Numericals

① $[R]_0 = 1.24 \times 10^{-2}$ (1st order given).
$[R] = 0.20 \times 10^{-2}$
$t = 1 \text{ hr} = 60 \text{ min}$.

$$k = \frac{2.303}{t} \log \frac{R_0}{R} = \frac{2.303}{60} \log \frac{1.24 \times 10^{-2}}{0.20 \times 10^{-2}}$$

$$= \frac{2.303}{60} \log 6.2$$

$$= 0.0384 \times (0.7924)$$

$$= 0.03043 \text{ min}^{-1}$$

②
$k = 1.20 \times 10^{-3} \text{ sec}^{-1}$ (1st order).
$R_0 = 5 \text{ gm}$ $t = ?$
$R = 3 \text{ gm}$.

$$k = \frac{2.303}{t} \log \frac{R_0}{R} = \frac{2.303}{t} \log \frac{5}{3}$$

$$1.20 \times 10^{-3} = \frac{2.303}{t} \log 1.667$$

$$t = \frac{2.303}{1.20 \times 10^{-3}} (0.2219)$$

$$t = 1.92 \times 10^{3} \times 0.2219 = 426 \text{ sec}.$$

③ → dib time given
→ dib conc given
} Pseudo 1st order.

(i) $r_{av} = -\frac{\Delta R}{\Delta t} = \frac{-(0.173 - 0.312)}{30} = \frac{0.139}{30}$

$$= 0.0046$$

$$= 4.6 \times 10^{-3} \text{ sec}^{-1}$$

(ii)

(a) $K = \frac{2.303}{t} \log \frac{R_0}{R}$

$= \frac{2.303}{30} \log \frac{0.551}{0.312}$

$= \frac{2.303}{30} \times 0.2455$

$= 0.019 \text{ sec}^{-1}$

(b) $K_2 = \frac{2.303}{30} \log \frac{0.312}{0.173}$

$= \frac{2.303}{30} \times 0.2560$

$= 0.2560 \text{ sec}^{-1}$

$= 0.01965$

$\approx 0.20 \text{ sec}^{-1}$

(c) $K_3 = \frac{2.303}{t} \log \frac{0.173}{0.085}$

$= \frac{2.303}{30} \times 0.3086$

$= 0.024 \text{ sec}^{-1}$

Av. $K = 0.19 + 0.20 + 0.024$

$= \frac{0.063}{3}$

$= \boxed{0.021 \text{ sec}^{-1}}$

(5) Suppose initial conc = 100 M.

(i) $R_0 = 100$

$R = 100 - 99 = 1$

$t_{99} = \frac{2.303}{K} \log \frac{100}{1}$

$t_{99} = \frac{2.303 \times 2}{K}$ — (1)

(ii) $R_0 = 100$

$R = 100 - 90 = 10$

$t_{90} = \frac{2.303}{K} \log \frac{100}{10}$

$t_{90} = \frac{2.303 \log 10}{K}$

$t_{90} = \frac{2.303}{K}$ — (2)

→ (1)/(2)

$\frac{t_{99}}{t_{90}} = \frac{\frac{2.303 \times 2}{K}}{\frac{2.303}{K}} = 2$

$t_{99} = 2 \times t_{99}$.

(6) $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{3} = 0.231 \text{ hour}^{-1}$

$K = \frac{2.303}{t} \log \frac{R_0}{R_t}$

$0.231 = \frac{2.303}{3} \log \frac{R_0}{R_t}$

$\log \frac{R_0}{R_t} = 0.9027$

Antilog

$\frac{R_0}{R_t} = 7.993. \quad \therefore R_0 = 7.993 \times R_t$

Suppose $R_0 = 100x.$

$\therefore 100x = 7.993 \times R_t$

$\boxed{R_t = 12.5\,x.}$

(7) $2\,NH_3 \rightarrow N_2 + 3H_2$. Zero order

→ It is zero order.

$\therefore -\frac{d[NH_3]}{dt} = K[NH_3]^0 = K$

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

$\therefore \frac{dN_2}{dt} = K, \quad \frac{dH_2}{dt} = 3K = 3 \times 2.5 \times 10^{-4}$

$= 2.5 \times 10^{-4}$

(3)

(8) $T_1 = 298K$ $K_1 =$
$T_2 = 308K$ $K_2 =$ } $K_2 = 2K_1$

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

$$\log 2 = \frac{Ea}{2.303 \times 1.987}\left[\frac{308 - 298}{308 \times 298}\right]$$

$$0.3010 = \frac{Ea}{2.303 \times 1.987} \times \frac{10}{308 \times 298}$$

$$Ea = 12642.075 \text{ cal.}$$

(9) C^{14} $t_{1/2} = 5370$ years.

$$\rightarrow K = \frac{0.693}{t_{1/2}} = \frac{0.693}{5370} = 1.29 \times 10^{-4} \text{ year}^{-1}$$

$\rightarrow$ Suppose $R_0 = 100$ y.
$R_t = 60$ y. $\Rightarrow R_0 = \frac{60 \times R_0}{100}$

$$t = \frac{2.303}{1.29 \times 10^{-4}} \log \frac{R_0}{R_t}$$

$$= \frac{2.303}{1.29 \times 10^{-4}} \log \frac{R_0 \times 100}{60 \times R_0}$$

$$K = \frac{2.303}{1.29 \times 10^{-4}} \log \frac{100}{60}$$

$$K = \frac{2.303}{1.29 \times 10^{-4}} \times 0.2219.$$

$$K = 2962 \text{ year}.$$

(10) $t_{1/2} = 28.1$ year — 1st order.

$R_0 = 1$ µg. (10^{-6} gm)

$t_{20} \rightarrow [R]_{20} = ?$

$t_{70} \rightarrow [R]_{70} = ?$

$$\rightarrow K = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} = 2.466 \times 10^{-2} \text{ year}^{-1}$$

$$\rightarrow K = \frac{2.303}{t} \log \frac{R_0}{R_t}$$

$$2.466 \times 10^{-2} = \frac{2.303}{20} \log \frac{1}{R_t}$$

$$20 \times \frac{2.466 \times 10^{-2} \times 2.303}{2.303} = \log 1 - \log R_t$$

$$0.00283 = -\log R_t$$

$$\log R_t =$$

$0.2142 = -\log R_t$

$\log R_t = -0.2142.$

$\log R_t = -1 + 0.7858$ $(1 - 0.2142) = 0.7858)$

$\log R_t = \bar{1}.7858$

Antilog

$R_t = R_{20} = 0.6106$ llg

$= 6.106 \times 10^{-7}$ gm.

Similar for R_{70}

$R_{70} = 1.780 \times 10^{-7}$ gm.

(11) $T_1 = 300K$, $K_1 = 2 \times 10^{-3}$

$T_2 = 320K$, $K_2 = 6 \times 10^{-3}$ (3-times)

$E_a = ?$

$T_3 = 310K$, $K_3 = ?$

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

$$\log \frac{6 \times 10^{-3}}{2 \times 10^{-3}} = \frac{E_a}{2.303 \times 1.987}\left[\frac{320 - 300}{320 \times 300}\right]$$

$$\log 3 = \frac{0.7 - 9}{4.576} \times \frac{20}{\times 320 \times 300}$$

$$Ea = \frac{0.4771 \times 4.576 \times 320 \times 300}{20}$$

$$\boxed{Ea = 10480 \text{ cal.}}$$

→

$$\Delta t = T_3 = 310 \text{ K.} \qquad T_1 = 300, \quad T_3 = 310$$

$$\log \frac{K_3}{K_1} = \frac{Eq}{4.576} \times \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{K_3}{2 \times 10^{-3}} = \frac{10480}{4.576} \left[\frac{310 - 300}{310 \times 300}\right]$$

$$\log K_3 - \log 2 \times 10^{-3} = 0.2462$$

$$\log K_3 \; \log 73 - \log 2 = 0.2462$$

$$\log K_3 + 2.6990 = 0.2462$$

$$\log K_3 = -2.4528$$

$$K_3 = \text{Antilog } (-2.4528)$$

$$K_3 = -3 + 0.5472$$

$$K_3 = \bar{3}.5472$$

$$K_3 = 3.526 \times 10^{-3} \text{ mint.}$$

(12) dist t - given
dB conc = given.

(1) 0 to 5.
0.80×10^{-3} to 0.160×10^{-3}

$$\text{Rate} = -\frac{dB}{dt} = -\frac{(0.80 \times 10^{-3} - 0.160 \times 10^{-3})}{5-0}$$

$$= \frac{(0.80)10^{-3}}{5}$$

$$= 0.016.$$

Similar calculate for
(2) 5 – 10
(3) 10 – 20
(4) 20 – 30.

(13) $K = 70 \text{ sec}^{-1}$

$$R = \frac{R_0}{18}$$

$$K = \frac{2.303}{t} \log \frac{R_0}{R_0/18}$$

$$70 = \frac{2.303}{t} \log 8$$

$$t = \frac{2.303}{70} \times 1.2553$$

$t = 0.0413$ sec.

(14)

$K = 2.428 \times 10^{-5}\ sec^{-1}$

$T = 550K.$

$Ea = 197.7$ kJoule/mole.

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

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

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

$$= \log (2.428 \times 10^{-5}) + \frac{197.7}{8.314 \times 550 \times 2.303}$$

$$= -5 + 0.3842 - \neq 18.77$$

$$= -4.6148 + 18.77$$

$$\log A = 14.1552$$

$A =$ Antilog of 14.1552

$$\boxed{A = 1.430 \times 10^{14}}$$

(15) $T_1 = 283$, $K_1 = 4.5 \times 10^3$ sec^{-1}

$T_2 = ?$ $K_2 = 3 \times 10^{10}$ sec^{-1}

$Ea = 60$ kJoule.

$$\log \frac{K_2}{K_1} = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log \frac{3 \times 10^{10}}{4.5 \times 10^3} = \frac{60 \times 10^3}{2.303 \times 8.314} \times \left[\frac{1}{283} - \frac{1}{T_2}\right]$$

$$6.8239 = 3133.63 \left[\frac{T_2 - 283}{283 T_2}\right]$$

$T_2 = 737.52$ K.

End.