

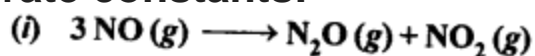
CHAPTER 3

CHEMICAL KINETICS

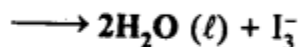
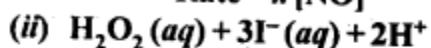
QUESTION AND ANSWERS

2MARKS

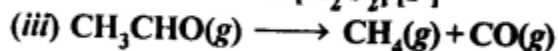
1. From the rate expression for the following reactions determine their order of reaction and the dimensions of the rate constants:



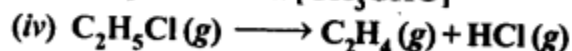
$$\text{Rate} = k [\text{NO}]^2$$



$$\text{Rate} = k [\text{H}_2\text{O}_2] [\text{I}^-]$$



$$\text{Rate} = k [\text{CH}_3\text{CHO}]^{3/2}$$



$$\text{Rate} = k [\text{C}_2\text{H}_5\text{Cl}]$$

Sol:

(i) Order = 2, dimension 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, dimension of

$$\begin{aligned} k_1 &= \frac{\text{Rate}}{[\text{H}_2\text{O}_2] [\text{I}^-]} \\ &= \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1}) (\text{mol L}^{-1})} = \text{L mol}^{-1} \text{s}^{-1} \end{aligned}$$

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

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

(iv) Order = 1, dimension 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. The decomposition of dimethyl ether leads to the formation of CH_4 , H_2 and CO and the reaction, rate is given by $\text{Rate} = k [\text{CH}_3\text{OCH}_3]^{3/2}$. The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also, be expressed in terms of the partial pressure of dimethyl ether, i.e., $\text{Rate} = k (P_{\text{CH}_3\text{OCH}_3})^{3/2}$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants?

Sol: As the concentration in the rate law equation is given in terms of pressure,

\therefore unit of rate = bar min^{-1}

$$\therefore \text{Unit of } k = \frac{\text{Rate}}{[P_{\text{CH}_3\text{OCH}_3}]^{3/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} \\ = \text{bar}^{-1/2} \text{min}^{-1}.$$

3. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half?

Sol:

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

(i) If $[\text{A}] = 2a$, rate = $k (2a)^2 = 4ka^2 = 4$ times.

(ii) If $[\text{A}] = a/2$, rate = $k \left(\frac{a}{2}\right)^2 = \frac{1}{4} ka^2 = \frac{1}{4}$ th.

4. What is the effect of temperature on the rate constant of reaction? How can this temperature effect on the rate constant be represented quantitatively?

Sol: The rate constant (k) for a reaction increases with rise in temperature and becomes nearly double with about every 10° rise in temperature. The effect is expressed with Arrhenius equation.

$$k = Ae^{-E_a/Rt}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \frac{0}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] = 0$$

$$\frac{k_2}{k_1} = \text{Antilog } 0 = 1 \text{ or } k_2 = k_1 = 1.6 \times 10^6 \text{ s}^{-1}$$

5. A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected on increasing the concentration of B three times?

(iii) How is the rate affected when the concentrations of both A and B is doubled?

Sol:

$$(i) \quad \frac{dx}{dt} = k[A][B]^2$$

$$(ii) \text{ Rate} = kab^2$$

$$\text{when } [B] \text{ becomes three times, rate} = ka(3b)^2 \\ = 9kab^2 = 9 \text{ times.}$$

$$(iii) \text{ When both } [A] \text{ and } [B] \text{ are doubled, rate} \\ = k2a(2b)^2 = 8kab^2 = 8 \text{ times.}$$

5MARKS

Question 1.

Show that for a first order reaction the time required for 99% completion of a reaction is twice the time required to complete 90% of the reaction. (C.B.S.E.Outside Delhi 2013)

Solution:

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

Ist case : $a = 100\%$; $x = 99\%$; $(a-x) = (100 - 99) = 1\%$

$$\begin{aligned} t_{99\%} &= \frac{2.303}{k} \log \frac{100}{1} = \frac{2.303}{k} \log 10^2 \\ &= \frac{2.303 \times 2}{k} = \frac{4.606}{k} \end{aligned}$$

IInd case : $a = 100\%$; $x = 90\%$; $(a-x) = (100 - 90) = 10\%$

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

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

$$\frac{t_{(99\%)}}{t_{(90\%)}} = \frac{4.606}{k} \times \frac{k}{2.303} = 2.$$

Question 2.

A first order reaction takes 40 min for 30% decomposition.
Calculate $t_{1/2}$.

Solution:

30% decomposition means that $x = 30\%$
of $[R_0]$ or, $[R] = [R_0] - 0.3[R_0] = 0.7[R_0]$

For reaction of 1st order,

$$\begin{aligned}k &= \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{40} \log \frac{[R_0]}{0.70[R_0]} \\&= \frac{2.303}{40} \log \frac{10}{7} \text{ min}^{-1} \\&= \frac{2.303}{40} \times 0.1549 \text{ min}^{-1} = 8.918 \times 10^{-3} \text{ min}^{-1}\end{aligned}$$

For a 1st order reaction,

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

Question 3.

The rate constant for the decomposition of a hydrocarbon is $2.418 \times 10^{-5} \text{ s}^{-1}$ at 546 K. If the energy of activation is $179.9 \text{ kJ mol}^{-1}$, what will be the value of pre-exponential factor?

Solution:

According to Arrhenius equation,

$$\begin{aligned}\log K &= \log A - \frac{E_a}{2.303RT} \\k &= 2.418 \times 10^{-5} \text{ s}^{-1}; E_a = 179900 \text{ J mol}^{-1}; R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}; T = 546 \text{ K} \\\log A &= \log K + \frac{E_a}{2.303RT} \\&= \log (2.418 \times 10^{-5} \text{ s}^{-1}) + \frac{(179900 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 546 \text{ K}} \\&= -4.6184 + 17.21 = 12.5916 \\A &= \text{Antilog } 12.5916 = 3.9 \times 10^{12} \text{ s}^{-1}.\end{aligned}$$

Question 4.

Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with $t_{1/2} = 3.00$ hours. What fraction of sample of sucrose remains after 8 hours?

Solution:

Sucrose decomposes according to first order rate law, hence

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}, t_{1/2} = 3 \text{ hrs}, t = 8 \text{ hrs}, \frac{[R]}{[R_0]} = ?$$

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

$$\text{Hence, } 0.231 = \frac{2.303}{8} \log \frac{[R_0]}{[R]}$$

$$\text{or, } \log \frac{[R_0]}{[R]} = 0.8024$$

$$\text{or, } \frac{[R_0]}{[R]} = \text{Antilog } (0.8024) = 6.345$$

$$\text{or, } \frac{[R]}{[R_0]} = \frac{1}{6.345} = 0.158$$

Question 5.

The decomposition of a hydrocarbon follows the equation

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K}/T}. \text{ Calculate } E_a.$$

Solution:

$$\text{Arrhenius equation, } k = A e^{-E_a/RT}$$

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

Comparing both the equations, we get

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

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

Question 6.

The decomposition of A into product has value of k as $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1} . At what temperature would k be $1.5 \times 10^4 \text{ s}^{-1}$?

Solution:

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,

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

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

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

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

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

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

Question 7.

The rate of a reaction quadruples when the temperature changes from 293 K to 313 K . Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Solution:

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

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

Using Arrhenius equation,

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

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

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

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

7MARKS

Question 1.

The time required for 10% completion of the first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the value of A is $4 \times 10^{10} \text{ s}^{-1}$, calculated at 318 K and E_a .

Solution:

$$t = \frac{2.303}{k_1} \log \frac{[R]_0}{\frac{90}{100}[R]_0},$$
$$t = \frac{2.303}{k_2} \log \frac{[R]_0}{\frac{75}{100}[R]_0}$$
$$t = \frac{2.303}{k_1} \log \frac{10}{9}, t = \frac{2.303}{k_2} \log \frac{4}{3}$$
$$\frac{2.303}{k_1} \log \frac{10}{9} = \frac{2.303}{k_2} \log \frac{4}{3}$$
$$\Rightarrow \frac{k_2}{k_1} = \frac{\log \frac{4}{3}}{\log \frac{10}{9}} = \frac{\log 1.333}{\log 1.111} = \frac{0.1249}{0.0457} = 2.733$$
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$
$$\Rightarrow \log 2.733 = \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{298 \times 308} \right)$$
$$E_a = \frac{2.303 \times 8.314 \times 308 \times 298}{10} \times 0.4367$$
$$= \frac{19.147 \times 308 \times 298}{10} \times 0.4367$$
$$= 76.75 \text{ kJ mol}^{-1}$$
$$\ln k = \ln A - \frac{E_a}{RT}$$
$$\log k = \log A - \frac{E_a}{2.303RT}$$
$$= \log(4 \times 10^{10}) - \frac{76.75 \times 1000}{2.303 \times 8.314 \times 318}$$

$$\begin{aligned}
 &= 10.6021 - \frac{76750}{6088.746} \\
 &= 10.6021 - 12.6051 = -2.003 \\
 k &= \text{Antilog}(-2.003) = 9.93 \times 10^{-3}
 \end{aligned}$$

Question 2.

The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 \text{ K}/T$$

Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

Solution:

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

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

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

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

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

Substituting this value in the given equation,

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

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

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

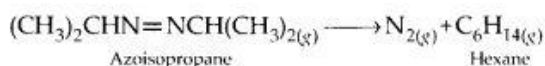
Question 3.

For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t (sec)	P (mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant

Solution:



Initial pressure P_0 0 0

Pressure $P_0 - p$ p p

after time t

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

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

When $t = 360$ sec,

$$k = \frac{2.303}{360} \log \frac{35.0}{2 \times 35.0 - 54.0} = \frac{2.303}{360} \log \frac{35.0}{16} \\ = 2.175 \times 10^{-3} \text{ s}^{-1}$$

When $t = 720$ sec,

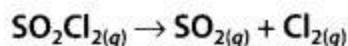
$$k = \frac{2.303}{720} \log \frac{35.0}{2 \times 35.0 - 63} = \frac{2.303}{720} \log 5 \\ = 2.235 \times 10^{-3} \text{ s}^{-1}$$

\therefore Average value of k

$$= \frac{2.175 + 2.235}{2} \times 10^{-3} \text{ s}^{-1} \\ = 2.20 \times 10^{-3} \text{ s}^{-1}$$

Question 4.

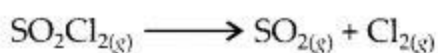
The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.



Experiment	Time/s ⁻¹	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

Solution:



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, $k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$

When $t = 100$ s,

$$\begin{aligned} k &= \frac{2.303}{100} \log \frac{0.5}{2 \times 0.5 - 0.6} = \frac{2.303}{100} \log(1.25) \\ &= \frac{2.303}{100} (0.0969) = 2.2316 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

When $P_t = 0.65$ atm,

\therefore Pressure of SO_2Cl_2 at time t ($p_{\text{SO}_2\text{Cl}_2}$),

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

Rate at that time $= k \times p_{\text{SO}_2\text{Cl}_2}$

$$= (2.2316 \times 10^{-3}) \times (0.35)$$

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

Question 5.

The rate constant for the decomposition of N_2O_5 at various temperatures is given below :

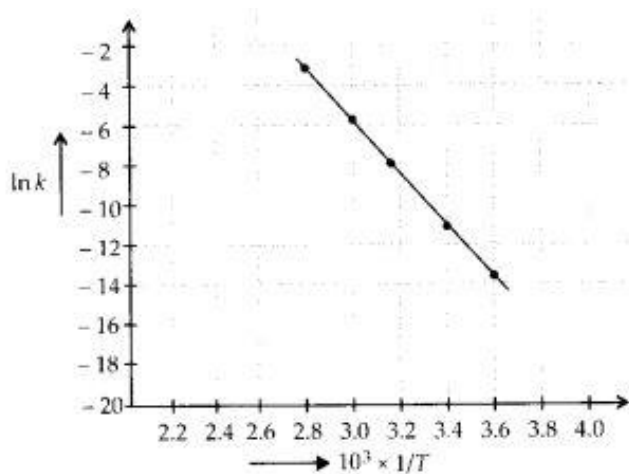
$T/^{\circ}\text{C}$	$10^5 \times k/\text{s}^{-1}$
0	0.0787
20	1.70
40	25.7
60	178
80	2140

Draw a graph between $\ln k$ and $1/T$ and calculate the value of A and E_a . Predict the rate constant at 30°C and 50°C .

Solution:

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

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



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

Slope of the line = $\tan \theta$

$$= \frac{y_2 - y_1}{x_2 - x_1} = \frac{-10.98 - (-14.08)}{3.4 - 3.6} \times 10^3$$

$$= -15.5 \times 10^3$$

$$E_a = -\text{slope} \times R = -(-15.5 \times 10^3 \times 8.314)$$

$$= 128.86 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned} \text{Again } \ln A &= \ln k + \frac{E_a}{RT} \\ &= -14.06 + \frac{128.86 \times 10^3 \text{ JK}^{-1} \text{ mol}^{-1}}{8.314 \times 273} \\ &= -14.06 + 56.77 = 42.71 \end{aligned}$$

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

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

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

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

$$\frac{1}{303 \text{ K}} \text{ and } \frac{1}{323 \text{ K}} \text{ and then } k \text{ is calculated.}$$

SUMMARY

1. Chemical kinetics is the branch of chemistry which deals with the study of rates (or fastness) of chemical reactions, the factors affecting it and the mechanism by which the reactions proceed.

2. Rate of reaction is the change in concentration of reactants or products per unit time.

For a general reaction, $A+B \rightarrow C$

The rate of reaction

$$= \frac{-\Delta[A]}{\Delta t} \text{ or } \frac{-\Delta[B]}{\Delta t} \text{ or } \frac{+\Delta[C]}{\Delta t}$$

The negative sign indicates that the concentration is decreasing with time.

Unit for reaction rate is $\text{mol L}^{-1}\text{s}^{-1}$.

3. The rate of reaction is not a constant quantity (except for zero order reactions). It decreases as the reaction proceeds in the forward direction.

4. A rate law expresses a mathematical relationship between the reaction rate and the molar concentration of one or more reactants.

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

Where m and n are determined experimentally and represent the order of reaction with respect to A and B respectively, $m + n$ represents the overall order of reaction.

5. Rate constant is the rate of reaction when the concentration of each of reacting species is unity. It is represented by 'k' It is also called specific reaction rate or velocity constant of reaction.