



Q. 01 A first order Reaction is 15% completed in 20 min. How long it will take to be 60% completed. (2K+6)

Soln. We know that,

$$K = \frac{2.303}{t} \cdot \log \frac{[A]_0}{[A]}$$

$$= \frac{2.303}{20} \log \frac{100}{85}$$

$$= 8.127 \times 10^{-3} \text{ min}^{-1}$$

Again, $t = \frac{2.303}{K} \log \frac{[A]_0}{[A]}$

$$\text{or, } t = \frac{2.303}{K} \cdot \log \frac{100}{40}$$

$$\text{or, } t = \frac{2.303}{8.127 \times 10^{-3}} \log \frac{100}{40}$$

$$\therefore t = 112.76 \text{ min (Ans.)}$$

Here, $t = 20 \text{ min}$

$$[A]_0 = 100$$

$$[A] = (100 - 15) = 85$$

for Second case

$$[A]_0 = 100$$

$$[A] = (100 - 60) = 40$$

Q. 02. Show that, for a first order reaction time required for 75% reaction is twice time for 50%, (2K+5)

Soln. We know, for first order reaction,

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

where, K is the rate constant of the reaction

Let,

$$\text{for time } t_1, K = \frac{2.303}{t_1} \log \frac{a}{a-x_1} \quad \rightarrow \textcircled{1}$$

$$\text{for time } t_2, K = \frac{2.303}{t_2} \log \frac{a}{a-x_2} \quad \rightarrow \textcircled{2}$$

$$\text{Here, } \alpha_1 = 75\% \text{ of } a = \frac{75}{100} \times a = 0.75a$$

so, equation ① taken the form

$$K = \frac{2.303}{t_1} \cdot \log \frac{a}{a - 0.75a}$$

$$\text{or, } K = \frac{2.303}{t_1} \log \frac{a}{0.25a}$$

$$\therefore t_1 = 1.38 \times \frac{1}{K} \quad \longrightarrow \text{(iii)}$$

$$\text{Again } \alpha_2 = 50\% \text{ of } a = 0.50a$$

so equation (ii) taken the form

$$K = \frac{2.303}{t_2} \log \frac{a}{a - 0.50a}$$

$$\therefore t_2 = \frac{0.69}{K} \quad \longrightarrow \text{(iv)}$$

Dividing (iii) by (iv) we get,

$$\frac{t_1}{t_2} = \frac{1.38}{0.69} = 2$$

$$\therefore t_1 = 2t_2$$

So, for a first order reaction time required for 75% reaction is twice the time for 50% reaction (Showed)

Q. 03. Find out the order of the reaction from the following chemical kinetic data (2K+2)

Initial pressure (mm Hg)

169

363

Half life (minute)

14.5

7.0

Soln. We know that,

$$n = 1 + \frac{\log \frac{\tau_1}{\tau_2}}{\log \frac{a_2}{a_1}}$$

$$\text{or, } n = 1 + \frac{\log \left(\frac{14.5}{7.0} \right)}{\log \left(\frac{363}{169} \right)}$$

$$\text{or, } n = 1 + 0.952$$

$$\text{or, } n = 1.952 \approx 2$$

Hence,

$$\tau_1 = 14.5 \text{ min}$$

$$\tau_2 = 7.0 \text{ min}$$

$$a_1 = 169 \text{ mm Hg}$$

$$a_2 = 363 \text{ mm Hg}$$

So the reaction is of the Second order reaction.

Q. 04 Determine the order and the rate constant from the following data.

Initial conc

0.01 M

0.05 M

Half life

200 sec

90 sec

Soln. We know, $n = 1 + \frac{\log \frac{\tau_1}{\tau_2}}{\log \frac{a_2}{a_1}}$

$$\text{or, } n = 1 + \frac{\log \frac{200}{90}}{\log \frac{0.05}{0.01}}$$

$$= 1 + 1 = 2$$

Here,

$$\tau_1 = 200 \text{ sec}$$

$$\tau_2 = 90 \text{ sec}$$

$$a_1 = 0.01 \text{ M}$$

$$a_2 = 0.05 \text{ M}$$

So the reaction is of the Second order (Ans)

$$\text{Again } \frac{1}{t} = \frac{1}{K} \cdot \frac{1}{a}$$

$$\text{or } K = \frac{1}{ta}$$

$$\text{or, } K = \frac{1}{2} = 0.5 \text{ M}^{-1} \text{ s}^{-1} (\text{L mol}^{-1} \text{ s}^{-1})$$

Q.05. The rate constant of a reaction is $2.5 \times 10^4 \text{ L mol}^{-1} \text{ sec}^{-1}$

(i) What is the order of the reaction

(ii) calculate the initial rate of the reaction if the concentration

$$is 0.06 \text{ M}$$

(iii) calculate the half life. $(2K+1)$

Soln. (i) Since the Unit of the rate constant of the reaction
is $\text{mol}^{-1} \text{ L sec}^{-1}$. So it is a Second order reaction $n=2$

(ii) Half life, $t_{1/2} = \frac{1}{K \cdot a}$

$$\text{or, } t_{1/2} = \frac{1}{2.5 \times 10^4 \times 0.06}$$

$$\therefore t_{1/2} = 6.67 \times 10^4 \text{ sec (Ans)}$$

(iii) We know that,

$$K = \frac{1}{t} \cdot \frac{n}{a(a-n)}$$

$$\text{or } t = \frac{1}{K} \cdot \frac{n}{a(a-n)}$$

$$\text{or, } t = \frac{0.06}{K} = \frac{0.06}{2.5 \times 10^4}$$

$$= 2.4 \times 10^{-6} \text{ sec (Ans)}$$

Here,
 $K = 2.5 \times 10^4 \text{ mol}^{-1} \text{ L sec}^{-1}$

$$a = 0.06 \text{ mol L}^{-1}$$

$$n = ?$$

$$t_{1/2} = ?$$

$$\frac{n}{a(a-n)} = 0.06$$



Q. 06. In a reaction 50% reaction is completed in 108 Sec.
When initial concentration is 0.336 g/L and in 147 sec
when initial conc is 0.288 g/L

Soln: We know that,

$$n = 1 + \frac{\log \left(\frac{t_1}{t_2} \right)}{\log \left(\frac{a_2}{a_1} \right)}$$

$$= 1 + \frac{\log \left(\frac{108}{147} \right)}{\log \left(\frac{0.288}{0.336} \right)}$$

$$= 1 + \frac{-0.1339}{-0.0669}$$

$$= 1 + 2 = 3 \quad (\text{Ans})$$

Here,
 $a_1 = 0.336 \text{ g/L}$
 $a_2 = 0.288 \text{ g/L}$
 $t_1 = 108 \text{ sec}$
 $t_2 = 147 \text{ sec}$

So it is the 3rd order reaction.

Q. 07. for a first order reaction $t_{\frac{1}{2}} = 35 \text{ min}$. After 75 min
what of initial conc will be rest?

We know that,

$$t_{\frac{1}{2}} = \frac{0.693}{K}$$

$$\text{or, } K = \frac{0.693}{t_{\frac{1}{2}}}$$

$$\text{or } K = \frac{0.693}{35}$$

$$\text{or, } K = 0.0198 \text{ min}^{-1}$$

$$\text{Again, } t = \frac{2.303}{K} \log \frac{[A]_0}{[A]}$$

$$\text{or, } \log \frac{[A]_0}{[A]} = -\frac{t \times K}{2.303}$$

$$= \frac{75 \times 0.0198}{2.303} = 0.6448$$

Here,
 $t_{\frac{1}{2}} = 35 \text{ min}$
 $t = 75 \text{ min}$

$$\text{or, } \frac{[A]_0}{[A]} = \text{antilog } (0.6498) = 4.413$$

$$\text{or, } [A] = \frac{[A]_0}{4.413} = 0.226 [A]_0$$

i.e. 22.6% will react.

Q.8 The rate constants for a reaction at 500°C and 600°C are $3 \text{ L mol}^{-1} \text{ s}^{-1}$ and $4.5 \text{ L mol}^{-1} \text{ s}^{-1}$ respectively. Calculate the energy of activation for the reaction $2K + g, 2K + o$

Soln. We know that,

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\text{or, } \log \frac{4.5}{3} = \frac{E}{2.303 \times 8.314} \left[\frac{873 - 723}{873 \times 723} \right]$$

$$\text{or, } 0.176 = \frac{E \times 100}{12921046}$$

$$\text{or, } E = \frac{0.176 \times 12921046}{100}$$

$$\therefore E = 22.74 \times 10^3 \text{ J/mol (Ans)}$$

Here,
 $T_1 = 500^\circ\text{C} = (500 + 273) \text{ K}$
 $= 773 \text{ K}$

$T_2 = 873 \text{ K}$
 $k_1 = 3 \text{ mol}^{-1} \text{ sec}^{-1}$
 $k_2 = 4.5 \text{ mol}^{-1} \text{ sec}^{-1}$
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 $E = ?$



Q.09. At 550°C the rate constant is $1.11 \text{ mol}^{-1} \text{ s}^{-1}$ and at 625°C the rate constant is $6.41 \text{ L mol}^{-1} \text{ s}^{-1}$. Find out the activation Energy.

Soln. We know that,

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

$$\text{or, } \log\left(\frac{6.41}{1.11}\right) = \frac{E}{2.303 \times 8.314} \times \left(\frac{898 - 823}{898 \times 823} \right)$$

$$\text{or, } 0.762 = \frac{E}{19.15} \times \frac{75}{799054}$$

$$\text{or, } E = \frac{19.15 \times 0.762 \times 799054}{75}$$

$$\text{or, } E = 1.45 \times 10^5 \text{ J mol}^{-1} \quad (\text{Ans})$$

Hence,

$$T_1 = 550^{\circ}\text{C} = 823 \text{ K}$$

$$T_2 = 898 \text{ K}$$

$$k_1 = 1.11 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_2 = 6.41 \text{ mol}^{-1} \text{ sec}^{-1}$$

$$E = ?$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Q.10. For a reaction $k_{556} = 3.512 \times 10^2 \text{ s}^{-1}$

$$\text{and } k_{281} = 4.954 \times 10^{-2} \text{ s}^{-1}$$

Calculate the Activated Energy (E)

Soln. Same as above

$$\text{Ans } E = +190.23 \text{ kJ/mol}$$

Q. 11. The rate constant at 45°C is double than at 35°C . Calculate the E.

Soln. We know that,

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\text{or, } \log \frac{k_2}{k_1} = \frac{E}{2.303 \times 8.314} \left[\frac{318 - 308}{308 \times 318} \right]$$

$$\text{or, } 0.301 = \frac{E \times 10}{1.87 \times 10^6}$$

$$\therefore E = 5.82 \times 10^4 \text{ J mol}^{-1} \text{ (Ans)}$$

Here,

$$k_2 = 2k_1$$

$$T_1 = 35^{\circ}\text{C} = 308\text{ K}$$

$$T_2 = 45^{\circ}\text{C} = 318\text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Q. 12: For the reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$. Rate is directly proportional to $[\text{N}_2\text{O}_5]$. At 45°C 90% N_2O_5 react in 3600 sec. Find the value of the rate constant, K.

Soln. Since the rate is directly proportional to $[\text{N}_2\text{O}_5]$ so it is a first reaction, then,

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

$$\text{or, } k = \frac{2.303}{3600} \cdot \log \frac{a}{a - 0.9a}$$

$$\text{or, } k = \frac{2.303}{3600} \cdot \log \frac{a}{0.1a}$$

$$\text{or, } k = \frac{2.303}{3600} \log \frac{a}{0.1a}$$

$$= \frac{2.303}{3600} \times \log 10$$

Here,

$$t = 3600 \text{ sec}$$

since 90% of N_2O_5 reacts then

$$x = 90\% \text{ of } a$$

$$= \frac{90a}{100}$$

$$= 0.9a$$

Where, a = initial concentration.

$$k = ?$$

$$\therefore k = 6.4 \times 10^{-9} \text{ sec}^{-1} \text{ (Ans)}$$

Part 1B
Engineering Chemistry

for a reaction $k_{300} = 1.59 \times 10^5 \text{ sec}^{-1}$ and $E = 50 \text{ kJ mol}^{-1}$
calculate k_{400}

Soln

We know that,

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

$$\text{or, } \frac{k_2}{k_1} = \text{antilog} \left[\frac{50000}{2.303 \times 8.314} \times \frac{400 - 300}{400 \times 300} \right]$$

$$\text{or, } k_2 = k_1 \times \text{antilog} \left[\frac{50000 \times 100}{2.303 \times 8.314 \times 120000} \right]$$

$$\text{or, } k_2 = 150.01 \times 1.59 \times 10^5$$

$$\therefore k_2 = 2.38 \times 10^3 \text{ sec}^{-1} \text{ (Ans)}.$$

Here,

$$T_1 = 300 \text{ K}$$

$$T_2 = 400 \text{ K}$$

$$E = 50 \times 10^3 \text{ J/mol}$$

$$k_1 = 1.59 \times 10^5 \text{ s}^{-1}$$

$$k_2 = ?$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Q. 14. The rate law for decomposition of A is : rate = $k[A]$
where $k = 6.22 \times 10^4 \text{ sec}^{-1}$. Calculate the half life
of A and the number of seconds it will take for the
initial concentration of A of 0.1M drops to 0.01M

Soln

We know that,

$$T_h = \frac{0.693}{k}$$

$$= \frac{0.693}{6.22 \times 10^4}$$

$$= 111 \text{ sec (Ans)}$$

Here,

$$k = 6.22 \times 10^4 \text{ sec}^{-1}$$

$$a = 0.1 \text{ M}$$

$$(a-n) = 0.01 \text{ M}$$

Again,

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

$$\text{or, } t = \frac{2.303}{K} \cdot \log \frac{0.1}{0.01}$$

$$\text{or, } t = \frac{2.303}{0.000622} \log 10$$

$$\text{or, } t = 3702 \text{ See (Ans.)}$$

Q. 15. $\frac{1}{5}$ th of a first order reaction is reacted in 40 min. calculate the time required for 100% completion.

Soln. We can write it from the 1st order reaction,

$$K = \frac{2.303}{t_1} \log \frac{a}{a-x_1}$$

$$\text{or, } K = \frac{2.303}{40} \cdot \log \frac{a}{a-\frac{a}{5}}$$

$$\text{or, } K = \frac{2.303}{40} \cdot \log \frac{5}{4}$$

$$\therefore K = 5.58 \times 10^{-3} \text{ min}^{-1}$$

Here,

$$x_1 = 40 \text{ min}$$

Let the initial concentration is a then

$$x_1 = \frac{a}{5}$$

for 100% completion
 $x_2 = ?$

Here,

$$x_2 = 100\% \text{ of } a = a$$

for 100% completion,

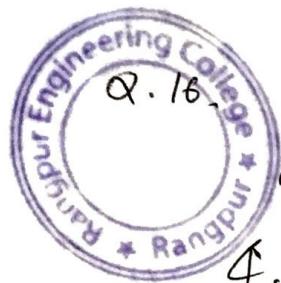
$$K = \frac{2.303}{t_2} \log \frac{a}{a-x_2}$$

$$\text{or, } t_2 = \frac{2.303}{K} \log \frac{a}{a-x_2}$$

$$\text{or, } t_2 = \frac{2.303}{5.58 \times 10^{-3}} \log \frac{a}{a-a}$$

$$= \frac{2.303}{5.58 \times 10^{-3}} \cdot \log \frac{a}{0}$$

= ∞
So a first order reaction does not finish.



Q. 16.

For the following rate data, calculate order and rate constant (given that molecular weight of reactant is 150)

| | | | | |
|---------------------|-----|-----|------|------|
| Initial conc (g/L) | 1.0 | 0.2 | 0.5 | 0.3 |
| conc after 5s (g/L) | 0.9 | 0.6 | 0.45 | 0.27 |

| | | | | | |
|-------|----------------------|--------|--------|--------|-------|
| Soln: | Initial conc (g/L) : | 1.0 | 0.7 | 0.5 | 0.3 |
| " " | (mol/L) : | 0.0067 | 0.0042 | 0.0033 | 0.002 |

$$\text{conc after 5s (g/L)} : 0.9 \quad 0.6 \quad 0.45 \quad 0.27$$

$$\text{conc after 5s (mol/L)} : 0.666 \quad 0.0042 \quad 0.0033 \quad 0.0018$$

$$dc \text{ mol/L} : 0.0007 \quad 0.0005 \quad 0.0003 \quad 0.0002$$

$$\frac{dc}{dt} \text{ mol L}^{-1} \text{s}^{-1} : 0.00014 \quad 0.001 \quad 0.0006 \quad 0.00004$$

$$\log \left(\frac{dc}{dt} \right) \text{ mol L}^{-1} \text{s}^{-1} : -3.85 \quad -4 \quad -4.22 \quad -4.9$$

$$\log c : -2.12 \quad -2.33 \quad -2.48 \quad -2.69$$

If $\log \left(\frac{dc}{dt} \right)$ is plotted against $\log c$ then n is obtained from the graph.

Other method:

We know for the 1st order reaction,

$$K = \frac{2.303}{t} \cdot \log \frac{a}{a-n} \quad \text{Here, } t = 5 \text{ sec}$$

putting $a = 0.10062$ and $(a-n) = 0.066 \text{ mol/L}$

$$K = \frac{2.303}{5} \log \frac{0.066}{0.006} \\ = 0.022 \text{ sec}^{-1}$$

putting $a = 0.0047 \text{ mol/L}$ and $(a-n) = 0.0042 \text{ mole/L}$

$$K = \frac{2.303}{5} \log \frac{0.0046}{0.0042} = 0.022 \text{ sec}^{-1}$$

putting $a = 0.0033 \text{ mole/L}$ and $(a-n) = 0.003 \text{ mol/L}$

$$K = \frac{2.303}{5} \log \frac{0.0033}{0.003} \\ = 0.02 \text{ sec}^{-1}$$

putting $a = 0.002 \text{ mole/L}$ and $(a-n) = 0.0018 \text{ mole/L}$

$$K = \frac{2.303}{5} \log \frac{0.002}{0.0018} = 0.021 \text{ sec}^{-1}$$

We see that, for all these data K is almost constant. Here
so hence the order of the reactant or reaction is one
and the value of $K = 0.022 \text{ sec}^{-1}$