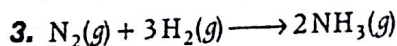


chemical kinetics-CBSE(solutions)

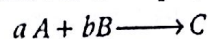
Order wrt $A = \frac{1}{2}$; Order wrt $B = 2$

\therefore Overall order of a reaction $= 1/2 + 2 = 5/2$



$$\text{Rate} = \frac{-d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = +\frac{1}{2} \frac{d[NH_3]}{dt}$$

4. **Order of a reaction** The sum of the powers of the concentration i.e. stoichiometric coefficients of reactants of a chemical reaction in rate law expression is called the order of that chemical reaction. For example, for the reaction given below



$$\text{Rate} = k[A]^x[B]^y$$

Order of reaction $= x + y$

Where x and y are actual stoichiometric coefficients for the reaction.

5. It is the second order reaction because unit of rate constant for second order reaction is $L \text{ mol}^{-1} \text{ s}^{-1}$.

6. $\therefore r \propto [\text{concentration}]^{\text{Order}}$

i.e. $\frac{\text{change in concentration}}{\text{time}}$

time

$\propto [\text{concentration at time } t]$

Hence, as time increases rate decreases.

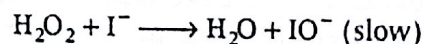
7. **Rate of a reaction** Change in concentration of reactants or products in unit time is known as rate of a reaction. Its unit is $(\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$.

8. (i) Rate law for the given reaction is

$$R = k[H_2O_2][I^-]$$

- (ii) Overall order of the reaction is 2. Since the reaction is first order w.r.t. H_2O_2 as well as w.r.t. I^- .

- (iii) The overall rate of the reaction is determined by the slowest step. Here, out of steps (1) and (2),



is the rate determining step.

9. For the reaction, $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

overall rate of reaction is

$$-\frac{1}{2} \frac{d[N_2O_5]}{dt} = +\frac{1}{4} \frac{d[NO_2]}{dt} = +\frac{d[O_2]}{dt}$$

Given, $\frac{d[NO_2]}{dt} = 2.8 \times 10^{-3} \text{ Ms}^{-1}$ $-\frac{d[N_2O_5]}{dt} = ?$

$$\therefore -\frac{1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt}$$

Putting the given values in the above equation, we get

$$\begin{aligned} -\frac{d[N_2O_5]}{dt} &= \frac{1}{4} \times 2 \times 2.8 \times 10^{-3} \text{ Ms}^{-1} \\ &= 1.4 \times 10^{-3} \text{ Ms}^{-1} \end{aligned}$$

Explanation

1. $r_1 = k[A]^x$... (i)

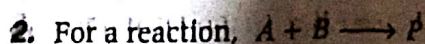
$r_2 = k[9A]^x$... (ii)

On dividing eqn. (ii) by eqn. (i), we get

$$\frac{r_2}{r_1} = \frac{k[9A]^x}{k[A]^x} \Rightarrow 3 = (9)^x \Rightarrow (3^1) = (3^2)^x$$

$$\Rightarrow 2x = 1 \Rightarrow x = 1/2$$

Thus, the order of reaction is 1/2



Given, rate of a reaction, $r = k[A]^{1/2}[B]^2$

10. (i) For a reaction, $H_2 + Cl_2 \xrightarrow{h\nu} 2HCl$
 Rate = k , suggests that the reaction is of zero order. Further, the molecularity of a given reaction is 2 as two molecules are participating in the reaction.

Hence, order = zero and molecularity = two. (1)

- (ii) The unit of k for zero order reaction is equal to the rate of a reaction which is $\text{mol L}^{-1}\text{s}^{-1}$.
 Hence, the unit of k for the given reaction is $\text{mol L}^{-1}\text{s}^{-1}$. (1)

11. (i) Refer to solution 10 (i) (1)
 (ii) Refer to solution 10 (ii) (1)

12. (i) Refer to solution 7. (1)
 (ii) Two factors on which rate of reaction depends are:

(a) **Concentration of reactants** Generally rate increases with the increase in concentration. (1/2)

(b) **Temperature** Generally rate of reaction increases about 2-3 times for every 10°C rise in temperature. (1/2)

13. Unit of rate constant (k)

$$k = \frac{\text{Concentration}}{\text{Time}} \times \frac{1}{(\text{Concentration})^n}$$

Unit of rate constant for zero order

$$= \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1}\text{s}^{-1} \quad (1)$$

Unit of rate constant for second order

$$= \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1}\text{L s}^{-1} \quad (1)$$

14. **S. No. Molecularity of a reaction Order of reaction**

(i) The number of reacting species which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction. The sum of powers of the concentrations of the reactants in the rate law expression is called the order of that chemical reaction.

(ii) Molecularity is always a whole number value. Order may have zero, whole number, negative or fractional, values.

(2)

15. (i) The sum of the powers of the concentrations of reactants in the rate law expression is called order of that chemical reaction.

$$\text{Rate} = k[A]^1[B]^2 \quad (1)$$

$$\text{Order of reaction} = (1 + 2) = 3$$

- (ii) Unit of rate constant for first order reaction is s^{-1} or min^{-1} or time^{-1} . (1)

16.

- (i) Write the rate law for initial concentration of reactant and for the conditions, when concentration is doubled or reduced to half.
 (ii) Now, compare the initial concentration condition with changed concentration to find the effect on rate.

Let R be the initial concentration of reactant and r be the initial rate. So, the rate law for the second order reaction is,

$$\text{Rate, } r = [R]^2 \quad (1)$$

- (i) When the concentration of the reactant is doubled, i.e. $R' = 2R$

Then new rate,

$$r' = [R']^2 = [2R]^2 = 4[R]^2 \quad (2)$$

From Eqs. (1) and (2),

$$\frac{r'}{r} = \frac{[R']^2}{[R]^2} = \frac{4}{1} \quad \text{or } r' = 4r$$

Hence, the rate becomes four times of the initial rate on doubling the concentration of reactant. (1)

- (ii) When the concentration is reduced to half,

$$R'' = \frac{R}{2}$$

$$\text{New rate, } r'' = [R'']^2 = \left[\frac{R}{2}\right]^2 = \frac{1}{4}[R]^2 \quad \dots (3)$$

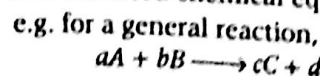
From eqs. (1) and (3),

$$\frac{r''}{r} = \frac{[R'']^2}{[R]^2} = \frac{1}{4}$$

$$\text{or } r'' = \frac{r}{4}$$

Hence, the rate becomes one fourth of the initial rate when concentration of the reactant is reduced to half. (1)

17. **Rate law** is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may be or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.



$$\text{Rate} = k[A]^a[B]^b \quad (1)$$

Rate constant (k) is equal to the rate of reaction when molar concentration of reactants is unity. Its unit depends upon the order of reaction.

(i) **Zero order** $-L^{-1} \text{ mol s}^{-1}$ (1/2)

(ii) **Second order** $-L \text{ mol}^{-1} \text{ s}^{-1}$ (1/2)

18. Refer to solution 16 (ii) (1)

The unit of rate constant is $L \text{ mol}^{-1} \text{ s}^{-1}$ (second order reaction). (1)

19. (i) Refer to solution 4. (1)

(ii) Each step of a complex reaction is called the elementary step of the reaction. (1)

20. (i) Unit of k indicates that the reaction is of second order reaction. (1)

(ii) Unit of k indicates that it is a first order reaction. (1)

21. (i) The slowest step in the reaction mechanism is the **rate determining step** of a reaction. (1)

(ii) **Molecularity of a reaction** Refer to solution 14. (1)

22.

- (i) Write the rate law for initial concentration of reactants and for the conditions when concentration of reactants are changed.
(ii) Now compare them.

Since, the reaction is of first order wrt A and second order wrt B , then the rate law can be given as, $(\text{Rate})_1 = k [A] [B]^2$

(i) When the concentration of B is increased to three times ($3B$), the rate would be

$$(\text{Rate})_2 = k [A] [3B]^2$$

$$(\text{Rate})_2 = 9k [A] [B]^2 = 9 \times (\text{Rate})_1$$

\therefore Rate is increased by 9 times. (1)

(ii) $(\text{Rate})_3 = k [2A] [2B]^2$

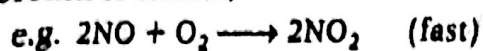
$$(\text{Rate})_3 = 2 \times 2 \times 2 \times k [A] [B]^2 = 8 \times (\text{Rate})_1$$

\therefore Rate is increased by 8 times. (1)

23. Factors influencing the rate of a chemical reaction are

(i) **Nature of reactants** Different reactants require different amount of energies for breaking the old bonds and for the formation of new bonds.

Hence, the reactivity of a substance is related to the ease with which the specific bonds are broken or formed,



(ii) **Concentration of reactants** Rate of reaction is directly proportional to the concentration of the reactants. (1/2)

(iii) **Temperature** Rate of reaction increases with increase in temperature. (1/2)

(iv) **Catalyst** It alters the rate of reaction without being consumed in the reaction. It provides an alternative path to the reaction with a low energy barrier. (1/2)

24. **Average rate of reaction** It is defined as the change in the concentration of any one of the reactants or products over a long time interval.

$$\text{Average rate of reaction} = \frac{\text{Change in concentration}}{\text{Time interval}}$$

For a reaction, $R \longrightarrow P$

$$r_{\text{av}} = -\frac{\Delta [R]}{\Delta t} = \frac{+\Delta [P]}{\Delta t} \quad (1)$$

Instantaneous rate of reaction It is defined as the rate of change in concentration of any one of the reactants or products at that particular instant of time.

For a reaction, $R \longrightarrow P$

$$r_{\text{inst}} = -\frac{d[R]}{dt} = +\frac{d[P]}{dt} \quad (dt = \text{very small interval of time}) \quad (1)$$

25. A reaction is first order in A and second order in B
(i) Differential rate equation = (Rate),

$$= \frac{-d[R]}{dt} = k[A][B]^2 \quad (1)$$

(ii) Refer to solution 22 (i). (1)

(iii) Refer to solution 22 (ii). (1)

26. A reaction is second order w.r.t. A and first order w.r.t. B .

(i) Differential rate equation = (Rate)₁ = $\frac{-d[R]}{dt} = k[A]^2[B]$ (1)

(ii) When the concentration of A is increased three times, i.e. $3A$ then

$$(\text{Rate})_2 = k [3A]^2 [B] = 9k[A]^2 [B] = 9 (\text{Rate})_1$$

This shows that rate will be increased 9 times to the initial rate. (1)

(iii) When concentrations of both A and B are doubled then,

$$(\text{Rate})_3 = k [2A]^2 [2B] = k 8[A]^2 [B]$$

$$= 8k [A]^2 [B] = 8 (\text{Rate})_1$$

This shows that rate will be increased 8 times to the initial rate. (1)

27. First, write the rate law, then find out the order w.r.t. each reactant, then find out the value of rate constant, put the values of concentration of reactants in any experiment and find its value.

Rate law may be written as

$$\text{Rate} = k [\text{NO}]^p [\text{Cl}_2]^q$$

The initial rate becomes

$$(\text{Rate})_0 = k [\text{NO}]^p [\text{Cl}_2]^q$$

Comparing experiments 1 and 2,

$$(\text{Rate})_1 = k (0.15)^p (0.15)^q = 0.60 \quad \dots(i)$$

$$(\text{Rate})_2 = k (0.15)^p (0.30)^q = 1.20 \quad \dots(ii)$$

Dividing Eq. (ii) by Eq. (i),

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k (0.15)^p (0.30)^q}{k (0.15)^p (0.15)^q} = \frac{1.20}{0.60}$$

or $2^q = 2^1 \Rightarrow q = 1$

\therefore Order with respect to Cl_2 is 1

Comparing experiments 1 and 3,

$$(\text{Rate})_1 = k (0.15)^p (0.15)^q = 0.60 \quad \dots(iii)$$

$$(\text{Rate})_3 = k (0.30)^p (0.15)^q = 2.40 \quad \dots(iv)$$

Dividing Eq. (iv) by Eq. (iii)

$$\frac{(\text{Rate})_3}{(\text{Rate})_1} = \frac{k (0.30)^p (0.15)^q}{k (0.15)^p (0.15)^q} = \frac{2.40}{0.60}$$

or $2^p = 4 \Rightarrow 2^p = 2^2$

$\Rightarrow p = 2$

Thus, order with respect to NO is 2.

(i) The rate law for the given reaction

$$\text{Rate} = k [\text{NO}]^2 [\text{Cl}_2] \quad (1)$$

(ii) Rate constant can be calculated by substituting the value of rate, $[\text{NO}]$ and $[\text{Cl}_2]$ for any of the experiments.

$$k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{Cl}_2]} = \frac{0.60}{(0.15)^2 (0.15)} = \frac{0.60}{0.00338} = 177.51 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1} \quad (1)$$

(iii) Let initial rate of disappearance of Cl_2 in experiment 4 is r_4 .

$$\therefore r_4 = k [\text{NO}]^2 [\text{Cl}_2] = 177.51 \times (0.25)^2 (0.25) = 2.77 \text{ M/min} \quad (1)$$

28. Rate law may be written as

$$\text{Rate} = k [A]^p [B]^q$$

Comparing experiments (2) and (3), we get

$$(\text{Rate})_2 = k (0.2)^p (0.2)^q = 3 \times 10^{-3} \quad \dots(i)$$

$$(\text{Rate})_3 = k (0.2)^p (0.4)^q = 6 \times 10^{-3} \quad \dots(ii)$$

Dividing Eq. (ii) by Eq. (i), we get

$$(\text{Rate})_3 = k (0.2)^p (0.4)^q = 6 \times 10^{-3}$$

$$(\text{Rate})_2 = k (0.2)^p (0.2)^q = 3 \times 10^{-3}$$

or $2^q = 2, q = 1$

Comparing experiments (1) and (2)

$$(\text{Rate})_1 = k (0.1)^p (0.1)^q = 1.5 \times 10^{-3} \quad \dots(iii)$$

$$(\text{Rate})_2 = k (0.2)^p (0.2)^q = 3.0 \times 10^{-3} \quad \dots(iv)$$

Dividing Eq. (iv) by Eq. (iii), we get

$$\frac{3 \times 10^{-3}}{1.5 \times 10^{-3}} = \frac{k (0.2)^p (0.2)^q}{k (0.1)^p (0.1)^q}$$

$$2 = (2)^p (2)^q$$

where, $q = 1, 1 = 2^p, 2^0 = 2^p, p = 0$

(i) Thus, the rate law is

$$\text{rate} = k [A]^0 [B] = k [B] \quad (1)$$

(ii) $\text{Rate} = k [B]$

$$k = \frac{\text{Rate}}{[B]} = \frac{3 \times 10^{-3}}{0.2} = 15 \times 10^{-3} \text{ min}^{-1} \quad (1)$$

(iii) $B \longrightarrow C + E$ (slow) is the possible reaction which is consistent with the rate law,

$$\text{rate} = k [B] \quad (1)$$

29. Let the rate law in terms of rate of formation of D be

$$\frac{d[D]}{dt} = k [A]^a [B]^b \quad (1)$$

$$1. 6.0 \times 10^{-3} = k (0.1)^a (0.1)^b \quad \dots(i)$$

$$2. 7.2 \times 10^{-3} = k (0.3)^a (0.2)^b \quad \dots(ii)$$

$$3. 2.88 \times 10^{-2} = k (0.3)^a (0.4)^b \quad \dots(iii)$$

$$4. 2.40 \times 10^{-2} = k (0.4)^a (0.1)^b \quad \dots(iv)$$

Divide Eq. (iv) by Eq. (i), we get

$$4 = (4)^a$$

$\therefore a = 1$

Divide Eq. (iii) by Eq. (ii), we get

$$4 = (2)^b$$

$$2^2 = (2)^b$$

$\therefore b = 2$

Order with respect to $A = 1$

Order with respect to $B = 2$

$$\text{Rate law} = \frac{d[D]}{dt} = k [A] [B]^2 \quad (1)$$

On putting the value of 'A' and 'B' in any equation, say (i)

$$6.0 \times 10^{-3} \text{ M min}^{-1} = k (0.1 \text{ M}) (0.1 \text{ M})^2$$

$\therefore k = 6 \text{ M}^{-2} \text{ min}^{-1} \quad (1)$

Explanations

- For a reaction $R \rightarrow P$, half-life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. Thus, it follows first order reaction.
- Given, $k = 5.5 \times 10^{-14} \text{ s}^{-1}$

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.5 \times 10^{-14}}$$

$$= 0.126 \times 10^{14} \text{ s} = 1.26 \times 10^{13} \text{ s}$$

- First, find out the value of k by using the formula

$$k = \frac{0.693}{t_{1/2}}, \text{ where } t_{1/2} = x.$$

- Putting the value of k in the formula,

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

find out the value of t which is given as y .

- Then from the above points, relate x and y .

For first order reaction, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{x}$

For $\frac{3}{4}$ th life period, $x = \frac{3}{4}a$

$$a - x = a - \frac{3}{4}a = \frac{1}{4}a$$

$$\therefore k = \frac{2.303}{y} \log \frac{a}{(a-x)} \Rightarrow \frac{0.693}{x} = \frac{2.303}{y} \log \frac{a}{a/4}$$

$$\frac{0.693}{x} = \frac{2.303}{y} 2 \log 2$$

$$\frac{0.693}{x} = \frac{0.693 \times 2}{y} \Rightarrow y = 2x$$

Alternate Method

\therefore For first order,

$t_{1/2} = x$ and amount left $(a-x)$ after the period y

$$a - x = 1 - \frac{3}{4} = \frac{1}{4}$$

$$\frac{a-x}{a} = \frac{1}{2^n} \Rightarrow \frac{1}{4} = \frac{1}{2^n}$$

(where, n = number of half-life)

On comparing $\frac{1}{4} = \frac{1}{2^n}, \frac{1}{2^2} = \frac{1}{2^n}, n = 2$

$\therefore y = T = n \times t_{1/2} = 2 \times x$

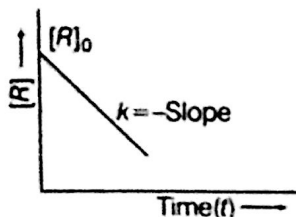
i.e.

$$y = 2x$$

4. (i) **Half-life ($t_{1/2}$) of a reaction** is the time in which the concentration of a reactant is reduced to one half of its initial concentration. (1)
- (ii) **Rate constant (k)** is equal to the rate of reaction when molar concentration of reactants is unity. Its unit depends upon the order of reaction. (1)

5. (i) The reaction is of zero order. (1)

- (ii) For zero order reaction, $[R] = -kt + [R]_0$
Compare with equation of a straight line ($y = mx + c$). If we plot $[R]$ against t , we get a straight line with slope $= -k$ and intercept equal to $[R]_0$.



Variation in the concentration vs time plot for a zero order reaction. (1)

6. (i) When 15% of a sample of H_2O_2 is decomposed.

For a first order reaction,

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

Given, $k = 1.06 \times 10^{-3} \text{ min}^{-1}$,

$$[R]_0 = 100 \text{ M,}$$

$$[R] \text{ (after time, } t) = 100 - 15 = 85 \text{ M}$$

$$t = \frac{2.303}{1.06 \times 10^{-3}} \log \frac{100}{85}$$

$$t = \frac{2.303}{1.06 \times 10^{-3}} \log 1.176$$

$$t = \frac{2.303 \times 0.0704}{1.06 \times 10^{-3}} = 153.3 \text{ min} \quad (1)$$

- (ii) When 85% of a sample of H_2O_2 is decomposed,

$$[R] = 100 - 85 = 15 \text{ M}$$

$$t = \frac{2.303}{1.06 \times 10^{-3}} \log \frac{100}{15}$$

$$= \frac{2.303}{1.06 \times 10^{-3}} \log 6.667$$

$$t = \frac{2.303 \times 0.8240}{1.06 \times 10^{-3}} = 1790.05 \text{ min} \quad (1)$$

7. **Half-life ($t_{1/2}$) of a reaction** is the time in which the concentration of reactant is reduced to one half of its initial concentration.

(i) For a zero order reaction, $t_{1/2} = \frac{[R]_0}{2k}$ (1)

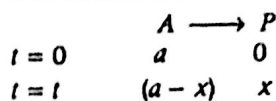
(ii) For first order reaction, $t_{1/2} = \frac{0.693}{k}$ (1)

8. (i) To find $t_{1/2}$, first calculate k by using the formula,

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

(ii) Calculate $t_{1/2}$ by using the formula, $t_{1/2} = \frac{0.693}{k}$

For a reaction,



For 30% decomposition, it takes 40 min which means after 40 min, reactant left is 70% of its initial concentration.

Thus, $(a - x) = \frac{70}{100} \times a = \frac{7}{10} a$ (1/2)

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

or, $k = \frac{2.303}{40} \log \frac{a}{(7/10)a}$ (1/2)

$$= \frac{2.303}{40} \log 1.428$$

$\Rightarrow k = 0.00891 \text{ min}^{-1}$ (1/2)

\therefore Half-life of the reactant ($t_{1/2}$)

$$= \frac{0.693}{k} = \frac{0.693}{0.00891}$$

$$= 77.76 \text{ min} \quad (1/2)$$

Alternate Method

$\therefore a - x = \frac{100}{2^n}$

$\Rightarrow 70 = \frac{100}{2^n}$

[where, $a - x$ = amount left, n = no. of half-life]

$$2^n = \frac{100}{70}$$

$\Rightarrow n \log 2 = \log 1.43$

$$n \times 0.3010 = 0.1533,$$

i.e. $n = \frac{0.1533}{0.3010}$

$$= 0.515$$

\therefore Total time (T) = $n \times t_{1/2}$

$\therefore t_{1/2} = \frac{40}{0.515} = 77.7 \text{ min} \quad (1)$

9. (i) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$ (1)

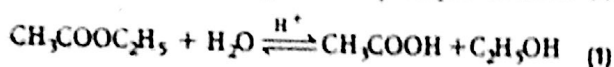
(ii) $N = N_0 \left(\frac{1}{2}\right)^n$

where, $n = \frac{\text{Total time}}{t_{1/2}} = \frac{60}{10} = 6$

$\frac{N}{N_0} = \left(\frac{1}{2}\right)^6 = \frac{1}{64}$ (1)

[where, N_0 = initial amount of reactant and
 N = amount of reactant left after time, t]

10. **Pseudo first order reaction** The reaction which is bimolecular but has order one, is called pseudo first order reaction, e.g. acidic hydrolysis of ester. (1)



11. Rate constant,

$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$ (1/2)

Given, $[R]_0 = 0.6 \text{ mol L}^{-1}$

$[R] = 0.2 \text{ mol L}^{-1}$, $t = 5 \text{ min}$

$k = \frac{2.303}{5} \log \frac{0.6}{0.2}$ (1/2)

$k = \frac{2.303}{5} \log 3$ ($\log 3 = 0.4771$) (1/2)

$k = \frac{2.303}{5} \times 0.4771$
 $= 0.2197 \text{ min}^{-1}$ (1/2)

12. For zero order reaction,

rate constant, $k = \frac{[R]_0 - [R]}{t}$

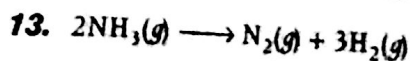
Given, $[R]_0 = 0.10 \text{ M}$,

$[R] = 0.075 \text{ M}$ and

$k = 0.0030 \text{ mol L}^{-1} \text{ s}^{-1}$

$\therefore t = \frac{[R]_0 - [R]}{k}$ (1)

$t = \frac{0.10 - 0.075}{0.0030} = 8.33 \text{ s}$ (1)



Given $k = 4 \times 10^{-3} \text{ Ms}^{-1}$

$[A_0] = 0.1 \text{ M}$; $[A] = 0.064 \text{ M}$

$\therefore k = \frac{[A_0] - [A]}{t}$ [For zero order reaction]

$\therefore t = \frac{0.1 - 0.064}{4 \times 10^{-3}} = \frac{0.036 \times 1000}{4} = 9 \text{ s}$ (1)

14. For a first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a-x}$

where, k = Rate constant

a = initial concentration

$(a-x)$ = concentration after time ' t '.

When a first order reaction is 25% completed in 20 min.

$a = 100$, $a-x = 100 - 25 = 75$, $t = 20 \text{ min}$.

$\therefore k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{20} \log \frac{100}{75}$

$= \frac{2.303}{20} [\log 4 - \log 3] = 0.0143 \text{ min}^{-1}$

For 75% completion of reaction,

$a = 100$, $a-x = 100 - 75 = 25$, $k = 0.0143 \text{ min}^{-1}$

$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{0.0143} \log \frac{100}{25}$

$= \frac{2.303}{0.0143} \log 4 = 96.968 \text{ min}$.

15. Using data, to find out the rate constant.

t/s	0	300	600
$[\text{N}_2\text{O}_5] / \text{mol L}^{-1}$	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

Using hit and trial method,

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

Here, $t = 300 \text{ s}$, $[R]_0 = 1.6 \times 10^{-2} \text{ mol L}^{-1}$
and $[R] = 0.8 \times 10^{-2} \text{ mol L}^{-1}$

$k = \frac{2.303}{300} \log \frac{(1.6 \times 10^{-2}) \text{ mol L}^{-1}}{(0.8 \times 10^{-2}) \text{ mol L}^{-1}}$

$= \frac{2.303}{300} \log 2 = \frac{2.303}{300} \times 0.3010$

$k = 2.31 \times 10^{-3} \text{ s}^{-1}$

Similarly, $k = \frac{2.303}{600} \log \frac{(1.6 \times 10^{-2}) \text{ mol L}^{-1}}{(0.4 \times 10^{-2}) \text{ mol L}^{-1}}$

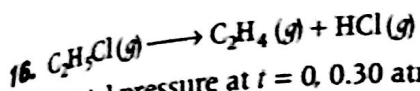
$k = 2.31 \times 10^{-3} \text{ s}^{-1}$

Thus, it is proved that reaction proceed through first order kinetics as the rate constant remains same.

(b) Half-life ($t_{1/2}$) = $\frac{0.693}{k}$

$t_{1/2} = \frac{0.693}{2.31 \times 10^{-3} \text{ s}^{-1}}$

$t_{1/2} = 300 \text{ s}$



Initial pressure at $t = 0$, 0.30 atm

After 300s, $P_{\text{total}} = (0.30 - p + p + p)$ atm
 $= (0.30 + p)$ atm

P_{total} (given) = 0.50 = 0.30 + p

$\Rightarrow p = 0.50 - 0.30$ atm = 0.20 atm

Pressure of $\text{C}_2\text{H}_5\text{Cl}(g)$ at 300 sec

$(P_{\text{C}_2\text{H}_5\text{Cl}}) = 0.30 - 0.20$ atm = 0.10 atm

$$k = \frac{2.303}{t} \log \frac{(P_{\text{C}_2\text{H}_5\text{Cl}})_0}{(P_{\text{C}_2\text{H}_5\text{Cl}})_{300}}$$

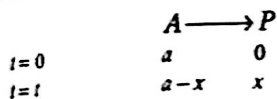
$$= \frac{2.303}{300} \log \frac{0.30 \text{ atm}}{0.10 \text{ atm}}$$

$$= \frac{2.303}{300} \log 3 = \frac{2.303}{300} \times 0.4771$$

$$= 3.66 \times 10^{-3} \text{ s}^{-1}$$

(3)

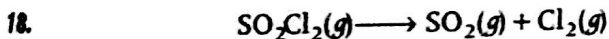
17. For a reaction,



Here, $a-x = \frac{a}{10}$

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303}{60} \log \frac{a}{a/10}$$

$$t = \frac{2.303}{60} \log 10 \quad t = 0.0384 \text{ s} \quad (3)$$



Initial pressure p_i 0 0

After time, t $p_i - p$ p p

Total pressure after time t ,

i.e. $p_t = p_i - p + p + p = p_i + p$

$\Rightarrow p = p_t - p_i$

Thus, $a = p_i$ and $a-x = p_i - p = p_i - (p_t - p_i)$

$$= p_i - p_t + p_i = 2p_i - p_t$$

Substituting the values of a and $(a-x)$ in equation,

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

$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)} \quad (1)$$

Calculating rate constant (k), when $t = 100$ s

Given, $p_i = 0.4$ atm and $p_t = 0.7$ atm

$$\text{Then, } k = \frac{2.303}{100} \log \frac{p_i}{(2p_i - p_t)} \quad (1/2)$$

$$= \frac{2.303}{100} \log \frac{0.4}{(2 \times 0.4 - 0.7)} \quad (1/2)$$

$$= \frac{2.303}{100} \log \frac{0.4}{0.1} = \frac{2.303}{100} \log 4$$

$$= \frac{2.303}{100} \times 0.6021 = 0.01387$$

$$= 1.387 \times 10^{-2} \text{ s}^{-1}$$

(1)

19.

(i) First, find out the value of $a-x$ from the given percentage, then the value of k by using the formula,

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

(ii) Again find out the value of $a-x$ from the given percentage then the value of t by using the formula,

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

and keeping the value of k in this formula.

For the first order reaction, when $t = 100$ min

$$\text{rate constant, } k = \frac{2.303}{100} \log \frac{a}{a-x} \quad (1)$$

For 60% completion of the reaction, if $a = 100\%$

$$a-x = 100 - 60 = 40\%$$

$$\text{Then, } k = \frac{2.303}{100} \log \frac{100}{40} \quad \dots(i) \quad (1/2)$$

For 90% completion of the reaction,

$$a = 100\%$$

and $a-x = 100 - 90 = 10\%$

$$\text{Then, } k = \frac{2.303}{t} \log \frac{100}{10} \quad \dots(ii) \quad (1/2)$$

Substituting the value of k in Eq. (ii), we have,

$$\frac{2.303}{100} \log \frac{100}{40} = \frac{2.303}{t} \log \frac{100}{10} \quad [\because \log 10 = 1]$$

$$\text{or } \frac{1}{t} = \frac{1}{100} \log \frac{100}{40}$$

$$\frac{1}{t} = \frac{0.3979}{100}$$

$$\Rightarrow t = \frac{100}{0.3979}$$

$$t = 251.2 \text{ min} \quad (1)$$

20.

(i) Find rate constant of each experiment using the formula, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$, then find the average value of k .

(ii) Find the concentration of N_2O_5 after the given time by putting the value of k in the above formula.

(iii) Then find the initial rate of reaction.

$$(i) k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$[R]_0 = 0.400 \text{ M}$$

When $[R] = 0.289 \text{ M}$, $t = 20 \text{ min}$

$$k = \frac{2.303}{20} \log \frac{0.400}{0.289}$$

$$k = \frac{2.303}{20} \times \log 1.384$$

$$= \frac{2.303}{20} \times 0.1411 = 0.01625 \text{ min}^{-1}$$

When $t = 40 \text{ min}$, $[R] = 0.209 \text{ M}$

$$k = \frac{2.303}{40} \log \frac{0.400}{0.209} = \frac{2.303}{40} \log 1.914$$

$$= \frac{2.303}{40} \times 0.2819 = 0.01623 \text{ min}^{-1}$$

Similarly, when $t = 60 \text{ min}$, $[R] = 0.151$

$$k = \frac{2.303}{60} \log \frac{0.400}{0.151}$$

$$k = \frac{2.303}{60} \times 0.4231 = 0.01623 \text{ min}^{-1}$$

$$k = \frac{0.01625 + 0.01623 + 0.01623}{3}$$

$$= 0.016236 \text{ min}^{-1}$$

$$(ii) k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$1.6236 \times 10^{-2} = \frac{2.303}{100} \log \frac{0.4}{[R]}$$

$$\log \frac{0.4}{[R]} = \frac{1.6236}{2.303} = 0.705$$

$$\frac{0.4}{[R]} = \text{antilog } 0.705$$

$$\frac{0.4}{[R]} = 5.070$$

$$\text{or } [R] = \frac{0.4}{5.070} = 0.07889 \text{ M}$$

$$(iii) \text{ Initial rate} = k [N_2O_5] = 0.016236 \times 0.4$$

$$= 0.00649 \text{ mol L}^{-1} \text{ min}^{-1}$$

21. Three fourth of initial quantity of HCOOH is decomposed means that (where, initial concentration = $[R]_0$) concentration after t time,

$$[R] = \frac{[R]_0}{4}$$

$$k = 2.4 \times 10^{-3} \text{ s}^{-1}$$

Thus, for the first order reaction, rate constant,

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

$$2.4 \times 10^{-3} \text{ s}^{-1} = \frac{2.303}{t} \log \frac{[R]_0}{[R]_0/4}$$

$$t = \frac{2.303}{2.4 \times 10^{-3}} \times \log 4$$

$$\text{or } t = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6021$$

$$= 5.77 \times 10^2 \text{ s}$$

22. (i) Refer to solution 20 (i).

(ii) Refer to solution 20 (iii).

$$(iii) k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$t = \frac{2.303}{1.6236 \times 10^{-2}} \log \frac{0.400 \text{ M}}{0.350 \text{ M}}$$

$$t = \frac{2.303}{1.6236 \times 10^{-2}} \times \log 1.143$$

$$t = \frac{2.303}{1.6236 \times 10^{-2}} \times 0.0581$$

$$t = 8.24 \text{ min}$$

23. Given, $k = 0.00510 \text{ min}^{-1}$, $[R]_0 = 0.10 \text{ M}$ and $t = 3 \text{ h} = 3 \times 60 \text{ min}$

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

$$3 \times 60 = \frac{2.303}{0.00510} \log \frac{0.10}{[R]}$$

$$\log \frac{0.1}{[R]} = \frac{180 \times 0.00510}{2.303} = 0.3986$$

$$\frac{0.1}{[R]} = \text{antilog } 0.3986$$

$$\frac{0.1}{[R]} = 2.503$$

$$[R] = \frac{0.1}{2.503} = 0.0399 \text{ M}$$

24. (i) Find the value of k by using formula, $k = 0.693/t_{1/2}$, then the value of t by using formula, $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$.

(ii) From the value of k and $t = 60 \text{ s}$, find the % concentration of PH_3 by using the above formula.

Given, $t_{1/2} = 37.9 \text{ s}$, initial concentration = $[R]_0$ concentration after time, $t = \frac{[R]_0}{4}$ (because $\frac{3}{4}$ th of PH_3 is decomposed).

(1)

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} = \frac{2.303}{0.093} \log 4$$

$$t = \frac{2.303 \times 37.9 \times 0.6030}{0.093} = 75.83 \text{ s} \quad (1)$$

(ii) $t = 1 \text{ min} = 60 \text{ s}$ and $k = \frac{0.093}{37.9} = 0.0183 \text{ s}^{-1}$

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \quad (1/2)$$

$$60 = \frac{2.303}{0.0183} \log \frac{[R]_0}{[R]}$$

$$\log \frac{[R]_0}{[R]} = \frac{60 \times 0.0183}{2.303} = 0.4761$$

$$\frac{[R]_0}{[R]} = \text{antilog } 0.4761 \quad (1/2)$$

$$\frac{[R]_0}{[R]} = 2.994$$

Let the initial amount is 100.

$$\frac{100}{2.994} = [R]$$

$$\Rightarrow [R] = 33.40\% \quad (1)$$

Alternate method

(i) (a) $a - x$ (amount left) = $\frac{a}{2^n} = 1 \cdot \frac{1}{4} = \frac{1}{4}$

$$\frac{1}{4} = \frac{1}{2^n} \Rightarrow \frac{1}{2^2} = \frac{1}{2^n}$$

On comparing powers

$$n = 2 \text{ (no. of half-life's)}$$

(b) Total time (T) = $n \times t_{1/2}$ (half-life)

$$\therefore T = 2 \times 37.9 = 75.8 \text{ sec.} \quad (1)$$

(ii) (a) To find fraction left ($a - x$) after 1 min (i.e. 60 s)

$$T = n \times t_{1/2}$$

$$n = \frac{T}{t_{1/2}} = \frac{60}{37.9} = 1.583$$

$$(b) (a - x) = \frac{1}{2^{1.583}} \Rightarrow 2^{1.583} = \frac{1}{(a - x)}$$

Taking log of both the sides

$$1.583 \log 2 = \log \frac{1}{a - x}$$

$$1.58 \times 0.3010 = \log \frac{1}{a - x} \quad (1/2)$$

$$\frac{1}{a - x} = \text{antilog } 0.476$$

$$2.992 = \frac{1}{a - x}$$

$$a - x = \frac{1}{2.992} = 0.3342$$

Hence % left after 60 sec = 33.42% (1)
or fraction left after 1 min = 0.3342

25.

(i) First, find rate constant by using formula.

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}, \text{ where } [R] = a - x \text{ and } [R]_0 = a$$

(ii) From the value of k and using the above formula, find the value of time at which 10% of the original material remains unreacted

(i) 20% decomposition means $[R]_0 = 100$,
and $[R] = 100 - 20 = 80$

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

$$= \frac{2.303}{15} \log \frac{100}{80} \quad (1/2)$$

$$k = \frac{2.303}{15} \times \log 1.25$$

$$= \frac{2.303}{15} \times 0.0969$$

$$= 0.0148 \text{ min}^{-1} \quad (1)$$

(ii) Time at which 10% of the original material remains unreacted, i.e.

$$[R]_0 = 100, [R] = 10$$

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \quad (1/2)$$

$$t = \frac{2.303}{0.0148} \log \frac{100}{10} \quad (\log 10 = 1)$$

$$t = \frac{2.303 \times 1}{0.0148} = 155.6 \text{ min} \quad (1)$$

Alternate method

(i) Given, amount left ($a - x$)

$$\text{after 15 min} = 100 - 20 = 80\%$$

$$t(\text{min}) = 15 \text{ min}, n = \text{no. of half-life's}$$

$$(a) a - x = \frac{100}{2^n} \Rightarrow 2^n = \frac{100}{80} = 1.25$$

Taking log of both the sides

$$n \log 2 = \log 1.25$$

$$\Rightarrow n \times 0.3010 = 0.0969$$

$$\therefore n = \frac{0.0969}{0.3010} = 0.321 \quad (1)$$

(b) $\therefore T = n \times t_{1/2}$ (Half-life)

$$15 = 0.321 \times t_{1/2} = 0.321 \times \frac{0.693}{k}$$

$$\therefore k = 0.0148 \text{ min}^{-1} \quad (1/2)$$

(ii) (a) When, $a - x = 10$ and $a - x = \frac{100}{2^n}$

$$10 = \frac{100}{2^n}, \text{ i.e. } 2^n = \frac{100}{10} = 10$$

Taking log of both the sides

$$n \log 2 = \log 10 \Rightarrow n = \frac{1}{0.3010} = 3.32 \quad (1)$$

(b) $\therefore T = n \times t_{1/2} = 332 \times 46.8 = 1554 \text{ min (1/2)}$

26. (i) Average rate of reaction between the time interval 30 to 60 s is

$$r_{av} = -\frac{(0.17 - 0.31)}{60 - 30} = \frac{-(-0.14)}{30} = 4.67 \times 10^{-3} \text{ s}^{-1} \quad (1)$$

(ii) $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

At $t = 30 \text{ s}$, $[R] = 0.31 \text{ M}$, $[R]_0 = 0.55 \text{ M}$

$$k = \frac{2.303}{30} \log \frac{0.55}{0.31}$$

$$= \frac{2.303}{30} \log 1.774$$

$$= \frac{2.303}{30} \times 0.2490 = 1.91 \times 10^{-2} \text{ s}^{-1}$$

At $t = 60 \text{ s}$, $[R] = 0.17 \text{ M}$

$$k = \frac{2.303}{60} \log \frac{0.55}{0.17} = \frac{2.303}{60} \log 3.235$$

$$k = \frac{2.303}{60} \times 0.5099 = 1.96 \times 10^{-2} \text{ s}^{-1}$$

Average

$$k = \frac{1.91 \times 10^{-2} + 1.96 \times 10^{-2}}{2} = 1.93 \times 10^{-2} \text{ s}^{-1} \quad (2)$$

27. (i) For the hydrolysis of methyl acetate to be a pseudo first order reaction, the reaction should be first order with respect to ester when $[H_2O]$ is constant. The rate constant (k) for a first order reaction is given by

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

where, $[R]_0$ = initial concentration of the reactant

$[R]$ = final concentration of the reactant

At $t_1 = 10 \text{ s}$

$$k_1 = \frac{2.303}{10} \log \frac{0.10}{0.05} = 6.93 \times 10^{-2} \text{ s}^{-1}$$

At $t_2 = 20 \text{ s}$

$$k_2 = \frac{2.303}{20} \log \frac{0.10}{0.025} = 6.93 \times 10^{-2} \text{ s}^{-1}$$

It can be seen that the rate constant (k) for the reaction has a constant value under any

given time interval. Hence, the given reaction follows the pseudo first order kinetics.

(ii) Average rate of reaction between the time interval of 10 - 20 s is given by

$$\text{Average rate} = \frac{-\Delta[\text{Ester}]}{\Delta t} = -\left(\frac{0.025 - 0.05}{20 - 10}\right) = \frac{0.025}{10} = 0.0025 \text{ mol L}^{-1} \text{ s}^{-1}$$

28. (i) $A + B \longrightarrow P$

$$\text{Rate} = k[A][B]^2 \text{ (given)}$$

(a) If concentration of B is doubled, then rate of reaction = $k[A][2B]^2 = 4k[A][B]^2$

\therefore Rate becomes 4 times the original rate.

(b) If A is present in large excess, then the reaction will be independent of the concentration of A and will be dependent only on the concentration of B . As $[B]^2$ will be the only determining factor in the order of reaction, the overall order of the reaction will be two.

(ii) For the given first order reaction, the rate constant for 50% completion is given by

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad \dots(i)$$

Here, t = time taken for 50% completion = 30 min

$[R]_0$ = initial concentration of reactant

$[R]$ = final concentration of reactant

Let $[R]_0$ be 100 and due to 50% completion of reaction, $[R]$ will be

$$100 - 50, \text{ i.e. } 50$$

Putting values in (i), we get

$$k = \frac{2.303}{30} \log \frac{100}{50} = \frac{2.303}{30} \log 2 = 0.023 \text{ min}^{-1} \quad (1)$$

For same reaction, the time required for 90% completion of reaction can be computed using the expression,

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

Here, $[R]$ = final concentration of reactant

$$= 100 - 90 = 10$$

$$0.023 = \frac{2.303}{t} \log \frac{100}{10}$$

$$\Rightarrow t = \frac{2.303}{0.023} \log 10 = 100.13 \text{ min}$$

Therefore, the time required for 90% completion of the given first order reaction is 100.13 min.

29. (i) $2.3 \times 10^{-2} \text{ s}^{-1}$ (2½)

Refer to solution 27 (i).

(ii) $0.005 \text{ mol L}^{-1} \text{ s}^{-1}$; Refer to solution 27 (ii). (2½)

30. (i) The first order rate constant is given by,

$$k = \frac{1}{t} \ln \frac{[R]_0}{[R]}$$

where, $[R]_0$ is the initial concentration of reactant and $[R]$ is the concentration of reactant at time t .

∴ $\ln[R] = \ln[R]_0 - kt$

$$y = c + mx$$

(a) The order of the reaction is first order. (1)

(b) Slope of the curve = $-k$. (1)

(c) Unit of rate constant for first order reaction = time^{-1} or s^{-1} or min^{-1} . (1)

(ii) Let $[R]_0 = 100$

For the reaction which is 99% completed, $[R] = 1\%$ of $[R]_0 = 1$ and for the reaction which is 90% completed, $[R] = 10\%$ of $[R]_0 = 10$.

$$\begin{aligned} \therefore k &= \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{t_{99\%}} \log \frac{100}{1} \\ &= \frac{2.303}{t_{99\%}} \log(10^2) \end{aligned} \quad \dots (1)$$

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad \dots (1)$$

$$= \frac{2.303}{t_{90\%}} \log \frac{100}{10} = \frac{2.303}{t_{90\%}} \log(10) \quad \dots (ii)$$

Equating Eqs. (1) and (ii)

$$\frac{2.303}{t_{99\%}} \log(10^2) = \frac{2.303}{t_{90\%}} \log(10)$$

$$\frac{2}{t_{99\%}} = \frac{1}{t_{90\%}}$$

$$\Rightarrow t_{99\%} = 2t_{90\%}$$

Hence, time required for 99% completion of a reaction of first order is double the time required for 90% completion of the reaction. (1)

Explanations

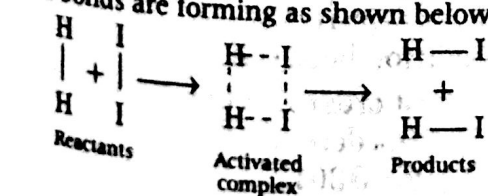
- Catalyst lowers the activation energy and changes the path of the reaction. (1/2)
 - A catalyst does not alter Gibbs energy (ΔG) of a reaction. (1/2)
- It is due to improper orientation, or due to another factor P called steric factor, which refers to the orientation of the colliding molecules. These are the two main factors which are responsible for a reaction to occur slowly. (1)
- It is the extra energy contained by reactant molecules that results into effective collisions between them to form the products. It is denoted by E_a . (1)
- Rate constant is the coefficient of proportionality related to the rate of reaction at a given temperature to the concentrations of reactants. (1)
 - Refer to solution 3. (1)
- Rate of chemical reaction when concentration of each reactant is unity is called rate constant. It is also known as specific rate of reaction. (1)
 - Refer to solution 3. (1)
- Rate of reaction increases with temperature. (1)
Temperature coefficient is the ratio of rate constant at temperature $(T + 10)$ K to the rate constant at temperature (T) K.
 Temperature coefficient

$$= \frac{\text{Rate constant at } (T + 10) \text{ K}}{\text{Rate constant at } (T) \text{ K}}$$

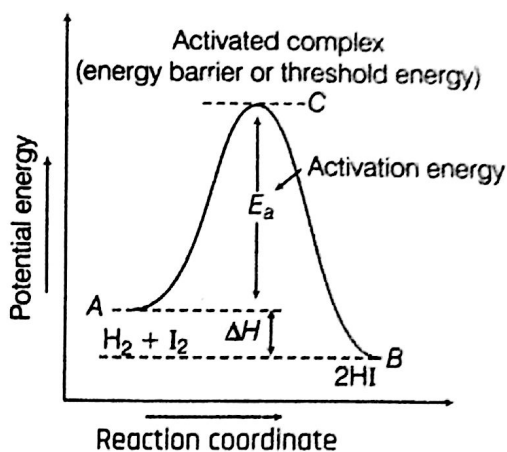
It is observed that for a chemical reaction with rise in temperature by 10° , the rate constant is nearly doubled. (1)

- When the colliding molecules possess the kinetic energy less than the threshold Energy (E_t), they require the energy to achieve E_t . This amount of energy (energy required) is known as activation energy (E_a). After achieving the activation energy (i.e. E_a), they reach to an activated stage. This stage is different from the reactant as well as from the product.

e.g. in the reaction between $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$, activated complex has configuration in which $\text{H}-\text{H}$ and $\text{I}-\text{I}$ bonds are breaking and $\text{H}-\text{I}$ bonds are forming as shown below:



Potential energy diagram of this reaction is shown below



- Given, $T_1 = 298 \text{ K}$, $T_2 = 308 \text{ K}$ and $k_2/k_1 = 2$ and $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

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

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \left[\frac{308 - 298}{298 \times 308} \right]$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{298 \times 308}$$

$$E_a = 52903.05 \text{ J mol}^{-1} \quad (1)$$

- Refer to solution 8. **Ans.** $55327.581 \text{ J mol}^{-1}$

$$\left[\text{Hint } \frac{k_2}{k_1} = 4, T_1 = 300 \text{ K}, T_2 = 320 \text{ K} \right]$$

- Given, $t_{1/2} = 40 \text{ min}$ at $T = 300 \text{ K}$

$$\therefore \text{For first order, } k_1 = \frac{0.693}{(t_{1/2})_1} = \frac{0.693}{40 \text{ min}}$$

$$k_1 = 0.0173 \text{ min}^{-1}$$

Similarly, at $T = 320 \text{ K}$

$$k_2 = \frac{0.693}{(t_{1/2})_2} = \frac{0.693}{20 \text{ min}} = 0.0346 \text{ min}^{-1}$$

Now, for calculation of activation energy

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

Putting values in above equation

$$\log \left(\frac{0.0346}{0.0173} \right) = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}}$$

$$\left(\frac{320 - 300}{300 \times 320} \right)$$

$$0.301 = \frac{E_a}{19.147 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{20}{96000 \text{ K}} \right)$$

$$E_a = 27663.58 \text{ J or } 27.663 \text{ kJ mol}^{-1}$$

11. Calculation of activation energy, E_a

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

$$\log k = \log A - \frac{E_a}{2.303 RT} \quad \dots (1)$$

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \quad \dots (ii)$$

On comparing Eqs. (i) and (ii)

$$\begin{aligned} \frac{E_a}{2.303 RT} &= \frac{1.0 \times 10^4}{T} \text{ K} \\ E_a &= 2.303R \times 1.0 \times 10^4 \text{ K} \\ &= 2.303 \times 1.0 \times 10^4 \text{ K} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \\ &= 1914 \times 10^4 \text{ J mol}^{-1} \\ &= 191.4 \text{ kJ mol}^{-1} \end{aligned} \quad (2)$$

Calculation of rate constant, k

Given, $t_{1/2} = 200 \text{ min} = 200 \times 60 \text{ s}$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{200 \times 60} \Rightarrow k = 5.775 \times 10^{-5} \text{ s}^{-1} \quad (1)$$

12. Use formula, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 \times T_2} \right)$ to calculate E_a .

Given, $k_1 = 0.02 \text{ s}^{-1}$, $k_2 = 0.07 \text{ s}^{-1}$

$T_1 = 500 \text{ K}$, $T_2 = 700 \text{ K}$

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

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

$$\log \frac{0.07}{0.02} = \frac{E_a}{2.303 \times 8.314} \left[\frac{700 - 500}{500 \times 700} \right] \quad (1)$$

$$E_a = 18230.35 \text{ J mol}^{-1} \quad (1)$$

13. Given, $k_1 = 2.15 \times 10^{-8} \text{ L}/(\text{mol s})$ at 650 K

$k_2 = 2.39 \times 10^{-7} \text{ L}/(\text{mol s})$ at 700 K

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

$$\begin{aligned} \log \frac{2.39 \times 10^{-7} \text{ L}/(\text{mol} \cdot \text{s})}{2.15 \times 10^{-8} \text{ L}/(\text{mol} \cdot \text{s})} \\ = \frac{E_a}{2.303 \times 8.314 \times 10^{-3} \text{ kJ/mol}} \left(\frac{1}{650} - \frac{1}{700} \right) \end{aligned} \quad (1)$$

$$\begin{aligned} \log 11.12 = \frac{E_a}{2.303 \times 8.314 \times 10^{-3} \text{ kJ/mol}} \\ \times \frac{700 - 650}{4.55 \times 10^5} \end{aligned}$$

$$E_a = \frac{1.046 \times 2.303 \times 8.314 \times 10^3 \times 4.55}{50}$$

$$E_a = 182.25 \text{ kJ/mol}$$

14. Using formula, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$ first find out the value of T_2 in Kelvin, then in Celsius.

Given, $T_1 = 10^\circ\text{C} + 273 = 283 \text{ K}$

$$k_{T_1} = 4.5 \times 10^3 \text{ s}^{-1}$$

$$E_a = 60 \text{ kJ mol}^{-1} = 60 \times 10^3 \text{ J mol}^{-1}$$

$$T_2 = ?$$

$$k_{T_2} = 1.5 \times 10^4 \text{ s}^{-1}$$

We know that,

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

On putting values,

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314} \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$0.523 = 3133.63 \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$\frac{T_2 - 283}{283 T_2} = 1.67 \times 10^{-4}$$

$$T_2 - 283 = 0.0472 T_2$$

$$0.953 T_2 = 283$$

$$T_2 = 297 \text{ K} \text{ or } T_2 = 24^\circ\text{C}$$

15. Given, Slope = -4250 K ,

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

From equation,

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

Comparing with straight line equation, $y = mx + c$

$$-\frac{E_a}{2.303R} = -4250$$

$$\begin{aligned} \Rightarrow E_a &= 2.303 \times 8.314 \times 4250 \\ &= 81.37 \text{ kJ mol}^{-1} \end{aligned}$$

16. Given, $T_1 = 293 \text{ K}$

$$T_2 = 313 \text{ K}$$

$$k_2/k_1 = 4$$

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

$$\log 4 = 0.6021$$

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

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

$$0.6021 = \frac{E_a}{19.147} \left(\frac{20}{91709} \right)$$

$$E_a = \frac{0.6021 \times 19.147 \times 91709}{20}$$

$$= 52862.94 \text{ J mol}^{-1} \quad (1)$$

17. Given, $E_a = 209.5 \text{ kJ mol}^{-1} = 209500 \text{ J mol}^{-1}$

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

$$T = 581 \text{ K}$$

Fraction of molecules = x

$$\log x = \frac{-E_a}{2.303 RT} \quad (1)$$

$$\log x = \frac{-209500}{2.303 \times 8.314 \times 581}$$

$$\log x = -18.8323 \quad (1)$$

$$x = \text{antilog}(\overline{19.1677})$$

$$= 1.471 \times 10^{-19} \quad (1)$$

Alternative method

$$\begin{aligned} \text{Fraction of molecules} &= e^{-E_a/RT} \\ &= e^{\frac{-209.5 \times 1000}{8.314 \times 581}} \\ &= e^{-43.37} = 1.461 \times 10^{-19} \quad (3) \end{aligned}$$

18. (i) (a) **Activation energy** Refer to solution 3. (1)

(b) **Rate constant** Refer to solution 4 (i). (1)

(ii) Given, $t = 10 \text{ min}$,

amount of reactant decomposed in time ($t = 10 \text{ min}$) = 25% if $[R]_0 = 100$, then amount of reactant left = 75% of $[R]_0 = 75$

$$k = \frac{2.303}{t} \log \frac{[R]_0}{R} = \frac{2.303}{10} \log \frac{100}{75}$$

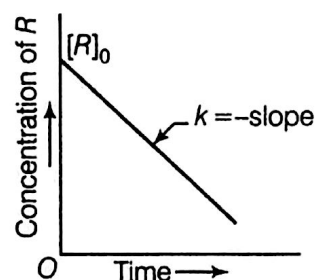
$$= 0.2303 \times 0.124$$

$$k = 0.028 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.028} = 24.75 \text{ min} \quad (3)$$

19. (a) The reaction is of zero order. Since, the integrated rate equation for zero order reaction is $k = \frac{[R_0] - [R]}{t}$.

(i) If we plot $[R]$ against t , we get a straight line with slope equal to $-k$ and intercept equals to $[R_0]$ as shown below



Variation in the concentration vs time plot for a zero order reaction

(ii) Slope of curve indicate that concentration of reactant decrease with the time (t) and is numerically equal to the value of k .

$$\text{i.e. slope of the graph} = -k = -\frac{d[R]}{dt}$$

(b) Given, $T_1 = 293 \text{ K}$, $T_2 = 313 \text{ K}$, $k_2/k_1 = 4$,
 $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $\log 4 = 0.6021$

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

$$\therefore \log 4 = \frac{E_a}{2.303 \times 8.314} \left[\frac{313 - 293}{313 \times 293} \right]$$

$$0.6021 = \frac{E_a}{19.147} \left[\frac{20}{91709} \right]$$

$$E_a = \frac{0.6021 \times 19.147 \times 91709}{20}$$

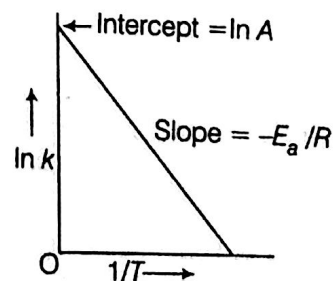
$$= 52862.94 \text{ J mol}^{-1}$$

Hence, $E_a = 52.86294 \text{ kJ mol}^{-1}$

20. (a) The plot of $\ln k$ vs $1/T$ gives a straight line.

Slope of this plot gives the value of $-\frac{E_a}{R}$ and the intercept gives the value of $\ln A$.

E_a and A can also be determined from the rate constants at two different temperatures.



A plot between $\ln k$ and $1/T$

(b) Given, reactant decomposes = 20% in 30 minutes (x)

Let initial quantity (a) = 100.

Then after 30 minutes ($a - x$) = $100 - 20 = 80$.

Time (t_{30}) = 30 minutes

For first order reaction,

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

$$\therefore k = \frac{2.303}{30} \log \frac{100}{80} \Rightarrow k = 7.439 \times 10^{-3}$$

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

On substituting the value of k in above equation,
we get

$$t_{1/2} = \frac{0.693}{7.439 \times 10^{-3}} = 9315 \text{ minutes.}$$

objectives

4. (d) Nature and concentration of the reactants and temperature of the reaction influence the rate of reaction. But molecularity does not affect the rate of reaction as it includes the number of atoms, ions or molecules that must collide with one another to result into a chemical reaction.

$$5. (b) r = k[A]^x [B]^y \Rightarrow \frac{dx}{dt} = k[A]^x [B]^y$$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k (\text{mol L}^{-1})^x (\text{mol L}^{-1})^y$$

$$k = (\text{mol L}^{-1})^{1-(x+y)} \text{ s}^{-1}$$

where, $(x + y)$ is the order of reaction.

Thus, unit of rate constant depends upon order of reaction.

6. (a) Given, rate constant for a first order reaction,

$$k = 2.303 \times 10^{-2} \text{ s}^{-1}$$

Let the initial concentration be a

Then, final concentration $(a - x) = \frac{1}{10}$ of $a = \frac{a}{10}$

Integrated rate law expression for first order reaction is

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

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

On substituting values we get,

$$t = \frac{2.303}{2.303 \times 10^{-2}} \log \frac{a}{a/10} \text{ or } t = 10^2 \log 10$$

$$t = 100 \text{ s} \quad (\because \log 10 = 1)$$

7. (c) For first order,

$$\text{rate} = \frac{d[R]}{dt} = k[R]$$

$$\text{or } \frac{d[R]}{[R]} = k dt \quad \dots (i)$$

On integrating Eq. (i)

$$\int \frac{d[R]}{[R]} = k \int dt$$

$$\ln [R] = -kt + C \quad \dots (ii)$$

At $t = 0, [R] = [R_0]$

(where, R = final concentration, i.e. $a - x$ and R_0 is the initial concentration, i.e. a .)

$$\ln [R_0] = C$$

On putting the value of C in Eq. (ii), we get

$$\ln [R] = -kt + \ln [R_0]$$

$$-kt = \ln [R] - \ln [R_0]$$

$$kt = \ln [R_0] - \ln [R]$$

Explanations

$$1. (b) \text{ Rate} = k[A][B] = r_1 \quad \dots (i)$$

when, $[B] = [2B]$, then,

$$\text{new rate} = k[A][2B] = r_2 \quad \dots (ii)$$

Divide Eq. (ii) by (i) to get,

$$\frac{r_2}{r_1} = \frac{k[A][2B]}{k[A][B]} \Rightarrow \frac{r_2}{r_1} = 2$$

$$r_2 = 2r_1$$

Hence, the rate doubles on doubling the concentration of B , thus we can say that the value of rate constant is also doubled

[as rate constant depends upon the rate of the reaction]

2. (a) For the reaction, $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$

Rate of reaction

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

$$\text{or } -\frac{d[\text{H}_2]}{dt} = \frac{3}{2} \frac{d[\text{NH}_3]}{dt}$$

$$\left(\because \frac{d[\text{NH}_3]}{dt} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \right)$$

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

3. (d) $2\text{H}_2\text{S} + \text{O}_2 \longrightarrow \text{Product}$

$$\text{Rate} = k p_{\text{H}_2\text{S}}^2 \times p_{\text{O}_2} = x$$

On increasing the pressure three fold

$$\text{Rate} = k [3p_{\text{H}_2\text{S}}]^2 \times [3p_{\text{O}_2}]$$

$$= k \times 9p_{\text{H}_2\text{S}}^2 \times 3p_{\text{O}_2}$$

$$= k \times 27 \times p_{\text{H}_2\text{S}}^2 \times p_{\text{O}_2} = 27x$$

Hence, rate will increase 27 times.

$$k = \frac{1}{t} \ln \frac{[R_0]}{[R]}$$

$$\therefore k = \frac{1}{t} \ln \frac{a}{a-x}$$

8. (b) For n th order reaction,
the unit of rate constant = $(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$

where, n = order of reaction

\therefore For first order reaction, $n = 1$

Thus, the unit of rate constant

$$= (\text{mol L}^{-1})^0 \text{s}^{-1} = \text{s}^{-1}$$

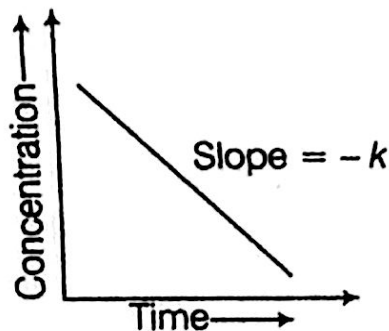
9. Expression for rate constant for zero order reaction is

$$k = \frac{1}{t} \{[A]_0 - [A]\}$$

$$kt = [A]_0 - [A]$$

$$[A] = -kt + [A]_0$$

It is an equation of straight line $[y = mx + c]$,
the plot of $[A]$ versus t will be a straight line with
slope = $-k$ and intercept on the concentration axis
= $[A]_0$.



10. (b) For first order reaction $t_{1/2}$ is independent of
initial concentration $t_{1/2} = \frac{0.693}{k}$.

11. (d) In general, $t_{1/2} \propto \frac{1}{(a)^{n-1}}$.

Here, n = order of reaction

$$\text{Given, } t_{1/2} \propto \frac{1}{a}$$

$$\text{On comparing } (a)^{n-1} = a \Rightarrow n-1 = 1$$

$$\therefore n = 2$$

12. (a) Arrhenius equation is $k = Ae^{-E_a/RT}$

On taking log both sides,

$$\text{we get, } \log k = \log A - \frac{E_a}{2.303RT}$$

When $\log k$ is plotted with $1/T$, the slope of the
reaction will be $-E_a/2.303R$ and intercept is given
by $\log A$.

$$13. (b) \log k = \log A - \frac{E_a}{2.303RT}$$

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

$$\log \left(\frac{k}{A} \right) = -\frac{2.303RT}{2.303RT} = -1$$

$$\frac{k}{A} = \text{antilog}(-1.0) = 1 \times 10^{-1} = 0.1$$