

4



Chemical Kinetics

Facts that Matter

- **Average rate:** It is obtained by dividing the change in concentration of any of the reactant or product by the time taken for the change, *i.e.* $\Delta x/\Delta t$

For a reaction of the type



the average rate expressions are:

$$\begin{aligned}r_{\text{ave}} &= -\frac{\Delta A}{\Delta t} \cdot \frac{1}{a} = -\frac{\Delta B}{\Delta t} \cdot \frac{1}{b} \\ &= +\frac{\Delta C}{\Delta t} \cdot \frac{1}{c} = +\frac{\Delta D}{\Delta t} \cdot \frac{1}{d}\end{aligned}$$

The negative sign implies that change in concentration of the reactant is negative.

Average rate does not give the true rate of the reaction.

- **Instantaneous rate of a reaction:** The rate of a reaction at a particular moment of time is called the instantaneous rate of a reaction. Average rate expression becomes instantaneous rate expression as $\Delta t \rightarrow 0$

Instantaneous rate $r_{\text{inst}} = dx/dt$

dx – infinitesimally small change in concentration

dt – infinitesimally small interval of time

Instantaneous rate is experimentally obtained by taking the tangent at any instant on the curve obtained by plotting the curve of concentration vs time.

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

For a general reaction



The rate law expression is

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

k – rate constant, ‘ x ’ may or may not be equal to ‘ a ’, ‘ y ’ may or may not be equal to ‘ b ’.

- **Order of a reaction:** The sum of exponents of the concentration of the reactants in the rate law expression.

In the rate law expression; rate = $[A]^x [B]^y$

‘ x ’ — order of the reaction w.r.t. reactant A, ‘ y ’ order of the reaction w.r.t. reactant B
 $x + y$ is the overall order of the reaction, and for a n^{th} order reaction the unit of rate constant ‘ k ’ is $(\text{mol L}^{-1})^{1-n} \text{ s}^{-1}$

- **Molecularity of a reaction.** The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction.
- Complex reactions involving more than three molecules in the stoichiometric equation, must (is assumed to be) take(ing) place in more than one step (elementary reactions.)

- The overall order of the reaction is controlled by the slowest step which is called the rate determining step.
- The rate can be written from the slowest step.
- For a single step (or elementary) reaction, the order and molecularity will be the same.
- **Integrated rate expression for zero order reactions**

$$k = \frac{[R]_0 - [R]}{t} \text{ where } k - \text{rate constant for zero order reaction}$$

$[R]_0$ – initial concentration of the reactant

$[R]$ – concentration of the reactant at time 't'

- For a first order reaction
- For a first order gas phase reaction of the type:
 $A(g) \longrightarrow B(g) + C(g)$

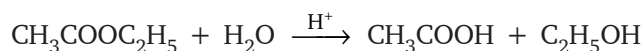
$$k = \frac{2.303}{t} \log \frac{p_i}{(2p_i - p_t)}$$

P_i = initial pressure of gas A

P_t = partial pressure of gas A at time 't'.

- **Half life of a reaction:** Time taken for reducing the concentration of a reactant to one half of its concentration:
 - For a zero order reaction, half life, $t_{1/2} = [R]_0/2k$
 - For a first order reaction, $t_{1/2} = 0.693/k$
 - For an n^{th} order reaction, $t_{1/2} \propto [R]_0^{1-n}$
- **Pseudo first order reactions.** Reactions which appears to be of second order, but actually are of first order are called pseudo first order reactions.

E.g., hydrolysis of esters:



Rate law for this reaction is: Rate = $k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$

But the concentration of water does not change during the course of the reaction.

So; $[\text{H}_2\text{O}]$ is a constant.

Therefore, rate = $k_1[\text{CH}_3\text{COOC}_2\text{H}_5]$. where, $k_1 = k[\text{H}_2\text{O}]$

Therefore, the reaction behaves as a first order reaction.

- **Arrhenius equation for temperature dependence of rate constant:**

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

Or $\log k = \log A - E_a/2.303RT$

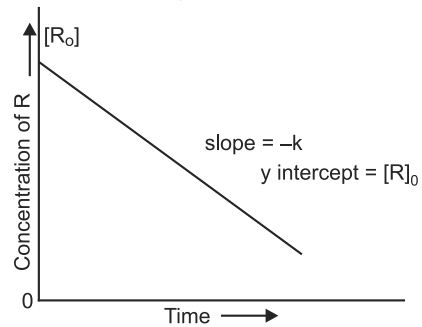
$$\log k_2/k_1 = E_a/2.303[T_2 - T_1/T_1T_2]$$

A = pre exponential factor;

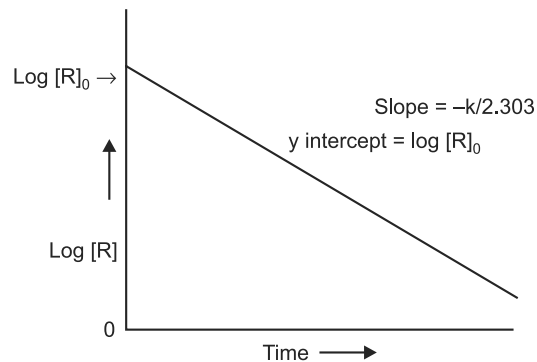
E_a = Activation energy

$$\text{slope} = -E_a/2.303R$$

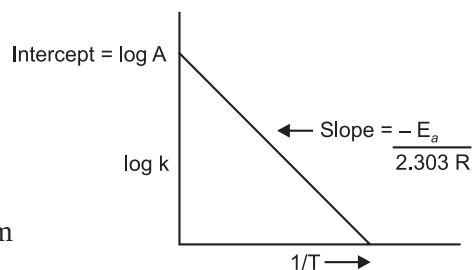
- **Activation energy:** The energy required to form the activated complex.



Plot of variation of $[R]$ vs time (t) for a zero order reaction.

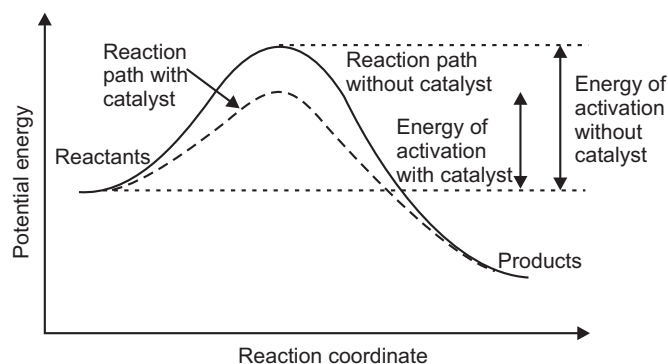


Plot of variation of $\log[R]$ Vs time for a first order reaction.



Plot of variation of $\log k$ Vs $1/T$

- **Effect of catalyst on reaction rate:** A catalyst alters the rate of a reaction as it provides an alternate pathway for the reaction mechanism by reducing the activation energy between reactants and products and hence lowers down the potential energy barrier

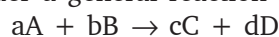


— A catalyst

- (a) does not alter the Gibb's energy (ΔG) of a reaction.
 - (b) catalyses only spontaneous reactions.
 - (c) does not change the equilibrium constant of a reaction.
 - (d) is highly specific.
- **Collision theory of chemical reactions:**
 - (a) **Collision frequency:** The number of collisions per second per unit volume of the reaction mixture.
 - (b) According to the collision theory; rate = $P Z_{AB} e^{-E_a/RT}$
 P —probability factor; Z —collision frequency of reactants A & B.
 $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a .

- **Important Formulae**

Rate law: Consider a general reaction



Where a, b, c, d are the stoichiometric coefficients of reactants and products.

Rate $\propto [A]^x [B]^y$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants.

$$-\frac{d[R]}{dt} = k[A]^x [B]^y$$

For Zero Order Reactions

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

This can be derived as follows:

Let the reaction



The rate of zero order reaction is directly proportional to zero power of concentration of reactants.

$$\therefore \text{Rate} = \frac{-d[R]}{dt} = k[R]^0$$

As $[R]^0 = 1$

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

$$d[R] = -kdt$$

Integrating both sides, we get

$$[R] = -kt + I \quad \dots(i)$$

At

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

$$[R_0] = -k \times 0 + I = [R_0] = I$$

Substituting in equation (i) we get

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

$$[R]_0 - [R] = kt$$

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

$$t_{1/2} = \frac{[R]_0}{2k}$$

Rate law for first order reactions

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

Considering a first order gas phase reaction, we have

$$k = \left(\frac{2.303}{t} \right) \left(\log \frac{P_i}{P_t} \right)$$

or

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

Where P_i is the initial pressure of the reactant A and P_t is the total pressure at time t .

Arrhenius Equation:

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

where 'A' is the frequency factor, E_a is the energy of activation, R is the gas constant and T is absolute temperature.

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

where k_1 and k_2 are the values of rate constant at temperature T_1 and T_2 respectively.

NCERT IN-TEXT QUESTIONS SOLVED

- 4.1.** For the reaction $R \rightarrow P$ the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

Ans.

$$\begin{aligned} \text{Average rate} &= \frac{\Delta[R]}{\Delta t} = \frac{[R]_2 - [R]_1}{t_2 - t_1} \\ &= \frac{0.02\text{M} - 0.03\text{M}}{25 \text{ min}} = \frac{-0.01\text{M}}{25 \text{ min}} = 4 \times 10^{-4} \text{ M min}^{-1} \end{aligned}$$

or

$$\frac{-0.01\text{M}}{25 \times 60} = 6.66 \times 10^{-6} \text{ M}^{-1}.$$

4.2. In a reaction, $2A \rightarrow$ products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Average rate = $-\frac{1}{2} \frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{[A]_2 - [A]_1}{t_2 - t_1}$

$$= -\frac{1}{2} \left(\frac{0.4 \text{ M} - 0.5 \text{ M}}{10 \text{ min}} \right) = -\frac{1}{2} \left(\frac{-0.1 \text{ M}}{10 \text{ min}} \right) = 5 \times 10^{-3} \text{ M min}^{-1}$$

4.3. For a reaction, $A + B \rightarrow$ product; the rate law is given by $r = k[A]^{1/2} [B]^2$. What is the order of the reaction?

Ans. Order of the reaction = $\frac{1}{2} + 2 = 2\frac{1}{2}$ or 2.5

4.4. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

Ans. For the reaction, $X \rightarrow Y$ as it follows second order kinetics, therefore the rate law equation will be

$$\text{Rate} = k[X]^2 = ka^2$$

if $[X] = a \text{ mol L}^{-1}$

If the concentration of X is increased three times, then

$$[X] = 3a \text{ mol L}^{-1}$$

\therefore Rate = $k(3a)^2 = 9ka^2$.

Thus, the rate of the reaction will become 9 times. Hence the rate of formation of Y will increase by 9 times.

4.5. A first order reaction has a rate constant, $1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

Ans. Here, $[R]_0 = 5\text{g}$, $[R] = 3\text{g}$
 $k = 1.15 \times 10^{-3} \text{ s}^{-1}$. As the reaction is of first order,

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

$$t = \frac{2.303}{1.15 \times 10^{-3} \text{ s}^{-1}} \log \frac{5\text{g}}{3\text{g}} = 2.00 \times 10^3 (\log 1.667) \text{ s}$$

$$= 2.0 \times 10^3 \times 0.2219 \text{ s} = 443.85 = 444 \text{ s}$$

4.6. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Ans. For a first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60 \text{ min}} = 1.155 \times 10^{-2} \text{ min}^{-1} = \frac{0.693}{60 \times 60} = 1.925 \times 10^{-4} \text{ s}^{-1}$$

4.7. What will be the effect of temperature on rate constant?

Ans. Rate constant of a reaction is nearly doubled with rise in temperature by 10°C . The exact dependence of the rate constant on temperature is given by Arrhenius equation:

$$(\text{Rate constant}), k = Ae^{-E_a/RT}$$

Where A is called the frequency factor and E_a is the activation energy of the reaction.

4.8. The rate of the chemical reaction doubles for an increase of 10K in absolute temperature from 298 K. Calculate E_a .

Ans.

$$T_1 = 298 \text{ K}, k_1 = k$$

$$T_2 = 308 \text{ K}, k_2 = 2k$$

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

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{308 \text{ K} - 298 \text{ K}}{308 \text{ K} \times 298 \text{ K}} \right)$$

or

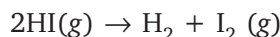
$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{298 \times 308} \text{ (J mol}^{-1}\text{)}$$

or

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{298 \times 308}$$

$$E_a = 5.290 \text{ kJ mol}^{-1}$$

4.9. The activation energy for the reaction:



is $209.5 \text{ kJ mol}^{-1}$ at 581 K . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Ans. Fraction of molecules having energy equal to or greater than the activation energy.

$$= n = \frac{N_E}{N_T} = e^{-E_a/RT}$$

\therefore

$$\ln \frac{N_E}{N_T} = -\frac{E_a}{RT}$$

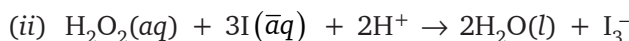
or

$$\log \frac{N_E}{N_T} = -\frac{E_a}{2.303 RT} = -\frac{209.5 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 581 \text{ K}}$$
$$= -18.8323$$

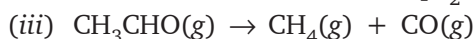
$$\frac{N_E}{N_T} = \text{Antilog}(-18.8323) = \text{Antilog } \overline{19.1677} = 1.471 \times 10^{-19}.$$

NCERT TEXTBOOK QUESTIONS SOLVED

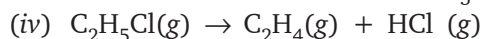
4.1. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants:



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



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



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

Ans. (i) Order = 2

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

(ii) Order = 2

$$\text{Dimension of } k = \frac{\text{Rate}}{(\text{mol L}^{-1})^2} = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^2} = \text{L mol}^{-1} \text{ s}^{-1}.$$

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

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

(iv) Order = 1

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

4.2. For the reaction:



The rate = $k[\text{A}][\text{B}]^2$ with $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$. Calculate the initial rate of the reaction when $[\text{A}] = 0.1 \text{ mol L}^{-1}$, $[\text{B}] = 0.2 \text{ mol L}^{-1}$. Calculate the rate of reaction after $[\text{A}]$ is reduced to 0.06 mol L^{-1} .

Ans.

$$\begin{aligned} \text{Initial rate} &= k[\text{A}][\text{B}]^2 \\ &= (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) (0.1 \text{ mol L}^{-1}) \times (0.2 \text{ mol L}^{-1})^2 \\ &= 8 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

When $[\text{A}]$ is reduced from 0.10 mol L^{-1} to 0.06 mol L^{-1} , i.e. 0.04 mole L^{-1} of A has reacted, then

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

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

Now, $\text{rate} = (2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}) \cdot (0.06 \text{ mol L}^{-1}) (0.18 \text{ mol L}^{-1})^2$
 $= 3.89 \times 10^{-9} \text{ mol L}^{-1} \text{ s}^{-1}.$

4.3. The decomposition of NH_3 on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$?

Ans. The chemical reaction is: $2 \text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$

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

For a zero order reaction, Rate = k

$$\therefore -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

$$\text{Rate of production of } \text{N}_2 = \frac{d[\text{N}_2]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

Rate of production of H₂

$$\frac{1}{3} \frac{d[\text{H}_2]}{dt} = k$$

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= 3k = 3 \times 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} \\ &= 7.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

- 4.4.** The decomposition of dimethyl ether leads to the formation of CH₄, H₂ 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.*

$$\text{Rate} = k(\text{PCH}_3\text{OCH}_3)^{3/2}$$

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

Ans. In terms of pressure,

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

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

- 4.5.** Mention the factors that affect the rate of a chemical reaction.

Ans. (i) Nature of reactants (ii) Physical state of reactants (iii) Concentration
(iv) Temperature (v) Catalyst (vi) Surface area

- 4.6.** A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is: [AI 2014]

(i) doubled (ii) reduced to half.

Ans. (i) Reaction is second order with respect to the reactant

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

$$\text{when } [\text{A}] = 2a$$

$$\text{Rate} = k(2a)^2 = 4ka^2 = 4 \text{ times}$$

Therefore, when concentration of the reactant is doubled the rate will become 4 times.

$$(ii) \text{ when } [\text{A}] = \frac{1}{2} a$$

$$\text{Rate} = k \left(\frac{1}{2} a \right)^2 = \frac{1}{4} ka^2 = \frac{1}{4} k$$

Therefore, rate will be reduced to one-fourth of the initial rate.

- 4.7.** What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

Ans. Rate constant of a reaction increases with increase of temperature. The effect of temperature can be represented quantitatively by Arrhenius equation,

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

- 4.8.** In a pseudo first order hydrolysis of ester in water, the following results were obtained.

t/s	0	30	60	90
Ester/mol L ⁻¹	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

Ans. (i) Average rate during the interval 30-60 seconds.

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

$$= 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

(ii)
$$k' = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

In which $[R]_0 = 0.55 \text{ M}$
 $t = 30 \text{ seconds}$

$$\therefore k' = \frac{2.303}{30 \text{ s}} \log \frac{0.55}{0.31} = 1.96 \times 10^{-2} \text{ s}^{-1}$$

At $t = 60 \text{ seconds}$,

$$k' = \frac{2.303}{60 \text{ s}} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2} \text{ s}^{-1}$$

At $t = 90 \text{ seconds}$,

$$k' = \frac{2.303}{90 \text{ s}} \log \frac{0.55}{0.085} = 2.07 \times 10^{-2} \text{ s}^{-1}$$

So, Average value of $k' = \frac{(1.91 + 1.96 + 2.07)}{3} \times 10^{-2} = 1.98 \times 10^{-2} \text{ s}^{-1}$.

4.9. 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 are doubled?

[Delhi 2013]

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

(ii) If concentration of 'B' is tripled, then the rate will become 9 times.

(iii) When concentration of both A and B are doubled, then the rate will become 8 times.

4.10. In a reaction between A and B, the initial rate of reaction (r_0) was measured for different initial concentrations of A and B as given below:

A/mol L ⁻¹	0.20	0.20	0.40
B/mol L ⁻¹	0.30	0.10	0.05
r_0 /mol L ⁻¹ s ⁻¹	5.07×10^{-5}	5.07×10^{-5}	1.43×10^{-4}

What is the order of the reaction with respect to A and B?

Ans.

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

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

$$\text{Also, } 5.07 \times 10^{-5} = k [0.2]^x [0.1]^y \quad \dots(ii)$$

Dividing (i) and (ii) we get

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

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

$$\text{Also, } 1.43 \times 10^{-4} = K [0.4]^x [0.05]^0 \quad \dots(iv)$$

Dividing (iii) and (iv) we get

$$\frac{1}{2.8} = \frac{1}{2^x}$$

\Rightarrow

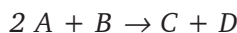
$$2.8 = 2^x$$

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

$$x = \frac{\log 2.8}{\log 2.0} = \frac{0.4472}{0.3010} = 1.48 = 1.5.$$

Therefore, the order of reaction is 1.5 w.r.t. 'A' and zero w.r.t. 'B'.

4.11. The following results have been obtained during the kinetic studies of the reaction:



Experiment	[A]/mol L ⁻¹	[B]/ mol L ⁻¹	Initial rate of formation of D/mol L ⁻¹ min ⁻¹
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Determine the rate law and the rate constant for the reaction.

Ans. From experiments I and IV, it may be noted that when [B] is kept the same but [A] has been made four times, then the rate of reaction becomes four times. This means

$$\text{Rate} \propto [A] \quad \dots(i)$$

From experiments II and III it may also be noted that when [A] is kept the same and [B] has been doubled, then the rate of reaction becomes four times. This means

$$\text{Rate} \propto [B]^2 \quad \dots(ii)$$

Combining (i) and (ii), we get the rate law for the given reaction as:

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

Thus, order w.r.t. A = 1

order w.r.t. B = 2

Overall order of the reaction = 1 + 2 = 3

The values of rate constant and its unit can be calculated from the data of each experiment using the expression;

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

Expt.	$k(\text{mol}^{-2} \text{L}^2 \text{min}^{-1})$
I	$\frac{6.0 \times 10^{-3}}{0.1 \times (0.1)^2} = 6.0$
II	$\frac{7.2 \times 10^{-2}}{0.3 \times (0.2)^2} = 6.0$
III	$\frac{2.88 \times 10^{-1}}{0.3 \times (0.4)^2} = 6.0$
IV	$\frac{2.4 \times 10^{-2}}{0.4 \times (0.1)^2} = 6.0$

So, rate constant $k = 6.0 \text{ mol}^{-2} \text{L}^2 \text{min}^{-1}$

4.12. The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A]/mol L ⁻¹	[B]/mol L ⁻¹	Initial rate/ mol L ⁻¹ min ⁻¹
I	0.1	0.1	2.0×10^{-2}
II	—	0.2	4.0×10^{-2}
III	0.4	0.4	—
IV	—	0.2	2.0×10^{-2}

Ans. The rate expression will be;

$$\text{Rate} = k [\text{A}] [\text{B}]^0 = k [\text{A}]$$

From expt. I, $2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = k (0.1 \text{ M})$ or $k = 0.2 \text{ min}^{-1}$

From expt. II, $4.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = (0.2 \text{ min}^{-1}) [\text{A}]$

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

From expt. III, $\text{Rate} = (0.2 \text{ min}^{-1}) (0.4 \text{ mol L}^{-1}) = 0.08 \text{ mol L}^{-1} \text{ min}^{-1}$

From expt. IV, $2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = 0.2 \text{ min}^{-1} [\text{A}]$

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

4.13. Calculate the half-life of a first order reaction from their rate constants given below:

(i) 200 s^{-1} (ii) 2 min^{-1} (iii) 4 years^{-1}

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

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

$$(i) \quad t_{1/2} = \frac{0.693}{200 \text{ s}^{-1}} = 0.346 \times 10^{-2} \text{ s} = 3.46 \times 10^{-3} \text{ s}$$

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

$$(iii) \quad t_{1/2} = \frac{0.693}{4 \text{ years}^{-1}} = 0.173 \text{ year.}$$

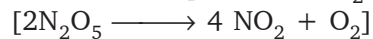
4.14. The half-life for radioactive decay of ^{14}C is 5730 years. An archaeological artifact containing wood had only 80% of the ^{14}C found in a living tree. Estimate the age of the sample.

Ans. Radioactive decay follows first order kinetics.

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

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \\ &= \frac{2.303}{0.693/5730 \text{ year}^{-1}} \log \frac{100}{80} \\ &= \frac{2.303 \times 5730}{0.693} \times 0.0969 \text{ year} \\ &= 1845 \text{ years.} \end{aligned}$$

4.15. The experimental data for decomposition of N_2O_5

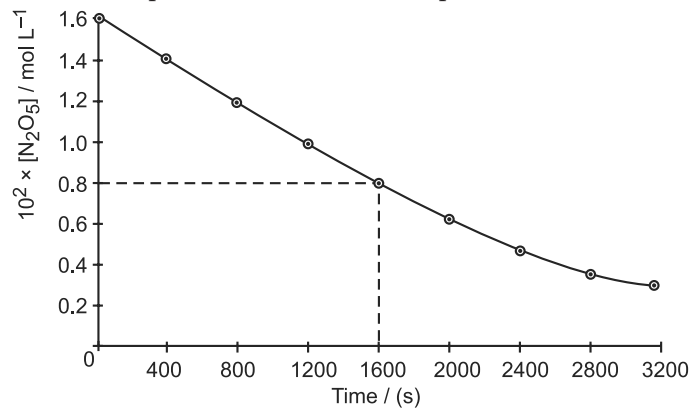


in gas phase at 318 K are given below:

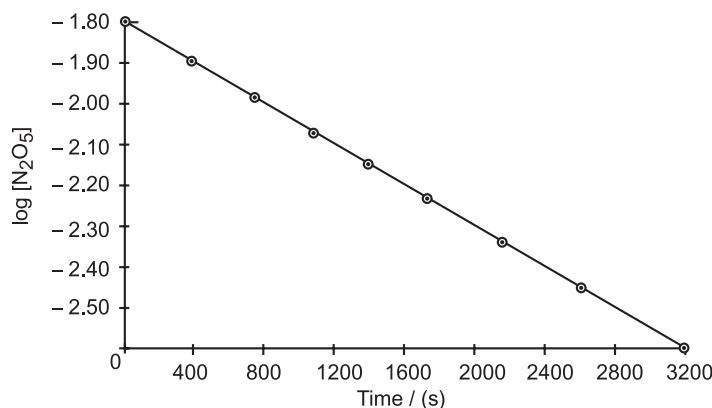
t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [\text{N}_2\text{O}_5]/\text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

- Plot $[\text{N}_2\text{O}_5]$ against t .
- Find the half-life period for the reaction.
- Draw a graph between $\log [\text{N}_2\text{O}_5]$ and t .
- What is the rate law?
- Calculate the rate constant.
- Calculate the half-life period from k and compare it with (ii).

Ans. (i)



- Initial concentration of $\text{N}_2\text{O}_5 = 1.63 \times 10^{-2} \text{ M}$
Half of this concentration = $0.815 \times 10^{-2} \text{ M}$
Time corresponding to this concentration = 1440 s
Hence, $t_{1/2} = 1440 \text{ s}$
- Plot of $\log [\text{N}_2\text{O}_5]$ vs time.



(iv) As plot of $\log [\text{N}_2\text{O}_5]$ vs time is a straight line. Hence it is a reaction of first order, *i.e.* rate law is

$$\text{Rate} = k [\text{N}_2\text{O}_5]$$

(v) Slope of the line = $-\frac{k}{2.303}$

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

i.e. $\frac{k}{2.303} = \frac{0.67}{3200}$

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

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

4.16. The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of the reactant to its $1/16^{\text{th}}$ value?

Ans. $t = \frac{2.303}{k} \log \frac{x}{x/16} = \frac{2.303}{60 \text{ s}^{-1}} \log 16 = 4.62 \times 10^{-2} \text{ s.}$

4.17. During nuclear explosion, one of the products is ^{90}Sr with half life of 28.1 years. If $1 \mu\text{g}$ of ^{90}Sr was absorbed in the bones of newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically?

Ans. As radioactive disintegration follows the first order kinetics,

$$\therefore \text{Decay constant of } ^{90}\text{Sr}, (k) = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.14} = 2.466 \times 10^{-2} \text{ year}^{-1}$$

To calculate the amount left after 10 years,

$$\begin{aligned} a &= 1 \mu\text{g}, t = 10 \text{ years} \\ k &= 2.466 \times 10^{-2} \text{ years}^{-1} \\ (a - x) &= ? \end{aligned}$$

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

$$2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{(a - x)}$$

$$\text{or} \quad \log (a - x) = - 0.1071$$

$$(a - x) = \text{Antilog } \bar{1}.8929 = 0.7814 \mu\text{g}$$

To calculate the amount left after 60 years.

$$2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{a - x}$$

$$\text{or} \quad \log (a - x) = - 0.6425$$

$$(a - x) = \text{Antilog } \bar{1}.3575 = 0.2278 \mu\text{g}.$$

4.18. For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction. [Delhi 2013]

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

99% completion means that

$$x = 99\% \text{ of } a = 0.99 a$$

$$\therefore t_{99\%} = \frac{2.303}{k} \log \frac{a}{a - 0.99a} = \frac{2.303}{k} \log 10^2 = 2 \times \frac{2.303}{k}$$

90% completion means that

$$x = 90\% \text{ of } a = 0.90 a$$

$$t_{90\%} = \frac{2.303}{k} \log \frac{a}{a - 0.90a} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}$$

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

4.19. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$. [Delhi 2013]

Ans. 30% decomposition means that $x = 30\% \text{ of } a = 0.30 a$

As the reaction is of first order

$$\begin{aligned} \therefore k &= \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{40 \text{ min}} \log \frac{a}{a - 0.30 a} \\ &= \frac{2.303}{40} \log \frac{10}{7} \text{ min}^{-1} = \frac{2.303}{40} \times 0.1549 \text{ min}^{-1} \\ &= 8.918 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

For a first order reaction,

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

4.20. 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.



Initial pressure (P_0) 0 0

After time t , $(P_0 - P)$ P P

Total pressure after time (t)

$$P_t = (P_0 - P) + P + P = P_0 + P$$

$$P = P_t - P_0$$

$$a \propto P_0$$

$$(a - x) \propto P_0 - P$$

i.e. $(a - x) \propto 2P_0 - P_t$

As decomposition of azoisopropane is a first order reaction

$$\therefore k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

When $t = 360$ sec

$$\begin{aligned} k &= \frac{2.303}{360 \text{ sec}} \log \frac{35.0}{2 \times 35.0 - 54.0} \\ &= \frac{2.303}{360 \text{ sec}} \log \frac{35}{16} = \frac{2.303}{360} (0.3400) \\ &= 2.175 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

When $t = 720$ sec

$$\begin{aligned} k &= \frac{2.303}{720 \text{ sec}} \log \frac{35.0}{2 \times 35.0 - 63.0} \\ &= \frac{2.303}{720 \text{ s}} \log 5 = \frac{2.303}{720} (0.6990) = 2.235 \times 10^{-3} \text{ s}^{-1} \end{aligned}$$

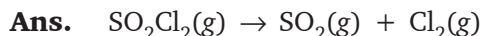
Average value of $k = \frac{2.175 + 2.235}{2} \times 10^{-3} \text{ s}^{-1} = 2.20 \times 10^{-3} \text{ s}^{-1}$

4.21. 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.



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

Where P_i is the initial pressure at time $t = 0$

P_t = total pressure

When

$t = 100$ s

$$k = \frac{2.303}{100 \text{ sec}} \log \frac{0.5}{2 \times 0.5 - 0.6} = \frac{2.303}{100 \text{ s}} \log (1.25)$$

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

When

$$P_t = 0.65 \text{ atm}$$

$$P_i + P = 0.65$$

$$P = 0.65 - P_1 = 0.65 - 0.50 = 0.15 \text{ atm}$$

Pressure of SO_2Cl_2 at time (t)

$$(P_{\text{SO}_2\text{Cl}_2}) = P_1 - P$$

$$= 0.5 - 0.15 = 0.35 \text{ atm}$$

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

$$= (2.2316 \times 10^{-3} \text{ s}^{-1}) (0.35 \text{ atm}) = 7.8 \times 10^{-5} \text{ atm s}^{-1}$$

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

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

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

Ans. Graph between $\ln k$ and $1/T$ will be a straight line with $-ve$ slope.

$$\text{Slope of the line} = \frac{y_2 - y_1}{x_2 - x_1}$$

From Arrhenius equation, E_a can be calculated by using formula:

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

$$E_a = -\text{slope} \times R$$

$$= -12.30 \times 8.314 = 102.27 \text{ kJ mol}^{-1}$$

Now, At

$$T = 273 \text{ K}$$

$$\ln k = -7.147$$

$$\therefore \ln A = -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273} = 37.91$$

$$\therefore A = \text{antilog} [37.91] = 2.91 \times 10^6$$

$$\text{At } 303 \text{ K, } \frac{1}{T} = 3.3 \times 10^{-3} \text{ K}^{-1} \text{ and}$$

$$\ln k = -2.8 \text{ k} = 6.06 \times 10^{-2} \text{ s}^{-1}$$

At

$$T = 323 \text{ K}$$

$$\ln k = -0.5$$

$$k = 0.607 \text{ s}^{-1}$$

4.23. 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 kJ/mol , what will be the value of pre-exponential factor?

Ans. Here

$$A = 2.418 \times 10^{-5} \text{ s}^{-1}$$

$$E_a = 179.9 \text{ kJ mol}^{-1}$$

$$T = 546 \text{ K}$$

According to the Arrhenius equation,

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

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

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

$$\begin{aligned} &= \log (2.418 \times 10^{-5} \text{ s}^{-1}) + \frac{179.9 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \times 546 \text{ K}} \\ &= (-5 + 0.3834) \text{ s}^{-1} + 17.2081 = 12.5924 \text{ s}^{-1} \end{aligned}$$

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

4.24. Consider a certain reaction $A \rightarrow \text{products}$ with $k = 2.0 \times 10^{-2} \text{ s}^{-1}$. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L^{-1} .

Ans. The units of k show that the reaction is of first order.

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

$$\therefore 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \log \frac{1.0 \text{ mol L}^{-1}}{[R]}$$

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

$$\therefore [R] = \text{Antilog} (-0.8684) = \text{Antilog} (\bar{1}.1316) = 0.1354 \text{ mol L}^{-1}$$

4.25. 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 the sample of sucrose remains after 8 hours?

Ans. As sucrose decomposes according to the first order rate law,

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

The aim is to find $[R]/[R]_0$

$$\text{As } t_{1/2} = 3.00 \text{ hour}$$

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

$$\text{Hence,} \quad 0.231 \text{ hr}^{-1} = \frac{2.303}{8 \text{ hr}} \log \frac{[R]_0}{[R]}$$

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

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

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

4.26. The decomposition of hydrocarbon follows the equation.

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

Calculate E_a .

Ans. According to Arrhenius equation

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

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

$$E_a = 28000 \text{ K} \times 8.3145 \text{ JK}^{-1} \text{ mol}^{-1} = 232.79 \text{ kJ mol}^{-1}.$$

4.27. 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?

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

According to the Arrhenius equation,

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

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

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

Comparing with the given equation,

$$\frac{E_a}{2.303 RT} = \frac{1.25 \times 10^4 \text{ K}}{T}$$

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

When

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

Substituting this value in the given equation,

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

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

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

or $T = 669 \text{ K}$

4.28. 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 $1.5 \times 10^4 \text{ s}^{-1}$?

[Delhi 2013 C]

Ans.

$$k_1 = 4.5 \times 10^3 \text{ s}^{-1}$$

$$T_1 = 10 + 273 \text{ K} = 283 \text{ K}$$

$$k_2 = 1.5 \times 10^4 \text{ s}^{-1}$$

$$T_2 = ? \quad , \quad E_a = 60 \text{ kJ mol}^{-1}$$

According to Arrhenius equation,

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

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left[\frac{T_2 - 283}{283 T_2} \right]$$

$$\text{or} \quad \log 3.333 = 3133.63 \left[\frac{T_2 - 283}{283 T_2} \right]$$

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

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

$$\text{or} \quad 0.9528 T_2 = 283$$

$$\text{or} \quad T_2 = \frac{283}{0.9528} = 297 \text{ K} = (297 - 273)^\circ\text{C} = 24^\circ\text{C}.$$

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

Ans.

$$\begin{aligned} k_{298 \text{ K}} &= \frac{2.303}{t_1} \log \frac{a}{a - 0.10a} \\ &= \frac{2.303}{t_1} \log \frac{10}{9} = \frac{2.303}{t_1} (0.0458) = \frac{0.1055}{t} \quad \text{or} \quad t_1 = \frac{0.1055}{k_{298 \text{ K}}} \end{aligned}$$

$$\begin{aligned} k_{308 \text{ K}} &= \frac{2.303}{t_2} \log \frac{a}{a - 0.25a} = \frac{2.303}{t_2} \log \frac{4}{3} \\ &= \frac{2.303}{t_2} (0.125) = \frac{0.2879}{t_2} \end{aligned}$$

$$\text{or} \quad t_2 = \frac{0.2879}{k_{308 \text{ K}}}$$

$$\begin{aligned} \text{But} \quad t_1 &= t_2 \\ \text{Hence} \quad \frac{0.1055}{k_{298 \text{ K}}} &= \frac{0.2879}{k_{308 \text{ K}}} \end{aligned}$$

$$\text{or} \quad \frac{k_{308 \text{ K}}}{k_{298 \text{ K}}} = 2.7289$$

Now, applying Arrhenius equation

$$\log \frac{k_{308 \text{ K}}}{k_{298 \text{ K}}} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore \log (2.7289) = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left[\frac{308 - 298}{298 \times 308} \right]$$

$$0.4360 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{298 \times 308}$$

or $E_a = 76.623 \text{ kJ mol}^{-1}$

Calculation of k at 318 K

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

$$= \log (4 \times 10^{10}) - \frac{76.623 \text{ J K}^{-1} \text{ mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times 318 \text{ K}$$

$$= 10.6021 - 12.5843 = -1.9822$$

or $k = \text{Antilog} (-1.9822)$

$$= \text{Antilog} (\bar{2}.0178) = 1.042 \times 10^{-2} \text{ s}^{-1}.$$

4.30. 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.

Ans.

$$k_2 = 4 k_1$$

$$T_1 = 293 \text{ K} \quad k_1 = k$$

$$T_2 = 313 \text{ K} \quad k_2 = 4k$$

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

$$\log \frac{4k}{k} = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \frac{(313 - 293)}{(313 \times 293)}$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \frac{20}{313 \times 293}$$

$$E_a = 53.6 \text{ kJ mol}^{-1}$$

ADDITIONAL QUESTIONS SOLVED

I. Very Short Answer Type Questions

(1 Mark)

Q1. The decomposition reaction of ammonia gas on platinum surface has a rate constant, $k = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. What is the order of the reaction?

[CBSE 2009]

Ans. The order of the reaction is zero.

Q2. Define 'order of a chemical reaction'.

[AI CBSE 2008]

Ans. The order of a reaction is equal to the sum of the power (exponents) to which the various concentration terms are raised in the rate law expression of the reaction.

Q3. The reaction $A + 2B \rightarrow C$ obeys the rate equation,

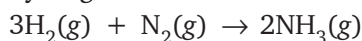
$$\text{Rate} = k [A]^{1/2} [B]^{3/2}$$

What is the order of the reaction?

[AI 2007]

Ans. Order of the reaction = $\frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2$.
The reaction is of second order.

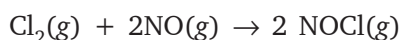
Q4. Express the rate of the following reaction in terms of disappearance of hydrogen in the reaction.



[AI 2007]

Ans. Rate = $-\frac{1}{3} \frac{d[\text{H}_2]}{dt}$

Q5. For the reaction



The rate law is expressed as:

$$\text{rate} = k[\text{Cl}_2][\text{NO}]^2$$

What is the overall order of this reaction? [CBSE 2007]

Ans. Overall order of this reaction = $1 + 2 = 3$.

Q6. Define activation energy of a reaction.

[AI 2006]

Ans. The minimum extra energy over and above the average potential energy of the reactants which must be supplied to the reactant molecules to enable them to cross over the energy barrier such that reactants can form products is called the activation energy.

Q7. What is meant by elementary step in a reaction? [CBSE 2006]

Ans. A complex reaction occurs through a sequence of steps. Each step is an elementary step which involves the simultaneous collision of two or three species only.

Q8. A reaction is 50% completed in 2 hours and 75% completed in 4 hours. What is the order of the reaction?

[AI 2006, 2017]

Ans. First order.

Q9. The reaction $\text{A} + \text{B} \rightarrow \text{C}$ has zero order. What is the rate equation?

[CBSE 2006]

Ans. Rate = $k[\text{A}]^0[\text{B}]^0 = k$

Q10. How does the value of rate constant vary with reactant concentration?

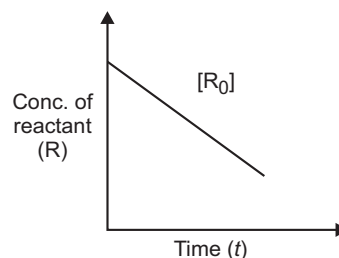
[CBSE 2005]

Ans. For n th order reaction

$$k \propto \frac{1}{C^{n-1}}$$

Q11. A reaction:

Reactant \rightarrow Product is represented as:



Predict (i) The order of the reaction in this case.

(ii) What does the slope of the graph represent? [CBSE 2005]

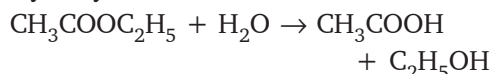
Ans. (i) The reaction is of zero order.

(ii) Slope of straight line graph.

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

Q12. Give one example of a pseudo first order reaction. [AI 2004]

Ans. Hydrolysis of ester:



$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^1[\text{H}_2\text{O}]^0$$

Q13. What is meant by an elementary reaction? [AI 2004]

Ans. A reaction which takes place in a single step is called the elementary reaction. For example, the reaction between H_2 and I_2 to form 2HI is an elementary reaction.

Q14. What is meant by order of a reaction being zero? [Foreign 2007]

Ans. It means that the reaction is extremely fast and rate of the reaction does not vary with the concentration of the reactant.

Q15. For the reaction $A \rightarrow B$, the rate of reaction becomes twenty-seven times when the concentration of A is increased three times. What is the order of the reaction? [CBSE 2006]

Ans. Order = 3.

Q16. The rate of reaction $X \rightarrow Y$ becomes 8 times when the concentration of the reactant X is doubled. Write the rate law of the reaction. [Foreign 2006]

Ans. $\frac{dx}{dt} = k [X]^3$

Q17. Is there any reaction for which reaction rate does not decrease with time? [AI 2006 C]

Ans. Zero order reactions.

Q18. Express the relation between the half-life period of a reactant and its initial concentration if the reaction involved is of second order. [CBSE 2005]

Ans. $t_{1/2}$ is inversely proportional to the initial concentration for a second order

reaction, i.e. $t_{1/2} \propto \frac{1}{[R]_0}$.

Where $[R]_0$ is the initial concentration.

Q19. State the "rate law" for chemical reactions. [Foreign 2005 F]

Ans. The relationship between rate of a reaction and the concentration of reactants is called the rate law.

Q20. How does the value of rate constant vary with reactant concentration? [AI 2004 C]

Ans. Rate constant is not affected by the concentration of reactants.

Q21. A substance with initial concentration 'a' follows zero order kinetics with the rate constant 'k' mol L⁻¹ s⁻¹. In how much time will the reaction go to completion? [CBSE 2005 (C)]

Ans. $\frac{a}{t} = k \Rightarrow t = \frac{a}{k}$

In time $\frac{a}{k}$, the reaction will go to completion.

Q22. When does the rate of reaction equal to the specific reaction rate? [CBSE 2005 C]

Ans. Rate of reaction becomes equal to the rate constant when molar concentration of reactants is equal to unity.

Q23. The reaction $A + B \rightarrow C$ has zero order. What is the rate equation? [AI 2005 C]

Ans. $\frac{dx}{dt} = k [A]^0 [B]^0$

Q24. In some cases, it is found that a large number of colliding molecules have energy more than the threshold value, yet the reaction is slow. Why? [AI 2005 C]

Ans. It is because effective collisions takes place only if molecules have energy more than the activation energy as well as they collide in proper orientation. In some cases reaction is slow because molecules overcome the energy barrier but they may not overcome orientation barrier.

Q25. For a reaction $A + H_2O \rightarrow B$, rate $\propto [A]$ What is its

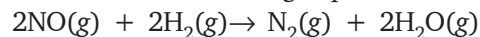
(i) molecularity

(ii) Order of reaction?

Ans. (i) Molecularity = 2

(ii) Order of reaction = 1

Q26. Consider the following equation:



The rate law for this reaction is first order with respect to H_2 and second order with respect to NO. Write the rate law for this reaction.

Ans. $\frac{dx}{dt} = k [NO]^2 [H_2]^1$

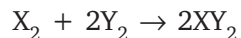
Q27. The rate constant of a reactant is 2×10^{-2} L mol⁻¹ s⁻¹. What is the order of the reaction?

Ans. Second order reaction.

Q28. Define rate of a reaction.

Ans. Rate of a reaction is defined as the change in the concentration of reactants or products per unit time.

Q29. For the assumed reaction,



Write the rate equation in terms of rate of disappearance of Y_2 .

Ans. Rate of reaction = $-\frac{1}{2} \frac{d[Y_2]}{dt}$

Q30. State four factors which affect the rate of a chemical reaction.

Ans. (i) Nature of reactants
(ii) Temperature
(iii) Catalyst
(iv) Physical state of the reactants.

Q31. Identify the reaction order if the unit of rate constant is sec^{-1} .

Ans. First order reaction.

Q32. Define half-life of a reaction ($t_{1/2}$).

Ans. Half life is the time in which 50% of the reaction is completed.

Q33. According to Arrhenius, rate of a reaction increases with increase in temperature. Give reason.

Ans. Rate of a reaction increases with increase in temperature because kinetic energy of the molecules increases, number of molecules possessing activation energy increases, i.e. the number of effective collisions increases.

Q34. For a reaction, $A \rightarrow B$

The rate of reaction can be denoted by $-\frac{d[A]}{dt}$ or $+\frac{d[B]}{dt}$. State the significance of plus and minus signs.

Ans. Minus sign indicates the decrease in concentration of the reactant 'A' with time whereas plus sign indicates the increase in concentration of product 'B' with time.

Q35. For the homogeneous decomposition of N_2O_5 into NO_2 and O_2 :



$$\text{Rate} = -\frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = k [N_2O_5]$$

Find out the order of reaction with respect to N_2O_5 .

Ans. It is first order with respect to N_2O_5 .

Q36. Give the units of specific reaction rate constant for a zero order reaction.

Ans. Unit of k for zero order reaction is $\text{mol L}^{-1} \text{s}^{-1}$.

Q37. What is the order of reaction if the rate of reaction is independent of concentration of all the reactants?

Ans. Zero order reaction.

Q38. On what factors $t_{1/2}$ of a first order reaction depends?

Ans. $t_{1/2}$ of a first order reaction depends on the rate constant k.

$$\therefore t_{1/2} = \frac{0.693}{k}$$

Q39. What is the order of radioactive decay?

Ans. First order.

Q40. $t_{1/2}$ of the reaction increases with increase in initial concentration. What is the order of reaction?

Ans. Zero order reaction.

Q41. Define effective collision.

Ans. Those collisions which lead to the formation of products are called effective collisions.

Q42. What is the effect of catalyst on the rate of reaction?

Ans. A catalyst increases the rate of reaction by lowering down the activation energy. It provides an alternative path to the reaction.

Q43. What is the shape of the graph between $10 \log k$ vs $\frac{1}{T}$? What is the relationship between its slope and activation energy (E_a)?

Ans. It is a straight line whose slope

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

Q44. Give the example of a reaction which has fractional order of reaction.

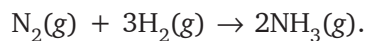
Ans. $\frac{dx}{dt} = k[\text{H}_2]^{1/2} [\text{Br}_2]^{1/2}$

$\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$ is a fractional order reaction.

Q45. The rate of a reaction is given by: Rate = $k[\text{N}_2\text{O}_5]$. In this equation what does k stands for?

Ans. 'k' stands for rate constant of the reaction.

Q46. For the reaction:



Express the rate of reaction in terms of formation of ammonia.

Ans. $+\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$

Q47. State any one condition under which a bimolecular reaction may be kinetically first order.

Ans. If one of the reactant is present in excess, then a bimolecular reaction will kinetically a first order reaction.

Q48. In a reaction $2\text{A} \rightarrow \text{Products}$, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval.

Ans. Rate = $-\Delta[\text{A}]/\Delta t \times 1/2$

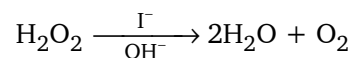
$$= -\frac{1}{2} \frac{(0.4 - 0.5) \text{ mol L}^{-1}}{10 \text{ min}}$$

$$= 0.005 \text{ mol L}^{-1} \text{ min}^{-1}$$

Q49. The rate constant of a reaction is $2.3 \times 10^{-5} \text{ mol}^{-1} \text{ L s}^{-1}$. What is the order of the reaction?

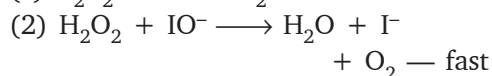
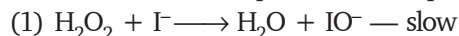
Ans. Here $1-n = -1$, so $n = 2$ i.e., the reaction is of second order.

Q50. Suggest a probable mechanism for the reaction:



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

Ans. This reaction takes place in 2 steps



Q51. For a reaction $\text{A} + \text{B} \rightarrow \text{Products}$, the rate law is given by

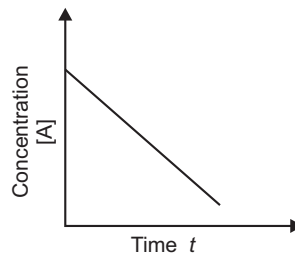
Rate = $k[\text{A}]^{1/2} [\text{B}]^2$, what is the order of the reaction?

Ans. Order = $1/2 + 2 = 2.5$

II. Short Answer Type Questions

(2 or 3 Marks)

Q1. Consider the reaction $\text{A} \xrightarrow{k} \text{P}$. The change in concentration of A with time is shown in the following plot:



(i) Predict the order of the reaction.

(ii) Derive the expression for the time required for the completion of the reaction. [CBSE 2009]

Ans. (i) The reaction $\text{A} \rightarrow \text{P}$ is a zero order reaction.

(ii) For the reaction $\text{A} \xrightarrow{k} \text{P}$

$$\text{Rate} = -\frac{d[\text{A}]}{dt} = k[\text{A}]^0$$

$$-d[\text{A}] = kdt$$

integrating both sides

$$[\text{A}] = -kt + C \quad \dots(i)$$

Where C = constant of integration at $t = 0$

$$[\text{A}] = [\text{A}]_0$$

Substituting this in the equation

$$[\text{A}] = -kt + [\text{A}]_0$$

$$kt = [\text{A}]_0 - [\text{A}]$$

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

Q2. The decomposition of $N_2O_5(g)$ is a first order reaction with a rate constant of $5 \times 10^{-4} \text{ sec}^{-1}$ at 45°C , i.e. $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$.

If the initial concentration of N_2O_5 is 0.25 M , calculate its concentration after 2 min . Also calculate half life for decomposition of $N_2O_5(g)$. [CBSE 2009]

Ans. For a first order reaction,

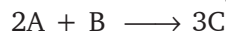
$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$$

$$5 \times 10^{-4} = \frac{2.303}{2 \times 60} \log \frac{0.25}{[R]_t}$$

$$[R]_t = 0.23 \text{ M}$$

$$t_{1/2} = \frac{0.693}{5 \times 10^{-4}} \text{ sec} = 1386 \text{ sec.}$$

Q3. For an elementary reaction



The rate of appearance of C at time 't' is $1.3 \times 10^{-4} \text{ mol}^{-1} \text{ s}^{-1}$. Calculate at this time,

(i) Rate of reaction

(ii) Rate of disappearance of A.

[CBSE 2009]

Ans. (i) Rate = $\frac{1}{3} \frac{d[x]}{dt}$

$$= \frac{1}{3} \times 1.3 \times 10^{-4}$$

$$= 0.43 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

(ii) $-\frac{dA}{dt} = \frac{2}{3} \times \frac{d[x]}{dt}$

$$= 8.87 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$$

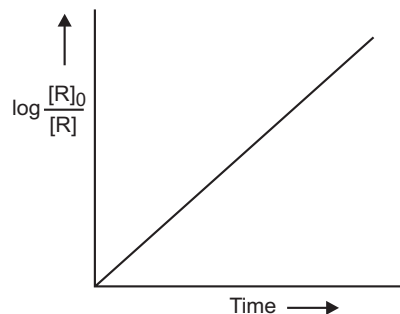
Q4. Answer the following questions on the basis of curve for a first order reaction.



(i) What is the relation between slope of this line and rate constant?

(ii) Calculate the rate constant of the above reaction if the slope is $2 \times 10^{-4} \text{ s}^{-1}$.

(iii) Derive the relationship between half life of a first order reaction and its rate constant. [CBSE 2009]



Ans. (i) Slope = $\frac{k}{2.303}$

(ii) As slope = $2 \times 10^{-4} \text{ s}^{-1}$

$$\therefore k = 2.303 \times 2 \times 10^{-4} \text{ s}^{-1}$$

$$k = 4.606 \times 10^{-4} \text{ s}^{-1}.$$

(iii) For a first order reaction:

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

At $t_{1/2}$, $[R] = \frac{[R]_0}{2}$

$$t_{1/2} = \frac{2.303}{k} \log 2$$

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

Q5. For a decomposition reaction the values of rate constant k at two different temperatures are given below:

$$k_1 = 2.15 \times 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 650 \text{ K}$$

$$k_2 = 2.39 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1} \text{ at } 700 \text{ K}$$

Calculate the value of activation energy for this reaction.

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

[AI 2009]

Ans. Here

$$k_1 = 2.15 \times 10^{-8} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$k_2 = 2.39 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1}$$

$$T_1 = 650 \text{ K}, T_2 = 700 \text{ K} \text{ and}$$

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

Using the formula

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

$$\log \frac{2.39 \times 10^{-7}}{2.15 \times 10^{-8}} = \frac{E_a}{2.303 \times 8.314} \left[\frac{700 - 650}{650 \times 700} \right]$$

$$\log 1.111 \times 10 = \frac{E_a}{19.147} \times \frac{50}{455000}$$

$$1.0457 = \frac{E_a}{19.147} \times \frac{1}{9100}$$

$$E_a = 182202.812 \text{ J or } 182.203 \text{ kJ}$$

Q6. A first order reaction has rate constant of 0.0051 min^{-1} . If we begin with 0.10 M concentration of the reactant what concentration of the reactant will be left after 3 hours? [AI 2009]

Ans. Here $[R]_0 = 0.10 \text{ M}$
 $t = 3 \text{ hours}$
 $= 3 \times 60 = 180 \text{ min}$
 $k = 0.0051 \text{ min}^{-1}$

Using the formula

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

$$0.0051 = \frac{2.303}{180} \log \frac{0.10}{[R]}$$

$$\log \frac{0.10}{[R]} = \frac{0.0051 \times 180}{2.303}$$

$$\log \frac{0.10}{[R]} = \frac{0.918}{2.303} = 0.3986$$

$$\therefore \frac{0.10}{[R]} = \text{antilog } (0.3986)$$

$$\frac{0.10}{[R]} = 2.503$$

$$\Rightarrow [R] = \frac{0.10}{2.503} = 0.039 \text{ M}$$

Q7. The data given below is for the reaction,
 $2 \text{ N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ at 298 K .

S. No.	$[\text{N}_2\text{O}_5]$ (mol L^{-1})	Rate of disappearance of N_2O_5 ($\text{mol L}^{-1} \text{ min}^{-1}$)
1.	1.13×10^{-2}	34×10^{-5}
2.	0.84×10^{-2}	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine for this reaction:

(i) Order of reaction

(ii) Rate constant

(iii) Rate law [CBSE 2008 C]

Ans. (i) The rate law for the disappearance of N_2O_5 is

$$\text{Rate} = k [\text{N}_2\text{O}_5]^a$$

$$34 \times 10^{-5} = k [1.13 \times 10^{-2}]^a \quad \dots(i)$$

$$25 \times 10^{-5} = k [0.84 \times 10^{-2}]^a \quad \dots(ii)$$

Dividing (i) by (ii) we get

$$\frac{34 \times 10^{-5}}{25 \times 10^{-5}} = \frac{[1.13 \times 10^{-2}]^a}{[0.84 \times 10^{-2}]^a}$$

$$\frac{34}{25} = \left[\frac{1.13 \times 10^{-2}}{0.84 \times 10^{-2}} \right]^a$$

$$\frac{34}{25} = \left(\frac{113}{84} \right)^a$$

$$(1.36) = (1.36)^a$$

$$\therefore a = 1$$

Order of the reaction = 1

(ii) Rate = $k [\text{N}_2\text{O}_5]$

$$34 \times 10^{-5} = k [1.13 \times 10^{-2}]$$

$$k = \frac{34 \times 10^{-5}}{1.13 \times 10^{-2}}$$

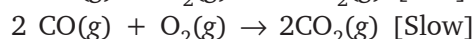
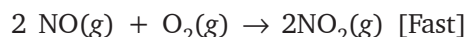
$$= 30.08 \times 10^{-3}$$

$$= 0.03 \text{ min.}$$

(iii) Rate law = $0.03 \times [\text{N}_2\text{O}_5]$

Q8. List four factors which affect the rate of a reaction. [CBSE 2008]

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



(ii) **Concentration of reactants:** Higher the concentration of reactant, faster would be the rate of reaction.

(iii) **Temperature:** Rate of reaction increases with increase of temperature.

(iv) **Presence of catalyst.** The presence of catalyst can increase the rate of reaction.

Q9. The decomposition of phosphine, $4\text{PH}_3(\text{g}) \rightarrow \text{P}_4(\text{g}) + 6\text{H}_2(\text{g})$ has the rate law, Rate, $R = k [\text{PH}_3]$. The rate constant is $6.0 \times 10^{-4} \text{ s}^{-1}$ at 300 K and the activation energy is $3.05 \times 10^5 \text{ J mol}^{-1}$. Calculate the value of rate constant at 310 K.

[Given: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

[CBSE 2008 C]

Ans. Here $T_1 = 300 \text{ K}$

$T_2 = 310 \text{ K}$

$k_1 = 6.0 \times 10^{-4} \text{ s}^{-1}$

$E_a = 3.05 \times 10^5 \text{ J mol}^{-1}$

and $k_2 = ?$

We know that

$\log k_2 - \log k_1$

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

$\log k_2 - \log 6.0 \times 10^{-4}$

$$= \frac{3.05 \times 10^5}{2.303 \times 8.314} \left(\frac{310 - 300}{310 \times 300} \right)$$

$\log k_2 - (4.7782)$

$$= \frac{3.05 \times 10^5}{19.147} \times \frac{10}{93000}$$

$\log k_2 - (-4 + 0.7782)$

$$= \frac{3.05 \times 1000}{19.147 \times 93}$$

$\log k_2 + 3.2218 = 1.7128$

$\log k_2 = -1.5090$

$\log k_2 = -2 + 2 - 1.5090$

$$= \bar{2}.4910$$

$k_2 = \text{antilog}(\bar{2}.4910)$

$$= 3.097 \times 10^{-2} \text{ s}^{-1}.$$

Q10. The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the concentration of the reactant to $1/10^{\text{th}}$ of its initial value? [AI 2007]

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

Here $k = 60 \text{ s}^{-1}$ $[\text{R}] = \frac{1}{10} [\text{R}]^0$

or $[\text{R}_0] = 10[\text{R}]$

$$t = \frac{2.303}{60} \log \frac{10[\text{R}]}{[\text{R}]}$$

$$t = \frac{2.303}{60} \log 10$$

$$= \frac{2.303 \times 1}{60} = 0.0384 \text{ s}.$$

Q11. The first order rate constant for the decomposition of ethyl iodide as per the reaction



at 600 K is $1.60 \times 10^{-5} \text{ s}^{-1}$. Its energy of activation is 209 kJ/mol, calculate the rate constant of the reaction at 700 K.

Ans. Here $T_1 = 600 \text{ K}$,

$T_2 = 700 \text{ K}$,

$E_a = 209 \text{ kJ/mol}$

$= 209000 \text{ J mol}^{-1}$

$k_1 = 1.60 \times 10^{-5} \text{ s}^{-1}$

$k_2 = ?$

Using the formula

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

$$\log k_2 - \log k_1 = \frac{E_a}{2.303 R} \left[\frac{700 - 600}{600 \times 700} \right]$$

$\log k_2 - \log 1.60 \times 10^{-5}$

$$= \frac{209000}{2.303 \times 8.314} \left[\frac{100}{600 \times 700} \right]$$

$\log k_2 = \log 1.60 \times 10^{-5} + 2.599$

$\log k_2 = -4.796 + 2.599$

$= -2.197$

$= -3 + 3 - 2.197$

$k_2 = \text{antilog}(\bar{3}.803)$

$$= 6.36 \times 10^{-3} \text{ s}^{-1}$$

Q12. A first order reaction is 15% completed in 20 minutes. How long will it take to get 60% completed?

Ans.

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

$$20 = \frac{2.303}{k} \log \frac{100}{100-15}$$

$$20 \text{ min} = \frac{2.303}{k} \log \frac{20}{17}$$

$$k = \frac{2.303 \times 1.306}{20} \text{ min}^{-1}$$

Now time taken for 60% completion:

$$t = \frac{2.303}{k} \log \frac{100}{100-60}$$

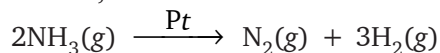
$$t = \frac{2.303}{k} \log \frac{10}{4}$$

$$= \frac{2.303 \times 20}{2.303 \times 1.306} \log \frac{10}{4}$$

$$= \frac{20 \times 0.398}{1.306}$$

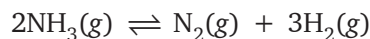
$$= 6.09 \text{ min.}$$

Q13. The decomposition of NH_3 on platinum surface,



is a zero order reaction with $k = 2.5 \times 10^{-4} \text{ M s}^{-1}$. What are the rate of production of N_2 and H_2 ?

Ans. The reaction is



Here $k = 2.5 \times 10^{-4} \text{ M s}^{-1}$

Since the reaction is of zero order, i.e.

$$\text{Rate} = k [\text{Reactant}]^0$$

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

$$\therefore \frac{d}{dt} [\text{N}_2] = \frac{1}{3} \frac{d}{dt} [\text{H}_2]$$

The rate of formation of N_2

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

$$\therefore 2.5 \times 10^{-4} = \frac{1}{3} \frac{d}{dt} [\text{H}_2]$$

$$\frac{d}{dt} [\text{H}_2] = 7.5 \times 10^{-4}$$

Therefore, rate of formation of H_2

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

Q14. Define activation energy of a reaction. [CBSE 2007]

Ans. Activation Energy (E_a). The minimum extra amount of energy which is required by the reactant molecules to make their energy equal to the threshold energy is known as activation energy. It is represented by E_a . It is independent of temperature.

Q15. Calculate the half life of a first order reaction whose rate constant is 200 s^{-1} . [CBSE 2007]

Ans. Here rate constant

$$k = 200 \text{ s}^{-1}.$$

\therefore Half-life of a first order reaction is

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{200}$$

$$= 3.46 \times 10^{-3} \text{ sec.}$$

Q16. Define zero order reaction. Give the unit for its rate constant(k).

Ans. Zero Order Reaction. The reaction in which the rate of reaction is independent of the concentration of the reactants is called zero order reaction.

$$\text{Rate} = k [\text{A}]^0$$

$$= k$$

Where k is the rate constant.

Its unit is $\text{mol L}^{-1} \text{ s}^{-1}$.

Q17. Write units of rate constant k for zero order, first order, second order and n^{th} order reaction.

Order of Reaction	Unit of k
1. Zero order reaction	$\text{mol L}^{-1} \text{ s}^{-1}$
2. First order reaction	s^{-1}
3. Second order	$\text{mol}^{-1} \text{ L s}^{-1}$
4. n^{th} order reaction	$(\text{mol/L})^{1-n} \text{ s}^{-1}$

Q18. What is rate constant? On what factors it will depend?

Ans. Rate constant or specific reaction

rate: Suppose A and B are two reactants in a reaction. The rate of the reaction depends on the concentration of $[A]^x$ and $[B]^y$. Then the rate equation is

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

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

Here k is called the rate constant or specific reaction rate.

The value of rate constant (k) is independent of the concentration of the reactant but it is dependent upon the;

- (i) temperature of the reaction.
- (ii) the particular reaction considered.

Q19. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is again 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction.

[$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\log 4 = 0.602$] [CBSE 2006]

Ans. At 300 K, $t_{1/2} = 20 \text{ min}$

At 350 K, $t_{1/2} = 5 \text{ min}$

$$\text{At 300 K, } k_1 = \frac{0.693}{20} \text{ min}^{-1}$$

$$\text{At 350 K, } k_2 = \frac{0.693}{5} \text{ min}^{-1}$$

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

$$\log \frac{20}{5} = \frac{E_a}{2.303 \times 8.314} \times \frac{350 - 300}{300 \times 350}$$

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \times \frac{50}{300 \times 350}$$

$$E_a = 24.2 \text{ kJ mol}^{-1}$$

Q20. The rate of a particular reaction triples when the temperature changes from 50°C to 100°C . Calculate the activation energy of the reaction.

[Given $\log 3 = 0.4771$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$] [CBSE 2006]

Ans. $T_1 = 273 + 50 = 323 \text{ K}$

$$T_2 = 273 + 100 = 373 \text{ K}$$

$$k_1 = k$$

$$k_2 = 3k$$

Using the formula,

$$E_a = 24.2 \text{ kJ mol}^{-1}$$

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

$$\log \frac{3k}{k} = \frac{E_a}{2.303 \times 8.314} \left[\frac{373 - 323}{373 \times 323} \right]$$

$$\log 3 = \frac{E_a \times 50}{2.303 \times 8.314 \times 373 \times 323}$$

$$E_a = 22011.76 \text{ J mol}^{-1}$$

$$\text{or } 22.01 \text{ kJ mol}^{-1}.$$

Q21. The rate of a particular reaction doubles when temperature changes from 27°C to 37°C . Calculate the activation energy of such a reaction.

[CBSE 2005 C]

Ans. Here $k_1 = k$

$$k_2 = 2k$$

$$T_1 = 27 + 273 = 300 \text{ K}$$

$$T_2 = 37 + 273 = 310 \text{ K}$$

Using the formula

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

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left[\frac{310 - 300}{300 \times 310} \right]$$

$$E_a = \frac{2.303 \times 8.314 \times 300 \times 310}{10} \log 2$$

$$= 53598.65 \text{ mol}^{-1}$$

$$= 53.6 \text{ kJ mol}^{-1}.$$

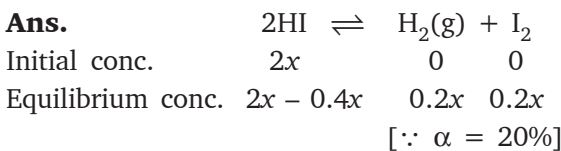
Q22. Show that in case of first order reactions, the time required for 99.9% of the reaction to complete is 10 times to that required for half of the reaction to take place.

[$\log 2 = 0.301$] [Foreign 2006]

$$\begin{aligned} \text{Ans. } t_{99.9\%} &= \frac{2.303}{k} \log \frac{[R]_0}{\left([R]_0 - \frac{99.9}{100} [R]_0\right)} \\ &= \frac{2.303}{k} \log 1000 = \frac{6.909}{k} \\ t_{1/2} &= \frac{0.693}{k} \\ \frac{t_{99.9\%}}{t_{1/2}} &= \frac{6.909}{k} \times \frac{k}{0.693} = 10 \end{aligned}$$

Q23. At 300°C the thermal dissociation of HI is found to be 20%. What will be the equilibrium concentration of H₂ and I₂ in the system

H₂ + I₂ ⇌ 2HI, at this temperature if the equilibrium concentration of HI in it be 0.96 mol L⁻¹? [AI CBSE 2006 C]



$$[H_2] \text{ at equilibrium} = 0.2x$$

$$[I_2] \text{ at equilibrium} = 0.2x$$

At equilibrium

$$[HI] = 0.96 \text{ mol L}^{-1}$$

$$2x - 0.4x = 0.96$$

$$1.6x = 0.96$$

$$x = 0.60$$

$$= 0.60 \text{ mol L}^{-1}$$

$$[H_2] = 0.2 \times 0.60$$

$$= 0.12 \text{ mol L}^{-1}$$

$$[I_2] = 0.2 \times 0.60$$

$$= 0.12 \text{ mol L}^{-1}$$

Q24. Prove that the time required for the completion of 3/4th of the reaction of a first order is twice the time required for the completion of half of the reaction. [AI 2006, 2005 C]

$$\begin{aligned} \text{Ans. } t_{3/4} &= \frac{2.303}{k} \log \frac{[R]_0}{\frac{1}{4} [R]_0} \\ t_{3/4} &= \frac{2.303}{k} \log 4 \end{aligned}$$

$$\begin{aligned} &= \frac{2.303 \times 0.6021}{k} = \frac{1.386}{k} \\ &= 2 \times \frac{0.693}{k} = 2 t_{1/2} \end{aligned}$$

Q25. A first order reaction takes 69.3 minutes for 50% completion. Set up an equation determining the time needed for 80% completion of this reaction. (Calculation of result is not required). [CBSE 2005]

Ans.

$$\begin{aligned} k &= \frac{0.693}{t_{1/2}} \\ &= \frac{0.693}{69.3 \text{ min}} = 1 \times 10^{-2} \text{ min}^{-1} \\ k &= \frac{2.303}{t} \log \frac{a}{a-x} \\ t &= \frac{2.303}{1 \times 10^{-2} \text{ min}^{-1}} \log \frac{100}{(100-80)} \\ &= \frac{2.303}{1 \times 10^{-2} \text{ min}^{-1}} \log \frac{100}{20} \\ &= \frac{2.303}{1 \times 10^{-2}} \log 5 \\ &= 160.97 \text{ min} \end{aligned}$$

Q26. The activation energy of a reaction is 75.2 kJ mol⁻¹ in the absence of a catalyst and 50.14 kJ mol⁻¹ in the presence of a catalyst. How many times will the rate of reaction grow in the presence of the catalyst, if the reaction proceeds at 25°C? [R = 8.314 J K⁻¹ mol⁻¹] [AI 2005]

Ans.

$$\begin{aligned} \ln k_1 &= \ln A - \frac{E_{a_1}}{RT} \\ \ln k_2 &= \ln A - \frac{E_{a_2}}{RT} \\ \ln k_2 - \ln k_1 &= \frac{1}{RT} (E_{a_2} - E_{a_1}) \\ \log \frac{k_2}{k_1} &= \frac{1}{2.303 RT} \\ &= \frac{1}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} \\ &= \frac{1}{5715.8} \end{aligned}$$

(75.2 kJ mol⁻¹ - 50.14 kJ mol⁻¹)

$$\log \frac{k_2}{k_1} = \frac{25100}{5705.8}$$

$$\frac{k_2}{k_1} = \text{Antilog } 4.40 = 2.5 \times 10^4$$

Therefore, the rate of reaction will grow by 25000 times in the presence of catalyst. The decrease in the activation energy takes place by 25.1 kJ mol⁻¹.

Q27. A reaction is first order in A and second order in B.

- Write the differential rate equation.
- How is the rate affected if the concentration of B is tripled?
- How is the rate affected when the concentration of both A and B are doubled? What is the significance of rate constant in the rate expression?

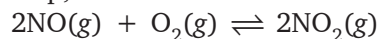
[CBSE 2004]

Ans. (i) $\frac{dx}{dt} = k [A]^1 [B]^2$

- If concentration of B is tripled, then the rate of reaction will become 9 times.
- If the concentration of 'A' and 'B', both are doubled, then rate of reaction becomes 8 times.

Rate constant is equal to rate of the reaction when molar concentration of the reactants is unity.

Q28. Following reaction takes place in one step,



How will the rate of the above reaction change if the volume of the reaction vessel is diminished to one-third of its original volume? Will there be any change in the order of the reaction with the reduced volume?

[AI 2004]

Ans. If volume of the reaction vessel is reduced to one third of its initial value, the concentration per unit volume will become 3 times.

$$\begin{aligned} \text{Rate} &= k[\text{NO}_2]^2 [\text{O}_2]^1 \\ &= k [3A]^2 [3A]^1 \end{aligned}$$

$$= 27 \times k [A]^3$$

The rate will become 27 times.

Q29. 60% of a first order reaction was completed in 60 minutes. When was it half completed?

Ans.

$$k = \frac{2.303}{60 \text{ min}} \log \frac{100}{100 - 60}$$

$$k = \frac{2.303}{60} \log \frac{100}{40}$$

$$k = \frac{2.303}{60} \log \frac{5}{2} = 0.01527$$

$$t_{1/2} = \frac{0.693}{0.01527} = 45.38 \text{ min.}$$

Q30. For a first order reaction, it takes 5 minutes for the initial concentration of 0.6 mol L⁻¹ to become 0.4 mol L⁻¹. How long will it take for the initial concentration to become 0.3 mol L⁻¹?

Ans.

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

$$k = \frac{2.303}{5} \log \frac{0.6}{0.4}$$

$$k = 0.081$$

$$t_{1/2} = \frac{0.693}{0.081} = 8.55 \text{ min}$$

Q31. What is meant by order and molecularity of a reaction? Distinguish between order and molecularity.

Ans.	Order	Molecularity
(i)	It is sum of powers to which concentration terms are raised in rate law or rate equation.	(i) It is the number of molecules taking part in the reaction.
(ii)	It is determined experimentally.	(ii) It is determined theoretically.
(iii)	It can be zero or even in fraction.	(iii) It is always in whole number.
(iv)	The order of complex reaction can be determined and slowest step is the rate determining step.	(iv) Molecularity of each step is determined separately.

Q32. What is the effect of catalyst on the activation energy? Why?

Ans. Catalyst lower down the activation energy. It provides an alternate path to the reaction. It forms an unstable intermediate which readily changes into products.

Q33. What is temperature coefficient of a reaction?

Ans. Temperature coefficient is the ratio of two rate constants at two different temperatures that differ by 10 K. If its value is two, it means that the reaction rate gets almost doubled and so on.

Q34. What is known as 'activation energy'? How is the activation energy affected by:

- The use of a catalyst and
- A rise in temperature? [AI 2003]

Ans. Activation energy is the extra energy which must be supplied to the reactants so that they can change into products.

- Catalyst lowers down the activation energy.
- There is no effect on the activation energy with rise in temperature but number of molecules possessing the activation energy will increase.

Q35. For the reaction at 500 K, $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{NO}(\text{g})$, the proposed mechanism is as follows:

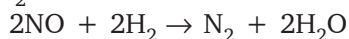
- $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$ (slow)
- $\text{NO}_3 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}_2$ (fast)

What is the rate law for the reaction?

Ans. Rate law = $\frac{dx}{dt} = k [\text{NO}_2]^2$

It is because slowest step will determine the rate law.

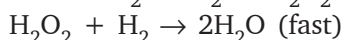
Q36. Nitric oxide reacts with H_2 to give N_2 and H_2O



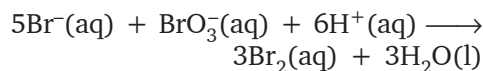
The rate law for the above reaction is

$$-\frac{d[\text{NO}]}{dt} = k[\text{NO}]^2[\text{H}_2]. \text{ Explain the mechanism of the reaction.}$$

Ans. Mechanism of reaction.



Q37. Write the average and instantaneous rate expressions of the following reactions



$$\begin{aligned} r_{\text{av}} &= -\Delta[\text{Br}^-]/\Delta t \times 1/5 \\ &= -\Delta[\text{BrO}_3^-]/\Delta t \\ &= -\Delta[\text{H}^+]/\Delta t \times 1/6 \\ &= +\Delta[\text{Br}_2]/\Delta t \times 1/3 \\ &= +\Delta[\text{H}_2\text{O}]/\Delta t \times 1/3 \end{aligned}$$

$$\begin{aligned} r_{\text{inst}} &= -d[\text{Br}^-]/dt \times 1/5 \\ &= -d[\text{BrO}_3^-]/dt \\ &= +d[\text{Br}_2]/dt \times 1/3 \\ &= +d[\text{H}_2\text{O}]/dt \times 1/3 \end{aligned}$$

Q38. A chemical reaction $2\text{A} \longrightarrow 4\text{B} + \text{C}$ in gas phase occurs in a closed vessel. The concentration of B is found to increase by $5 \times 10^{-3} \text{ mol L}^{-1}$ in 10 seconds. Calculate (a) the rate of appearance of B (b) the rate of disappearance of A.

Ans. rate = $-1/2 \times \Delta[\text{A}]/\Delta t$
 $= +1/4 \times \Delta[\text{B}]/\Delta t$
 $= +\Delta[\text{C}]/\Delta t$

Rate of appearance of

$$\begin{aligned} \text{B} &= 5 \times 10^{-3} \text{ mol L}^{-1}/10 \text{ s} \\ &= 5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1} \end{aligned}$$

Rate of disappearance of A,

$$\begin{aligned} \text{i.e. } \Delta[\text{A}]/\Delta t &= 2/4 \times \Delta[\text{B}]/\Delta t \\ &= 1/2 \times 5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1} \\ &= 2.5 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1} \end{aligned}$$

Q39. Write any three important differences between order and molecularity.

Order	Molecularity
1. It is determined experimentally.	1. It is a theoretical concept.
2. It can be zero or fractional number	2. Always whole numbers.
3. For complex reactions, order is applicable for both the elementary and overall reaction.	3. Applicable only for elementary reactions and no meaning for overall complex reactions.

Q40. The rate constant of a reaction w.r.t. the reactant A is 6 min^{-1} . If we start with $[A] = 0.8 \text{ mol L}^{-1}$, when would $[A]$ reach the value of 0.08 mol L^{-1} ?

Ans. For first order reaction

$$t = 2.303/k \log [R]_0/[R]$$

$$[R]_0 = 0.8 \text{ mol L}^{-1},$$

$$[R] = 0.08 \text{ mol L}^{-1},$$

$$k = 6 \text{ min}^{-1}$$

$$t = 2.303/6 \text{ min}^{-1} \log [0.8 \text{ mol L}^{-1}/0.08 \text{ mol L}^{-1}]$$

$$= 2.303/6 \text{ min}^{-1} \times \log 10$$

$$= 0.38 \text{ min.}$$

Q41. If half life period for a first order reaction in A is 2 minutes. How long will it take $[A]$ to reach 25% of its initial concentration?

Ans. For first order reaction

$$k = 0.693/t_{1/2}$$

$$k = 0.693/2 \text{ min.}$$

$$k = 0.3465 \text{ min}^{-1}$$

$$[R]_0 = 100 \quad [R] = 25$$

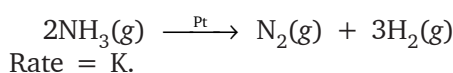
$$t = 2.303/k \log [R]_0/[R]$$

$$= 2.303/0.3465 \text{ min}^{-1} \log 100/25$$

$$= 2.303/0.3465 \text{ min}^{-1} \log 4$$

$$= 6.65 \text{ min}$$

Q42. For a reaction:



(i) Write the order and molecularity of this reaction.

(ii) Write the unit of K. [CBSE 2016]

Ans. (i) Order of reaction = Zero order.

Molecularity = 2

(ii) Unit of K = $\text{mol L}^{-1} \text{ sec}^{-1}$.

Q43. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

$$\log k = 14.2 - \frac{1.0 \times 10^4 \text{ K}}{T}$$

Calculate E_a for this reaction and rate constant K if its half period be 200 minutes.

(Given: $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

[CBSE 2016]

Ans. $2\text{H}_2\text{O}_2 \xrightarrow{\Delta} 2\text{H}_2\text{O} + \text{O}_2$

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

$$\log k = 14.2 - \frac{1.0 \times 10^4}{T} \text{ K}$$

$$\frac{E_a}{2.303 R} = 1.0 \times 10^4$$

E_a (Activation Energy)

$$= 1.0 \times 10^4 \times 2.303 \times 8.314$$

$$= 19.14 \times 10^4 \text{ s mol}^{-1}$$

Half life ($t_{1/2}$)

$$= 200 \text{ minutes}$$

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{200 \times 60}$$

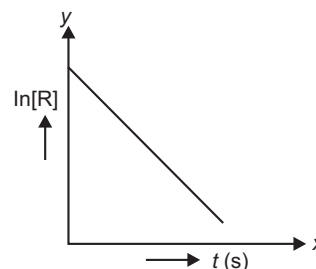
$$= 5.78 \times 10^{-5} \text{ sec}^{-1}$$

III. Long Answer Type Questions

(5 Marks)

Q1. For a certain chemical reaction variation in concentration, $\ln [R]$ Vs time (s) plot is given below:

For this reaction write/draw



(i) What is the order of the reaction?

(ii) What are the units of rate constant (k)?

(iii) Give the relationship between k and $t_{1/2}$ (half-life period).

(iv) What does the slope of the above line indicate?

(v) Draw the plot of $\log [R_0]/[R]$ vs time (s).

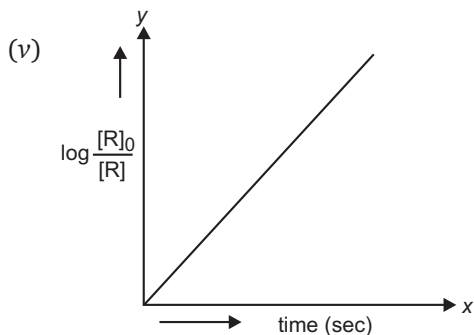
[CBSE 2009]

Ans. (i) First order

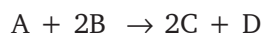
(ii) $\text{time}^{-1} (\text{s}^{-1})$

(iii) $k = \frac{0.693}{t_{1/2}}$

(iv) Rate constant (k) of reaction.



Q2. For a certain chemical reaction:



The experimentally obtained information is tabulated as follows:

Experiment	[A]₀	[B]₀	Initial rate of reaction
1.	0.30	0.30	0.096
2.	0.60	0.30	0.384
3.	0.30	0.60	0.192
4.	0.60	0.60	0.768

For this reaction:

- Derive the order of reaction w.r.t. both the reactants A and B.
- Write the rate law.
- Calculate the value of rate constant (k).
- Write the expression for the rate of reaction in terms of A and C.

[CBSE 2009]

Ans. (i) Rate = k [A]^x [B]^y
 0.096 = k [0.30]^x [0.30]^y ... (i)
 0.384 = k [0.60]^x [0.30]^y ... (ii)

On dividing eqns. (ii) by (i) we get

$$x = 2$$

$$0.192 = k [0.30]^x [0.60]^y \dots (iii)$$

On dividing eqn. (iii) by (i) we get

$$y = 1$$

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

$$(iii) \quad \text{Rate of reaction} = -\left\{ \frac{\Delta[A]}{\Delta t} \right\}$$

$$0.096 = k (0.30)^2 (0.30)^1$$

$$k = 3.56$$

(iv) Rate of reaction,

$$R = -\left\{ \frac{\Delta[A]}{\Delta t} \right\} = \frac{1}{2} \left\{ \frac{\Delta[C]}{\Delta t} \right\}$$

Q3. (a) A first order reaction $A \rightarrow B$ requires activation energy of 70 kJ mol^{-1} when 20% solution of 'A' was kept at 25°C for 20 min., 25% of decomposition took place. What will be the percentage decomposition of 30% solution at 40°C in the same time? Assume activation energy remains constant in the range of temperature.

(b) Give two differences between zero order and first order reaction.

Ans. (a) $k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$

$$= \frac{2.303}{20} \log \frac{100}{75}$$

$$= \frac{2.303}{20} \log \frac{4}{3}$$

$$= \frac{2.303}{20} \log 4 - \log 3$$

$$= 0.01439 \text{ min}^{-1}$$

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

$$= \frac{70,0005 \times [313 - 298]}{2.303 \times 8.314 [313 \times 298]}$$

$$= 0.5879$$

$$\frac{k_2}{0.01439} = \text{Antilog } 0.5879 = 3.872$$

$$k_2 = 3.872 \times 0.01439$$

$$= 0.0557 \text{ min}^{-1}$$

$$k_2 = \frac{2.303}{20} \log \frac{[R_0]}{R}$$

$$\log \frac{100}{x} = \frac{0.0557 \times 20}{2.303} = \frac{1.114}{2.303}$$

$$\frac{100}{x} = \text{Antilog } 0.4837 = 3.045$$

$$x = \frac{100}{3.045} = 32.84$$

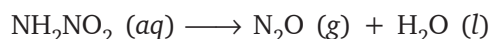
Final conc. = 32.84%

% decomposition

$$= 100 - 32.84 = 67.16\%$$

(b) Zero order	Ist order
(i) Its 'k' has unit = mol L ⁻¹ s ⁻¹	(i) Its 'k' has unit = time ⁻¹ = sec ⁻¹
(ii) Its t _{1/2} is directly proportional to initial conc. of reactant.	(ii) Its half life is independent of the initial conc. of the reactant.

Q4. (a) The half life for the decomposition of nitramide is 2.1 hours at 15°C:



If 6.2 g of NH₂NO₂ is allowed to decompose, calculate:

(i) Time taken for NH₂NO₂ to decompose 99%.

(ii) Volume of N₂O (dry) produced at STP

(b) The conversion of X to Y follows second order kinetics. If concentration of 'X' is increased to three times, then how will it affect the rate of formation of 'Y' and why?

Ans. (a) (i) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1 \text{ hr}} = 0.33 \text{ hr}^{-1}$

$$t_{99\%} = \frac{2.303}{k} \log \frac{100}{100 - 99}$$

$$= \frac{2.303}{0.33} \log 100$$

$$= \frac{4.606}{0.33 \text{ hr}^{-1}} = 13.96 \text{ hr}$$

(ii) Amount decomposed = 99% of 6.2 g

$$= \frac{6.2 \times 99}{100} = 6.138 \text{ g}$$

1 mole of NH₂NO₂ (62 g) produces 22.4 L at STP

$$6.138 \text{ g will produce} = \frac{22.4}{62} \times 6.138$$

= 2.217 L at STP

(b) X → Y

$$\text{rate} = k [x]^2 = k [3x]^2 = k \times 9x^2$$

The rate of formation of 'Y' will increase by 9 times because the reaction is of second order and the conc. of the reactants is increased by 3 times.

Q5. (a) Consider the data for the reaction between A and B.

A (mol L ⁻¹)		B (mol L ⁻¹)		Initial rate in mol L ⁻¹ s ⁻¹	
				T = 300 K	T = 320 K
2.5 × 10 ⁻⁴	3.0 × 10 ⁻⁵	5 × 10 ⁻⁴	2 × 10 ⁻³		
5.0 × 10 ⁻⁴	6.0 × 10 ⁻⁵	4 × 10 ⁻³	—		
1.0 × 10 ⁻³	6.0 × 10 ⁻⁵	1.6 × 10 ⁻²	—		

Calculate

(i) order w.r.t. 'A' and 'B'.

(ii) rate constant at 300 K.

(iii) the energy of activation (E_a).

(iv) the pre-exponential factor (A).

(b) What will be the effect of temperature on rate constant?

Ans. (a)(i) Let the rate law be:

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

From expt 2:

$$4 \times 10^{-3} = k[5 \times 10^{-4}]^x (6.0 \times 10^{-5})^y \quad \dots(i)$$

From expt 3:

$$1.6 \times 10^{-2} = k(1.0 \times 10^{-3})^x (6.0 \times 10^{-5})^y \quad \dots(ii)$$

Dividing (i) by (ii) we get

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

$$x = 2$$

From expt 1:

$$5 \times 10^{-4} = k(2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})^y \quad \dots(iii)$$

From expt 2

$$4 \times 10^{-3} = k(5.0 \times 10^{-4})^2 (6.0 \times 10^{-5})^y \quad \dots(iv)$$

On dividing (iii) by (iv)

$$\frac{5}{40} = \frac{1}{2^2} \times \frac{1}{2^y}$$

$$\frac{1}{2} = \frac{1}{2^y} \text{ or } 2^y = 2^1$$

$$y = 1$$

∴ Order w.r.t. 'A' is 2 and w.r.t. 'B' is 1

(ii) From expt 1:

$$5 \times 10^{-4} = k_1 (2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})^1$$

$$k_1 = \frac{5 \times 10^{-4}}{2.5 \times 2.5 \times 10^{-8} \times 3.0 \times 10^{-5}}$$

$$= 2.67 \times 10^8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

(iii) From expt. 1:

$$k_2 = \frac{2 \times 10^{-3}}{2.5 \times 2.5 \times 10^{-8} \times 3 \times 10^{-5}}$$

$$= 1.07 \times 10^9 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

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

$$\log \frac{1.07 \times 10^9}{2.67 \times 10^8} = \frac{E_a}{19.147} \times \frac{320 - 300}{320 \times 300}$$

$$E_a = 55.407 \text{ kJ}$$

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

$$\log A = \log (2.67 \times 10^8)$$

$$+ \frac{554075}{19.147 \times 300}$$

$$A = 1.181 \times 10^{18}$$

(b) 'k' increases with increase in temperature.

Q6. (a) At 380°C, the half period for the first order decomposition of H_2O_2 is 360 min. The energy of activation is 200 kJ mol⁻¹. Calculate the time required for 75% decomposition of H_2O_2 at 450°C.

(b) Consider the following data for the reaction:



Conc. of A (mol L ⁻¹)	Conc. of B (mol L ⁻¹)	Initial rate (mol L ⁻¹ s ⁻¹)
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	1.0×10^{-2}
0.5	0.5	1.0×10^{-2}

Calculate:

(i) order w.r.t. A and B for the reaction.

(ii) rate constant

(iii) The reaction rate when conc. of A is 0.2 M and conc. of B is 0.35 M

Ans. (a) $k_1 = \frac{0.693}{t_{1/2}} = 1.92 \times 10^{-3} \text{ min}^{-1}$

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

$$\log \frac{k_2}{k_1} = \frac{200000}{19.147} \times \frac{723 - 653}{723 \times 653}$$

$$= 1.5487$$

$$\frac{k_2}{k_1} = \text{Antilog } 1.5487 = 35.38$$

$$k_2 = k_1 \times 35.38$$

$$= 1.92 \times 10^{-3} \times 35.38$$

$$= 6.793 \times 10^{-2} \text{ min}^{-1}$$

$$t = \frac{2.303}{k_2} \log \frac{[R_0]}{\frac{25}{100} [R_0]}$$

$$t = 20.411 \text{ min}$$

(b) (i) Rate = $[A]^x [B]^y$

From expt 3:

$$1 \times 10^{-2} = k (0.5)^x (0.1)^y \quad \dots(i)$$

From expt 4:

$$1.0 \times 10^{-2} = k (0.5)^x (0.5)^y \quad \dots(ii)$$

Dividing (i) by (ii) we get

$$\frac{1 \times 10^{-2}}{1 \times 10^{-2}} = \frac{1}{5^y} \Rightarrow 5^y = 5^0$$

$$y = 0$$

From expt 1:

$$4.0 \times 10^{-4} = k (0.1)^x (0.1)^y \quad \dots(iii)$$

From expt 3:

$$1.0 \times 10^{-2} = k (0.5)^x (0.1)^y \quad \dots(iv)$$

Dividing (iii) by (iv)

$$\frac{1}{25} = \frac{1}{5^x}$$

$$\Rightarrow 5^x = 5^2$$

$$x = 2$$

∴ Order w.r.t. 'A' is 2 and w.r.t. 'B' is 0

(ii) Rate = $k[A]^2 [B]^0$

$$4.0 \times 10^{-4} = k (0.1)^2$$

$$k = 4.0 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$

(iii) Rate = $k (0.2)^2 (0.35)^0$

$$= 4.0 \times 10^{-2} \times (0.2)^2$$

$$= 1.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

Q7. (a) The vapour pressure of two miscible liquids A and B are 300 and 500 mm of Hg respectively. In a flask 10 moles of 'A' is mixed with 12 moles of B. When 'B' is added, A starts polymerising into insoluble solid by first order kinetics. After 100 min, 0.525 mole of solute dissolves and polymerisation is stopped completely. The final vapour pressure of the solution is 400 mm of Hg. Calculate the rate constant of polymerisation reaction assuming the ideal behaviour of solution.

(b) The rate constant for an isomerisation reaction:



If the initial conc. of A is 1 M, calculate the rate of reaction after 1 hr.

Ans. (a) Let the number of moles of 'A' left after 100 min = x

Total number of moles after 100 min.
 $= 12 + x + 0.525$

$$P_{\text{Total}} = P_A + P_B$$

$$400 = \frac{x}{12 + x + 0.525} \times 300$$

$$+ \frac{12}{12 + x + 0.525} \times 500$$

$$400 = \frac{300x + 6000}{12 + x + 0.525}$$

$$4800 + 400x + 210$$

$$= 300x + 6000$$

$$x = 9.9$$

$$k = \frac{2.303}{100} \log \frac{10}{1.9}$$

$$= 1.013 \times 10^4 \text{ min}^{-1}$$

(b) $k = 4.5 \times 10^{-3} \text{ min}^{-1}$

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

$$4.5 \times 10^{-3} = \frac{2.303}{60 \text{ min}} \log \frac{1}{[R]}$$

$$\log \frac{1}{[R]} = \frac{4.5 \times 10^{-3} \times 60}{2.303} = \frac{0.270}{2.303}$$

$$\frac{1}{[R]} = \text{Antilog } (0.1172) = 1.31$$

$$[R] = \frac{1}{1.31} = 0.7633 \times 4.5 \times 10^{-3}$$

$$= 3.44 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

Q8. (a) For the reaction



Calculate the mole fraction of $\text{N}_2\text{O}_5(\text{g})$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

(b) A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction, if the catalyst lowers the activation energy, E_a by 20 kJ mol⁻¹.

Ans. (a) $\text{N}_2\text{O}_5(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

Initial : P 0 0

Final : P-x 2x 0.5x

Total pressure = $P + 1.5x = 960$

$$600 + 1.5x = 960$$

$$x = 240 \text{ mm Hg}$$

Mole fraction of N_2O_5 decomposed

$$= \frac{240}{600} = 0.4$$

(b) Let E_{a_1} be the activation energy in the absence of a catalyst.

E_{a_2} be the activation energy in the presence of a catalyst.

$$k = Ae^{\frac{E_{a_1}}{500R}}$$

$$k = Ae^{\frac{E_{a_2}}{400R}}$$

$$\therefore \frac{E_{a_1}}{500R} = \frac{E_{a_2}}{400R}$$

$$\therefore E_{a_2} = \frac{4}{5} E_{a_1}$$

Now, $E_{a_1} - E_{a_2} = 20 \text{ kJ mol}^{-1}$

$$E_{a_1} - \frac{4}{5} E_{a_1} = 20 \text{ kJ mol}^{-1}$$

$$E_{a_1} = 100 \text{ kJ mol}^{-1}$$

Q9. (a) The rate of the first order reaction is $0.04 \text{ mol L}^{-1}\text{s}^{-1}$ at 10 min and $0.03 \text{ mol L}^{-1}\text{s}^{-1}$ at 20 min after initiation. Find the half life of the reaction.

(b) Some $\text{PH}_3(\text{g})$ is introduced into a flask at 600°C containing an inert gas. $\text{PH}_3(\text{g})$ decomposes to $\text{P}_4(\text{g})$ and $\text{H}_2(\text{g})$ and the reaction goes to completion. The total pressure given below as a function of time.

Find the order of the reaction and calculate the rate constant.

Time (sec)	0	60	120	∞
P(mm Hg)	262.40	272.90	275.51	276.40

$$\begin{aligned} \text{Ans. (a) } k &= \frac{2.303}{t_2 - t_1} \log \frac{(\text{rate})_1}{(\text{rate})_2} \\ &= \frac{2.303}{20 - 10} \log \frac{0.04}{0.03} \\ &= 2.878 \times 10^{-2} \text{ min}^{-1} \end{aligned}$$

$$t_{1/2} = \frac{0.693}{2.878 \times 10^{-2}} = 1444.7 \text{ sec.}$$

$$\begin{aligned} \text{(b) } R_0 &\propto P_\infty - P_0 \\ R_0 &\propto (276.40 - 262.40) \end{aligned}$$

$$R_0 \propto 14.0 \text{ mm of Hg}$$

$$P_t - P_0 \propto 'x' \text{ (amount decomposed)}$$

$$R \propto [P_\infty - P_0] - [P_t - P_0]$$

$$R \propto P_\infty - P_t$$

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

$$= \frac{2.303}{t} \log \frac{P_\infty - P_0}{P_\infty - P_t}$$

$$k = \frac{2.303}{60} \log \frac{276.4 - 262.4}{276.4 - 272.9}$$

$$= 2.31 \times 10^{-2} \text{ s}^{-1}$$

$$k = \frac{2.303}{120} \times \log \frac{14}{0.89}$$

$$= 2.296 \times 10^{-2} \text{ s}^{-1}$$

The reaction is of first order,

\therefore Average value of

$$k = \frac{2.310 + 2.296}{2} \times 10^{-2} \text{ s}^{-1}$$

$$k = 2.302 \times 10^{-2} \text{ s}^{-1}$$

Q10. For the hydrolysis of methyl acetate in aqueous solution, the following results were obtained:

t/s	0	30	60
$\text{CH}_3\text{COOCH}_3 \text{ mol}^{-1}$	0.60	0.30	0.15

(a) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(b) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

[Given $\log 2 = 0.3010$, $\log 4 = 0.6021$]
[CBSE 2015]

$$\text{Ans. (a) } k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$k = k'[\text{H}_2\text{O}]$$

For $t = 0$ to 30

$$k = \frac{2.303}{30} \log \frac{0.60}{0.30}$$

$$k = 0.07677 \log 2$$

$$k = 0.0231$$

For $t = 30$ to 60

$$k = \frac{2.303}{30} \log \frac{30}{0.15}$$

$$k = 0.07677 \log 2$$

$$k = 0.0231$$

∴ k is same for both the cases hence it is a pseudo first order reaction

$$\begin{aligned} (b) \quad k &= \frac{-\Delta[\text{CH}_3\text{COOCH}_3]}{\Delta t} \\ &= \frac{-(0.30 - 0.60)}{30 - 0} \\ &= \frac{0.30}{30} = 0.01 \end{aligned}$$

Q11. (a) For a reaction $A + B \longrightarrow P$, the rate is given by

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

(i) How is the rate of reaction affected if the concentration of B is doubled?

(ii) What is the overall order of the reaction if A is present in large excess?

(b) A first order reaction take 30 minutes for its 50% completion. Calculate the time required for 90% completion of this reaction (Given: $\log 2 = 0.3010$)

[CBSE 2015]

Ans. (a) $\text{Rate} = K[A][B]^2$

(i) $B' = 2B$

$$\begin{aligned} \text{Rate} &= K[A][2B]^2 \\ &= 4K[A][B]^2 \\ &= 4 \text{ times the rate of reaction.} \end{aligned}$$

(ii) If A is present in large excess, then overall order of reaction will be two.

$$(b) \quad K = \frac{2.303}{t_{50\%}} \log \frac{[A]_0 \times 100}{50[A]_0}$$

$$\begin{aligned} K &= \frac{2.303}{30} \log 2 \\ &= 0.0231 \text{ min}^{-1} \end{aligned}$$

$$t_{90\%} = \frac{2.303 \log [A]_0 \times 100}{K \cdot 10[A]_0}$$

$$\begin{aligned} &= \frac{2.303}{0.0231} \log 10 \\ &= 99.69 \text{ min} \end{aligned}$$

IV. HOTS Questions

Q1. The decomposition of dinitrogen pentoxide (N_2O_5) follows the first order rate law. Calculate the rate constant from the given data:

$$t = 800 \text{ sec}$$

$$[\text{N}_2\text{O}_5] = 1.45 \text{ mol L}^{-1} = [A_1]$$

$$t = 1600 \text{ sec}$$

$$[\text{N}_2\text{O}_5] = 0.88 \text{ mol L}^{-1} = [A_2]$$

Ans. Applying the formula,

$$\begin{aligned} k &= \frac{2.303}{(t_2 - t_1)} \log_{10} \frac{[A_1]}{[A_2]} \\ &= \frac{2.303}{(1600 - 800)} \log_{10} \frac{1.45}{0.88} \\ &= \frac{2.303}{800} \times 0.2169 \\ &= 6.24 \times 10^{-4} \text{ sec}^{-1}. \end{aligned}$$

Q2. The decomposition of N_2O_5 according to the equation:



is a first order reaction. After 30 minutes from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.4 mm Hg and on completion, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

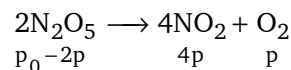
Ans. $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$

On decomposition of 2 moles of N_2O_5 , 4 moles of NO_2 and 1 mole of O_2 are produced. Thus, the total pressure after completion corresponds to 5 moles and initial pressure to 2 moles.

Initial pressure of N_2O_5 ,

$$\begin{aligned} P_0 &= \frac{2}{5} \times 584.5 \\ &= 233.8 \text{ mm Hg} \end{aligned}$$

After 30 minutes, the total pressure = 284.5 mm Hg



$$\text{or } p_0 + 3p = 284.5$$

$$\begin{aligned} \text{or } 3p &= 284.5 - 233.8 \\ &= 50.7 \text{ mm Hg} \end{aligned}$$

$$\text{or } p = \frac{50.7}{3} = 16.9 \text{ mm Hg}$$

$$\begin{aligned} \text{Pressure of N}_2\text{O}_5 \text{ after 30 minutes} \\ &= 233.8 - (2 \times 16.9) \\ &= 200 \text{ mm Hg} \end{aligned}$$

$$\begin{aligned} k &= \frac{2.303}{30} \log_{10} \frac{233.8}{200.0} \\ &= 5.2 \times 10^{-3} \text{ min}^{-1}. \end{aligned}$$

Q3. The gas phase decomposition of dimethyl ether follows first order kinetics.



The reaction is carried out in a constant volume container at 500°C and it has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure after 12 minutes? Assume ideal gas behaviour.

$$\begin{aligned} \text{Ans. } k &= \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5} \\ &= 0.047793 \text{ min}^{-1} \end{aligned}$$

Let the pressure of the dimethyl ether after 12 minutes be p atm. Applying first order equation,

$$k = \frac{2.303}{t} \log_{10} \frac{p_0}{p}$$

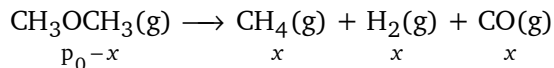
$$\log_{10} \frac{0.4}{p} = \frac{0.047793 \times 12}{2.303} = 0.2490$$

$$\text{or } \frac{0.4}{p} = 1.7743$$

$$\text{or } p = \frac{0.4}{1.7743} = 0.2254 \text{ atm}$$

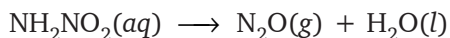
Decrease in pressure,

$$\begin{aligned} x &= 0.4 - 0.2254 \\ &= 0.1746 \text{ atm} \end{aligned}$$



$$\begin{aligned} \text{Total pressure} &= p_0 + 2x \\ &= 0.4 + 2 \times 0.1746 \\ &= 0.7492 \text{ atm} \end{aligned}$$

Q4. The half life of first order decomposition of nitramide is 2.1 hours at 15°C.



If 6.2 g of NH_2NO_2 is allowed to decompose, calculate (i) time taken for NH_2NO_2 to decompose 99% and (ii) the volume of dry N_2O produced at this point, measured at STP.

$$\begin{aligned} \text{Ans. (i) } k &= \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1} \\ &= 0.33 \text{ hr}^{-1} \end{aligned}$$

Applying kinetic equation of first order reaction,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

$$\begin{aligned} \text{or } t &= \frac{2.303}{0.33} \log_{10} \frac{100}{(100 - 99)} \\ &= 13.96 \text{ hrs.} \end{aligned}$$

(ii) No. of moles of NH_2NO_2 decomposed

$$= 0.99 \times \frac{6.2}{62} = 0.099$$

No. of moles of N_2O formed

$$= 0.099$$

Volume of N_2O at STP

$$\begin{aligned} &= 0.099 \times 22400 \text{ mL} \\ &= 2217.6 \text{ mL} \end{aligned}$$

Q5. A substance reacts according to the first order rate law and the specific reaction rate for the reaction is $1 \times 10^{-2} \text{ s}^{-1}$. If the initial concentration is 1.0 M.

(a) What is the initial rate?

(b) What is the reaction rate after 1 minute?

$$\begin{aligned} \text{Ans. (a) Initial rate of a first order reaction} \\ &= kC \end{aligned}$$

$$= 1 \times 10^{-2} \times 1.0$$

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

(b) Concentration after 60 seconds is calculated by applying the first order kinetic equation,

$$k = \frac{2.303}{60} \log_{10} \frac{1}{(1-x)}$$

$$\text{or } 1 \times 10^{-2} = \frac{2.303}{60} [-\log(1-x)]$$

$$\text{or } \frac{60 \times 10^{-2}}{2.303} = -\log(1-x) = 0.2605$$

$$\log(1-x) = -0.2605 = \bar{1}.73395$$

$$(1-x) = \text{antilog of } (\bar{1}.73395)$$

$$= 0.5489 \text{ mol L}^{-1}$$

Rate of reaction after 1 minute

$$= k \times C$$

$$= 1 \times 10^{-2} \times 0.5489$$

$$= 5.489 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

Q6. A first order reaction is 50% completed in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the reaction rate constant at 27°C and the energy of activation of the reaction in kJ mol⁻¹.

Ans. For a first order reaction

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

At 27°C,

$$k_{27^\circ\text{C}} = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}$$

At 47°C,

$$k_{47^\circ\text{C}} = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$$

Now applying the following equation:

$$\log_{10} \frac{k_1}{k_2} = \frac{-E_a}{2.303 \times R} \cdot \left(\frac{T_2 - T_1}{T_2 \cdot T_1} \right)$$

$$\text{or } \log_{10} \frac{0.0231}{0.0693}$$

$$= \frac{-E_a}{2.303 \times 8.314} \cdot \left(\frac{320 - 300}{320 \times 300} \right)$$

$$\text{or } -\log_{10} 0.3333 = \frac{E_a}{19.1471} \times \frac{20}{96000}$$

$$E_a = \frac{19.1471 \times 96000}{20}$$

$$\times \log 0.3333$$

$$= -91906 \times (-0.4772)$$

$$= 43857 \text{ J mol}^{-1}$$

$$= 43.857 \text{ kJ mol}^{-1}$$

Q7. In Arrhenius equation for a certain reaction, the values of A and E_a (activation energy) are 4 × 10¹³ sec⁻¹ and 98.6 kJ mol⁻¹ respectively. If the reaction is of first order, at what temperature will its half life period be 10 minutes? [IIT 1990]

Ans. According to the Arrhenius equation,

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

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

$$\text{or } 2.303 \log_{10} k$$

$$= 2.303 \log_{10} A - \frac{E_a}{RT}$$

For a first order reaction

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

$$\text{So, } k = \frac{0.693}{600} \text{ sec}^{-1}$$

$$(t_{1/2} = 10 \text{ min} = 600 \text{ sec.})$$

$$= 1.1 \times 10^{-3} \text{ sec}^{-1}$$

Hence, $\log(1.1 \times 10^{-3})$

$$= \log(4 \times 10^{13}) - \frac{98.6 \times 10^3}{2.303 \times 8.314 \times T}$$

$$T = 310.95 \text{ K}$$

Q8. A second order reaction in which both the reactants have same concentration, is 20% completed in 500 seconds. How much time it will take for 60% completion?

Ans. The second order equation when both the reactants have same concentration is

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

If $a = 100$, $x = 20$, $t = 500$ seconds.

$$\text{Then, } k = \frac{1}{500} \times \frac{20}{100 \times (100 - 20)}$$

When $a = 100$, $x = 60$, $t = ?$

$$t = \frac{1}{k} \cdot \frac{60}{100 \times 40}$$

Substituting the value of k ,

$$t = \frac{500 \times 100 \times 80}{20} \times \frac{60}{100 \times 40}$$

or $t = 3000$ seconds

Q9. A first order reaction is 20% completed in 10 minutes. Calculate the time taken for the reaction to go to 80% completion.

Ans. Applying the first order equation,

$$k = \frac{2.303}{t} \log \left[\frac{R_0}{R} \right]$$

At $t = 10$ min, $R = 100 - 20$.

$$\begin{aligned} \therefore k &= \frac{2.303}{t} \log_{10} \frac{100}{(100 - 20)} \\ &= \frac{2.303}{10} \log_{10} \frac{100}{80} \\ &= 0.0223 \text{ min}^{-1} \end{aligned}$$

□□