Chemical kinetics. [solutions]

LEVEL - I

Q(3) $r = -\frac{1}{3}\frac{d[H_2]}{dt}$ or $-\frac{d[H_2]}{dt} = 3 \times r = 3 \times 2.5 \times 10^{-4} M s^{-1}$

Q(4) $-\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{d[SO_3]}{dt}$ or $-\frac{d[SO_3]}{dt} = -2 \times \frac{d[O_2]}{dt} = 2 \times 2.5 \times 10^{-4}$

Q(14) rate of production of 'c' = $K_1[A]$, depends on slow step.

Q(16) $r = K[A]^2$, $\therefore$ O.R. = 2

Q(25) $k = \frac{1}{t}\log_e \frac{V_\infty}{V_\infty - V_t} = \frac{1}{15}\log_e \frac{35}{26}$

Q(26) $\log\frac{K_2}{K_1} = \frac{E_a}{2.303R} \times \left[\frac{T_2 - T_1}{T_1 T_2}\right]$, $E_a = ?$

Q(27) Two because unit of 'k' is $L mol^{-1} s^{-1}$.

Q(28) $t = \frac{1 \times 2.303}{k}\log\frac{[A]_0}{[A]}$, $32 = \frac{2.303}{K}\log\frac{100}{25}$ —(I)

$t_{1/2} = \frac{2.303}{K}\log\frac{100}{50}$ —(II)

By (II)/(I)

$\frac{t_{1/2}}{32} = \frac{\log 2}{\log 4} \Rightarrow t_{1/2} = 32/2 = 16$ min.

Q(29) $r = K[A]^2[B]$, $r_2 = 27 r_1$

Q(34) $k = \frac{0.6932}{t_{1/2}} = \frac{0.6932}{100} s^{-1} = 6.93 \times 10^{-3} s^{-1}$.

Q.(38) $t_{1/2} = 12$ min. Total half lives = $\frac{60}{12} = 5$.

$\frac{[A]}{[A]_0} = \left(\frac{1}{2}\right)^n$ = $[A] = 100 \times \frac{1}{2^5} = \frac{100}{32}\% \approx 3\%$

Q(42) $r = K[A]^n$ As conc. ↑. rate ↓. It means $n < 1$. ($n = \frac{1}{2}$)

Q(46) $r = K[A][B]^2$

Q(51) $k_3 > k_2 > k_1$ $\therefore$ A → B is the slowest step.

↓ smallest

(54) $K_{310} = 2.3K$

(55) $0.30 = K(0.2)^2$ & $r = K(0.3)^2$

$\Rightarrow \frac{r}{0.30} = \frac{(0.6)^2}{(0.2)^2}$ or $r = 0.30 \times 9 = 2.7$

(56) $K_{H_2SO_4} > K_{HCl} \Rightarrow r_{H_2SO_4} > r_{HCl}$.

$\Rightarrow$ H_2SO_4 is stronger than HCl.

(57) $\frac{-E_a}{2.303R} = -5000 \Rightarrow E_a = 2.303 \times 8.314 \times 5000 \text{ J} = 95.7 \text{ kJ}$

(59) $\frac{-dx}{dt} = k_1(a-x) + k_2(a-x)$

(62) $A = A_0 e^{-kt}$ or $\ln A = \ln A_0 - kt$ or $\log A = \log A_0 - \frac{kt}{2.303}$

$\Rightarrow \frac{k}{2.303} = 0.03$ or $k = 0.03 \times 2.303$
$= 0.069$

(64) $32 = \frac{2.303}{k} \log \frac{100}{1}$ & $t = \frac{2.303}{k} \log \frac{100}{0.1}$

$\Rightarrow \frac{t}{32} = \frac{\log 1000}{\log 100} = \frac{3}{2}$ or $t = 1.5 \times 32 = 48$ min.

(69) zero

(70) second order

(71) $k = Ae^{-E_a/RT} = Ae^{-40000/T}$ $\Rightarrow \frac{E_a}{R} = 40000$ or $E_a = \frac{40000 \times 8.314}{4.18}$ cal. $= 80,000$ cal.

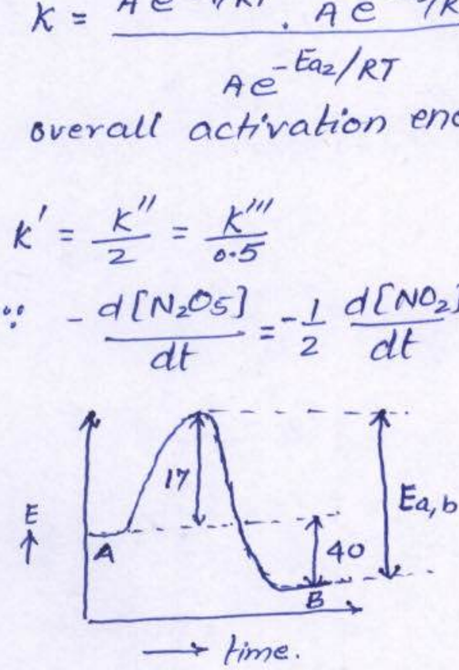
(72) $k = \frac{Ae^{-E_{a1}/RT} \cdot Ae^{-E_{a3}/RT}}{Ae^{-E_{a2}/RT}} = Ae^{+(E_{a2} - E_{a1} - E_{a3})/RT}$

overall activation energy, $E_a = -(E_{a2} - E_{a1} - E_{a3})$
$= E_{a3} + E_{a1} - E_{a2} = 60 + 10 - 30$
$= 40$

(73) $k' = \frac{k''}{2} = \frac{k'''}{0.5}$

$\because -\frac{d[N_2O_5]}{dt} = -\frac{1}{2}\frac{d[NO_2]}{dt} = +\frac{1}{0.5}\frac{d[O_2]}{dt}$

(75)



$E_{a,b} = 17 + 40 = 57$ kJ.

(LEVEL - II)

(1.) Hydrolysis of RX by NaOH (base) is second order kinetics.
$r = k[RX][NaOH]$. Ans (b).

(3) $rate = \frac{\Delta C}{\Delta t} = \frac{0.2-0.1}{10} = \frac{0.1}{10} = 10^{-2}$ M min^{-1}.

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

$\Rightarrow -\frac{d[H_2]}{dt} = +\frac{3}{2}\times\frac{d[NH_3]}{dt} = 1.5\times 40\times 10^{-3}\ mol\,L^{-1}s^{-1}$
$= 60\times 10^{-3}\ mol\,L^{-1}s^{-1}$

(8) $+\frac{d[NH_3]}{dt} = \frac{10^{-3}\times 10^{3}}{17}\ mol\,hr^{-1}$

$-\frac{d[H_2]}{dt} = \frac{3}{2}\times\frac{1}{17}\ mol\,hr^{-1} = \frac{3}{34}\times 2\ g/h = \frac{3}{17}\times 10^{-3}\ kg/hr.$
$= 1.76\times 10^{-4}\ kg\,h^{-1}$.

(9) 2^5 times.

(15) $k = \frac{2.303}{t}\log\frac{P_0}{P}$ or $3.38\times 10^{-5} = \frac{2.303}{10\times 60}\log\frac{500}{P}$

or $\log\frac{500}{P} = 0.0088 = \log 1.02 \Rightarrow \frac{500}{P} = 1.02$
or $P = 490$ atm.

(19) $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]} = \frac{2.303}{200}\log\frac{800}{50}$

(23) For the reverse reaction, $K = \frac{1}{49}$

(24) $r = k[N_2O_5]$ or $[N_2O_5] = \frac{r}{k} = \frac{2.4\times 10^{-5}}{3\times 10^{-5}} = 0.8$.

(27) order of reaction $= \frac{3}{2}+\frac{3}{2} = 3$.

(33) $t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{1.1\times 10^{-9}}$ sec.

(39) $0.4 \xrightarrow{1hr} 0.2 \longrightarrow 0.1$ (2hr overall). It is first order because half life ~~concentration~~ does not depend on conc.

(52) $t_{1/2} = \frac{2.303}{k}\log 2$ —(I)
$t = \frac{2.303}{k}\log\frac{0.08}{0.01}$ —(II)
By (II)/(I) $\frac{t}{t_{1/2}} = \frac{\log 8}{\log 2} = 3 \therefore t = 3\times t_{1/2} = 3\times 10 = 30$

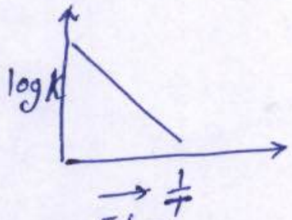
(55) $r = k[A]$ or $k = \frac{10^{-2}}{0.2} = 5\times 10^{-2}$, $t_{1/2} = \frac{0.6932}{k} = \frac{0.6932}{5\times 10^{-2}}$ min.

(59) $t_{1/2} \propto (a_0)^{1-n} \Rightarrow \frac{0.1}{0.4} = \left(\frac{200}{50}\right)^{1-n}$ or $\frac{1}{4} = \left(\frac{4}{1}\right)^{1-n}$
$\Rightarrow 1-n = -1$ or $\boxed{n=2}$

(61) $t_{1/2} = \frac{2.303}{k} \log 2$

$t_{1/4} = \frac{2.303}{k} \log 4/3 = \frac{2.303}{k} * 0.125 = \frac{0.288}{k}$

(77) $k = A e^{-Ea/RT}$ or $\log k = \log A - \frac{Ea}{2.303RT}$



(87) $K = A e^{-E/RT}$; as $T \to \infty$, $K = A = 6 \times 10^{4}$.

(89) $k = \frac{2.303}{t} \log \frac{0.100}{0.025}$ or $k = \frac{2.303}{40} \times \log 4$.

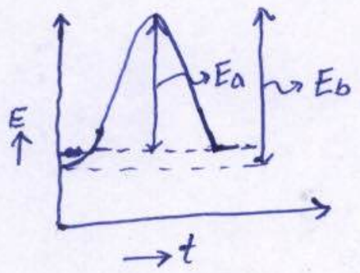
$r = \frac{2.303}{40} \times 2 \times 0.30 \times 0.01$ M min^{-1} $= 3.47 \times 10^{-4}$ M min^{-1}.

(91) $\log \frac{K_2}{K_1} = \frac{Ea}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$, $\log 2 = \frac{Ea}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$, $Ea = ?$

(93) $t_{1/2} \propto \frac{1}{(a_0)^{n-1}}$ $\Rightarrow$ $n-1 = 3$ or $n = 4$.

(95) $t_{1/2} \propto [a_0]^{1-n}$ or $t_{1/2} = k[a_0]^{1-0} = k[a_0]$ $\Rightarrow n = 0$.

(96)



$E_b > E_f$

(99) $k = A e^{-Ea/RT}$ or $\log K = \log A - \frac{Ea}{2.303RT}$

slope $= -Ea/2.303R$.

(100) $k = A e^{-E/RT}$; As $Ea \uparrow$, $k \downarrow$

$\Rightarrow Ea' < Ea''$

Previous years questions.

(1) More 'K' means reaction is achieving completion quickly.

(2) $r_1 = K[A]$, $r_2 = K[3A]$ or $\frac{r_2}{r_1} = 3$

(5) $r = k[A]$ or $[A] = r/k = \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} \approx 3.$

(8) order of reaction $= \frac{3}{2} - \frac{1}{2} = 1.0$

(10) $K = \frac{1}{t}\left[\frac{1}{[A]} - \frac{1}{[A]_0}\right]$ or $t = \frac{1}{8 \times 10^{-5}}\left[\frac{1}{0.5} - \frac{1}{1}\right] = \frac{10^5}{8}$ min.

(13) $30 = \frac{2.303}{K}\log\frac{100}{25}$ & $t = \frac{2.303}{K}\log\frac{100}{6.25}$

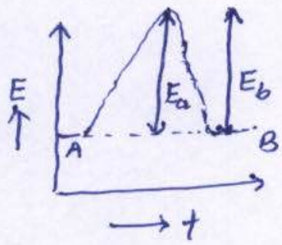
Now $\frac{t}{30} = \log\left(\frac{100}{6.25}\right) / \log\left(\frac{100}{25}\right) = \frac{\log 16}{\log 4} = 2$ or $t = 60$ min.

(19) $-\frac{d[SO_2]}{dt} = \frac{1.28 \times 10^{-3}}{64}$ mol/sec. $= 10^{-5}$ mol/sec.

$+\frac{d[SO_3]}{dt} = -\frac{d[SO_2]}{dt} = 10^{-5}$ mol/sec. $= 10^{-5} \times 80$ g/sec $= 0.80 \times 10^{-3}$ g/sec.

(31) For second order of reaction, unit of K is $L\,mol^{-1}s^{-1}$.

(33)



$A \rightarrow B$, $\Delta H = 0$

(37) $3A \rightarrow 2B$, $-\frac{1}{3}\frac{d[A]}{dt} = +\frac{1}{2}\frac{d[B]}{dt}$ or $+\frac{d[B]}{dt} = -\frac{2}{3}\frac{d[A]}{dt}$

(38) The increase in reaction rate is 2^9 times (i.e. 512 times).

(44) K for first order $= 10^{-3}\,s^{-1}$.

Now $t_{2/3} = \frac{2.303}{K}\log\frac{1}{1/3} = \frac{2.303}{10^{-3}}\log 3 = 1100$ sec.

(52) $1\text{ hr} = \frac{2.303}{K}\log\frac{0.8}{0.2}$ & $t = \frac{2.303}{K}\log\frac{0.900}{0.225}$

Now $\frac{t}{1} = \log\left(\frac{900}{225}\right) / \log\left(\frac{8}{2}\right) = \log 4 / \log 4 = 1$ or $t = 1$ hr.

(56) $\log K$ vs $\frac{1}{T}$ will produce straight line.

(59) $\frac{K_{T+10}}{K_T} \approx 2$. $\therefore$ $K_{300K} = 2 \times K_{290K} = 2 \times 3.2 \times 10^{-3} = 6.4 \times 10^{-3}$

(62) $r = K[A] = 3 \times 10^{-6} \times 0.1 = 3 \times 10^{-7}$

(66) $15 = \frac{2.303}{k} \log \frac{0.8}{0.4}$ —(i) $t = \frac{2.303}{k} \log \frac{0.100}{0.025}$ —(ii)

By (ii)/(i), $t = 30$ min.

(70) $r = K[A]$ or $K = \frac{r}{[A]} = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2}$

$t_{1/2} = \frac{0.6932}{K} = \frac{0.6932}{3 \times 10^{-2}} = \frac{69.32}{3}$ min $= 23.1$ min.

(72) $A = [A]_0 e^{-kt}$ or $[N_2O_5]_t = [N_2O_5]_0 e^{-kt}$.

(73) $\% B = \frac{k_1}{k_1 + k_2} \times 100$ and $\% C = \frac{k_2}{k_1 + k_2} \times 100$

$= \frac{1.26 \times 10^{-4}}{(1.26 + 10^{-4}) + (3.8 \times 10^{-5})}$ $= 23.17\%$.

$= 76.83\%$

(78) $K_{310} = 4 \times K_{290} = 4 \times 3.2 \times 10^{-3}\ s^{-1} = 1.28 \times 10^{-2}$.

(84) $-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt}$ $\therefore$ $-\frac{d[B]}{dt} = 2 \times 5 \times 10^{-4} = 10^{-3}$.

(87) $r = K[A]^n \Rightarrow 2.4 = K(2.2)^n$ & $0.6 = K(1.1)^n$

$\Rightarrow \frac{2.4}{0.6} = \left(\frac{2.2}{1.1}\right)^n$ or $4 = 2^n$ or $2^n = 2^2$ or $n = 2$

(90) No. of half lives $= \frac{12}{3} = 4$. or $\frac{N}{N_0} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^4 = \frac{1}{32}$.

(97) Rate of appearance of 'B' is $= +\frac{d[B]}{dt} = \frac{5 \times 10^{-3}}{10} = 5 \times 10^{-4}$.

(99) $r = K[A]^1[B]^{-1}$ $\therefore$ O.R. = 0

(101) $-\frac{1}{2}\frac{d[I^-]}{dt} = +\frac{d[I_2]}{dt}$ or $\frac{d[I_2]}{dt} = \frac{1}{2} \times \frac{0.02}{20} = 5 \times 10^{-4}$.

(106) Exothermic reaction; $E_b = E_a + \Delta H = (50+22)$ kcal $= 72$ kcal.

(112) $rate = k[A]^x[B]^y[C]^z$

$= k[A]^1[B]^0[C]^2 \Rightarrow$ O.R. = 3.

(113) $k_1 = k_2$ or $10^{16} e^{-2000/T} = 10^{15} e^{-1000/T}$

$T = \frac{1000}{2.303} K.$

(114) $\frac{T_{27}}{T_{17}} = 2$ or $T_{17} = \frac{T_{27}}{2} = \frac{10^{-3}}{2} = 5\times10^{-4}.$

(118) $-\frac{1}{5}\frac{d[Br^-]}{dt} = +\frac{1}{3}\frac{d[Br_2]}{dt}$

(125) $t_{75\%} = \frac{2.303}{k}\log\frac{1}{1/4}$

$t_{25\%} = \frac{2.303}{k}\log\frac{1}{3/4}$

$\frac{t_{75\%}}{t_{25\%}} = \frac{\log 4}{\log 4/3} = \frac{2\log 2}{2\log 2 - \log 3} = 4.8$

(126) $k = Ae^{-E_a/RT}$ or $k/A = e^{-E_a/RT} = e^{\frac{-2.303RT}{RT}} = e^{-2.303} \approx 0.10$

(128) $-\frac{d[N_2O_5]}{dt} = +\frac{1}{2}\frac{d[NO_2]}{dt} = +\frac{1}{0.5}\frac{d[O_2]}{dt}$

(130) $\frac{k_1}{1} = \frac{k_1'}{2} = \frac{k_1''}{1/2}$ or $2k_1 = k_1' = 4k_1''$

(134) $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$\log\left(\frac{k_2}{1.6\times10^{-5}}\right) = \frac{209\times10^3}{2.303\times8.314}\times\left[\frac{1}{600} - \frac{1}{700}\right]$, $k_2 = ?$

(136) $r = k_1[X][B]$ From slow step.

From fast step, $K_{eq} = \frac{[X]}{[A]^2}$ or $[X] = K_{eq}.[A]^2$

Now $r = k_1 k_{eq}[A]^2[B]$ or $r = k[A^2][B]$.

(140) $\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right].$

$\log 2 = \frac{E_a}{2.303\times8.314}\left[\frac{1}{298} - \frac{1}{308}\right]$, $E_a = ?$