A_2} = e^{(E_2-E_1)/RT}$; A_1 and A_2 are not given.

15. For reaction, $A \longrightarrow B$.

$E_a = 10$ kJ/mole , $\Delta H = 5$ kJ/mole

Rxn endothermic because ΔH (+)

$\Delta H = E_a - E_b$

$5 = 10 - E_b$

$E_{ab} = 10 - 5 = 5$ kJ/mole. Then [B].

16. Clearly, $t_{1/2} \propto a^{1-n}$

18.✍ Rate = $K[X][Y_2]$

$K_{eq} = \frac{[X]^2}{[X_2]} \Rightarrow [X] = \sqrt{K_{eq}} \times [X_2]^{1/2}$

Rate = $K \times \sqrt{K_{eq}}\ [X_2]^{1/2}[Y_2]$ So the order of overall reaction is 1.5

19. $H_2(g) + 2ICl(g) \longrightarrow 2HCl(g) + I_2(g)$

Proposed mechanism

Mechanism ५ $H_2(g) + ICl(g) \xrightarrow{\text{slow}} HCl(g) + HI(g)$

21. Half life is not depend upon initial concentration.

22. $C_3 = \frac{C_0}{2^3} = \frac{C_0}{8} \Rightarrow \quad \frac{C_3}{C_0} = \frac{1}{8}$

23. Since 0.01 M of X changes to 0.0025 M in 40 minutes, $t_{1/2}$ of reaction = 40/2 = 20 minutes Rate of reaction of $r = k[X] = \frac{0.693}{t_{1/2}} \times [X] = \frac{0.693}{20} \times 0.01 = 3.47 \times 10^{-4}$ M min^{-1}.

24. From Arrhenius equation

$$K = Ae^{-Ea/RT}$$

$$\ell nk = \ell nA - \frac{Ea}{RT}$$

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

$$\log K = \frac{-Ea}{2.303 \ \ R} \times \frac{1}{T} + \log A \qquad \text{....... (1)}$$

$$\log K = -(2000)\frac{1}{T} + 6 \qquad \text{........(2)}$$

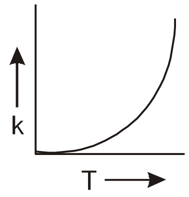
On comparing equation (1) and (2)

$$\frac{-Ea}{2.303 \ \ R} = -2000.$$

Ea = 2.303 × 8.314 × 2000 = 38.29 kJ and log A = 6 $A = 10^6$

25. $k = Ae^{-Ea/RT}$

So, variation will be



26. $M \longrightarrow N$

$r = K[M]^x$

as [M] is doubled, rate increases by a factor of 8.

i.e. $8r = K[2M]^x \quad \Rightarrow \quad 8 = (2)^x$

$x = 3$

EXERCISE # 3

PART - I

1. $-\frac{1}{5} = \frac{d[Br^-]}{dt} + \frac{1}{3}\frac{d[Br_2]}{dt}$ or $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

2. $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$-\frac{-d[N_2O_5]}{dt} = k \, . \, [N_2O_5] \quad \Rightarrow \quad 1.02 \times 10^{-4} = 3.4 \times 10^{-5} \, s^{-1} \times [N_2O_5]$

$[N_2O_5] = \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3$

3. For reaction,

$3A \longrightarrow 2B$

$\text{Rate} = -\frac{1}{3}\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt} \quad \therefore \quad +\frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$

4. For reaction $3A \longrightarrow B + C$

If it is zero order reaction, then the rate remains same at any concentration of 'A' or $\frac{dx}{dt} = k\,[A^0]$. It means that rate is independant on concentration of reactants.

5. Rate constant of first order reaction

$$k = \frac{2.303}{t}\log_{10}\frac{(A)_0}{(A)_t}$$

or $k = \frac{2.303}{1} \times \log_{10}\frac{0.8}{0.2}$ ... (1)

(because 0.6 mole of B is formed)

Suppose t_1 hour are required for changing the concentration of A from 0.9 mole to 0.675 mole of B.

Remaining mole of A = 0.9 – 0.675 = 0.225

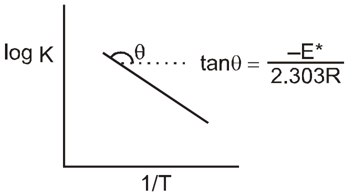
$\therefore\ k = \frac{2.203}{t_1}\log_{10}\frac{0.9}{0.225}$ ... (2)

From Eqs (i) and (ii)

$$\frac{2.303}{1}\log_{10}\frac{0.8}{0.2} = \frac{2.303}{t_1}\log_{10}\frac{0.9}{0.225} \Rightarrow 2.303\log_{10}4 = \frac{2.303}{t}\log_{10}4$$

$t_1 = 1$ h

6. Arrhenius equation $k = Ae^{-E^*/RT}$



$\ln k = \ln A - \frac{E^*}{RT}$ or $\log k = \log A - \frac{E^*}{2.303RT}$

Hence, E is calculated with the help of following slope.

7. rate of reaction is equal to the rate constant for zero order reaction.

Let us consider the following hypothetic change.

$A \rightarrow B + C$

suppose this reaction is zero order, then rate $[A]^0$ $\therefore$ rate = $\left(\frac{dx}{dt}\right)k\,[A]^0 = k$

8. For the first order reaction rate = k [A]

[A] – concentration of reactant k = rate constant

Given that $\frac{dx}{dt} = 1.5 \times 10^{-2}$ mol L^{-1} min^{-1}

k = ? and [A] = 0.5 M

$\therefore$ 1.5 ´ $10^{-2} = k \times 0.5$ $\therefore\ k = \frac{1.5\times10^{-2}}{0.5} = 3 \times 10^{-2}$ min^{-1}

For first order reaction half-life period, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3\times10^{-2}} = 23.1$ min

9. $t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{\left(\frac{2\times10^{-5}}{0.01}\right)} = \frac{693}{2} = 347$ s

10. $A + B \longrightarrow$ product

Rate, $r \propto [A]^x[Y]^y$ .... (i)

The rate decrease by a factor 4 if the concentration of reactant 'B' is doubled

$\frac{r}{4} \propto [A]^x[2B]^y$ .... (ii)

From eqs. (i) and (ii)

$$4 = \left(\frac{1}{2}\right)^y \quad y = -2$$

Hence, order of reaction wrt B is –2

11. For the reaction $2A + B \rightarrow 3C + D$

The reaction rate is written as follows

The reaction rate wrt A = $-\frac{1}{2}\frac{d[A]}{dt}$

The reaction rate wrt B = $-\frac{d[B]}{dt}$

The reaction rate wrt C = $+\frac{1}{3}\frac{d[C]}{dt}$

The reaction rate wrt D = $\frac{d[D]}{dt}$

Hence, the answer (1) is not correct expression to represent the rate of the reaction.

12. For the reaction,

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

The rate of reaction wrt $N_2 = -\frac{d[N_2]}{dt}$

The rate of reaction wrt $H_2 = -\frac{1}{3}\frac{d[H_2]}{dt}$

The rate of reaction wrt $NH_3 = +\frac{1}{2}\frac{d[NH_3]}{dt}$

Hence, at a fixed time

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

or $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

or $-\frac{2d[N_2]}{dt}$

13. $k = \frac{1}{60}\ln\left(\frac{100}{40}\right)$, $t_{50\%} = \frac{1}{k}\ln 2 = \frac{\ln 2}{\ln 2.5}\ 60 = \frac{60 \times 0.3010}{2 \times 0.7 - 1}$

$t_{50\%} = \frac{60 \times 0.3}{0.4}$ = 45 min [log2 = 0.3 log 2.5 = log 25 –log10 = 0.4]

14. $t_{\frac{1}{2}} = \frac{1}{k}\ln\left(\frac{100}{100-50}\right) = \frac{\ln 2}{k}$

15. $10^{16}\, e^{-2000/T} = 10^{15} e^{-1000/T} \Rightarrow 10 = e^{1000/T} \Rightarrow T = \frac{1000}{2.303}$

16. Specific rate constant, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386} = 0.5 \times 10^{-3}\ s^{-1}$

17. For the reaction,

$A + B \rightarrow$ Products

on doubling the initial concentration of A only the rate of the reaction is also doubled, therefore

Rate $\propto [A]^1$ ...(i)

Let initial rate law is

Rate $k[A][B]^y$ ...(ii)

If concentration of A and B both are doubled, the rate gets changed by a factor of 8

$8 \times \text{rate} = k\,[2A]\,[2B]^y$ ...(iii)
$[\therefore \text{Rate } [A]^1]$

Dividing Eq. (iii) by eq. (ii)
$8 = 2 \times 2^y$
$4 = 2^y$
$y = 2$
Hence, rate law is, rate = $k\,[A][B]^2$

18. For the reaction,

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$\text{Rate} = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt} \quad \text{or} \quad -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

$$-\frac{d[H_2]}{dt} = \frac{3}{2} \times 2 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1} = 3 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

19. Order of the Reaction may be zero, whole No. or fraction number.

20. $\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

21.

[A]	[B]	Rate
x	y	R_1
x	2y	$2R_1$
2x	2y	$8R_1$

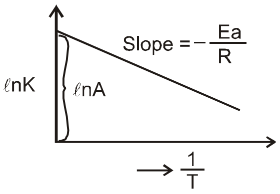
That means order of reaction with respect to B is 1 and w.r.t A is 2. Hence, Rate = $k[A]^2\,[B]^1$

22. $\frac{r_{100°C}}{r_{10°C}} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512$

23. $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \Rightarrow \log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{293} - \frac{1}{308}\right]$

$0.3 = \frac{E_a}{2.303 \times 8.314} \times \frac{15}{293 \times 308}$ = 34673 J mole^{-1} = 34.7 kJ mole^{-1}

24.



$K = A\,e^{-Ea/RT}$

$\ell n\,K = \ell n\,A - \frac{Ea}{RT}\,\ell n_e e \quad \Rightarrow \quad \ell n\,K = \ell n\,A - \frac{Ea}{R} \times \frac{1}{T}$

25. $t_{½} = \frac{0.6932}{k}$

Half life of first order reaction is independent on initial conc. of reactant.

26. $\frac{r_2}{r_1} = \frac{C_2}{C_1}$ (for first order reaction)

$$k = \frac{1}{t_2 - t_1}\ell n\frac{C_2}{C_1} = \frac{1}{t_2 - t_1}\ell n\frac{r_2}{r_1}$$

$$k = \frac{1}{20 - 10}\ell n\frac{0.04}{0.03} = \frac{1}{10}\ell n\frac{4}{3}$$

$$t_{1/2} = \frac{\ell n2}{k} = \frac{\ell n2}{\ell n4/3} \times 10 = \frac{2.3 \times 0.3}{2.3(0.6 - 0.477)} \times 10 = 24.4\ \text{sec.}$$

27. $PH_3 \xrightarrow{W} P + \frac{3}{2}H_2$

Rate = $k[PH_3]$.

It is independent of the surface coverage because zero order reaction depend on surface area covered by reactant.

28. $K = 10^{-2} \quad = \frac{0.693}{t_{1/2}}$

So, $t_{1/2} = \frac{0.693}{10^{-2}} = 69.3$ sec.

Two half lives are required for the reduction of 20g of reactant into 5g.

So, time required = 2 x 69.3 = 138.6 sec

29.

	1st order	2nd order
Rate	rate = $K[A]^1$	rate = $K[A]^2$
Half life	$T_{\frac{1}{2}} = \frac{\ell n2}{K}$	$T_{\frac{1}{2}} = \frac{1}{KC_0}$

As $T_{\frac{1}{2}}$ of 1st order reaction does not depends on C_0 while. $T_{\frac{1}{2}}$ of 2nd order reaction depends on C_0.

30. For zero order reaction

$T_{\frac{1}{2}} = \frac{C_0}{2K}$ so $T_{\frac{1}{2}} \, \alpha \, C_0$

On doubling initial concentration $T_{\frac{1}{2}}$ is double

31. **The 1st order reaction**

$$t = \frac{2.303}{k}\log\frac{a}{a-x} = \frac{2.303}{k}\log\frac{100}{100-99} = \frac{2.303}{k}\log 10^2 = \frac{2.303}{k}\times 2\times\log 10$$

$$\frac{2.303\times 2}{k} = \frac{4.606}{k}$$

32. $K = 2.303 \times 10^{-3}$

Time required for Ist order reaction :-

$t = \frac{2.303}{K}\log\frac{a}{a-x}$ value of k = 2.305×10^{-3} sec. = $10^3 \times 0.602$

t = 602 sec.

33. Activation energy $E_a = 0$

$T_1 = 200$ K $K_1 = 1.6 \times 10^{-6}$

$T_2 = 400$ K $K_2 = ?$

$$\log \frac{k_2}{k_1} = \frac{eq}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \Rightarrow \quad \log \frac{k_2}{k_1} = 0 \quad \Rightarrow \quad \frac{k_2}{1.6 \times 10^{-6}} = 1$$

$k_2 = 1.6 \times 10^{-6}\ S^{-1}$

PART - II

1. Reactions which involve absorption of heat energy are called endothermic reactions. For such reactions

$$\Sigma H_P > \Sigma H_R$$

In graph (3) and (4) the heat of products is more than heat of reactants

$\therefore$ They represents endothermic reaction. But in (4) only small amount of energy is absorbed (less difference between energy of reactants and products). Thus, (3) represent maximum activation energy.

2. $aA \rightarrow xP$

rate $\propto [A]^a = \dfrac{[A]_1^a}{[A_2]^a}$ k $[A]^a$

Initially $[A]_1 = 2.2$ mM $r_1 = 2.4$ mM/s

If $[A]_2 = = 1.1$ mM $r_2 = 0.6$ mM/s

We have

$\dfrac{r_1}{r_2} = \dfrac{[A]_1^a}{[A]_2^{\ a}}$ (a is the order) $\Rightarrow$ $\dfrac{r_1}{r_2} = \dfrac{(2.2)^a}{(1.1)^a}$ or $= \dfrac{2.4}{0.6}$ $(2)^a$

$4 = 2^a$ $\Rightarrow$ $2^2 = 2^a$ or $a = 2$. The reaction is of second order.

3. $t_{1/2} \propto a^{1-n}$

for $n = 3$ $t_{1/2} \propto \frac{1}{a^2}$

Graph (4) represent graph between $t_{1/2}$ and initial concentration for 3rd order reaction :

(1) Zero order reaction (2) 1st order reaction (3) 2nd order reaction

4. $2N_2O_5 \longrightarrow 4NO_2 + O_2$

rate of reaction is :

$$\frac{1}{2}\frac{d\ [N_2O_5]}{dt} = \frac{1}{4}\frac{d\ [NO_2]}{dt}$$

So, rate of disappearance of N_2O_5 is represented either by $-\dfrac{1}{2}\dfrac{d\ [N_2O_5]}{dt}$ or by .

5. Mole of $N_2O_5 = \dfrac{10.8}{108} = 0.1$ and, $n = \dfrac{9.6}{2.4} = 4$ here n = numbers of half-life.

$N_2O_5 \longrightarrow 2NO_2 + \dfrac{1}{2}\ O_2$ $\therefore N_t = 0.1 \times \left(\dfrac{1}{2}\right)^n$

Moles of N_2O_5 left $= \dfrac{0.1}{16}$

Moles of N_2O_5 changed to product $= \left(0.1 - \dfrac{0.1}{16}\right) = \dfrac{1.5}{16}$ mol

Moles of O_2 formed $= \dfrac{1.5}{16} \times \dfrac{1}{2} = \dfrac{1.5}{32}$

Volume of oxygen $= \dfrac{1.5}{32} \times 22.4 = 1.05$ L

6. $k = Ae^{-E_a/RT}$

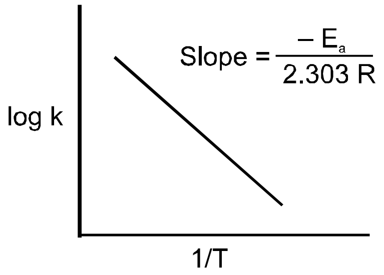
$$\log k = \log A - \frac{E_a}{2.303\ \ RT}$$

Comparing this equation with straight line

y = mx + c

y = log k and x = $\frac{1}{T}$

$\therefore$ E_a is calculated with the help of slope by plotting the curve between log k and $\frac{1}{T}$.



7. It is an experimentally determined value and depends upon the concentration change of reactant. It changes with pressure, temperature and concentration and it can have the fractional value.

8. $3BrO^- \longrightarrow BrO_3^- + 2Br^-$

$$\text{Rate} = -\frac{d\ \ [BrO^-]}{3dt} = +\frac{d\ \ [BrO_3^-]}{dt} = +\frac{[Br^-]}{2\ \ dt}$$

or $$\frac{k_1\ \ [BrO^-]^2}{3} = k_2\ [BrO^-]^2 = \frac{k_3[BrO^-]^2}{2}$$

or $k_1 = 3k_2 = 1.5\ k_3$

$3BrO^- \longrightarrow BrO_3^- + 2Br^-$

10. For a first-order reaction, the rate expression is log{$[A]_t$ M} – log {$[A]_0$M} = – {kt/ 2.303}.

Thus, the plot of log {$[A]_t$ / M} versus t is linear with a negative slope $\left(-\frac{k}{2.303}\right)$ and non zero intercept.

11. $$\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2}$$

As E_a increases, rate of increase in k also increases so k_1 will increase faster than k_2 but always will remain less than k_2.

12. $A_{(g)} \longrightarrow \mathbf{2B_{(B)} + C_{(g)}}$

Initial : P_0 0 0

$P_0 – P$ 2P P

Total pressure at time (t) = $P_0 - P + 2P + P = P_1 \Rightarrow P_t = P_0 + 2P$

$$P_t - P_0 = 2P \Rightarrow P = \frac{P_t - P_0}{2} \qquad \Rightarrow \qquad k = \frac{2.303}{t}\ \log\left[\frac{P_0}{P_0 - P}\right] = \frac{2.303}{t}\log\left[\frac{P_0}{P_0 - \left(\frac{P_t - P_0}{2}\right)}\right]$$

$$= \frac{2.303}{t}\ \log\left[\frac{2P_0}{2P_0 - P_t + P_0}\right] = \frac{2.303}{t}\log\left[\frac{2P_0}{3P_0 - P_t}\right]$$

13. Two different reactions can have same rate of reaction. Rate of reaction depends upon many factors like nature and concentration of reactants, temperature, catalyst, energy factors, orientation factor, etc.

14. Let the rate law be $r = k\ [A]^x\ [B]^y$

Divide (3) by (1) $\frac{0.10}{0.10} = \frac{[0.024]^x[0.035]^y}{[0.012]^x[0.035]^y}$ $\therefore$ $1 = [2]^x$, x = 0

Divide (2) by (3) $\frac{0.80}{0.10} = \frac{[0.24]^x[0.070]^y}{[0.024]^x[0.035]^y}$ $\therefore$ $8 = (2)^y$, $y = 3$

Hence, rate equation, $R = k[A]^0\,[B]^3 = k[B]^3$

15. According to Arrhenius equation, $k = Ae^{-ERT}$

When $E_a = 0$, $k = A$.

16.

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

$$= \frac{2.303}{6}\log\frac{0.5}{0.05} = 0.384\,\text{min.}$$

23. For zero order

$A = A_0 - kt$

$$t_{\frac{1}{2}} = \frac{A_0}{2k} \quad \Rightarrow \quad t_{\frac{1}{4}} = \frac{A_0}{4k} \quad \Rightarrow \quad \frac{t_{\frac{1}{2}}}{t_{\frac{1}{4}}} = \frac{2}{1}$$

24.

$$\frac{r_A}{r_B} = \frac{A_1e^{-E_A/RT}}{A_2e^{-E_B/RT}} \quad \Rightarrow \quad \frac{2}{1} = \frac{e^{-E_A/RT}}{e^{-E_B/RT}}$$

$\ln 2 = E_B - E_A / RT$

$E_B - E_A = RT\ell n2$

$E_A - E_B = -RT\ell n2$

25.

$$\frac{t}{t^{\frac{1}{2}}} = \frac{\ell n\frac{C_0}{t_t}}{\ell n\,2} \qquad \frac{60}{t^{\frac{1}{2}}} = \frac{\log\frac{100}{20}}{\log 2}$$

26. In presence of catalyst :

$$\log\frac{k_2}{k_1} = \log\frac{A_2}{A_1} + \frac{Ea_2 - Ea_1}{2.3\,RT} \quad \Rightarrow \quad \text{Log } 1 = \log\frac{A_2}{A_1} - \frac{2RT}{2.3RT}\;\ell n\frac{A_2}{A_1} = 2$$

27. For first order reaction :

$$\log\frac{r_2}{r_1} = -k\log\frac{t_2}{t_1} \quad \Rightarrow \quad \log\frac{0.04}{0.4} = -k\log\frac{30}{10} \quad \Rightarrow \quad t_{\frac{1}{2}} = \frac{\ell n2}{k} = 6\text{ min.}$$

28.

$$\log\frac{K_A}{K_B} = \frac{E_A - E_B}{2.3\,RT} = \frac{5.75\times1000}{2.3\times8.31\times300} = 1 \quad \frac{K_A}{K_B} = 10$$

29.

$$\frac{0.4}{12.8} = \left(\frac{1}{2}\right)^n \quad = n = 5$$

$$\therefore\ t = 5\,t_{\frac{1}{2}} \quad = 5 \times 138\text{ s} \quad = 690\text{ s.}$$

PART - III

1. Generally, molecularity of simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation. Thus, a reaction involving two different reactants can never be unimolecular.

2. Given rate = $k\,[CO]^2$

Thus, according to the rate law expression doubling the concentration of CO increases the rate by a factor of 4.

3. $NO(g) + Br_2(g) \rightleftharpoons NOBr_2(g)$

$NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$ [rate determining step]

Rate of the reaction (r) = $k\,[NOBr_2]\,[NO]$

where $[NOBr_2] = K_c\,[NO]\,[Br_2]$

$r = k.\,K_C.\,[NO]\,[Br_2]\,[NO]$

$r = k'\,[NO]^2\,[Br_2]$.

The order of the reaction with respect to NO(g) = 2.

4. $\Delta H_R = E_f - E_b = 180 - 200 = -20\ \text{kJ mol}^{-1}$

The correct answer for this question should be -20kJ mol^{-1}. But no option given is correct. Hence we can ignore sign and select option

5. Let A be the activity for safe working.

Given $A_o = 10$ A   Ao × No and A × N

$$t = \frac{2.303}{\lambda}\log\frac{N_o}{N} = \frac{2.303}{\lambda}\log\frac{A_o}{A}$$

$$= \frac{2.303}{\frac{0.693}{30}}\log\frac{10A}{A} = \frac{2.303\times 30}{0.693}\log 10 = \frac{2.303\times 30}{0.693} = 99.69 \text{ days} \approx 100 \text{ days.}$$

6. $$\frac{1}{2}A \longrightarrow 2B \quad \Rightarrow \quad -\frac{1}{1/2}\frac{d(A)}{dt} = \frac{1}{2}\frac{d(B)}{dt}$$

$$\boxed{-\frac{d(A)}{dt} = \frac{1}{4}\frac{d(B)}{dt}}$$

7. In first order reaction for X% complation

$$k = \frac{2.303}{t}\log\left(\frac{100}{100 - x\%}\right) \quad \Rightarrow \quad \frac{0.693}{t_{1/2}} = \frac{2.303}{t}\log\left(\frac{100}{100-99}\right) = \frac{0.693}{6.93} = \frac{2.303\times 2}{t}$$

So, t = 46.06 min.

8. $A \longrightarrow$ product

For zero order reaction

$t_{1/2} \propto \frac{1}{a^{n-1}}$ a = initial concentration of reactant

$t_{1/2} \propto a$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_1}{a_2}\ ;\ \frac{1}{(t_{1/2})_2} = \frac{2}{0.50} \quad \Rightarrow \quad t_{1/2} = \frac{0.5}{2} = 0.25\text{ h.}$$

9. Mechanism (1) rate = $K\,[Cl_2]\,[H_2S]$

Mechanism (2) rate = $K_1\,[Cl_2]\,[HS^-]$

$$K_{eq} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$[HS^-] = \frac{K_{eq}[H_2S]}{[H^+]} = K_1K_{eq}\frac{[Cl_2][H_2S]}{[H^+]}$$ ∴ Mechanism (1) is consistent with this rate equation.

10. $$\frac{\text{Rate at } 50^\circ C}{\text{Rate at } T_1\ ^\circ C} = (2)^{\frac{\Delta T}{T_1}} = (2)^{\frac{50}{10}} = 2^5 = 32 \text{ times}$$

11. $K_1 = A_1e^{-Ea_1/RT}$

$K_2 = A_2e^{-Ea_2/RT}$

$$\frac{K_1}{K_2} = \frac{A_1}{A_2}e^{(E_{a_2} - E_{a_1})/RT}$$

$K_1 = K_2A \times e^{E_{a_1}/RT}$

12. $$K = \frac{1}{40}\ln\frac{0.1}{0.025} = \frac{1}{40}\ln 4$$

$$R = K[A]^1 = \frac{1}{40}\ln 4(.01) = \frac{2\ln 2}{40}(.01) = 3.47 \times 10^{-4}$$

13. $$\log\frac{K_2}{K_1} = \frac{-E_a}{2.030R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\frac{K_2}{K_1} = 2$; $T_2 = 310$ K $\quad T_1 = 300$ K

$\Rightarrow \log 2 = \frac{-E_a}{2.303 \times 8.134}\left(\frac{1}{310} - \frac{1}{300}\right) \Rightarrow E_a = 53598.6$ J/mol = 53.6 KJ/mol **Ans is (1)**

14. $1.2 \times 10^{-3} = K\,(0.1)^x\,(0.1)^y$
$1.2 \times 10^{-3} = K\,(0.1)^x\,(0.2)^y$
$2.4 \times 10^{-3} = K\,(0.2)^x\,(0.1)^y$
$R = K\,[A]^1\,[B]^0$

15. Higher order (> 3) reactions are rare due to low probability of simultaneous collision of all the reacting species.

16. In 50 minutes, concentration of H_2O_2 becomes $\frac{1}{4}$ of initial.

$\Rightarrow \quad 2 \times t_{1/2} = 50$ minutes $\quad \Rightarrow \quad t_{1/2} = 25$ minutes $\quad \Rightarrow \quad K = \frac{0.693}{25}$ per minute

$r_{H_2O_2} = \frac{0.693}{25} \times 0.05 = 1.386 \times 10^{-3}$

$2H_2O_2 \rightarrow 2H_2O + O_2$

$r_{O_2} = \frac{1}{2} \times r_{H_2O_2} \quad \Rightarrow \quad r_{O_2} = 0.693 \times 10^{-3}$

$r_{O_2} = 6.93 \times 10^{-4}$ mol/minute × litre

17. $k_1 = Ae^{-Ea_1/RT}$

$k_2 = Ae^{-(Ea_1-10)/RT} \quad \Rightarrow \quad \text{Ln}\left(\frac{k_2}{k_1}\right) = \frac{10}{RT} = \frac{10}{8.314 \times 10^{-3} \times 300} = 4$

18. Rate = K (pressure)^n
$R_1 = K(P_1)^n$
$R_2 = K(P_2)^n$

$\frac{R_1}{R_2} = \left[\frac{P_1}{P_2}\right]^n \quad \Rightarrow \quad P_1 = 363 - \frac{363 \times 5}{100} = 344.85$, $P_2 = 363 - \frac{363 \times 33}{100} = 243.21 \Rightarrow \frac{1}{0.5} = \left(\frac{344.85}{243.21}\right)^n$

$2 = (\sqrt{2})^n \quad \Rightarrow \quad (n = 2)$

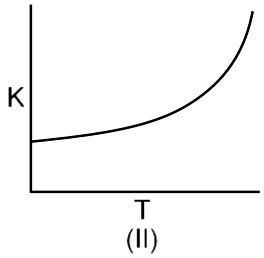
19. $R = k[A]^x\,[B]^y$
$6.93 \times 10^{-3} = k\,(0.1)^x\,(0.2)^y$ (i)
$6.93 \times 10^{-3} = k\,(0.1)^x\,(0.25)^y$ (ii)
$1.386 \times 10^{-2} = k\,(0.2)^x\,(0.3)^y$ (iii)
$\Rightarrow y = 0$ (from (i) & (ii))
$x = 1$ (from (i) & (iii))
$\Rightarrow$ First order wrt A $\quad \Rightarrow 6.93 \times 10^{-3} = k\,(0.1)$
$\Rightarrow k = 6.93 \times 10^{-2}\ \text{min}^{-1} \Rightarrow t_{1/2} = \frac{\ell n2}{k} = \frac{0.693}{6.93 \times 10^{-2}} = 10$

20. $2A + B \longrightarrow$ products
$r = K[A]^x\,[B]^y$
$0.3 = K[A]^x\,[B]^y$ ….(1)
$2.4 = K[2A]^x\,[2B]^y$ ….(2)
$\frac{(2)}{(1)}$
$8 = 2^x \times 2^y$
or $8 = 2^{x+y} \Rightarrow x + y = 3$
$x = 1 \quad \therefore y = 2$

21. $k = Ae^{-E_a/RT}$

k decreases exponentially with E_a

$\therefore$ First graph is correct.



(II)

But temperature is given in °C So, $k \neq 0$ at 0°C.

$\therefore$ For temperature between 0°C and 300°C, graph will come like (II)

22. $\frac{d[A]}{dt} = 2k_1[A_2] - 2\,k_{-1}\,[A]^2$

23. Slope of ℓnk v/s $\frac{1}{RT} = -y = -E_a$

$\therefore E_a = y$

24. $t_{\frac{1}{2}} = \frac{C_0}{2k} \Rightarrow 6 = \frac{0.2}{2k} \Rightarrow k = \frac{1}{60}$

Now, $C_t = C_0 - Rk$

$0.2 = 0.5 - \frac{1}{60} \times t$

$0.3 = \frac{t}{60} \Rightarrow t = 18\text{hrs}$

25. According to unit of rate constant it is a zero order reaction then half life of reaction will be

$t_{1/2} = \frac{C_0}{2k} = \frac{5\mu g}{2 \times 0.05\mu g/\text{year}}$ = 50 years

26. $\ell nk = \ell nA - \frac{Ea}{RT} = \ell nA - \frac{4606}{T}$ $\left[\therefore \frac{E_A}{R} = 4606\right]$

$\ell n\left(\frac{k}{10^{-5}}\right) = \left(\frac{E_a}{R}\right) \times \frac{500-400}{500 \times 400} \Rightarrow \ell n\left(\frac{k}{10^{-5}}\right) = 4606 \times \frac{1}{2000} = 2.303$

$\ell n\left(\frac{k}{10^{-5}}\right) = \ell n10$

$k = 10^{-4}\,s^{-1}$