UNIT # 08 (PART - I)

CHEMICAL KINETICS

EXERCISE # 1

2.
$$r = \frac{-1}{3} \frac{d[H_2]}{dt}$$

$$\frac{-d[H_2]}{dt} = 3 \quad 2.5 \quad 10^{-4} = 7.5 \quad 10^{-4} \text{ mol } L^{-1} \text{ S}^{-1}$$

$$3. \qquad \frac{-d[O_2]}{dt} = \frac{1}{2} \frac{d[SO_3]}{dt}$$

$$\frac{d[SO_3]}{dt} = 2 \quad 2.5 \quad 10^{-4} = 5 \quad 10^{-4} \text{ mol } L^{-1} \text{ S}^{-1}$$

4.
$$\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

$$\frac{d[NH_3]}{dt} = \frac{2}{3} \times 0.3 \times 10^{-4}$$

$$= 2 \quad 10^{-5} = 0.2 \quad 10^{-4}$$

6.
$$r = k[A]^2 [B]$$

 $r = k[x]^2 [y]$

$$r' = k[3x]^2 [3y]$$

$$r' = 27 r$$

8.
$$r = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{2}$$
 1 = 0.5 mol L⁻¹ S⁻¹

$$10. \quad K = \frac{2.303}{t} log \left[\frac{a_0}{a} \right]$$

$$K = \frac{2.303}{500} \log \frac{\frac{1}{10}}{\frac{1}{100}}$$

$$= \frac{2.303}{500} \log 10 = 4.606 \quad 10^{-3} \text{ sec}^{-1}$$

12.
$$r = K[A] = 5 10^{-5} [1] = 5 10^{-5} M s^{-1}$$

13.
$$r = K_2[N_2O_2][O_2]$$
(i

$$\frac{K_1}{K_1} = \frac{[N_2 O_2]}{[NO]^2}$$
 or $[N_2 O_2] = \frac{K_1}{K_1} [NO]^2$ from eq. (i)

$$r = K_2 \frac{K_1}{K_{-1}} = [NO]^2 [O_2]$$

compair $r = K [NO]^2 [O_2]$

compair
$$r = K [NO]^2 [O_0]$$

$$K = K_2 \frac{K_1}{K_1}$$

15.
$$r = -\frac{1}{2} \frac{d[N_2 O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt} = K[N_2 O_5]$$

$$K_{\star} = 2K_{\star}$$

$$K_2 = 4K = 2K$$

$$K_3 = K = K_1/2$$

16.
$$\frac{-d[a-x]}{dt} = K_1[a-x] + K_2[a-x]$$

$$20. \quad r = K[X][C]$$

$$K' = \frac{[X]}{[A][B]}$$

$$r = K'[A][B][C]$$

21.
$$r = K[NO]_{2}[Cl_{2}]$$

$$K' = \frac{[NO]_2}{[NO]^2}$$

$$r = KK' [NO]^2 [Cl_0]$$

23. K 15 =
$$ln\left(\frac{35-0}{35-9}\right)$$

43. K
$$32 = \ln\left(\frac{100}{1}\right)$$
 ... (i

$$K t = ln\left(\frac{100}{0.1}\right) ... (ii)$$

$$\frac{t}{32} = \frac{3\ln 10}{2\ln 10}$$

$$t = 48 \text{ min}$$

44. Given
$$t_{\frac{1}{2}}\alpha \frac{1}{a^2}$$

$$\therefore t_{\frac{1}{2}} \alpha \frac{1}{a^{n-1}}$$

$$1 - 1 = 2$$

$$1 = 3$$

45.
$$t_{\frac{1}{2}} \alpha \frac{1}{a^{n-1}}$$
 $\frac{200}{100} = \left(\frac{1}{0.5}\right)^{n-1}$ $2 = 2^{n-1}$ $n - 1 = 1$ $n = 2$

51.
$$K = Ae^{-Ea/RT}$$

$$\ln K = \ln A - \frac{Ea}{RT}$$

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

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

slope
$$\frac{Ea}{2.303R} = 5000$$

Ea =
$$5000 ext{ 8.31} ext{ 2.303} = 95.7 ext{KJ k}^{-1} ext{ mol}^{-1}$$

52.
$$-\frac{Ea}{R} = -40000$$

Ea =
$$40000 2 = 8 10^4 cal$$

$$\begin{array}{lll} \textbf{53}. & K = Ae^{-Ea/RT} & \therefore & Ae^{-Ea/RT} = Ae^{\frac{-\epsilon_1 - \epsilon_3 + \epsilon_2}{RT}} \\ & \epsilon_a = E_1 + E_3 - E_2 = 60 + 10 - 30 = 40 \text{ kJ} \end{array}$$

1. A (g) ====

$$10^{-5}$$
 mole 100 mole

$$K_f = 1.5 \quad 10^{-3} \text{ s}^{-1}$$

$$K = \frac{[100]^2}{10^{-5} \times 10} = \frac{K_f}{K_h}$$

$$K_b = \frac{1.5 \times 10^{-3} \times 10^{-7}}{10^4}$$

$$K_b = 1.5 10^{-11} L mol^{-1} s^{-1}$$

2. A + B \longrightarrow C + D

rate =
$$k [A]^{1/2} [B]^{1/2}$$

$$\frac{\mathrm{dx}}{\mathrm{dt}} = k\sqrt{(a-x)(a-x)}$$

$$\frac{\mathrm{dx}}{\mathrm{dt}} = \mathrm{k}(\mathrm{a} - \mathrm{x})$$

 \Rightarrow $t = \frac{2.303}{k} \log_{10} \left(\frac{a}{a-x} \right)$

$$t = \frac{2.303}{2.31 \times 10^{-3}} log_{10} \left(\frac{1}{0.25} \right)$$

- and $Y \xrightarrow{k_2} C + D$ $3. X \xrightarrow{k_1} A + B$

$$\frac{k_1}{k_2} = \frac{\log(2)}{\log(100/4)}$$

$$\frac{k_1}{k_2} = \frac{\log(2)}{\log(100/4)} \qquad \frac{k_1}{k_2} = \frac{\log 2}{2\log 10 - 2\log 2}$$

$$\frac{k_1}{k_2} = 4.06$$

5. P(mmHg) 500 250 950

$$t_{1/2}$$
 (in min.) 235

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

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1} \qquad \frac{235}{950} = \left(\frac{250}{500}\right)^{n-1}$$

$$2^2 = (2)^{n-1}$$

950 (500)

$$n-1 = 2 \Rightarrow n = 3$$

20 $k_1 = 5 k_2$

6.
$$t_1 k_1 = t_2 k_2$$

$$20 \quad k_1 = 5 \quad k_2$$

$$\frac{k_1}{k_2} = 4$$

Now Arrhenius equation

$$\log_{10}\left(\frac{k_2}{k_1}\right) = \frac{Ea}{2.30 \times R}\left(\frac{T_2 - T_1}{T_1.T_2}\right)$$

$$\log_{10}(4) = \frac{\text{Ea}}{8.314 \times 2.3} \left(\frac{20}{300 \times 320} \right)$$

Ea = 55.332 kJ/mole

 $k = 3.0 10^{-4} s^{-1}$; $Ea = 104.4 \text{ kJ mol}^{-1}$ 7.

$$A = 6.0 \quad 10^{14} \, \text{s}^{-1} \qquad \qquad k_2 = A e^{-Ea/RT}$$
 But when T $\rightarrow \infty$ $e^{-\theta} \rightarrow 1$

$$k = A \implies k = 6.0 \quad 10^{14} \text{ s}^{-1}$$

10. $k = \frac{1}{t(n-1)} \left| \frac{1}{C^{n-1}} - \frac{1}{C^{n-1}} \right|$

$$t_{1/2} = \frac{1}{k(n-1)} \left[\frac{2^{n-1}}{Co^{n-1}} - \frac{1}{Co^{n-1}} \right] \dots (1)$$

$$t_{3/4} = \frac{1}{k(n-1)} \left[\frac{4^{n-1}}{Co^{n-1}} - \frac{1}{Co^{n-1}} \right] \dots (2)$$

equ.
$$(2) \div equ. (1)$$

$$\frac{t_{3/4}}{t_{1/2}} = \left[\frac{4^{n-1} - 1}{2^{n-1} - 1}\right] = \frac{2^{2(n-1)} - 1}{(2^{n-1} - 1)} = \frac{(2^{n-1} + 1)(2^{n-1} - 1)}{(2^{n-1} - 1)}$$

$$t_{3/4}^{-} = t_{1/2} [2^{n-1} + 1]$$

11. Fraction of reactant consume $f = \left(1 - \frac{C}{C_{c}}\right)$

for a reaction : $\frac{df}{dt} = k(1 - f)$ (Remaining amount).

12. $2 A + B \xrightarrow{K} C + D$

 $t = 30 \text{ min}, \frac{C_0}{2} \frac{7C_0}{4}$ Rate at that time

Rate =
$$k \left[\frac{C_0}{2} \right] \left[\frac{7C_0}{4} \right]^2 = \frac{49C_0^3}{32}$$

14.
$$A \rightarrow B$$
 $K_A = 10^{15} e^{-2000/T}$
 $C \rightarrow D$ $K_C = 10^{14} e^{-1000/T}$ At T $(K_A = K_C)$

$$C_0^{15} e^{-2000/T} = 10^{14} e^{-1000/T}$$

$$10 e^{-2000/T} = e^{-1000/T}$$

$$10 - a^{1000/T}$$

$$\log_{e} 10 = 1000/T$$
 $T = \frac{1000}{\log_{e} 10}$ $T = \left(\frac{1000}{2.303}\right) k$

15.
$$\log_{10} \frac{k_2}{k_1} = \frac{2.303 \, \text{Ea}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\frac{R\log 2 \times 280 \times 290}{2.303 \times 10} = Ea$$

$$\log \frac{k_4}{k_2} = \frac{2.303 \times R \log 2 \times 280 \times 290}{2.303 \times 10 \times R} \left(\frac{10}{290 \times 300} \right)$$

$$\log_{10}\left(\frac{k_4}{k_3}\right) = \frac{280}{300}\log 2$$
 $\frac{k_4}{k_3} = 1.91$

16. products

$$-\frac{d[A]}{dt} = k\sqrt{[A]} \sqrt{[B]}$$

Reactant are in their stoichiometric proportion

$$\Rightarrow \qquad -\frac{d(a-x)}{dt} = k\sqrt{(a-x)}\sqrt{2(a-x)}$$

$$\frac{dx}{dt} = \sqrt{2} k(a-x) \qquad \qquad t_{1/2} = \frac{0.693}{\sqrt{2}k}$$

17.
$$2A + B \rightarrow \text{products}$$
 $\frac{-d[A]}{dt} = k[A]$

$$A = A_0 e^{-kt} \qquad \text{when } t_2 l/k$$

$$A = A_0 e^{-1} \qquad A = A_0/e$$

24. Rate =
$$K[A][B_2]$$

$$K = \frac{[A]^2}{[A_2]}$$
 $\Rightarrow [A] = \{K[A_2]\}^{1/2}$

$$r = K' [A_2]^{1/2} [B_2]$$
 order = $1\frac{1}{2}$

26. For A
$$K_1$$
 $t = \ln \frac{100}{100 - 94}$...(1)
For B K_2 $t = \ln \frac{100}{100 - 50}$...(1)

$$\frac{K_1}{K_2} = \frac{\ln \frac{100}{6}}{\ln \frac{100}{50}} \implies \frac{K_1}{K_2} = 4.058$$

27. % B =
$$\frac{K_1}{K_1 + K_2} \times 100 = 76.83\%$$

$$%C = 100 - B\% = 23.17\%$$

28.
$$\frac{dt}{dt} = \alpha - \lambda N$$

For max. no of nuclei
$$\frac{dN}{dt} = 0$$

 $\alpha = \lambda N \Rightarrow N = \alpha/\lambda$

29. Let n is the moles of reagent
$$'R'$$
 when R is reacted with A at time $t=0$

$$\therefore 5n = n_2 \Rightarrow n = \frac{n_2}{5}$$

$$n + 4x = n_1 \Rightarrow x = \frac{n_1 - n}{4}$$

$$k = \frac{2.303}{t} log \left(\frac{n}{n-x} \right)$$

so
$$k = \frac{1}{t} \ln \left(\frac{4n_2}{5(n_2 - n_1)} \right)$$

30. Overall rate constant
$$=k=k_1+k_2+k_3=6.93$$
 10

$$t_{1/2} = \frac{0.693}{6.93 \times 10^{-3}} = 100 \text{ sec};$$

After half-life, $P_{R} + P_{C} + P_{D} = 4$ atm

$$\frac{P_B}{P_B + P_C + P_D} = \frac{k_1}{k_1 + k_2 + k_3} = \frac{200}{693}$$

$$P_{\rm B} = 4 - \frac{200}{693} = 1.154 \text{ atm}$$

CHEMICAL KINETICS

1.(a)
$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Rate = $\frac{\Delta[NH_3]}{\Delta t} = 2 \quad 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

$$-\frac{dH_2}{dt} = \frac{-1}{3}\frac{dH_2}{dt} = \frac{1}{2}\frac{dNH_3}{dt}$$

$$\frac{dN_2}{dt} = 1 \quad 10^{-4}$$

(b)
$$-\frac{dH_2}{dt} = -\frac{3}{2} \times 2 \times 10^{-1}$$
$$= -3 \quad 10^{-4}$$

$$\begin{array}{lll} \textbf{2.} & N_2O_5 \ (g) \longrightarrow 2 \ NO_2 \ (g) + \frac{1}{2} \ O_2 \ (g) \\ & -d \ [N_2O_5] \ / \ dt = k_1[N_2O_5] \\ & d \ [NO_2] \ / \ dt = k_2[N_2O_5] \\ & d \ [O_2] \ / \ dt = k_3[N_2O_5] \\ & -\frac{d \ N_2O_5}{dt} = \frac{1}{2} \frac{d \ NO_2}{dt} = 2 \frac{d \ O_2}{dt} \\ & K_1 = \frac{K_2}{2} = \ 2K_3 \\ \end{array}$$

 $2K_{1} = K_{2} = 4K_{2}$

3.
$$2A + B + C \rightarrow D + E$$

$$\left(\frac{dx}{dt}\right) = K_1 [A] [B]^2 [C]^0$$

if increases conc. 2 time

$$\left(\frac{dx}{dt}\right)_2 = K_1 [2A] [2B]^2 [2C]^0 = 8\left(\frac{dx}{dt}\right)_1$$

 \Rightarrow rate increase by 8 time

4.
$$2 A + B_2 \longrightarrow 2 AB$$
 $\left(\frac{dx}{dt}\right)_1 = K[A]^2[B_2]$

if V is decrease to $\frac{V}{3}$

$$\Rightarrow \left(\frac{dx}{dt}\right)_2 = [3A]^3[3B] \qquad \left(\frac{dx}{dt}\right)_2 = 27\left(\frac{dx}{dt}\right)_1$$

reaction increase by 27 times

5.
$$2H_2O_2 \longrightarrow 2H_2O + O_2 \frac{d_{O_2}}{dt} = 3.6 \text{ M min}^{-1}$$

$$\frac{d_{H_2O}}{dt}$$
 = 2 3.6 = 7.2 M min⁻¹

$$\frac{d_{H_2O_2}}{dt} = 7.2 \text{ M min}^{-1}$$

6.
$$A \longrightarrow B$$

$$K = 1.2 10^{-2} \text{ M s}^{-1}$$

initially = 10 M

from the unit of rate constant we find that reaction is of zero order $X_1 = kt$

remainng

$$= 10 - 1.2 \quad 10^{-2} \quad 10 \quad 60 = 10 - 7.2$$

[Remaining mole = 2.8 M]

If
$$10 = 1.2 10^{-2} t \frac{1000}{1.2} = t$$

$$t = \frac{1000}{60 \times 1.2} \, ddd$$
 $t = 13.88 \, min$

28.
$$H_2O + O \stackrel{Ea}{\rightleftharpoons} 2 HO \Delta H = 72kJ$$

 $T = 500 K$

Ea = 77 kJ/mole
$$\Rightarrow$$
 ΔH = Ea - Eb

$$72 = 77 - Eb$$

$$Eb = 77 - 72$$

$$Eb = 5 kJ$$

33. 2 NO +
$$Br_2 \longrightarrow 2NOBr$$

(i) NO + Br₂
$$\Longrightarrow$$
 NOBr₂ (East)

Rate is determined by the solwest step

$$\Rightarrow$$
 Rate = k [NOBr₉] [NO]

But NOBr₂ is a visible of Intermediate

$$k_2 = \frac{[NOBr_2]}{[NO][Br_2]}$$
 \Rightarrow Rate = k1 $[NO]^2$ $[Br_2]$

⇒ 3rd order RxN

45. A
$$\longrightarrow$$
 B Ea = 70 kJ/mole $t_{1/2}$ = 40 min (0.693)

$$k = \left(\frac{0.693}{40\,\text{min}}\right)$$

$$\log_{10} \frac{k_2}{k_1} = \frac{Ea}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$= \frac{70 \times 10^3}{2.303 \times 8.314} \left[\frac{15}{298 \times 313} \right]$$

$$\frac{k_2}{k_1} = 5.88 \quad 10^{-4} \quad 10^3 = 10^{0.588}$$

$$\frac{k_2}{k_1} = 3.87$$

$$\frac{k_2}{k_1} = \frac{\log(a/a-x)}{\log_{10}(a/3ka)}$$

$$3.87 = \frac{\log(a/a-x)}{\log(4/3)}$$

$$10^{.4835} = \left(\frac{a}{a-x}\right)$$

$$\left(\frac{a}{a-x}\right) = 10^{-.4835}$$
 $\left(\frac{a}{a-x}\right)$ 100=32.84%

$$\%$$
 decomposition = $100 - 82.84 = 67.16\%$

46. (i)
$$A \longrightarrow \text{product}$$

(ii)
$$B \longrightarrow product$$

$$\log\left(\frac{k_{2}}{k_{1}}\right) = \frac{Ea}{2.303R} \left[\frac{10}{310 \times 300}\right]$$

$$\log 2 \quad 2.303 \quad 8.314 \quad 31 \quad 300 = Ea$$

$$Ea = 53.6 \text{ kJ/mole}$$

$$k_{A_2} = \left(\frac{0.693}{30}\right)$$

$$k_{B_2} = \left(\frac{0.693}{15}\right)^{\min^{-1}}$$

$$Ea = 26.8 \text{ kJ/mole}$$

$$\log \frac{k_2}{k_B} = \frac{Ea}{2.303} \left[\frac{-10}{310 \times 300} \right]$$

$$log\left(\frac{k_2}{k_B}\right) = \frac{-26.8 \times 1000}{2.303 \times 8.314 \times 30 \times 3.10}$$

$$\log_{10}\left(\frac{k_2}{k_B}\right) = -0.151$$

$$k_2 = \left(\frac{0.706 \times .693}{15 \times 60}\right)^{\text{sec}^{-1}}$$

$$k_{2} = 0.0327 \text{ min}^{-1}$$

$$k=2.8875 \quad 10^{-4} \quad 47. \quad 2H_2O_2 \longrightarrow 2H_2O + O_2$$

ml. eq of H_2O_2 in 10 ml diluted

 $= M_1$ eq. of KMnO₄ titrated = 25 .025 5 = 3.125 ml. eq in 100 ml solu. = 31.25

but 22400 ml $O_2 = 68 \text{ gm H}_2O_2$

1 ml =
$$\frac{68}{22400}$$

$$20 \text{ ml} = \frac{68 \times 20}{22400} \quad \text{ln 1 ml } \text{H}_2\text{O}_2$$

$$= \frac{68 \times 20 \times 10}{22400} \text{ in } 10 \text{ ml } H_2O_2$$

No. of Meq. in 10 ml of 20%kg ml H_2O_2

Initialy =
$$\frac{68 \times 20 \times 10 \times 1000}{17 \times 22400} = 35.71$$

$$\Rightarrow \qquad k \ = \ \frac{2.303}{6} log \left(\frac{35.71}{31.25} \right)$$

$$k = 0.022 \text{ hr}^{-1}$$

CHEMICAL KINETICS

EXERCISE # 4[B]

 Initial m mol of cyclobutene (साइक्लोब्यूटीन के प्रारम्भिक m मोल) = 10

Let after 20 min, x m mol cyclobutene isomerized. (माना 20 मिनट पश्चात्, x m mol साइक्लोब्यूटीन समावयवीकृत हुआ।)

m mol of cyclobutene left = 10 - x and m mol of diene formed = x

(साइक्लोब्यूटीन के शेष m mol = 10 - x व निर्मित डाइईन के m mol = x)

m mol of Br_2 required after 20 min = 10 - x + 2x = 10 + x = 16

(20 मिनट पश्चात् आवश्यक Br_2 के m mol = 10 - x + 2x = 10 + x = 16)

 $\Rightarrow x = 6 \Rightarrow 20K = \ln \frac{10}{4} \qquad \dots \dots (i)$

If y m mol of cyclobutene isomerized after 30 min. (यदि 30 मिनट पश्चात् साइक्लोब्यूटीन के y m mol समावयवीकृत होते है।)

30 K =
$$\ln \frac{10}{10 - v}$$
(ii)

From Eqs. (i) and (ii) (समीकरण (i) व (ii) से) y = 7.47

- \Rightarrow m mol of Br₂ required (Br₂ के आवश्यक m mol) = 10 + y = 17.47
- ⇒ Vol. of bromine solution required (ब्रोमीन विलयन का आवश्यक आयतन) = 17.47 mL
- 2. $10^2 e^{-\frac{14000}{RT}} = 10^3 e^{-\frac{20000}{RT}}$ Solving (हल करने पर), T = 313.42 K
- \Rightarrow Rate constant (दर नियतांक) $K_1 = K_2 = 0.464 \text{ hr}^{-1}$

$$\Rightarrow K_1 t = \ln \frac{n_0(A_2)}{n_0(A_2) - n_1} \Rightarrow n_1 = 0.37$$

$$K_2 t = ln \frac{n_0(B_3)}{n_0(B_3) - n_2} \Rightarrow n_2 = 0.37$$

- ⇒ Total moles of gases after 1.0 hr. (1.0 घंटे पश्चात् गैसों के कुल मोल) = 1.37 + 1.74 = 2.11 P = 5.42 atm
- 3. Let rate constant in absence of catalyst is k_1 (माना उत्प्रेरक की अनुपस्थित में दर नियतांक k_1)
 Let rate constant in presence of first catalyst is k_2 (प्रथम उत्प्रेरक की उपस्थित में दर नियतांक k_2)
 Let rate constant in presence of second catalyst is k_3 (द्वितीय उत्प्रेरक की उपस्थित में दर नियतांक k_3) $k_1 = \ln \implies k_1 = 0.2231 \text{ hr}^{-1} \qquad \dots (i)$ $k_2 = 0.5 = \ln \frac{80}{40} \implies k_2 = 1.3862 \qquad \dots (ii)$

$$\frac{k_3 \times 1}{6} = \ln \frac{40}{10} \implies k_3 = 8.317 \qquad(iii)$$

$$k_1 = Ae^{-80,000/RT}$$

 $k_2 = A e^{-E_{a_1}/RT}$ $E_{a_1} \rightarrow$ Activation energy in presence of 1^{st} catalyst

(1st उत्प्रेरक की उपस्थिति में सक्रियण ऊर्जा)

$$ln\frac{k_2}{k_1} = \frac{80,000 - E_{a_1}}{RT} = ln\frac{1.3862}{0.2231}$$

$$E_{x} = 75443.8 \text{ J} = 75.44 \text{ kJ}$$

 $k_{_3}=Ae^{^{-E_{_{a_2}}/RT}}~E_{_{a_2}}\rightarrow~Activation~energy~in~$ presence of $2^{^{nd}}$ catalyst

(2nd उत्प्रेरक की उपस्थिति में सक्रियण ऊर्जा)

$$ln\frac{k_3}{k_1} = \frac{80,000 - E_{a_2}}{RT} = ln\frac{8.317}{0.2231}$$

$$E_{a_2} = 70974.9 J = 70.975 J$$

1.
$$N_2O_5 \stackrel{k_a}{\longleftarrow} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_b} NO_2 + O_2 + NO_3$$

$$NO + NO_3 \xrightarrow{k_c} 2NO_2$$

$$\frac{-d[N_2O_5]}{dt} = k_a[N_2O_5] - k_{-a}[NO_2][NO_3] \dots (i)$$

$$\frac{d[NO_3]}{dt} = k_a [N_2O_5] - k_{-a} [NO_2] [NO_3] - k_b [NO_2]$$

$$[NO_3] - k_c [NO] [NO_3] = 0$$
(ii)

$$\frac{d[NO]}{dt} = k_b[NO_2][NO_3] - k_c[NO][NO_3] = 0 \dots (iii)$$

From equation (iii) (समीकरण (iii) से)

$$[NO] = \frac{k_b}{k_a} [NO_2]$$

putting this in equation(ii)(इसे समीकरण (ii) में रखने पर) $k_a [N_2O_5] = [NO_3] \{k_a [NO_2] + 2k_a [NO_2]$

$$[NO_3] = \frac{k_a[N_2O_5]}{k_{-a}[NO_2] + 2k_b[NO_2]}$$

putting this in equation (i)(इसे समीकरण (i) में रखने पर)

$$\frac{-d[N_2O_5]}{dt} = k_a[N_2O_5] - \frac{k_ak_{-a}[N_2O_5]}{k + 2k_s}$$

$$\frac{-d[N_2O_5]}{dt} = \frac{2k_ak_b[N_2O_5]}{k_{-2} + 2k_b}$$

$$r = \frac{-1}{2} \frac{d[N_2 O_5]}{dt} = \frac{k_a k_b [N_2 O_5]}{k_{-a} + 2k_b}$$

$$\mathbf{5.} \qquad \tau^2 = \alpha t + \beta$$

$$2\tau \frac{d\tau}{dt} = \alpha \implies \frac{d\tau}{dt} = \frac{\alpha}{2\tau} = \frac{\alpha}{2}(\tau)^{-1}$$
 order (कोटि) = -1

$$t_{1/2} = \frac{\ln 2}{k'} = \frac{\ln 2}{k[H^+]b}$$

On doubling concentration of $[H^{+}]$ ion $t_{1/2}$ gets half so b = 1

([H $^{\uparrow}$] आयन की सान्द्रता दुगुनी करने पर $\mathbf{t}_{1/2}$ आधा हो जाता है, अत: b = 1)

7. Let at 20 C rate constant(माना 20 C पर दर नियतांक) =k then at 3 C rate constant (तो 3 C पर दर नियतांक)=k/3

$$ln \frac{k}{k/3} = \frac{E_a}{R} \left[\frac{1}{276} - \frac{1}{293} \right] \Rightarrow E_a = 43.45 \text{ kJ}$$

Let at 40 C rate constant is k_1 then $\ln \frac{k_1}{k} = \frac{43.45 \times 10^3}{8.314} \left[\frac{1}{293} - \frac{1}{313} \right]$

(माना 40 C पर दर नियतांक k_1 है तो)

$$k_1 = 3.125 \text{ k}$$

so time required for juice to get spoil at 40 C =

$$\frac{64}{3.125}$$
 = 20.47 hr.

(अत: 40 C पर जूस के खराब होने में लगा समय)

8. Given:

$$\frac{k_1}{k_2} = \frac{1}{9}, \qquad k_1 = 1.3 \quad 10^{-5}$$

$$k_2 = 9k_1$$

$$[A] = [A]_0 e^{-(k_1 + k_2)t}$$

$$[C] = \frac{k_2[A]_0}{k_1 + k_2} [1 - e^{-(k_1 + k_2)t}]$$

$$\frac{[C]}{[A]} = \frac{k_2}{k_1 + k_2} [e^{(k_1 + k_2)t} - 1] = \frac{9k_1}{10k_1} [e^{10k_1t} - 1] = 0.537$$

9. $k = 0.16, k_1 = 3.3 10^{-4}$

so
$$k_2 = k_1/k = 2.0625 10^{-3}$$

$$k_1 + k_2 = 0.0023925$$

$$[B]_{eq.} = \frac{k_1}{k_2} [A]_{eq.} = \frac{k_1 [A]_0}{k_1 + k_2}$$

given [B] =
$$\frac{[B]_{eq.}}{2} = \frac{k_1[A]_0}{2(k_1 + k_2)}$$

& [B] =
$$\frac{k_1[A]_0}{k_1 + k_2} \left[1 - e^{-(k_1 + k_2)t}\right]$$

so
$$\frac{1}{2} = 1 - e^{-(k_1 + k_2)t}$$
 $(k_1 + k_2) t = \ln 2$
 $t = 289.71 \text{ sec.} = 4.82 \text{ min.}$

10. A \longrightarrow B + C

$$t = 0$$
 a

$$t = 20$$
 min. $a-x$ x x

$$t = \infty$$
 – a a

$$60(a - x) + 40x - 80x = 5$$

$$40a - 80a = -20$$

on solving (हल करने पर) a = 0.5, x = 0.25

so
$$t_{1/2} = 20$$
 min.

Average life = $1/k = 1.443 t_{1/2} = 28.86 min.$

11. At $t = \infty$ when equilibrium is established

$$(t = \infty \ \text{पर जब साम्य स्थापित होता है।})$$

$$k = \frac{[P]}{[A]} = \frac{7}{3} = 2.33$$

&
$$\frac{k_1}{k_{-1}} = 2.33 \Rightarrow k_1 = 2.33 k_{-1}$$

[A] =
$$\frac{k_2[A]_0}{k_1 + k_2}$$
 [1 - $e^{-(k_1 + k_2)t}$]

$$0.725 = \frac{1}{3.33} [1 + 2.33 e^{-3.33 k_{-1} \times 3600}]$$

$$k_{-1} = 4.16 \quad 10^{-5} \text{ sec}^{-1}$$

$$k_1 = 2.33 k_{-1} = 9.7 10^{-5} sec^{-1}$$

13.
$$CH_3OCH_3 \longrightarrow CH_4 + CO + H_2$$

$$t = 0$$
 0.4

$$t = 4.5 hr. 0.11 0.29 0.29$$

$$kt = ln \frac{P_0}{P} \Rightarrow 4.78 \quad 10^{-3} \quad 4.5 \quad 60 = ln \frac{0.4}{P}$$

$$P = 0.11$$
 atm

at
$$t = 0 P_0 = 0.4$$

$$M_0 = 46$$

14.

at
$$t = 4.5 \text{ hr.}$$
 $P = 0.11 + 0.29$ $3 = 0.98 \text{ atm}$

$$M = \frac{0.11 \times 46 + 0.29(16 + 28 + 2)}{0.98} = 18.77$$

$$\frac{r_0}{r} = \frac{P_0}{P} \sqrt{\frac{M}{M_0}} = \frac{0.4}{0.98} \sqrt{\frac{18.77}{46}} = 0.26$$

A
$$k_1$$
 k_2 k_3 k_4 k_4 k_2 k_4 k_5 k_6 $k_$

16. A + B
$$\xrightarrow{k_1}$$
 C, C $\xrightarrow{k_3}$ D
 $r = k_1[A] [B] - k_2[C]$

$$\frac{d[C]}{dt} = k_1[A][B] - k_2[C] - k_3[C] = 0$$

[C] =
$$\frac{k_1[A][B]}{k_2 + k_3}$$

$$\frac{d[D]}{dt} = r = k_1[A] [B] - k_2 \frac{k_1[A][B]}{k_2 + k_3}$$

$$r = \frac{k_1 k_3 [A][B]}{k_2 + k_3}$$

since $\bar{k}_2 > k_3$

$$k_{net} = \frac{k_1 k_3}{k_2}$$

so
$$A_{\text{net}} = \frac{A_1 A}{A_2}$$

$$t = \infty - 2P_0$$
so $P_0 - P + 2P + P/2 = 317 - 32.5$

i.e.
$$P_0 + 1.5 P = 284.5$$
(i)

&
$$2.5 P_0 = 617 - 32.5 = 584.5$$

so
$$P_0 = 233.8$$

 $P = 33.8$

$$k \quad 30 = \ln \frac{233.8}{200} \implies k = 0.0052$$

At
$$t = 75 \text{ min}$$

$$0.0052 \quad 75 = \ln \frac{233.8}{P^{\circ} - P}$$

 $P - P = 158.23 \Rightarrow P = 75.57$

$$P_{T} = 32.5 + P_{0} + 1.5 P = 347.155 + 32.5$$

 $P_{T} = 379.65 \text{ mm Hg}$

(ii)
$$0.0052$$
 t = ln 8

t = 399.89 min.

t=10 min. a - x

v.f. of
$$B^{n+} = 2$$

v.f. of
$$B^{(n+4)+} = 5$$

Let normality of reducing agent (माना अपचायक की नॉर्मलता) = N

so
$$2a = 25 N$$

$$2(a - x) + 5x = 32 N$$

$$2a + 3x = 32 N$$
 $x = \frac{7}{2}N$

k 10 =
$$\ln \frac{a}{a-x} = \ln \frac{12.5N}{12.5N - \frac{7}{2}N}$$

$$k = 0.02 \text{ min}^{-1}$$
.

20. For reaction 1 (अभिक्रिया 1 के लिए)

$$k_2 = k_1 e^{+E_a/R\left(\frac{1}{T_1} - \frac{1}{T}\right)} = 2.79 \quad 10^{-3} e^{6000\left(\frac{1}{509} - \frac{1}{T}\right)}$$

For reaction 2 (अभिक्रिया 2 के लिए)

$$k_2 = 1.52 \quad 10^{-4} e^{\frac{12250(\frac{1}{510} - \frac{1}{T})}{}}$$

For given condition (दी गयी परिस्थिति के लिए)

2.79
$$10^{-3} e^{6000\left(\frac{1}{509} - \frac{1}{T}\right)} = 1.52 \quad 10^{-4} e^{12250\left(\frac{1}{510} - \frac{1}{T}\right)}$$

$$18.355 = e^{12250\left(\frac{1}{510} - \frac{1}{T}\right) - 6000\left(\frac{1}{509} - \frac{1}{T}\right)}$$

$$\ln 18.355 = 12.33 - \frac{6250}{T} = 2.9$$

$$T = 670.6 K = 397.6 C$$

P1.
$$A = \begin{bmatrix} k_1 \\ k_2 \end{bmatrix}$$
 [A] = [A]₀ $e^{-(k_1 + k_2)t}$ [B] = $\frac{2k_1[A]_0}{k_1 + k_2}[1 - e^{-(k_1 + k_2)t}]$

$$[B] \; = \; \frac{2k_1[A]_0}{k_1 + k_2}[1 - e^{-(k_1 + k_2)t}]$$

$$[C] = \frac{k_2[A]_0}{k_1 + k_2} [1 - e^{-(k_1 + k_2)t}]$$

since V & T are constant (चूंकि V व T नियत हैं) P α moles

at
$$t = 0$$
, $P = 1$ atm so

$$[A]_0 = 1$$

t = 10 sec. P = 1.4 atm so

at
$$t = 10$$
, [A] + [B] + [C] = 1.4(2)

$$t = \infty P = 1.5 \text{ atm...(3)}$$

at
$$t = \infty$$
, [B] + [C] = 1.5

from equation (समीकरण (3) से) (3)

$$\frac{2k_1}{k_1 + k_2} + \frac{k_2}{k_1 + k_2} = 1.5$$

$$\frac{2k_1 + k_2}{k_1 + k_2} = 1.5$$

$$1 + \frac{k_1}{k_1 + k_2} = 1.5$$

$$k_1 = k_2 \qquad \dots (4)$$

from equation (समीकरण से) (2) & (4)

$$e^{-(k_1+k_2)t} + \frac{2k_1}{k_1+k_2} \, \left(1 - e^{-(k_1+k_2)t}\right) + \frac{k_2}{k_1+k_2} (1 - e^{-(k_1+k_2)t}) = \ 1.4$$

$$t = 10 \text{ sec } \& k_1 = k_2 \text{ so}$$

$$e^{-20k_1} + 1 - e^{-20k_1} + 0.5 - 0.5e^{-20k_1} = 1.4$$

$$0.1 = 0.5 e^{-20 k_1}$$

$$0.2 = e^{-20k_1}$$

$$20k_1 = 1.6094$$

$$k_1 = 0.0804 = k_2$$
 $_{90}Th^{232} \longrightarrow _{82}Pb^{208} + 6_{2}He^4 + 4_{-1}\beta^0$

$$t = 0$$
 a

23.

time
$$t - x = 6x$$

given :

$$a - x = \frac{5 \times 10^{-7}}{232} = 2.155 \quad 10^{-9} \text{ mole}$$

$$6x = \frac{8 \times 10^{-5}}{22400} \implies x = 5.9523 \quad 10^{-10} \text{ mole}$$

so
$$a = 2.75 10^{-9}$$

$$k = \frac{0.693}{1.39 \times 10^{10}}$$

$$k = ln \frac{a}{a-x}$$

$$\frac{0.693}{1.39 \times 10^{10}} = \ln \frac{2.75 \times 10^{-9}}{2.155 \times 10^{-9}} = 0.2438$$

$$t = 4.89 10^9 \text{ year}$$

24.
$$k = \frac{0.693}{8}$$

$$kt = ln \frac{A_0}{A} = \frac{0.693}{8} \times 4 = ln \frac{A_0}{A}$$

$$\frac{A}{A_0} = 0.707$$

Total activity is 70.7% of the original activity but only 67.7% found in the thysoid so mass of stable iodide ion had migrated to the thyroid gland is (कुल सिक्रयता वास्तिवक सिक्रयता को 70.7% है लेकिन केवल 67.7% थाइरॉइड में पाया गया। अत: थाइरॉइड में प्रवेशित होने वाले स्थायी आयोडाइड का द्रव्यमान)

$$=\frac{67.7}{70.7}\times0.1 = 0.09575 \text{ mg}$$

25.
$$_{84}\text{Po}^{218} \xrightarrow{\lambda_1} _{82}\text{Pb}^{214} \xrightarrow{\lambda_2} _{83}\text{Bi}^{214}$$

Number of nuclei of Pb^{214} at time t are N_2

$$=\frac{\lambda_1 N_0}{(\lambda_2-\lambda_1)} \Big[e^{-\lambda_1 t}-e^{-\lambda_2 t}\Big]$$

(समय t पर Pb²¹⁴ के नाभिकों की संख्या N₂)

For max. value of N_2 (N_2 के अधिकतम मान कि लिए)

$$\frac{dN_2}{dt} = 0$$

so
$$t = \frac{1}{(\lambda_2 - \lambda_1)} \ln \frac{\lambda_2}{\lambda_1}$$

when
$$\lambda_2 = \frac{0.693}{2.68}$$
 , $\lambda_1 = \frac{0.693}{3.05}$,

on putting these values (यह मान रखने पर)

$$t = 31.87 \ln \frac{3.05}{2.68} = 4.12 \min$$

 ${\bf 26}$. Let the mass of sample in a g & initial mass of U^{238} is w g the

(माना नमूने का द्रव्यमान g में है व U^{238} का प्रारम्भिक द्रव्यमान w g है I)

$$U^{238} \longrightarrow Ph^{206}$$

$$t = 0$$
 w

t w-x
$$\frac{206x}{2.68}$$

given w - x = 0.5 a

$$\frac{206x}{238} = \frac{2.425\,\text{a}}{100} \times 0.93 = 0.0225525\,\text{a}$$

$$x = 0.026 a$$

$$w = 0.526 a$$

$$\lambda t = \ln \frac{w}{w - x}$$

1.52
$$10^{-10}$$
 t = ln $\frac{0.526 \, a}{0.5 \, a}$

$$t = 3.33 10^8$$
 year.

1. rate of appearance of HI = $\frac{1}{2} \frac{d[HI]}{dt}$

rate of formation of $H_2 = \frac{-d[H_2]}{dt}$

rate of formation of $I_2 = \frac{-d[I_2]}{dt}$

hence $\frac{-d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2} \frac{d[HI]}{dt}$

or
$$-\frac{2d[H_2]}{dt} = -\frac{2d[I_2]}{dt} = \frac{d[HI]}{dt}$$

2. Order is the sum of the power of the concentrations terms in rate law expression.

hence the order of reaction is = 1 + 2 = 3

3. For a zero order reaction.

rate = k [A] i.e., rate = k

hence unit of $k = M.sec^{-1}$

For a first order reaction

rate = k [A]

 $k = M.sec^{-1}/M = sec^{-1}$

4. Rt = $\log C_0 - \log C_1$

It is clear from the equation that if we plot a graph between log $C_{_{\! \! +}}$ and time, a straight line with a

slope equal to $-\frac{k}{2.303}$ and intercept equal to

 $log[A_0]$ will be obtained.

6. It is zero order reaction

Note: Adsorption of gas on metal surface is of zero order.

7. In equation $K = Ae^{-E_a/Rt}$; A = Frequency factorK = velocity constant,

R = gas constant and E_a = energy of activation

8. $r = k[O_2][NO]^2$. When the volume is reduced to 1/2, the conc. will double.

:. New rate = $k[2O_2][2NO]^2 = 8 k [O^2] [NO]^2$

The new rate increases to eight times of its initial.

- 10. As the concentration of reactant decreases from 0.8 to 0.4 in minutes hence the $t_{1/2}$ is 15 inutes. To fall the concentration from 0.1 to 0.025 we need two half lives i.e., 30 minutes.
- 11. The velocity constant depends on temperature only. It is independent of concentration of reactants.

12. $N_t = N_0 \left(\frac{1}{2}\right)^n$ where n is number of half life periods.

 $n = \frac{total\ time}{half\ life} = \frac{24}{4} = 6$

 $N_{t} = 200 \left(\frac{1}{2}\right)^{6} = 3.125g$

13. Enthalpy of reaction $(\Delta H) = Ea_{(f)} - Ea_{(b)}$ for an endothermic reaction $\Delta H = +ve$ hence for ΔH to be negative.

 $Ea_{(b)} \leq Ea_{(f)}$

14. The molecularity of a reaction is the number of reactant molecules taking part in a single step of the reaction.

Note: The reaction involving two different reactant can never be unimolecular.

15. $t_{1/4} = \frac{2.303}{K} \log \frac{1}{3/4} = \frac{2.303}{K} \log \frac{4}{3}$

$$= \frac{2.303}{K} (\log 4 - \log 3) = \frac{2.303}{K} (2 \log 2 - \log 3)$$

$$= \frac{2.303}{K}(2 \times 0.301 - 0.4771) = \frac{0.29}{K}$$

16. Since the reaction is 2nd order w.r.t. CO. Thus, rate law is given as

$$r = k [CO]^2$$

Let initial concentration of CO is a i.e. [CO] = a

$$\therefore r_1 = k(a)^2 = ka^2$$

when concentration becomes doubled, i.e.,

$$[CO] = 2a$$

$$\therefore r_2 = k(2a)^2 = 4ka^2 \qquad \therefore r_2 = 4r_1$$

So, the rate of reaction becomes 4 times.

- 17. In Arrhenius equation $K = Ae^{-E/RT}$, E is the energy of activation , which is required by the colliding molecules to react resulting in the formation of products.
- **18**. (i) $NO(g) + Br_2(g)$ NOBr₂(g)
 - (ii) $NOBr_2(g) + NO(g) \longrightarrow 2NOBr(g)$

Rate law equation = $K[NOBr_2]$ [NO]

But $NOBr_2$ is intermediate and must not appear in the rate law equation

from 1st step $K_C = \frac{[NOBr_2]}{[NO][Br_2]}$

$$\therefore [NOBr_2] = K_C[NO] [Br_2]$$

 \therefore Rate law equation = k.K_C [NO]² [Br₂]

hence order of reaction is 2 w.r.t. NO.

- **19.** $\Delta H_{p} = E_{t} E_{b} = 180 200 = -20 \text{ kJ/mol}$ The nearest correct answer given in choices may be obtained by neglecting sign.
- **20.** For a first order reaction $t_{1/2} = \frac{0.693}{K}$ i.e., for a first order reaction $t_{1/2}$ does not depend up on the concentration. From the given data, we can say that order of reaction with respect to B = 1because change in concentration of B does not change half life.

Order of reaction with respect to A = 1 because rate of reaction doubles when concentration of B is double keeping concentration of A constant.

 \therefore Order of reaction = 1 + 1 = 2 and units of second order reaction are L mol⁻¹ sec⁻¹.

21. The rates of reactions for the reaction

$$\frac{1}{2}A \longrightarrow 2B$$

can be written either as

$$-2\frac{d}{dt}[A]$$
 with respect to 'A'

or
$$\frac{1}{2} \frac{d}{dt} [B]$$
 with respect to 'B'

from the above, we have

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

or
$$-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$$

22. For first order reaction

$$k = \frac{2.303}{t} \log \frac{100}{100 - 99}$$
$$\frac{0.693}{693} = \frac{2.303}{t} \log \frac{100}{1}$$
$$\frac{0.693}{693} = \frac{2.303 \times 2}{t}$$

t = 46.06 minutes

23. Since the slow step is the rate determining step hence if we consider option (1) we find

Rate =
$$k[Cl_2][H_2S]$$

Now if we consider option (2) we find

Rate =
$$k[Cl_2]$$
 [HS⁻](i)

From equation (i)

$$k = \frac{[H^+][HS^-]}{H_0S}$$
 or $[HS^-] = \frac{k[H_2S]}{H^+}$

Substituting this value in eqution (i) we find

Rate =
$$k[Cl_2] K \frac{k[H_2S]}{H^+} = k' \frac{[Cl_2][H_2S]}{[H^+]}$$

hence only, mechanism (i) is consistent with the given rate equation.

24. For the reaction

 $A \rightarrow Product$

given $t_{1/2} = 1$ hour

for a zero order reaction

$$t_{completion} = \frac{[A_0]}{k} = \frac{initial conc.}{rate constant}$$

$$\therefore t_{1/2} = \frac{[A_0]}{2k}$$

or
$$k = \frac{[A_0]}{2t_{1/2}} = \frac{2}{2 \times 1} = 1 \,\text{mol lit}^{-1} \,\text{hr}^{-1}$$

Further for a zero order reaction

$$k = \frac{dx}{dt} = \frac{change in concentration}{time}$$

$$1 = \frac{0.50 - 0.25}{\text{time}}$$

 \therefore time = 0.25 hr.

Since for every 10 C rise in temperature rate 25. doubles for 50 C rise in temp increase in reaction rate = 2^5 = 32 times.

26.
$$k_1 = A_1 e^{-Ea_1/RT}$$
(i)

$$k_2 = A_2 e^{-Ea_2/RT}$$
(ii)

On dividing eq. (i) from eq. (ii)

$$\frac{k_1}{k_2} = \frac{A_1}{A_2} (Ea_2 - Ea_1) / RT \cdots (iii)$$

Given $Ea_2 = 2Ea$,

On substituting this value in eqn. (iii)

$$k_1 = k_2 A e^{Ea_1/RT}$$

27. For a first order reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{40} \log \frac{0.1}{0.025}$$

$$=\frac{2.303}{40}\log 4=\frac{2.303\times 0.6020}{40}=3.47\times 10^{-7}$$

$$R = K(A)^1 = 3.47 \quad 10^{-2} \quad 0.01 = 3.47 \quad 10^{-4}$$