

## Topic 1

1. (i) Order = 2,

$$\text{Dimensions of } k = \frac{\text{Rate}}{[\text{NO}]^2} = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1} \text{ s}^{-1}$$

(ii) Order = 2, Dimensions of  $k = \text{L mol}^{-1} \text{ s}^{-1}$

(iii) Order =  $\frac{3}{2}$ ,

$$\begin{aligned} \text{Dimensions of } k &= \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^{3/2}} = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^{3/2}} \\ &= \text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1} \end{aligned}$$

(iv) Order = 1,

$$\text{Dimensions of } k = \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{Cl}]} = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{\text{mol L}^{-1}} = \text{s}^{-1}$$

2. Initial rate =  $k[A][B]^2$

$$= (2.0 \times 10^{-6}) \times (0.1) \times (0.2)^2 = 8 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}$$

When  $[A]$  is reduced from  $0.10 \text{ mol L}^{-1}$  to  $0.06 \text{ mol L}^{-1}$ , i.e.  $0.04 \text{ mol L}^{-1}$  of  $A$  has reacted. Then according to equation, amount of  $B$  reacted is half of  $A$ .

$$[B] = \frac{1}{2} \times 0.04 \text{ mol L}^{-1} = 0.02 \text{ mol L}^{-1}$$

$$\text{Hence, } [B] \text{ left} = 0.2 - 0.02 = 0.18 \text{ mol L}^{-1}$$

$$\text{Now, again rate} = k[A][B]^2$$

$$\begin{aligned} \therefore \text{Rate} &= (2.0 \times 10^{-6}) \times (0.06) \times (0.18)^2 \\ &= 3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1} \end{aligned}$$

3. For the reaction,  $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} \quad \dots(1)$$

For zero order reaction,

$$\text{Rate} = k \quad \dots(2)$$

From equation (1) and (2)

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k \quad \dots(3)$$

$$\therefore \text{Rate of production of } \text{N}_2 = \frac{d[\text{N}_2]}{dt} = k$$

$$k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\begin{aligned} \therefore \text{Rate of production of } \text{N}_2 &= k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \\ &\quad \text{(From equation (3))} \end{aligned}$$

$$\text{Rate of production of } \text{H}_2 = \frac{d[\text{H}_2]}{dt} = 3k$$

$$= 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

4. In terms of pressure,

$$\text{Units of rate} = \text{bar min}^{-1}$$

$$\text{Units of } k = \frac{\text{Rate}}{(\rho_{\text{CH}_3\text{OCH}_3})^{3/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2} \text{ min}^{-1}$$

5. Following are the factors on which rate of reaction depends :

(i) Nature of the reactant : Rate of reaction depends on nature of reactant.

Example : Reactions of ionic compounds are faster than that of covalent compounds.

(ii) State of reactants : Solid reactions are slow, reactions of liquids are fast whereas that of gases are very fast.

(iii) Temperature : Rate of reaction largely depends on temperature. It has been observed that every  $10^\circ\text{C}$  rise in temperature increases rate of reaction by 2-3 times.

$$\frac{r_{t+10}}{r_t} = 2-3. \text{ This ratio is called temperature coefficient.}$$

There are two reasons for increasing rate of reaction with increasing temperature.

(a) Increase in temperature increases average kinetic energy of reactant molecules. Hence, rate of collision increases.

(b) With increase in temperature number of molecules having threshold energy also increases i.e., number of active molecules increases. As a result, number of effective collisions increases. Hence, rate of reaction increases.

(iv) Concentration : Rate of reaction also depends on concentration of reactants.

Rate =  $k \times C^n$ , where  $n$  = order of reaction,  $C$  = concentration of reactant.

(v) Presence of catalyst : Rate of reaction also depends on presence of catalyst. Catalyst increases rate of reaction by any of the following ways :

(a) Increasing surface area of reaction.

(b) Adsorbing the reactants on its surface and thus increasing chances of collision.

(c) By forming unstable intermediate with the substrate.

(d) By providing alternate path of lower activation energy.

6. Rate =  $kR^2$

(i) If  $[A] = 2R$ , rate =  $k(2R)^2 = 4kR^2$  i.e., rate of reaction increases 4 times when concentration is doubled.

(ii) If  $[A] = \frac{1}{2} R$ , rate =  $k\left(\frac{R}{2}\right)^2 = \frac{1}{4}kR^2$  i.e., rate becomes  $\frac{1}{4}$

when concentration is reduced to  $\frac{1}{2}$ .

7. (i) Reaction is first order in A and second order in B, hence, differential rate equation is  $\frac{dx}{dt} = k[A][B]^2$

(ii) Let rate =  $kab^2$

If [B] is tripled, Rate =  $ka(3b)^2 = 9kab^2$

i.e., Rate increases 9 times.

(iii) If both [A] and [B] are doubled,

Rate =  $k(2a)(2b)^2 = 8kab^2$

i.e. Rate of reaction increases 8 times.

8. Suppose order with respect to A is 'X' and with respect to B is 'Y'. Then the rate of law will be

$$r_0 = \frac{dx}{dt} = k[A]^x[B]^y$$

$$5.07 \times 10^{-5} = k(0.2)^x(0.3)^y \quad \dots(i)$$

$$5.07 \times 10^{-5} = k(0.2)^x(0.10)^y \quad \dots(ii)$$

Dividing (i) by (ii), we get

$$1 = 3^y \Rightarrow 3^0 = 3^y \Rightarrow y = 0$$

$$5.07 \times 10^{-5} = k(0.2)^x(0.1)^0 \quad \dots(iii)$$

$$1.43 \times 10^{-4} = k(0.4)^x(0.05)^0 \quad \dots(iv)$$

Dividing (iv) by (iii), we get  $2.8 = 2^x$

$$\log 2.8 = x \log 2$$

$$\text{or } x = \frac{\log 2.8}{\log 2.0} = \frac{0.4472}{0.3010} = 1.48 \approx 1.5$$

The order of reaction is 1.5 with respect to 'A' and zero with respect to 'B'.

9. Suppose order with respect to A is  $m$  and with respect to B is  $n$ . Then the rate law will be

$$\text{Rate} = k[A]^m[B]^n$$

Substituting the value of experiments I to IV, we get

$$\text{Expt. I : Rate} = 6.0 \times 10^{-3} = k(0.1)^m(0.1)^n \quad \dots(i)$$

$$\text{Expt. II : Rate} = 7.2 \times 10^{-2} = k(0.3)^m(0.2)^n \quad \dots(ii)$$

$$\text{Expt. III : Rate} = 2.88 \times 10^{-1} = k(0.3)^m(0.4)^n \quad \dots(iii)$$

$$\text{Expt. IV : Rate} = 2.4 \times 10^{-2} = k(0.4)^m(0.1)^n \quad \dots(iv)$$

Comparing equation (i) and equation (iv)

$$\therefore \frac{(\text{Rate})_I}{(\text{Rate})_{IV}} = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k(0.1)^m(0.1)^n}{k(0.4)^m(0.1)^n}$$

$$\text{or, } \frac{1}{4} = \frac{(0.1)^m}{(0.4)^m} = \left(\frac{1}{4}\right)^m \therefore m = 1$$

Comparing equation (ii) and equation (iii)

$$\frac{(\text{Rate})_{II}}{(\text{Rate})_{III}} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k(0.3)^m(0.2)^n}{k(0.3)^m(0.4)^n}$$

$$\text{or, } \left(\frac{1}{2}\right)^2 = \frac{(0.2)^n}{(0.4)^n} = \left(\frac{1}{2}\right)^n \therefore n = 2$$

$\therefore$  Rate law expression is : Rate =  $k[A][B]^2$ .

The rate constant can be calculated from the given data of any experiment using expression :

$$k = \frac{\text{Rate}}{[A][B]^2}$$

$$\text{From Expt. I, } k = \frac{6.0 \times 10^{-3}}{0.1 \times (0.1)^2} = 6.0$$

$$\therefore \text{Rate constant } k = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

$$\text{Unit of } k, k = \frac{\text{Rate}}{[A][B]^2} = \frac{\text{mol L}^{-1} \text{ min}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})^2} = \text{mol}^{-2} \text{ L}^2 \text{ min}^{-1}$$

10. The reaction is first order with respect to A and zero order with respect to B,

Hence the rate expression will be =  $k[A]^1[B]^0 = k[A]$

From expt. I :  $2.0 \times 10^{-2} = k(0.1)$

or,  $k = 0.2 \text{ min}^{-1}$

From expt. II :  $4.0 \times 10^{-2} = (0.2) \times [A]$

$\Rightarrow [A] = 0.2 \text{ mol L}^{-1}$

From expt. III : Rate =  $(0.2)(0.4)$

=  $0.08 \text{ mol L}^{-1} \text{ min}^{-1} = 8 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$

From expt. IV :  $2.0 \times 10^{-2} = (0.2) \times [A]$

$\Rightarrow [A] = 0.1 \text{ mol L}^{-1}$

## Topic 2

1. Average rate during the interval 30-60 sec

$$\text{Rate} = -\frac{C_2 - C_1}{t_2 - t_1} = -\frac{0.17 - 0.31}{60 - 30} = \frac{0.14}{30} \text{ mol L}^{-1} \text{ s}^{-1} = 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

2. Half-life period of a first order reaction is given by

$$t_{1/2} = \frac{0.693}{k}, \text{ hence}$$

$$(i) t_{1/2} = \frac{0.693}{200} = 3.46 \times 10^{-3} \text{ s}$$

$$(ii) t_{1/2} = \frac{0.693}{2} = 0.346 \text{ min}$$

$$(iii) t_{1/2} = \frac{0.693}{4} = 0.173 \text{ year}$$

3. Radioactive decay follows first order kinetics. Therefore,

$$\text{Decay constant } (\lambda) = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730} \text{ yr}^{-1}$$

Given,  $[R]_0 = 100 \therefore [R] = 80$

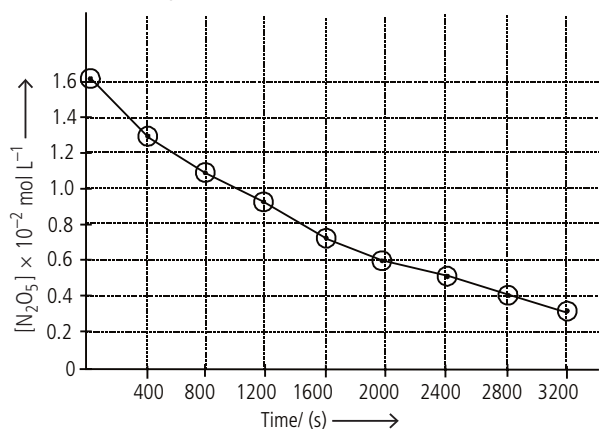
$$\text{and } t = \frac{2.303}{\lambda} \log \frac{[R]_0}{[R]} = \frac{2.303}{\left(\frac{0.693}{5730}\right)} \log \left(\frac{100}{80}\right) = \frac{2.303 \times 5730}{0.693} \times 0.0969 \text{ yr} = 1845 \text{ years}$$

4.

t/s	$[\text{N}_2\text{O}_5] \times 10^{-2} / \text{mol L}^{-1}$	$\log[\text{N}_2\text{O}_5]$
0	1.63	-1.79
400	1.36	-1.87

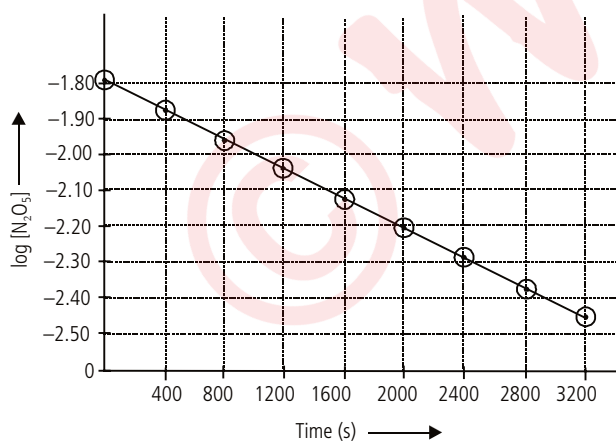
800	1.14	-1.94
1200	0.93	-2.03
1600	0.78	-2.11
2000	0.64	-2.19
2400	0.53	-2.28
2800	0.43	-2.37
3200	0.35	-2.46

(i) Plot of  $[N_2O_5]$  vs time



(ii) Initial conc. of  $N_2O_5 = 1.63 \times 10^{-2} \text{ M}$   
 Half of this concentration =  $0.815 \times 10^{-2} \text{ M}$   
 Time corresponding to this concentration = 1440 s.  
 Hence,  $t_{1/2} = 1440 \text{ s}$

(iii) Plot of  $\log [N_2O_5]$  vs time



(iv) As plot of  $\log [N_2O_5]$  vs time is a straight line, it is a reaction of first order, i.e. rate law is,  
 Rate =  $k[N_2O_5]$

(v) For first order reaction,

$$\log R = -\frac{k}{2.303}t + \log R_0$$

Therefore slope of the graph drawn between  $\log R$  and  $t$  will be  $\frac{-k}{2.303}$

$$\therefore \text{Slope of the line} = -\frac{k}{2.303} = \frac{y_2 - y_1}{t_2 - t_1}$$

$$\text{or, Slope} = \frac{-2.46 - (-1.79)}{3200 - 0} = -\frac{0.67}{3200}$$

$$\text{or, } \frac{k}{2.303} = \frac{0.67}{3200}$$

$$\text{or, } k = \frac{0.67}{3200} \times 2.303 = 4.82 \times 10^{-4} \text{ s}^{-1}$$

$$(vi) t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4}} = 1438 \text{ s}$$

The value of  $t_{1/2}$  calculated from the value of  $k$  is very close to that obtained from graph.

5. Given,  $k = 60 \text{ s}^{-1}$ ,  $[R] = \frac{[R]_0}{16}$ ,  $t = ?$

$$\text{Using formula, } t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} = \frac{2.303}{60} \log 16 = 4.62 \times 10^{-2} \text{ s}$$

Alternatively,

In general, amount of the substance left after  $n$  half lives,

$$R = \frac{[R]_0}{2^n} = \frac{[R]_0}{16}$$

$$\therefore n = 4 \text{ and } t = n \times t_{1/2}$$

$$t = n \times \frac{0.693}{k} = 4 \times \frac{0.693}{60} = 0.0462 \text{ s}$$

6. As radioactive disintegration follows first order kinetics. Hence

$$\text{Decay constant of } ^{90}\text{Sr}, (\lambda) = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} = 2.466 \times 10^{-2} \text{ yr}^{-1}$$

To calculate the amount left after 10 years

Given,  $[R]_0 = 1 \mu\text{g}$ ,  $t = 10$  years,

$$k = 2.466 \times 10^{-2} \text{ yr}^{-1}, [R] = ?$$

$$\text{Using formula, } \lambda = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\text{or } 2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{[R]}$$

$$\frac{2.466 \times 10^{-2} \times 10}{2.303} = -\log [R]$$

$$\text{or, } \log [R] = -0.1071$$

$$\text{or, } [R] = \text{Antilog}(-0.1071) = 0.7814 \mu\text{g}$$

To calculate the amount left after 60 years,  $t = 60$  years,

$$[R]_0 = 1 \mu\text{g}, [R] = ?$$

$$\text{or, } 2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{[R]}$$

$$\text{or, } \frac{2.466 \times 10^{-2} \times 60}{2.303} = -\log [R]$$

or,  $\log [R] = -0.6425$

or,  $[R] = \text{Antilog}(-0.6425) = 0.2278 \mu\text{g}$

7. 99% completion means that  $x = 99\%$  of  $[R]_0$  or,  
 $[R] = [R]_0 - 0.99[R]_0 = 0.01[R]_0$

For first order reaction,  $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

$$\therefore t_{99\%} = \frac{2.303}{k} \log \frac{[R]_0}{0.01[R]_0} = \frac{2.303}{k} \log 10^2 = 2 \times \frac{2.303}{k}$$

90% completion means that  $[R] = [R]_0 - 0.90[R]_0$   
 $= 0.1[R]_0$

$$\therefore t_{90\%} = \frac{2.303}{k} \log \frac{[R]_0}{0.1[R]_0} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}$$

$$\therefore \frac{t_{99\%}}{t_{90\%}} = \left( \frac{2 \times 2.303}{k} \right) / \left( \frac{2.303}{k} \right) = 2$$

or,  $t_{99\%} = 2 \times t_{90\%}$

8. 30% decomposition means that  $x = 30\%$  of  $[R]_0$  or,  
 $[R] = [R]_0 - 0.3[R]_0 = 0.7[R]_0$

For reaction of 1<sup>st</sup> order,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{40} \log \frac{[R]_0}{0.70[R]_0}$$

$$= \frac{2.303}{40} \log \frac{10}{7} \text{ min}^{-1}$$

$$= \frac{2.303}{40} \times 0.1549 \text{ min}^{-1} = 8.918 \times 10^{-3} \text{ min}^{-1}$$

For a 1<sup>st</sup> order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3} \text{ min}^{-1}} = 77.7 \text{ min}$$

9.  $(\text{CH}_3)_2\text{CHN} = \text{NCH}(\text{CH}_3)_{2(g)} \longrightarrow \text{N}_{2(g)} + \text{C}_6\text{H}_{14(g)}$

	Azoisopropane		Hexane
Initial pressure	$P_0$	0	0
Pressure after time $t$	$P_0 - p$	$p$	$p$

Total pressure after time  $t$  ( $P_t$ )

$$= (P_0 - p) + p + p = P_0 + p \text{ or } p = P_t - P_0$$

$$[R]_0 \propto P_0 \text{ and } [R] \propto P_0 - p$$

On substituting the value of  $p$ ,

$$[R] \propto P_0 - (P_t - P_0), \text{ i.e. } [R] \propto 2P_0 - P_t$$

As decomposition of azoisopropane is a first order reaction

$$\therefore k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{t} \log \left( \frac{P_0}{2P_0 - P_t} \right)$$

When  $t = 360$  sec,

$$k = \frac{2.303}{360} \log \left( \frac{35.0}{2 \times 35.0 - 54.0} \right) = \frac{2.303}{360} \log \frac{35.0}{16}$$

$$= 2.175 \times 10^{-3} \text{ s}^{-1}$$

When  $t = 720$  sec,

$$k = \frac{2.303}{720} \log \frac{35.0}{2 \times 35.0 - 63} = \frac{2.303}{720} \log 5$$

$$= 2.235 \times 10^{-3} \text{ s}^{-1}$$

$$\therefore \text{Average value of } k = \frac{2.175 + 2.235}{2} \times 10^{-3} \text{ s}^{-1}$$

$$= 2.20 \times 10^{-3} \text{ s}^{-1}$$

10.  $\text{SO}_2\text{Cl}_{2(g)} \longrightarrow \text{SO}_{2(g)} + \text{Cl}_{2(g)}$

Let initial pressure	$P_0$	0	0
Pressure at time $t$	$P_0 - p$	$p$	$p$

Let initial pressure  $P_0 \propto R_0$

Pressure at time  $t$ ,  $P_t = P_0 - p + p + p = P_0 + p$

$\therefore$  Pressure of reactant at time  $t$

$$= P_0 - p = 2P_0 - P_t \propto R$$

Using formula,  $k = \frac{2.303}{t} \log \left( \frac{P_0}{2P_0 - P_t} \right)$

When  $t = 100$  s,

$$k = \frac{2.303}{100} \log \left( \frac{0.5}{2 \times 0.5 - 0.6} \right) = \frac{2.303}{100} \log(1.25)$$

$$= \frac{2.303}{100} (0.0969) = 2.2316 \times 10^{-3} \text{ s}^{-1}$$

When  $P_t = 0.65$  atm,

$\therefore$  Pressure of  $\text{SO}_2\text{Cl}_2$  at time  $t$  ( $p_{\text{SO}_2\text{Cl}_2}$ ),

$$R = 2P_0 - p_t = 2 \times 0.50 - 0.65 \text{ atm} = 0.35 \text{ atm}$$

$$\text{Rate at that time} = k \times p_{\text{SO}_2\text{Cl}_2} = (2.2316 \times 10^{-3}) \times (0.35)$$

$$= 7.8 \times 10^{-4} \text{ atm s}^{-1}$$

11. The units of  $k$  shows that the reaction is of first order.

$$\text{Hence, } k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\text{or, } 2.0 \times 10^{-2} = \frac{2.303}{100} \log \frac{1.0}{[R]}$$

$$\text{or, } \log [R] = -0.8684$$

$$\therefore [R] = \text{Antilog}(-0.8684) = 0.1354 \text{ mol L}^{-1}$$

12. Sucrose decomposes according to first order rate law,  
Hence,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}, t_{1/2} = 3 \text{ hrs, } t = 8 \text{ hrs, } \frac{[R]}{[R]_0} = ?$$

$$t_{1/2} = 3.0 \text{ hrs, } \therefore k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3} = 0.231 \text{ hr}^{-1}$$

$$\text{Hence, } 0.231 = \frac{2.303}{8} \log \frac{[R]_0}{[R]}$$

$$\text{or, } \log \frac{[R]_0}{[R]} = 0.8024$$

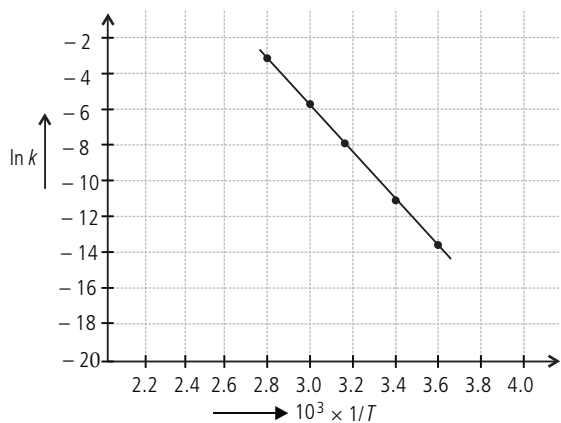
$$\text{or, } \frac{[R]_0}{[R]} = \text{Antilog}(0.8024) = 6.345$$

$$\text{or, } \frac{[R]}{[R]_0} = \frac{1}{6.345} = 0.158$$

## Topic 3

1. The values of rate constants for the decomposition of  $N_2O_5$  at various temperatures are given below :

$T(^{\circ}C)$	$T(K)$	$1/T$	$k(s^{-1})$	$\ln k (= 2.303 \log k)$
0	273	$3.6 \times 10^{-3}$	$7.87 \times 10^{-7}$	-14.06
20	293	$3.4 \times 10^{-3}$	$1.70 \times 10^{-5}$	-10.98
40	313	$3.19 \times 10^{-3}$	$25.7 \times 10^{-5}$	-8.266
60	333	$3.00 \times 10^{-3}$	$178 \times 10^{-5}$	-6.332
80	353	$2.8 \times 10^{-3}$	$2140 \times 10^{-5}$	-3.844



Graph between  $\ln k$  and  $1/T$

Slope of the line =  $\tan \theta$

$$= \frac{y_2 - y_1}{x_2 - x_1} = \frac{-10.98 - (-14.06)}{3.4 - 3.6} \times 10^3 = -15.5 \times 10^3$$

$$E_a = -\text{slope} \times R = -(-15.5 \times 10^3 \times 8.314) \\ = 128.86 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\text{Again } \ln A = \ln k + \frac{E_a}{RT}$$

$$= -14.06 + \frac{128.86 \times 10^3 \text{ JK}^{-1} \text{ mol}^{-1}}{8.314 \times 273}$$

$$= -14.06 + 56.77 = 42.71$$

$$\text{or, } \log A = 18.53$$

$$\text{or, } A = \text{antilog } 18.53 = 0.3388 \times 10^{19}$$

$$\text{or, } A = 3.388 \times 10^{18}$$

Value of rate constant  $k$  at 303 K and 323 K can be obtained from graph.

First of all  $\ln k$  is obtained corresponding to  $\frac{1}{303 \text{ K}}$  and  $\frac{1}{323 \text{ K}}$  and then  $k$  is calculated.

2. Here,  $k = 2.418 \times 10^{-5} \text{ s}^{-1}$ ,

$$E_a = 179.9 \text{ kJ mol}^{-1}, T = 546 \text{ K}, A = ?$$

According to Arrhenius equation,

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

$$= \log(2.418 \times 10^{-5}) + \frac{179.9}{2.303 \times 8.314 \times 10^{-3} \times 546}$$

$$= (-5 + 0.3834) + 17.2081 = 12.5924 \text{ s}^{-1}$$

$$\text{or, } A = \text{Antilog}(12.5924) \text{ s}^{-1} = 3.912 \times 10^{12} \text{ s}^{-1}$$

3. Arrhenius equation,  $k = Ae^{-E_a/RT}$

$$\text{Given equation is } k = (4.5 \times 10^{11} \text{ s}^{-1})e^{-28000K/T}$$

Comparing both the equations, we get

$$\frac{E_a}{RT} = \frac{28000 \text{ K}}{T}$$

$$\text{or, } E_a = 28000 \text{ K} \times R = 28000 \times 8.314 \\ = 232.79 \text{ kJ mol}^{-1}$$

4. According to Arrhenius equation,  $k = Ae^{-E_a/RT}$

$$\text{or, } \ln k = \ln A - \frac{E_a}{RT}$$

$$\text{or, } \log k = \log A - \frac{E_a}{2.303RT} \quad \dots(i)$$

Given equation is

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K}/T \quad \dots(ii)$$

$$\text{Comparing (i) with (ii), } \frac{E_a}{2.303RT} = \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\text{or, } E_a = 2.303R \times 1.25 \times 10^4 \text{ K} \\ = 2.303 \times (8.314) \times 1.25 \times 10^4 = 239.34 \text{ kJ mol}^{-1}$$

$$\text{When } t_{1/2} = 256 \text{ min, } k = \frac{0.693}{256 \times 60} = 4.51 \times 10^{-5} \text{ s}^{-1}$$

Substituting this value in the given equation,

$$\log(4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\text{i.e., } (-5 + 0.6542) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\text{or, } \frac{1.25 \times 10^4 \text{ K}}{T} = 18.6858 \text{ or, } T = 669 \text{ K}$$

5. Given  $k_1 = 4.5 \times 10^3 \text{ s}^{-1}$ ,

$$T_1 = 10 + 273 \text{ K} = 283 \text{ K}; k_2 = 1.5 \times 10^4 \text{ s}^{-1}, T_2 = ?,$$

$$E_a = 60 \text{ kJ mol}^{-1}$$

Applying Arrhenius equation,

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

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000}{2.303 \times 8.314} \left( \frac{T_2 - 283}{283 T_2} \right)$$

$$\text{or, } \log 3.333 = 3133.63 \left( \frac{T_2 - 283}{283 T_2} \right)$$

$$\text{or, } \frac{0.5228}{3133.63} = \frac{T_2 - 283}{283 T_2}$$

$$\text{or, } 0.0472 T_2 = T_2 - 283 \text{ or } 0.9528 T_2 = 283$$

$$\text{or, } T_2 = \frac{283}{0.9528} = 297 \text{ K} = 297 - 273 = 24^{\circ}C$$

$$6. \quad t = \frac{2.303}{k_1} \log \left( \frac{[R]_0}{\frac{90}{100}[R]_0} \right),$$

$$t = \frac{2.303}{k_2} \log \left( \frac{[R]_0}{\frac{75}{100}[R]_0} \right)$$

$$t = \frac{2.303}{k_1} \log \frac{10}{9}, \quad t = \frac{2.303}{k_2} \log \frac{4}{3}$$

$$\frac{2.303}{k_1} \log \frac{10}{9} = \frac{2.303}{k_2} \log \frac{4}{3}$$

$$\Rightarrow \frac{k_2}{k_1} = \frac{\log \frac{4}{3}}{\log \frac{10}{9}} = \frac{\log 1.333}{\log 1.111} = \frac{0.1249}{0.0457} = 2.733$$

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

$$\log 2.733 = \frac{E_a}{2.303 \times 8.314} \left( \frac{308 - 298}{298 \times 308} \right)$$

$$E_a = \frac{2.303 \times 8.314 \times 308 \times 298}{10} \times 0.4367$$

$$= \frac{19.147 \times 308 \times 298}{10} \times 0.4367 = 76.75 \text{ kJ mol}^{-1}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

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

$$= \log(4 \times 10^{10}) - \frac{76.75 \times 1000}{2.303 \times 8.314 \times 318}$$

$$= 10.6021 - \frac{76750}{6088.746}$$

$$= 10.6021 - 12.6051 = -2.003$$

$$k = \text{Antilog}(-2.003) = 9.93 \times 10^{-3}$$

$$7. \quad \text{Given } r_2 = 4r_1, T_1 = 293 \text{ K}, T_2 = 313 \text{ K}, E_a = ?$$

$$\text{We know, } \frac{r_2}{r_1} = \frac{k_2}{k_1} = \frac{4}{1}$$

Using Arrhenius equation,

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

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left( \frac{1}{293} - \frac{1}{313} \right)$$

$$\text{or, } E_a = \log 4 \times \frac{2.303 \times 8.314 \times 293 \times 313}{20}$$

$$\text{or, } E_a = 52.864 \text{ kJ/mol}$$

8. The rate constant increases with increase in temperature and becomes almost double for every 10° increase in temperature. Swedish chemist, Arrhenius derived a quantitative relation between rate of reaction and temperature. According to Arrhenius,

$$k = Ae^{-\frac{E_a}{RT}} \quad \text{or, } \log k = \log A - \frac{E_a}{RT}$$

$$\text{or, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$$

where  $k_1$  = rate constant at temperature  $T_1$ ,

$k_2$  = rate constant at temperature  $T_2$ ,

$E_a$  = energy of activation,  $R$  = universal gas constant.



