UNIT 4

CHEMICAL KINETICS

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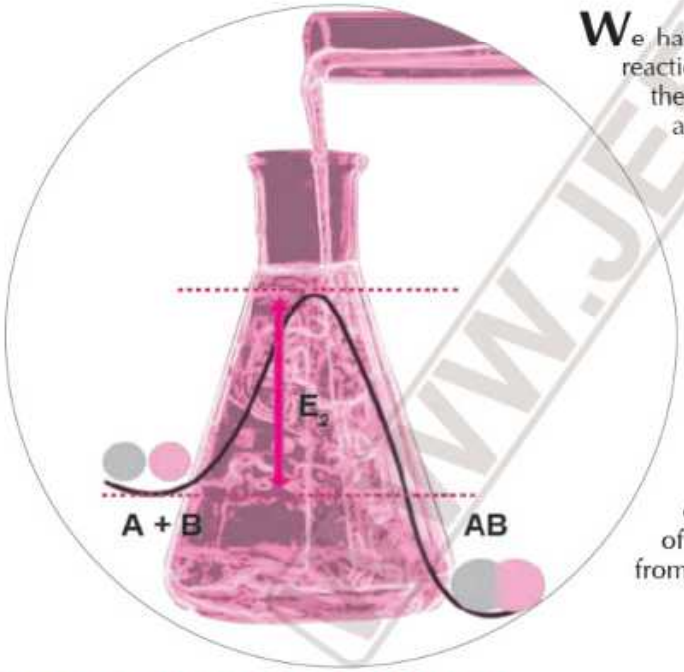

We have learnt some aspects of chemical reactions. The feasibility of a reaction under the given experimental conditions can be predicted on the basis of decrease in Gibbs energy ($\Delta G < 0$). The extent to which a reaction proceeds can be explained with the help of equilibrium constant of the reaction. The third important aspect of the chemical reactions is the speed with which the reactions proceed. Although thermodynamics answer the first two aspects satisfactorily, it cannot answer this important question; how fast a reaction can occur ?

The branch of chemistry which deals with the rates of chemical reactions and the factors which influence the rates of reactions and the mechanisms by which the reactions proceed is called **chemical kinetics.**

The word kinetics is derived from the Greek word 'kinesis' meaning movement. The kinetic studies not only help us to know the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates may be altered. The study of the rates of reactions also helps us to understand the pathways from reactants to products called mechanism of the reaction.

RATE OF A CHEMICAL REACTION

Everyday experience tells us that chemical reactions take place in widely varying rates. Some reactions are so rapid that they occur as soon as the reactants are mixed. For example, the reactions involving ionic species (known as **ionic reactions**) are very fast. For example, the precipitation of silver chloride occurs very quicky on mixing the solutions of silver nitrate and sodium chloride. Similarly, the neutralisation of an acid by a base occurs as soon as the two substances are mixed.

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$
$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$$
$$BaCl_2\ (aq) + H_2SO_4(aq) \longrightarrow BaSO_4\ (s) + 2HCl(aq)$$

It may be noted that *these reactions involve only the ions and no bonds are broken. Therefore, they occur very fast*. These reactions occur in about 10^{-12} to 10^{-16} seconds. On the other hand, there are certain reactions which occur at an extremely slow speed. For example, rusting of iron occurs so slowly that one could be misled into thinking that no reaction is taking place at all. However, there are some reactions which occur in a conveniently measurable time and their rates can be measured easily in the laboratory.

Reactions involving ionic species (known as ionic reactions) are very fast reactions. These generally occur in 10^{-12} to 10^{-16} seconds.

Some common examples of such reactions are :

(*i*) Hydrolysis of an ester in the presence of sodium hydroxide

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + \underset{\text{Ethanol}}{C_2H_5OH}$$

(*ii*) Decomposition of hydrogen peroxide

$$2H_2O_2\,(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

(*iii*) Inversion of cane sugar to give glucose and fructose

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(*iv*) Decomposition of nitrogen (V) oxide

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

These are the reactions which are focus of attention for us.

You must be knowing that speed of an automobile is expressed in terms of change in position of distance covered by it in a certain period of time. Similarly, the rate of a chemical reaction is a measure of the speed with which the reactants are converted into products.

Rate of reaction may be defined as

the change in any one of the reactants or products per unit time.

This may be obtained by dividing the change in concentration of a reactant or a product by the time interval over which the change occurs.

Consider a hypothetical reaction:

$$R \longrightarrow P$$

in which one mole of the reactant 'R' produces one mole of the product 'P'. The rate of the reaction may be expressed in either of the following two ways :

(*i*) *The rate of disappearance or decrease in concentration of R (reactants):*

$$\text{Rate of reaction} = \frac{\text{Decrease in concentration of R}}{\text{Time taken}}$$

(*ii*) *The rate of increase in concentration of P (products) :*

$$\text{Rate of reaction} = \frac{\text{Increase in concentration of P}}{\text{Time taken}}$$

If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their respective concentrations at time t_2, then

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1 \quad \text{and} \quad \Delta[P] = [P]_2 - [P]_1$$

where the square brackets express the molar concentrations and $\Delta[R]$ and $\Delta[P]$ are the changes in concentrations of R and P during time interval Δt. Then rate of the reaction may be obtained by dividing the change in concentration of a reactant or a product by the time interval over which the change occurs. This is expressed as a:

$$\text{Rate of reaction} = -\frac{\Delta[R]}{\Delta t} \qquad ...(1)$$

or

$$\text{Rate of reaction} = \frac{\Delta[P]}{\Delta t} \qquad ...(2)$$

where $\Delta[R]$ gives the decrease in concentration of R and $\Delta[P]$ represents increase in concentration of P. The square brackets around the substances are used to express the molar concentration (mol/litre). It may be noted *that in the case of concentration of reactants* **minus sign** is used. This implies that the concentration of reactants is decreasing with time.

The above rate is also called *average rate of the reaction*. It has the dimensions of concentration/time. The units of concentration and time are chosen according to the convenience.

NOTE

Significance of negative sign. The significance of negative sign in the case of expressing rate of reaction in terms of reactants may be understood. The concentration of reactants is decreasing as time passes and, therefore, ΔR, (*i.e.*, final concentration–initial concentration) will be negative.

This makes the expression $\frac{\Delta[R]}{\Delta t}$ (reaction rate) negative. But we know that rate is always positive, as also obtained from the rate of formation of products. Therefore, minus sign is put before $\frac{\Delta[R]}{\Delta t}$ so that the rate is positive [(–) × (–) = +ve]. Thus,

$$\text{Rate of reaction} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

In the above example, the stoichiometric coefficients for the reactants and products are same. Therefore, the rate at which the concentration of R decreases will be the same as the rate at which the concentration of P increases. Therefore, the rates expressed by the Eq. (1) and Eq. (2) are same.

For example, for the reaction :

$$PCl_5\ (g) \longrightarrow PCl_3\ (g) + Cl_2\ (g)$$

Rate may be expressed as :

$$\text{Rate} = -\frac{\Delta[PCl_5]}{\Delta t} = \frac{\Delta[PCl_3]}{\Delta t} = \frac{\Delta[Cl_2]}{\Delta t}$$

Similarly, for the reaction :

$$Hg\ (l) + Cl_2\ (g) \longrightarrow HgCl_2\ (s)$$

Rate may be expressed as :

$$\text{Rate} = -\frac{\Delta[Hg]}{\Delta t} = -\frac{\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

Reactions Involving Different Stoichiometric Coefficients of Reactants and Products

Consider the reaction

$$A + B \longrightarrow 2C$$

In this case, one mole of A reacts with one mole of B to form 2 moles of C. This means that the rates of disappearance of A and B are same but the rate of appearance of C must be twice the rate of disappearance of A and B. Thus,

2 Rate of disappearance of A = 2 Rate of disappearance of B
= Rate of appearance of C

To get **unique value** of the reaction rate (independent of the concentration terms chosen), *we divide the rate of reaction defined with any of the reactants or products by the stoichiometric coefficient of that reactant or product involved in the reaction.* Thus, for the above reaction,

$$\text{Rate of reaction} = \frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} = \frac{1}{2}\frac{\Delta[C]}{\Delta t}$$

For example, for the decomposition of gaseous nitrogen pentoxide (N_2O_5) as:

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

Similarly, for the reaction :

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

rate may be expressed as :

$$\text{Rate of reaction} = -\frac{1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species and hence, rate can also be expressed as rate of change in partial pressure of the reactant or the product.

Average Rate and Instantaneous Rate

The rate expressions given so far give the *average rate of reactions* over the time interval *(Δt)*. This may be expressed as :

$$\text{Rate} = \frac{\text{Change in concentration}}{\text{Time interval}} = \frac{\Delta x}{\Delta t}$$

However, it may be noted that average rate cannot be used to predict the rate of a reaction at a particular instant because the rate is generally not constant throughout the reaction. This is because rate of a reaction depends upon the molar concentration of reactants which keep on decreasing with the passage of time (while those of the products keep on increasing). Therefore, to express the rate at a particular moment of time, we determine the **instantaneous rate**. Thus, **instantaneous rate of a reaction** may be defined as

the rate of change of concentration of any one of the reactants or products at a particular moment of time.

Average rate concept and mechanical speed. The concept of average rate is similar to *mechanical speed*. For example, the average speed of a car can be easily calculated by knowing the distance covered by it in a given time. If the car covers 250 km in 5 hours, its average speed is = 250 km/5 hr = 50 km/hr. However, during the journey, the driver can look from the speedometer that the speed keeps on changing depending upon the conditions of the road, weather, traffic density etc. The needle of the speedometer indicating speed may vary from as low as 10 km/hr to 120 km/hr. For a chemical reaction also, the average rate depends on the values of t_2 and t_1 chosen. Like speed of the car, the rate also changes. This is due to the fact that in case of reactions, *the rate depends upon the concentration of the reactants.* As the reaction proceeds, the concentration of the reactants keeps on decreasing. Thus, the rate of a reaction may not be constant in the time interval which we measure.

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To express instantaneous rate of reaction, the time interval Δt is made as small as possible so that rate of reaction remains almost constant during that time interval.

Mathematically* instantaneous rates may be represented by $-\frac{d[R]}{dt}$ or $\frac{d[P]}{dt}$ instead of $-\frac{\Delta[R]}{\Delta t}$ or $\frac{\Delta[P]}{\Delta t}$ respectively. Here $d[R]$ or $d[P]$ represents infinitesimally small changes in concentration of R or P in infinitesimally small interval of time, dt. Thus, the average rate approaches the instantaneous rate as Δt becomes smaller and smaller *i.e.*,

REMEMBER

- Symbol Δ is used for larger change *i.e* for average rate.
- Symbol 'd' is used for smaller change *i.e.* for instantaneous rate.

$$-\left(\frac{\Delta[R]}{\Delta t}\right)_{\Delta t \to 0} = -\frac{d[R]}{dt} \quad \text{and} \quad \left(\frac{\Delta[P]}{\Delta t}\right)_{\Delta t \to 0} = \frac{d[P]}{dt}$$

$$\text{Thus,} \quad r_{\text{inst}} = -\frac{d[R]}{dt} \text{ or } = \frac{dP}{dt}$$

In general, if dx represents very small (infinitesimally small) change in concentration of any species during the very small (infinitesimally small) change of time, dt, the rate of the reaction may be expressed as :

$$\text{Rate of reaction} = \frac{dx}{dt}$$

If the rate is expressed in terms of concentration of any one of the reactants, which obviously, keeps on decreasing, the negative sign is used, as already discussed.

For a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

the rate of the reaction is defined as :

$$\text{Rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt}$$

$$= \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Let us write the instantaneous rate expressions for some reactions :

(*i*) $2N_2O_5 \rightleftharpoons 4NO_2 + O_2$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

$$= \frac{d[O_2]}{dt}$$

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* In differential calculas, when Δt becomes very small and approaches zero, the ratio $\frac{\Delta[R]}{\Delta t}$ may be replaced by the derivative, $\frac{d[R]}{dt}$. That is,

$$\underset{\Delta t \to 0}{\text{Limit}} \frac{\Delta[R]}{\Delta t} = \frac{d[R]}{dt}$$

In general, for change in concentration of any species

$$\underset{\Delta t \to 0}{\text{Limit}} \frac{\Delta x}{\Delta t} = \frac{dx}{dt}$$

where dx is the infinitesimally small change in concentration corresponding to infinitesimally small change in time, dt.

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(*ii*) $H_2 + I_2 \rightleftharpoons 2HI$

$$\text{Rate of reaction} = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$$

(*iii*) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

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

(*iv*) $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightleftharpoons 3Br_2(aq) + 3H_2O(l)$

$$\text{Rate of reaction} = -\frac{1}{5}\frac{d[Br^-]}{dt} = -\frac{d[BrO_3^-]}{dt} = -\frac{1}{6}\frac{d[H^+]}{dt} = +\frac{1}{3}\frac{d[Br_2]}{dt} = +\frac{1}{3}\frac{d[H_2O]}{dt}$$

REMEMBER

- The rate of a reaction can be expressed in terms of any reactant or product.
- As concentration of reactant decreases, a **negative sign** is used to express the rate of reaction in terms of reactants.
- As concentration of products increases, a positive sign is used to express the rate of reaction in terms of products.
- To make the different expressions for the rate of reaction to be equivalent, the rate expressions are divided by the stoichiometric coefficients of that reactant or product in the balanced chemical equation.

EXPERIMENTAL MEASUREMENT OF REACTION RATE

In order to measure the rate of a reaction, we have to monitor the concentration of the reactant (or product) as a function of time. The most common practice to do so is to withdraw a known small amount of the reaction mixture (1 to 2 mL) at different intervals of time, cool it down immediately to nearly 0°C to arrest the reaction and then measure the concentration of the reactant (or the product) by some suitable method. The most common method used is the titration of the solution against a suitable reagent. However, more convenient techniques have been developed that can continuously measure the changes in some physical property which is related to the concentration of one of the species, at different intervals of time without stopping the reaction. For example, if a gaseous reaction involves a change in number of molecules, the pressure of the system changes when the volume and the temperature are kept constant. By measuring the pressure changes as the reaction proceeds, we can measure the rate of the reaction. Some other commonly measurable properties are volume change, change in thermal or electrical conductivity, change in optical rotation, change in colour, pH or refractive index etc.

Calculation of average rate of reaction

As already studied, the average rate of reaction can be determined by calculating the change in concentration of a reactant or a product in a given interval of time. For example, if the concentration of a reactant decreases from C_1 to C_2 in a time from t_1 to t_2, then average rate of the reaction is

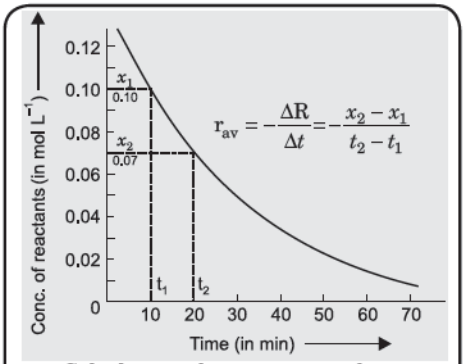
$$\text{Average rate} = -\frac{C_2 - C_1}{t_2 - t_1}$$

However, rate of reaction can be conveniently calculated by **graphical method.** A graph is plotted between the concentration of a reactant and time as shown in Fig. 1(*a*) ahead.

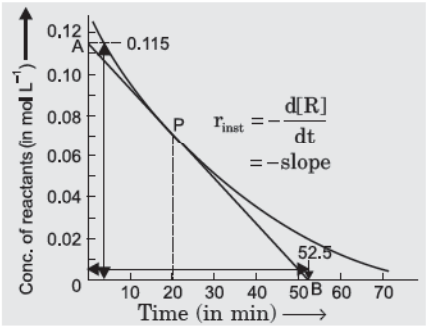
The average rate of reaction is determined by noting the concentration of reactants at two different times. In Fig. 1 (*a*), x_1 and x_2 are the concentrations in the time interval between t_1 and t_2. Then average rate is :

$$\text{Average rate of reaction} = -\frac{\Delta[x]}{\Delta t} = -\frac{x_2 - x_1}{t_2 - t_1}$$

It is clear that the concentration of reactant decreases with time making $(x_2 - x_1)$ a negative quantity. Thus, the minus sign makes the rate as a positive quantity. For example, from Fig. 1(*a*), it is clear that the concentration of the reactant at time 10 min is 0.10 mol L^{-1} and it decreases to 0.07 mol L^{-1} at time 20 min. The average rate over this time interval is



(*a*) Calculation of average rate of reaction.



(*b*) Calculation of instantaneous rate of reaction.

Fig. 1. Measurement of (*a*) average rate and (*b*) instantaneous rate of a reaction from the plot of conc. of a reactant with time.

Significance of negative and positive slopes and rates of reactions.

It may be noted from Fig. 1 that in the plot of concentration of reactant vs time, the tangent at any instant of time has a **negative slope** whereas in the plot of concentration of product vs time (Fig. 2), the tangent has a **positive slope.** Hence, we have :

$$r_{inst} = -\frac{d[R]}{dt} = -\text{ slope of tangent}$$

$$= +\frac{d[P]}{dt} = \text{slope of tangent}$$

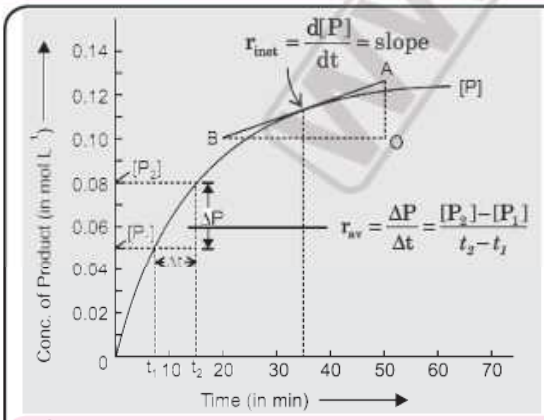


Fig. 2. Calculation of average and instantaneous rate of a reaction from the plot of conc. of products vs time.

$$\text{Average rate} = -\frac{0.07 - 0.10}{20 - 10}$$

$$= 0.003 \text{ mol L}^{-1} \text{ min}^{-1}$$

Similarly, it can be calculated at other time intervals.

Calculation of instantaneous rate of reaction

Since reaction rate is constantly changing, it is more appropriate to measure the instantaneous rate. The instantaneous rate gives the rate at any specific instant of time during a chemical reaction. It can be determined graphically by plotting concentrations of a reactant or a product against time. Then a tangent is drawn to the curve at time at which the rate of reaction is to be determined. Then the slope of this tangent gives the instantaneous rate of the reaction at that time. The slope can be determined by extending the tangent to intersect both the axes. Fig. 1 (b) shows the variation of the concentration of a reactant with time and tangent at a time corresponding to point P. The tangent is shown extended to intersect both the axes. The distance OA along the ordinates gives the change in concentration, Δx, while the distance along the abscissa OB gives the corresponding change in time, Δt.

The ratio $\frac{OA}{OB}$ or $\frac{\Delta x}{\Delta t}$ gives the slope of the tangent. Thus,

$$\text{Instantaneous rate of reaction} = \frac{OA}{OB}$$

$$\text{or} \qquad = \frac{\Delta x}{\Delta t}$$

For example from Fig. 1(*b*), it is clear that for tangent at point P corresponding to 20 min, the OA and OB distances are 0.115 mol L^{-1} and 52.5 min respectively. The instantaneous rate is

$$\text{Instantaneous rate} = \frac{0.115 \text{ mol L}^{-1}}{52.5 \text{ min}}$$

$$= 0.0022 \text{ mol L}^{-1} \text{ min}^{-1}$$

The instantaneous rate at any other time can be determined in a similar manner. It is clear from Fig. 1 that the concentration of reactant does not change linearly with time. Consequently, the slope of the curve and, thus, rate of the reaction keeps on changing with time.

Calculation of rate of reaction from plot of concentration of a product versus time

If concentration of one of the products is plotted against time, a curve as shown in Fig. 2 is obtained. The average rate of reaction between times t_1 and t_2 is calculated by noting the concentrations $[P_1]$ and $[P_2]$ corresponding to these times as:

$$\text{Average rate} = \frac{\Delta P}{\Delta t} = \frac{[P_2]-[P_1]}{t_2 - t_1}$$

Similarly, the rate of reaction at any instant of time, t i.e., instantaneous rate is calculated from the slope of the tangent at that point as

$$\text{Rate} = \frac{d[P]}{dt} = \frac{OA}{OB}$$

$$= \text{Slope of the tangent}$$

It is clear from the figure that the graph is not linear. This supports the observation that rate of the reaction is not constant with time.

SOLVED EXAMPLES

Example 1.

Express the rate of the following reactions :

(i) $4PH_3 \longrightarrow P_4 + 6H_2$

(ii) $2NO_2 \longrightarrow 2NO + O_2$

in terms of the concentration of reactants and products.

Solution :

(i) For the reaction,

$4PH_3 \longrightarrow P_4 + 6H_2$

$$\text{Rate of reaction} = -\frac{1}{4}\frac{d[PH_3]}{dt} = \frac{d[P_4]}{dt} = \frac{1}{6}\frac{d[H_2]}{dt}$$

(ii) For the reaction,

$2NO_2 \longrightarrow 2NO + O_2$

$$\text{Rate of reaction} = -\frac{1}{2}\frac{d[NO_2]}{dt}$$

$$= \frac{1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt}$$

Example 2.

The concentrations of a reactant R at different times are given below :

t(s)	[R] (mol L^{-1})	t(s)	[R] (mol L^{-1})
0	160×10^{-3}	5	80×10^{-3}
10	40×10^{-3}	20	10×10^{-3}
30	2.5×10^{-3}		

Calculate the average rate of reaction, $R \longrightarrow P$ during different intervals of time.

Solution : The average rate of reaction can be calculated as :

$$r_{av} = -\frac{[R]_2 - [R]_1}{\Delta t}$$

$[R_1] \times 10^{-3}$	$[R_2] \times 10^{-3}$	t_1 s	t_2 s	r_{av} (mol L^{-1} s^{-1})
160	80	0	5	$-\frac{(80-160)\times 10^{-3}}{5-0} = 16 \times 10^{-3}$
80	40	5	10	$-\frac{(40-80)\times 10^{-3}}{10-5} = 8 \times 10^{-3}$
40	10	10	20	$-\frac{(10-40)\times 10^{-3}}{10} = 3 \times 10^{-3}$
10	2.5	20	30	$-\frac{(2.5-10)\times 10^{-3}}{30-20} = 0.75 \times 10^{-3}$

It can be seen that the average rate decreases from 16×10^{-3} to 0.75×10^{-3} mol L^{-1} s^{-1} during the time interval 0 to 30 s.

Example 3.

From the concentration of C_4H_9Cl (butyl chloride) at different times given below, calculate the average rate of reaction:

$C_4H_9Cl + H_2O \longrightarrow C_4H_9OH + HCl$

during different intervals of time.

t(s)	C_4H_9Cl(mol L^{-1})	t(s)	C_4H_9Cl(mol L^{-1})
0	0.100	300	0.0549
50	0.0905	400	0.0439
100	0.0820	500	0.0335
150	0.0741	700	0.0210
200	0.0671	800	0.017

N.C.E.R.T.

Solution : Average rate of reaction in the interval t_1 to t_2 can be calculated as:

$$r_{av} = -\frac{\{[C_4H_9Cl]_{t_2} - [C_4H_9Cl]_{t_1}\}}{t_2 - t_1}$$

At $t = 0$ $[C_4H_9Cl] = 0.100$ mol L^{-1},

At $t = 50s$ $[C_4H_9Cl] = 0.0905$ mol L^{-1}

$$r_{av}(\text{in time interval } 0 - 50s) = -\frac{0.0905 - 0.100}{(50 - 0)}$$

$$= \mathbf{1.90 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

At $t = 50\ s$ $[C_4H_9Cl] = 0.0905$ mol L^{-1},

At $t = 100s$ $[C_4H_9Cl] = 0.0820$ mol L^{-1}

$$r_{av}(\text{in time interval } 50 - 100s) = -\frac{(0.0820 - 0.0905)}{100 - 50}$$

$$= \mathbf{1.70 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

At $t = 100s$ $[C_4H_9Cl] = 0.0820$ mol L^{-1},

At $t = 150s$ $[C_4H_9Cl] = 0.0741$ mol L^{-1}

$$r_{av}(\text{in time interval } 100 - 150s) = -\frac{(0.0741 - 0.0820)}{150 - 100}$$

$$= \mathbf{1.58\ mol\ L^{-1}\ s^{-1}}$$

At $t = 150s$ $[C_4H_9Cl] = 0.0741$ mol L^{-1},

At $t = 200s$ $[C_4H_9Cl] = 0.0671$ mol L^{-1}

$$r_{av}(\text{in time interval } 150 - 200s) = -\frac{(0.0671 - 0.0741)}{200 - 150}$$

$$= \mathbf{1.40\ mol\ L^{-1}\ s^{-1}}$$

Similarly, we can calculate in other time intervals

$r_{av}(200 - 300s) = 1.22 \times 10^{-4}$ mol L^{-1} s^{-1}

$r_{av}(300 - 400s) = 1.10 \times 10^{-4}$ mol L^{-1} s^{-1}

$r_{av}(400 - 500s) = 1.04 \times 10^{-4}$ mol L^{-1} s^{-1}

$r_{av}(500 - 700s) = 0.625 \times 10^{-4}$ mol L^{-1} s^{-1}

$r_{av}(700 - 800s) = 0.4 \times 10^{-4}$ mol L^{-1} s^{-1}

It is clear that the average rate of reaction decreases from

1.90×10^{-4} mol L^{-1} s^{-1} to 0.4×10^{-4} mol L^{-1} s^{-1}.

Example 4.

Ammonia and oxygen react at high temperature as :

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$$

In an experiment, rate of formation of NO is 3.6×10^{-3} mol L^{-1} s^{-1}. Calculate (i) rate of disappearance of ammonia, (ii) rate of formation of water.

(Pb.S.B. 2009, Assam S.B. 2012)

Solution : For the reaction,

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

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$$\text{Rate} = -\frac{1}{4}\frac{d[NH_3]}{dt} = -\frac{1}{5}\frac{d[O_2]}{dt}$$

$$= \frac{1}{4}\frac{d[NO]}{dt} = \frac{1}{6}\frac{d[H_2O]}{dt}$$

(*i*) *Rate of disappearance of ammonia*

Rate of disappearance of NH_3 = Rate of appearance of NO

$= \mathbf{3.6 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}}$.

(*ii*) *Rate of formation of water*

Rate of formation of $H_2O = \frac{d[H_2O]}{dt}$

From rate equation,

$$\frac{1}{6}\frac{d[H_2O]}{dt} = \frac{1}{4}\frac{d[NO]}{dt}$$

$$\therefore \frac{d[H_2O]}{dt} = \frac{6}{4} \times 3.6 \times 10^{-3} = \mathbf{5.4 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}}.$$

Example 5.

The decomposition of N_2O_5 in CCl_4 solution at 318 K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially, the concentration of N_2O_5 is 2.33 M and after 184 minutes, it is reduced to 2.08 M. The reaction takes place according to the equation:

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period ? **N.C.E.R.T.**

Solution : Rate of reaction

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

$$= -\frac{1}{2}\frac{(2.08 - 2.33)\ mol\ L^{-1}}{184\ min}$$

$$= 6.79 \times 10^{-4}\ mol\ L^{-1}\ min^{-1}$$

If time = 184 min = 3.067 hr

$$\text{Rate} = -\frac{1}{2}\frac{(2.08 - 2.33)\ mol\ L^{-1}}{3.067\ hr}$$

$$= 4.07 \times 10^{-2}\ mol\ L^{-1}\ hr^{-1}$$

If time = 184 × 60 = 11040 s

$$\text{Rate} = -\frac{1}{2}\frac{(2.08 - 2.33)\ mol\ L^{-1}}{11040\ s}$$

$$= 1.13 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$$

$$\text{Rate} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$$

$$\therefore \frac{\Delta(NO_2)}{\Delta t} = 4 \times \text{Rate}$$

$$= 4 \times 6.79 \times 10^{-4}\ mol\ L^{-1}\ min^{-1}$$

$$= \mathbf{2.72 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}}.$$

Example 6.

Dinitrogen pentoxide decomposes at 475K as :

$$N_2O_5(g) \longrightarrow N_2O_4(g) + \frac{1}{2}O_2(g)$$

If the initial pressure is 125 mm and after 30 minutes of the reaction, total pressure of the gaseous mixture is 148 mm, calculate the average rate of reaction in (i) atm min^{-1} (ii) mol L^{-1} s^{-1}.

Solution : (*i*) Let p is the decrease in pressure of N_2O_5 in 30 minutes then

	$N_2O_5(g)$	$\longrightarrow N_2O_4(g)$	$+ \frac{1}{2}O_2(g)$
Initial pressure	125 mm	0	0
After 30 min	$125-p$	p	$\frac{1}{2}p$

$$\text{Total pressure} = 125 - p + p + \frac{1}{2}p = 148$$

or $125 + \frac{1}{2}p = 148$

or $\frac{1}{2}p = 148 - 125 = 23$ mm

or $p = 2 \times 23$ mm $= 46$ mm

$\therefore$ Decrease in pressure in 30 min = 46 mm = $\frac{46}{760}$ atm

$$\text{Average rate of reaction} = \frac{46/760\ atm}{30\ min}$$

$$= \mathbf{2.02 \times 10^{-3}\ atm\ min^{-1}}$$

(*ii*) Applying pV = nRT

or $\frac{n}{V} = \frac{p}{RT}$

Decrease in molar concentration

$$= \frac{46/760\ atm}{0.0821\ L\ atm\ K^{-1}\ mol^{-1} \times 475K}$$

$$= 0.001552\ mol\ L^{-1}$$

$\therefore$ Average rate of reaction

$$= \frac{0.001552}{30 \times 60} = \mathbf{8.62 \times 10^{-7}\ mol\ L^{-1}\ s^{-1}}$$

Practice Problems

1. How can we express the rates of following reactions in terms of concentration of reactants and products ?

(*i*) $2O_3 \rightleftharpoons 3O_2$

(*ii*) $2NO + Br_2 \rightleftharpoons 2NOBr$

(*iii*) $2ICl(g) + H_2(g) \longrightarrow I_2(g) + 2HCl(g)$

2. For the reaction,

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

Answers to Practice Problems

2. (*i*) 1.2×10^{-4} mol L^{-1} s^{-1}.
(*ii*) 3.6×10^{-4} mol L^{-1} s^{-1}.

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the rate of reaction measured as $\frac{\Delta[NH_3]}{\Delta t}$ was found to be 2.4×10^{-4} mol L^{-1} s^{-1}. Calculate the rate of reaction expressed in terms of (*i*) N_2 and (*ii*) H_2.

(Pb.S.B.2011)

3. For the reaction :

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$,

the rate of formation of $NO_2(g)$ is 2.8 10^{-3} Ms^{-1}. Calculate the rate of disappearance of $N_2O_5(g)$. *(A.I.S.B. 2018)*

4. A reaction, $3X \longrightarrow 2Y + Z$ proceeds in a closed vessel. The rate of disappearance of X, $-\Delta[X]/\Delta t$ is found to be 0.072 mol L^{-1} s^{-1}. Calculate

$$\frac{\Delta[Y]}{\Delta t} \text{ and } \frac{\Delta[Z]}{\Delta t}$$ *(Pb.S.B. 2009)*

5. Consider the reaction:

$$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$$

In an experiment, rate of reaction of O_2 is 0.024 mol $L^{-1}s^{-1}$. Calculate (*i*) the rate disappearance of NO_2 and (*ii*) rate of formation of N_2O_5.

6. 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.

7. For an elementary reaction :

$$2A + B \longrightarrow 3C$$

the rate of appearance of C at time '*t*' is 1.3×10^{-4} mol $L^{-1}s^{-1}$. Calculate at this time

(*i*) rate of reaction (*ii*) rate of disappearance of A.

(C.B.S.E. Sample Paper 2008)

Answers to Practice Problems

3. 1.4×10^{-3} ms^{-1}.

4. 0.048, 0.024.

5. (*i*) 0.096 (*ii*) 0.048.

6. 4.0×10^{-4} mol L^{-1} min^{-1}, 6.6×10^{-6} mol L^{-1} s^{-1}.

7. (*i*) 4.33×10^{-5} mol L^{-1} s^{-1} (*ii*) 8.67×10^{-5} mol L^{-1} s^{-1}.

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FACTORS INFLUENCING RATES OF CHEMICAL REACTIONS

There are a number of factors which influence the rate of a reaction. Some of the important factors are :

1. *Concentration of the reacting species.*
2. *Temperature of the system.*
3. *Nature of the reactants and products.*
4. *Presence of a catalyst.*
5. *Surface area.*
6. *Exposure to radiation.*

Let us briefly discuss these factors.

1. Concentration of the reactants

The rate of a reaction is directly proportional to the concentration of the reactants. If the concentration of the reactants is large, the rate of reaction is large. As the concentration of the reactants decreases, the rate of the reaction also decreases. For example, the rate of burning of wood depends upon the concentration of oxygen. A piece of wood burns slowly in air (containing about 20% oxygen) but burns rapidly in pure oxygen (*i.e.*, 100% oxygen) because the concentration of oxygen in air is less (only about 1/5th of the concentration of pure oxygen).

2. Temperature of the system

In general, *an increase in the temperature increases the rate of almost all chemical reactions.* On the other hand, *a decrease in temperature decreases the rate.* This effect is observed for exothermic as well as for endothermic reactions. A general approximate rule for the effect of temperature on reaction rates is that the reaction rate for most of the chemical reactions becomes almost double, for every 10°C rise in temperature.

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- **Pieces of wood burn faster than a log of wood of the same mass.**
  - The total surface area of the wooden pieces is larger than log of wood of the same mass. Greater the surface area, faster is the reaction.

The reactions which are initiated by the absorption of radiation are called **photochemical reactions.**

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- **Generally ultraviolet or visible radiations are used for carrying out photochemical reactions. But infra-red radiations cannot be used.**
  - This is because the photons of ultraviolet or visible radiations possess energies approximately of the order of 420 kJ per mol which is comparable to most of the bond energies. Therefore, ultraviolet or visible radiation energies are capable of breaking the bonds. On the other hand, infra-red radiations are generally not used because their photons possess energy of the order of 60 kJ per mol which is quite less for breaking the bonds.

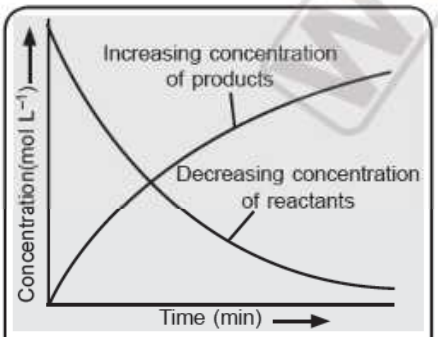

Fig. 3. The concentration of reactants decreases while concentration of products increases with time.

3. Nature of reactants and the products

Rates of reactions are influenced by the nature of reactants and products. A chemical reaction involves the breaking of old bonds and formation of new bonds. The reactivity of a substance can, therefore, be related to the ease with which the specific bonds are broken or formed and the number of such bonds involved. For example, the oxidation of nitric oxide to nitrogen dioxide takes place fairly **rapidly** while oxidation of carbon monoxide to carbon dioxide takes place **slowly :**

$$2NO + O_2 \longrightarrow 2NO_2 \quad \text{(Fast)}$$

$$2CO + O_2 \longrightarrow 2CO_2 \quad \text{(Slow)}$$

In these two reactions, the reacting species appear to be very similar to each other, still they differ in reaction rates.

4. Presence of catalyst

A catalyst is a substance which influences the rate of a reaction without undergoing any chemical change itself. It has been observed that many reactions are made to proceed at an increased rate by the presence of certain catalysts. For example, a mixture of H_2 and O_2 does not react at room temperature. However, in the presence of a catalyst such as finely divided platinum, the reaction becomes quite vigorous.

5. Surface area

The larger the surface area of the reactants, the faster is rate of reaction. It has been observed that if one of the reactants is a solid, then the rate of the reaction depends upon the state of sub-division of the solid. This fact is supported by the general observation that finely divided solids react faster than massive substances. For example, a log of wood burns slowly but if it is cut into small wooden chips, the burning takes place rapidly. This is due to the fact that the total surface area of the smaller particles is greater than that of large particles and this permits more molecules of the reactants to come in contact and form products.

6. Exposure to radiation

In some cases, the rate of a chemical reaction is considerably increased by the use of certain radiations. The photons of these radiations having frequencies (ν) possess sufficient energies ($E = h\nu$) to break certain bonds in reactants. For example, reaction of hydrogen and chlorine takes place very slowly in the absence of light. However, in the presence of light, the reaction takes place very rapidly.

$$H_2 + Cl_2 \xrightarrow{\text{light}} 2HCl$$

DEPENDENCE OF REACTION RATES ON CONCENTRATION : RATE LAW EXPRESSION

When a chemical reaction proceeds, the reactants get converted into the products. As a result, the concentration of reactants decreases while that of products increases. The general behaviour of the concentration of the reactants and the products is shown in Fig. 3.

From the figure, the following observations can be made :

(*i*) In the beginning of the reaction (*i.e.,* when time = 0), only reactants are present so that the concentration of the products is zero. As the reaction progresses, the concentration of the reactants decreases while the concentration of the products increases.

(*ii*) The change in concentration of the various species takes place rapidly in the beginning but very slowly as the reaction approaches the final stage.

From the above observations, it can be concluded that at the start of the reaction, the rate of the reaction is large and it decreases with passage of time. This means that *the rate of a reaction is directly proportional to the concentration of the reactants.* In the gas phase reaction, the increase in pressure of the reactant gases increases the rate of the reaction. With increase in pressure, the number of molecules per unit volume increases and, therefore, rate of reaction increases.

Law of Mass Action

The quantitative relationship between the rate of a reaction and the molar concentration of the reacting substances was given by two Norwegian chemists, Guldberg and Waage in 1867. This relationship is known as **law of mass action**. According to this law :

at a given temperature the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants.

The molar concentration of the reactant is also called **active mass.**

Let us consider a simple reaction of the type

$$A + B \longrightarrow 2AB$$

According to law of mass action, rate of the reaction may be written as :

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

where [A] and [B] are the molar concentrations of reactants, *k is constant of proportionality* and is called **rate constant.** The rate constant is also called **velocity constant** and is a measure of rate of the reaction.

Now, if concentration of each of the reactants involved in the reaction is unity, *i.e.* [A] = [B] = 1, then substituting these values in above expression, we get

$$\text{Rate of reaction} = k \times 1 \times 1 = k$$

Thus, **the rate constant** of a reaction at a given temperature may be defined as

rate of the reaction when the molar concentration of each of the reactants is unity.

That is why the rate constant is also called **specific reaction rate.**

Characteristics of Rate Constant

Some of the characteristics of rate constant are :

(i) *Rate constant is a measure of the rate of the reaction. Larger the value of k, faster is the reaction. Similarly, smaller value of k indicates slow reaction.*

(ii) *Different reactions have different values of k.*

(iii) *At a fixed temperature, the value of k is constant and is characteristic of the reaction. However, it changes with temperature.*

(iv) *For a particular reaction, the value of rate constant is independent of concentration.*

Differences between Rate of Reaction and Reaction Rate Constant

Let us sum up the differences between rate of reaction and reaction rate constant.

Rate of reaction	Reaction rate constant
1. It is the speed with which reactants are converted into products. It is measured as the rate of decrease in concentration of reactants or increase in concentration of products with time.	It is the proportionality constant in the rate law and is defined as the rate of reaction when the concentration of the reactants is unity.
2. It depends upon the initial concentration of the reactants.	It is independent of the initial concentration of the reactants.
3. Its units are always mol L^{-1} $time^{-1}$.	Its units depends upon the order of reaction.

Rate Law Expression

To express the rate of a reaction as a function of the concentration of the reactants, it is essential to measure experimentally the actual dependence of the concentration of the reacting species. For example, consider the reaction between NO_2 and F_2 to form NO_2F :

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

Experimental observations reveal that the rate of the reaction is proportional to the product of the concentrations of nitrogen peroxide and fluorine. Therefore, the rate of the reaction may be expressed as

$$\text{Rate} = k\,[NO_2][F_2]$$

This expression is called **rate law or rate equation.**

Similarly, consider the decomposition of dinitrogen pentoxide :

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Experimental studies have shown that the rate of this reaction is proportional to the $[N_2O_5]$ and not to $[N_2O_5]^2$. Therefore, the rate law is :

$$\text{Rate} = k\,[N_2O_5]$$

This expression is called **rate law** or **rate equation.**

Consider a general reaction,

$$aA + bB + cC \longrightarrow \text{Products}$$

where A, B and C are the reactants and a, b and c are stoichiometric coefficients of the balanced equation.

From the kinetic study of the reaction, the dependence of the concentration of reactants on the rate of the reaction have been found to be

$$\text{Rate} = k\,[A]^p\,[B]^q\,[C]^r \qquad ...(3)$$

where p, q and r are constant numbers or the powers of the concentrations of the reactants A, B and C respectively on which the rate of the reaction depends. It may be noted that the values of p, q and r are **determined experimentally** and may or may not be equal to a, b and c coefficients in the reaction. The expression (3) is the **rate law** or **rate equation.** It may be defined as

the mathematical expression which denotes the rate of a reaction in terms of molar concentrations of 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.

The power of concentration terms corresponds to experimentally observed rate of reaction.

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Differences between rate law expression and law of mass action

The *rate law gives the* **experimentally observed** *dependence of rate on the concentration of reactants.* The powers of concentrations of reactants in rate law expression may or may not be same as the coefficients of reactants in balanced chemical equation. On the other hand, *the law of mass action gives the rate expression on the basis of stoichiometry of overall balanced equation for the reaction :*

Consider for example, a general reaction :

$$aA + bB \longrightarrow cC + dD$$

where a, b, c and d are stoichiometric coefficients.

According to law of mass action :

$$\text{Rate} = k\,[A]^a\,[B]^b$$

The rate law expression is

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

where x and y are experimentally determined values. These may or may not be equal to the stoichiometric coefficients (a and b) of the reactants.

For example, for the reaction,

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F$$

rate law expression

$$\text{Rate} = k\,[NO_2]\,[F_2] \text{ and}$$

rate expression according to law of mass action

$$\text{Rate} = k\,[NO_2]^2\,[F_2]$$

Similarly, for the reaction :

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

The experimentally observed rate law is

$$\text{Rate} = k\,[Br^-]\,[BrO_3^-]\,[H^+]^2$$

As evident, the rate law does not correspond to stoichiometric coefficients in the balanced chemical equations.

Thus, rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation *i.e.*, theoretically but must be determined experimentally.

It may be noted that generally the rate law expressions are not simple. These may differ even for the same reaction depending upon the conditions of the reaction. For example, for the reaction :

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

$$\text{Rate} = k\ [H_2]\ [I_2]$$

However, for a similar type of reaction :

$$H_2\ (g) + Br_2\ (g) \rightleftharpoons 2HBr$$

The rate expression is

$$\text{Rate} = \frac{k_a[H_2][Br_2]^{1/2}}{1+k_b\{[HBr]/[Br_2]\}}$$

Here k_a and k_b are constants which depend upon the temperature of the reaction. It can be seen that in the absence of HBr, the initial rate of reaction may be given as :

$$\text{Rate} = k_a\ [H_2]\ [Br_2]^{1/2}$$

Rate law expressions for some other reactions are :

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

$$\text{Rate} = k\ [CHCl_3]\ [Cl_2]^{1/2}$$

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k\ [CH_3COOC_2H_5]\ [H_2O]^0$$

The rate expression becomes more complicated especially when a number of parallel reactions take place simultaneously. It may have more than one term on the right hand side.

ORDER OF A REACTION

The dependence of the reaction rates on concentration may be expressed in terms of order of a reaction. To calculate the order of a reaction, we must carry out the experiments to find out the dependence of reaction rate on the concentration of each individual reactant at a given temperature. Moreover, the concentration dependence of various reactants, as we have seen, is given by the rate law. Thus, the **order of a reaction** is defined as :

the sum of the powers to which the concentration terms are raised in the rate law equation to express the observed rate of the reaction.

The power of the concentration of a particular reactant in the rate law is called the **order of the reaction with respect to that reactant.**

Thus, if the rate of a reaction,

$$aA + bB + cC \longrightarrow \text{Products}$$

is given by the rate law as :

$$\text{Rate} = -\frac{dx}{dt} = k[A]^p\ [B]^q\ [C]^r$$

then, the order of the reaction, n, is :

$$n = p + q + r$$

where p, q and r are the orders with respect to individual reactants and overall order of the reaction is sum of these exponents, *i.e.*, $p + q + r$.

When $n = 1$, the reaction is said to be first order reaction, if $n = 2$, the reaction is said to be second order reaction and so on.

Some Examples of Reactions of Different Orders

Some common examples of reactions of different orders are given below :

(*a*) Reactions of first order

(*i*) Decomposition of nitrogen pentoxide (N_2O_5)

$$N_2O_5\ (g) \longrightarrow 2NO_2\ (g) + \frac{1}{2}O_2\ (g)$$

Rate $= k\ [N_2O_5]$

(*ii*) Decomposition of ammonium nitrite in aqueous solution

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Rate = $k\ [NH_4NO_2]$

(*iii*) Decomposition of H_2O_2 in the presence of I^- ions

$$H_2O_2 \xrightarrow{I^-} H_2O + \frac{1}{2}O_2$$

Rate = $k\ [H_2O_2]$

(*iv*) Decomposition of SO_2Cl_2 :

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

Rate = $k\ [SO_2Cl_2]$

(*b*) Reactions of second order

(*i*) Decomposition of nitrogen peroxide

$$2NO_2 \longrightarrow 2NO + O_2$$

Rate = $k\ [NO_2]^2$

(*ii*) Reaction between H_2 and I_2 to give HI

$$H_2 + I_2 \longrightarrow 2HI$$

Rate = $k\ [H_2]\ [I_2]$

(*iii*) Reaction between NO and O_3 :

$$NO + O_3 \longrightarrow NO_2 + O_2$$

Rate = $k\ [NO][O_3]$

(*c*) Reactions of third order

(*i*) Reaction between nitric oxide and oxygen

$$2NO + O_2 \longrightarrow 2NO_2$$

Rate = $k\ [NO]^2\ [O_2]$

(*ii*) Reaction between nitric oxide and Cl_2

$$2NO + Cl_2 \longrightarrow 2NOCl$$

Rate = $k\ [NO]^2\ [Cl_2]$

(*d*) Reactions of fractional order

(*i*) Decomposition of acetaldehyde is a fractional order reaction

$$CH_3CHO \longrightarrow CH_4 + CO$$

Rate = $k\ [CH_3CHO]^{3/2}$ **; Order** = 3/2 or 1.5

(*ii*) The reaction between hydrogen and bromine to form hydrogen bromide is a fractional order reaction

$$H_2(g) + Br_2(g) \longrightarrow 2HBr$$

Rate = $k\ [H_2]\ [Br_2]^{1/2}$ **; Order** = $1+\frac{1}{2} = 1\frac{1}{2}$ or 1.5

(*iii*) Dissociation of $COCl_2$:

$$COCl_2 \longrightarrow CO + Cl_2$$

Rate = $k\ [COCl_2]^{3/2}$, **Order** = $\mathbf{\frac{3}{2}}$

(*e*) Zero order reaction

A number of zero order reactions are known in which the rate of the reaction is independent of the concentration of the reactants. For example, the decomposition of ammonia at the surface of metals like gold, platinum etc., is a zero order reaction.

$$2NH_3 \xrightarrow[1130K]{\text{Platinum}} N_2 + 3H_2$$

It has been observed that the rate of the reaction is independent of the concentration of ammonia, *i.e.*,

$$\textbf{Rate} = -\frac{dx}{dt} = k\ [NH_3]^0 \quad \text{or} \quad \text{Rate} = k$$

Order = 0

In this reaction, platinum metal acts as a catalyst. At sufficiently high pressure of ammonia, the metal surface gets fully saturated with gas molecules. On further increasing the concentration of NH_3, the amount of NH_3 on the surface of the catalyst does not change. Therefore, the rate of

reaction becomes independent of the concentration and hence becomes zero order reaction. Similarly, thermal decomposition of HI on gold surface is also a zero order reaction :

$$2HI \underset{\text{Heat}}{\overset{\text{Gold}}{\rightleftharpoons}} H_2 + I_2$$

Many enzyme catalysed reactions and photochemical reactions (*e.g.*, formation of HCl from H_2 and Cl_2) are also examples of zero order reactions.

Units of reaction rate constants

Units of rate. The rate is the change in concentration with time. Therefore, the rate of reaction is expressed by concentration units divided by time units. If the concentrations are expressed in moles/litre and time in seconds, then the units for rate of a reaction are mol litre^{-1} s^{-1} as :

$$\text{Rate} = \frac{\text{Concentration}}{\text{Time}} = \frac{\text{mol L}^{-1}}{\text{s}} = \text{mol L}^{-1}\ \text{s}^{-1}.$$

Units of rate constant. The units of rate constants of different orders are different. This can be easily illustrated as :

(*i*) Units of rate constant for zero order reaction

For zero order reaction, rate may be expressed as

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

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

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

∴ *The units of rate constant of zero order reaction are* ***mol L^{-1} s^{-1}.***

(*ii*) Units of rate constant for first order reaction

For first order reaction, rate may be expressed as :

$$\text{Rate} = k\,[A]$$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k\,(\text{mol L}^{-1})$$

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

∴ *The units of rate constant of first order reaction are* **s^{-1}.**

(*iii*) Units of rate constant for second order reaction

For second order reaction, the rate may be expressed as

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

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

or $$k = \frac{1}{\text{mol L}^{-1}\text{s}} = \text{L mol}^{-1}\ \text{s}^{-1}.$$

∴ *The units of rate constant for second order reaction are* **L mol^{-1} s^{-1}**.

(*iv*) Units of rate constant for third order reaction

For third order reaction, rate may be expressed as :

$$\text{Rate} = k\,[A]^3$$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k\,(\text{mol L}^{-1})^3$$

or $$k = \frac{1}{\text{mol}^2\,\text{L}^{-2}\,\text{s}} = \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$$

The units of rate constant for third order reaction are **L^2 mol^{-2} s^{-1}.**

> In general, the units for rate constant for the reaction of ***n*th order are :**
>
> $$\text{Rate} = k[A]^n$$
>
> $$\frac{\text{mol L}^{-1}}{\text{s}} = k\,(\text{mol L}^{-1})^n$$
>
> or $$k = (\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}.$$

Units of Rate Constants for Gaseous Reactions

In case of gaseous reactions, the concentrations are expressed in terms of pressure in the units of atmosphere. Therefore, the rate has the units of atm per second. Thus, the unit of different rate constants would be :

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(*i*) Zero order reaction : **atm s^{-1}**
(*ii*) First order reaction : **s^{-1}**
(*iii*) Second order reaction : **atm^{-1} s^{-1}**
(*iv*) Third order reaction : **atm^{-2} s^{-1}** so on.

The units of rate constants for some reactions are summed up below :

Reaction	Units: Solution	Units: Gaseous reactions
Zero order reaction	mol L^{-1} s^{-1}	atm s^{-1}
First order reaction	s^{-1}	s^{-1}
Second order reaction	L mol^{-1} s^{-1}	atm^{-1} s^{-1}
Third order reaction	L^2 mol^{-2} s^{-1}	atm^{-2} s^{-1}
*n*th order	(mol L^{-1})$^{1-n}$ s^{-1}	(atm)$^{1-n}$ s^{-1}

In general, *for the gaseous reaction of* ***n*th order**, the *units of rate constant are* **(atm)$^{1-n}$ s^{-1}**.

MOLECULARITY OF A REACTION

According to 'collision theory,' for a chemical reaction to occur, the reacting molecules must collide with each other.

The number of reacting species (molecules, atoms or ions) which collide simultaneously to bring about a chemical reaction is called **molecularity of a reaction.**

If a reaction involves the decomposition of only a single species, the molecularity is one or it is called unimolecular reaction. For example, the decomposition of hydrogen peroxide involves single species which undergoes the change to form the products. Hence, it is a unimolecular reaction.

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2 \quad \textbf{unimolecular reaction}$$

Decomposition of ammonium nitrite is also unimolecular reaction because it involves only one reacting species :

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Similarly, if the reaction involves the collision of two species, it is **bimolecular** and if three species take part in a collision leading to the formation of the products, it is called **trimolecular** and so on. The examples of bimolecular and trimolecular reactions are given below :

(*i*) Dissociation of hydrogen iodide is a bimolecular reaction because two molecules collide to bring about the reaction.

$$2HI(g) \longrightarrow H_2(g) + I_2(g) \quad \textbf{bimolecular reaction}$$

(*ii*) Combination of NO and O_3 is a bimolecular reaction :

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

(*iii*) The reaction of nitric oxide and oxygen is a trimolecular reaction because it involves collision of three reacting molecules.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad \textbf{trimolecular reaction}$$

In a similar way, we can expect reactions which involve the collisions of four or more molecules. However, it has been observed that reactions involving three or more molecules are uncommon. The reason for this is that the occurrence of such reactions requires the ***simultaneous* collision** of three or more than three molecules. In other words, *simultaneous collision of three molecules means that the third molecule must collide the other two molecules at the same time when they are in the process of collision.* The chances of the occurrence of such collisions are very small. On this basis, we can say that reactions involving three or more than three reacting particles should be slow. However, it has been observed that some reactions involving more than three molecules are quite fast. For example, consider the reaction of bromide ions with bromate ions in the presence of an acid :

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

The experimentally measured rate law for this reaction is given as :

Rate = $k[Br^-]\ [BrO_3^-]\ [H^+]^2$

Therefore, this rate is first order with respect to Br^- and BrO_3^- ion and second order with respect to H^+ ions and the overall order of the reaction is 1 + 1 + 2 = 4. However, from the above equation, it is clear that if the reaction were to take place in a single step, the 12 particles (5 Br^- ions, 1 BrO_3^- ion and 6 H^+ ions) would have to collide simultaneously.

But chances of such events are extremely small, so much so that a reaction which takes place by such collision will not occur at all. However, the reaction is found to be quite fast. This means that even though the balanced equation involves a large number of molecules, yet the reaction does not proceed by simultaneous collision of all these reacting particles. In other words, it involves simultaneous collision of two or at the most three molecules. *Such type of reactions which take place through a sequence of two or more consecutive steps* are called **complex reactions.** *The detailed description of various steps by which reactants change into the products* is called **mechanism of the reaction.** *The steps which contribute to the overall reaction* are called **elementary processes.**

Mechanism and Rate Law

In case of multi-step reactions, since each elementary step involves quite different type of reactions, so each step will occur at its own distinctive rate. Some of the steps will be very fast while others will be slow. If one step takes place much more slowly then all other steps, *it will definitely control the overall reaction rate.* This means that all the steps have to wait for the occurrence of this step and the rate of the reaction cannot be less than the rate of this slowest step. But once this slowest step has occurred, the other steps will take place to form the products.

Thus, the **rate of the reaction** is

the rate of the reaction which is determined by the slowest step in the sequence. The slowest step is called ***rate determining step in the proposed mechanism***.

Let us consider reaction between NO_2 and F_2 to form NO_2F :

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

The experimental observations reveal that the rate of the reaction is proportional to the product of the concentrations of nitrogen peroxide and fluorine. This indicates that the rate determining step in the mechanism of this reaction must be the reaction between NO_2 and F_2 only. Keeping this in mind, a mechanism of this reaction may be suggested as :

$$NO_2 + F_2 \longrightarrow NO_2F + F \quad \text{Slow step}$$
$$NO_2 + F \longrightarrow NO_2F \quad \text{Fast step}$$
$$2NO_2 + F_2 \longrightarrow 2NO_2F \quad \text{Net reaction}$$

Although the above reaction proceeds through two steps but the rate of the overall reaction is determined by the first step which is the slower of the two steps. Each of the steps is called an **elementary process.** Elementary processes are almost always either unimolecular or bimolecular. Occassionally, they may be trimolecular.

All the steps taken together give the **mechanism** of the reaction. The sum of the equations for the separate consecutive steps give the overall reaction. Accordingly, the experimentally observed rate of the reaction is given by the expression :

$$\text{Rate} = -\frac{dx}{dt} = k[NO_2]\ [F_2]$$

This is the **rate law** for the reaction.

Let us consider some more examples :

(*i*) Reaction between NO_2 and CO to form CO_2 and NO

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

The experimental observations reveal that the rate of the reaction is proportional to the square of the concentration of nitrogen peroxide. This

Slowest step as rate determining step

This can be easily understood in terms of a simple **analogy.** Suppose a cycle factory manufactures different parts like handles, paddles, rims, seats, brakes parts etc. at the rate of 500, 600, 50, 800, 400 pieces per day respectively. The overall rate of cycle production cannot be more than 50 per day, which depends upon the slowest working section of the factory (*i.e.,* production of rims).

It may be noted that the mechanism of a reaction may involve the formation of certain molecules in one step which are later used up in the subsequent steps. These molecules are termed **intermediates** and donot appear in the overall reaction.

indicates that the rate determining step in the mechanism of this reaction must be independent of the concentration of CO. Keeping this in mind, a mechanism of the reaction may be suggested as :

Step 1. $NO_2 + NO_2 \longrightarrow NO + NO_3$ Slow step

Step 2. $NO_3 + CO \longrightarrow CO_2 + NO_2$ Fast step

$NO_2 + CO \longrightarrow CO_2 + NO$ Net reaction

Although the above reaction proceeds through two steps but the rate of the overall reaction is determined by the first step which is the slower of the steps. Accordingly, the experimentally observed rate of the reaction is given by the expression :

$$\text{Rate} = k[NO_2]^2$$

This is the rate law for the reaction.

(*ii*) Thermal decomposition of dinitrogen pentoxide,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

It has been found experimentally that

Rate of reaction = $k\ [N_2O_5]$.

If the reaction were to take place by the collisions of two N_2O_5 molecules as indicated by the balanced equation, it would be a second order reaction as

Rate = $k[N_2O_5]^2$

But the observed rate law suggests that it is a first order reaction. This means that the reaction is a complex reaction and proceeds by two or more successive steps.

The probable mechanism of the reaction is as follows :

Step 1. $N_2O_5 \longrightarrow NO_2 + NO_3$ Slow

Step 2. $N_2O_5 + NO_3 \longrightarrow 3NO_2 + O_2$ Fast

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

Hence, the above reaction is unimolecular reaction or reaction of first order.

(*iii*) Reaction of NO and H_2 as :

$$2NO(g) + 2H_2(g) \longrightarrow N_2(g) + 2H_2O(g)$$

It has been observed experimentally that

Rate of reaction = $k[NO]^2\ [H_2]$

The rate law expression suggests that it is a complex reaction and is believed to proceed by two step mechanism in which the first step is the rate determining step as :

Step 1. $2NO(g) + H_2(g) \longrightarrow N_2(g) + H_2O_2$ Slow

Step 2. $H_2O_2(g) + H_2(g) \longrightarrow 2H_2O\ (g)$ Fast

Since the first step is slow and rate determining, the rate law is

Rate = $k[NO]^2\ [H_2]$

(*iv*) Reaction of decomposition of hypochlorite (ClO^-)

$$3ClO^- \longrightarrow ClO_3^- + 2Cl^-$$

The various steps are :

$ClO^- + ClO^- \longrightarrow ClO_2^- + Cl^-$ Slow

$ClO_2^- + ClO^- \longrightarrow ClO_3^- + Cl^-$ Fast

The first step is slow and hence rate determining. Thus, the rate law is

Rate = $k\ [ClO^-]^2$

(*v*) Reaction of decomposition of hydrogen peroxide

The decomposition of H_2O_2 is catalysed by iodide ion in an alkaline medium:

$$2H_2O_2 \xrightarrow[\text{alkaline medium}]{I^-} 2H_2O + O_2$$

The rate of a reaction may depend not only on the reactants but also on the substances present as catalyst. For example, the decomposition of hydrogen peroxide is catalysed by I^- ion in an alkaline medium and the reaction rate depends upon the concentration of both H_2O_2 and I^-.

It has been found experimentally that

Rate = $k\ [H_2O_2]\ [I^-]$

The reaction is first order with respect to both H_2O_2 and I^-. This means that the reaction is a complex reaction and proceeds by two or more successive steps. The probable mechanism for the reaction is as :

$$H_2O_2 + I^- \xrightarrow{\text{slow}} H_2O + IO^-$$

$$H_2O_2 + IO^- \xrightarrow{\text{fast}} H_2O + I^- + O_2$$

Both the steps are bimolecular elementary reactions. Species IO^- is called as an intermediate because it is formed during the course of the reaction but not in the overall balanced equation. Since the first step is slow, it is rate determining. Thus, the rate of formation of intermediate (IO^-) will determine the rate of this reaction.

Let us sum up the important points of distinction between order and molecularity.

Molecularity	Order
1. Molecularity is the number of reacting species undergoing simultaneous collision in the elementary or simple reaction.	Order is the sum of the powers of the concentration terms in the rate law expression.
2. Molecularity is applicable only for elementary reactions. For complex reactions, molecularity has no meaning.	Order is applicable to elementary as well as complex reactions.
3. Molecularity is a theoretical concept.	Order of a reaction is determined experimentally.
4. Molecularity has whole number values only *i.e.*, 1, 2, 3, etc. It cannot be a non-integer.	Order of a reaction need not be a whole number *i.e.*, it can have fractional values also.
5. Molecularity of a reaction cannot be zero.	Order of a reaction can be zero.
6. For complex reactions, molecularity is given for elementary steps. Molecularity of the slowest step is same as the order of the reaction.	For complex reactions, order is given by slowest step.

SOLVED EXAMPLES

Example 7.

(a) Calculate the overall order of a reaction, which has the rate expression :

(i) Rate = $k[A]^{1/2}[B]^{3/2}$ (ii) Rate = $k[A]^{3/2}[B]^{-1}$

(b) The reaction $A + B \longrightarrow C$ has zero order. Write rate equation. **N.C.E.R.T.**

Solution :

(*a*) (*i*) Rate = $k\ [A]^{1/2}\ [B]^{3/2}$

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

i.e., second order.

(*ii*) Rate = $k\ [A]^{3/2}\ [B]^{-1}$

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

i.e., half order.

(*b*) For zero order reaction,

$A + B \longrightarrow C$

Rate equation is :

Rate = $k[A]^0\ [B]^0$

Example 8.

(a) If concentrations of A and B are expressed in terms of mol dm^{-3} and time in min, calculate the units for the rate constant for the following reaction:

$$A + B \longrightarrow AB$$

(b) What are the units for a zero order reaction ? (concentrations are expressed in mol L^{-1} and time in seconds).

Solution :

(*a*) For the reaction,

$$A + B \longrightarrow AB$$

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

$$\frac{\text{mol dm}^{-3}}{\text{min}} = k\ (\text{mol dm}^{-3})\ (\text{mol dm}^{-3})$$

or $k = (\text{mol dm}^{-3})^{-1}\ (\text{min}^{-1}) = \mathbf{mol^{-1}\ dm^3\ min^{-1}}$.

(*b*) For zero order reaction, the rate is independent of the concentration :

$$\text{Rate} = k$$

$\therefore$ Units of k are : $k = \text{Rate} = \dfrac{\text{mol L}^{-1}}{s} = \mathbf{mol\ L^{-1}\ s^{-1}}$.

Example 9.

Write the units of the rate constant for a nth order reaction. Deduce from this the units of rate constant for a (i) half or der reaction (ii) 3/2th order reaction (iii) third order reaction.

Solution : The units of the rate constant for nth order reaction are :

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

$$\frac{\text{mol L}^{-1}}{s} = k[\text{mol L}^{-1}]^n \text{ or } k = (\text{mol L}^{-1})^{1-n}\ \text{s}^{-1}$$

(*i*) $n = \dfrac{1}{2}$, the units are : $\mathbf{mol^{1/2}\ L^{-1/2}\ s^{-1}}$.

(*ii*) $n = \frac{3}{2}$, the units are : $\mathbf{mol^{-1/2}\ L^{1/2}\ s^{-1}}$

(*iii*) $n = 3$, the units are : $\mathbf{mol^{-2}\ L^{2}\ s^{-1}}$.

Example 10.

Identify the reaction order from each of the following rate constants.

(i) $k = 2.3 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$

(ii) $k = 3.2 \times 10^{-4}\ s^{-1}$ **N.C.E.R.T.**

Solution : Order of a reaction can be predicted from the units of rate constant.

(*i*) The unit of second order rate constant is $L\ mol^{-1}\ s^{-1}$ and therefore, $k = 2.3 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$ represents a **second order reaction.**

(*ii*) The unit of a first order rate constant is s^{-1} and therefore, $k = 3.2 \times 10^{-4}\ s^{-1}$ represents a **first order reaction.**

Example 11.

The rate law for a reaction of A, B and C has been found to be rate = k[A][B][C]². How would the rate of reaction change when

(i) concentration of C is doubled

(ii) concentration of A is halved

(iii) concentration of both B and C are doubled

(iv) concentration of each of A, B and C are tripled ?

Solution : Suppose the initial concentrations are :

$[A] = a\ mol\ L^{-1}$, $[B] = b\ mol\ L^{-1}$, $[C] = c\ mol\ L^{-1}$

$$\text{Rate} = k\,abc^2$$

(*i*) New $[C] = 2c$

$$\text{Rate} = k\,ab(2c)^2 = 4kabc^2 \qquad \therefore \text{ 4 times}$$

(*ii*) New $[A] = \frac{a}{2}$

$$\text{Rate} = k\,\frac{a}{2}\,bc^2 = \frac{1}{2}\,kabc^2 \qquad \therefore \text{ 1/2 times}$$

(*iii*) New $[B] = 2b$, $[C] = 2c$

$$\text{Rate} = k \times a \times 2b \times (2c)^2 = 8\,kabc^2 \quad \therefore \text{ 8 times}$$

(*iv*) New $[A] = 3a$, $[B] = 3b$, $[C] = 3c$

$$\text{Rate} = k \times 3a \times 3b \times (3c)^2 = 81\,kabc^2 \qquad \therefore \text{ 81 times}$$

Example 12.

The rate of a gaseous reaction becomes half when volume of the vessel is doubled. What is the order of the reaction ?

Solution : For the gaseous reaction; $A \longrightarrow$ Products

Suppose the order of reaction is n, so that

$$\text{rate} = k[A]^n$$

or $$r = k(a)^n \qquad ...(i)$$

When volume of vessel becomes double, molar concentration becomes half. Since rate becomes half, therefore,

$$\frac{r}{2} = k\left(\frac{a}{2}\right)^n \qquad ...(ii)$$

Dividing eq. (*i*) by eq. (*ii*), $2 = 2^n$

or $2^n = 2^1$

$\therefore$ $n = 1$

$\therefore$ Order = 1

Example 13.

A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is

(i) doubled

(ii) reduced to half ?

Solution : Rate = $k[A]^2$

(D.S.B. 2009, A.I.S.B. 2012, Hr. S.B.2013)

(*i*) When concentration of reactant is doubled, the rate becomes **4 times.**

(*ii*) When concentration is reduced to 1/2, the rate becomes **1/4 times.**

Example 14.

The decomposition of hydrogen peroxide in the presence of iodide ion has been found to be first order in H_2O_2 :

$$2H_2O_2(aq) \xrightarrow{I^-(aq)} 2H_2O(l) + O_2(g)$$

The rate constant has been found to be $1.01 \times 10^{-2}\ min^{-1}$. Calculate the rate of the reaction, when

(a) $[H_2O_2] = 0.4\ mol\ L^{-1}$ (b) $[H_2O_2] = 0.15\ mol\ L^{-1}$

(c) What concentration of $[H_2O_2]$ would give rate of $1.12 \times 10^{-2}\ mol\ L^{-1}\ min^{-1}$? (Pb.S.B. 2011, 2015)

Solution : The reaction is of first order in H_2O_2 so that

$$\text{Rate} = k[H_2O_2]$$

(*a*) $k = 1.01 \times 10^{-2}\ min^{-1}$, $[H_2O_2] = 0.4\ mol\ L^{-1}$

$\therefore$ Rate $= (1.01 \times 10^{-2}\ min^{-1}) \times (0.4\ mol\ L^{-1})$

$= \mathbf{4.04 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}}$.

(*b*) When $[H_2O_2] = 0.15\ mol\ L^{-1}$

Rate $= (1.01 \times 10^{-2}\ min^{-1}) \times (0.15\ mol\ L^{-1})$

$= \mathbf{1.5 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}}$.

(*c*) To obtain concentration of H_2O_2 when rate

$= 1.12 \times 10^{-2}\ min\ L^{-1}\ min^{-1}$

$$[H_2O_2] = \frac{\text{Rate}}{k} = \frac{1.12 \times 10^{-2}\ mol\ L^{-1}\ min^{-1}}{1.01 \times 10^{-2}\ min^{-1}}$$

$= \mathbf{1.11\ mol\ L^{-1}}$.

Example 15.

For the reaction

$$2A + B + C \longrightarrow A_2B + C$$

The rate law has been found to be

Rate = k[A] [B]² with $k = 2.0 \times 10^{-6}\ mol^{-2}\ L^2\ s^{-1}$

For this reaction, determine the initial rate of reaction with [A] = 0.1 mol L⁻¹, [B] = 0.2 mol L⁻¹, [C] = 0.8 mol L⁻¹. Determine the rate after 0.04 mol L⁻¹ of A has been reacted.

Solution : Rate law is :

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

where $k = 2.0 \times 10^{-6}\ mol^{-2}\ L^2\ s^{-1}$

Initial concentration,

$[A] = 0.1\ mol\ L^{-1}$, $[B] = 0.2\ mol\ L^{-1}$, $[C] = 0.8\ mol\ L^{-1}$

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

$= 8 \times 10^{-9}\ mol\ L^{-1}\ s^{-1}$

Conc. of A after 0.04 mol L⁻¹ of A has been reacted

$[A] = 0.1 - 0.04 = 0.06\ mol\ L^{-1}$

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Now, we know that when 2 moles of A are consumed then one mole of B gets consumed. Therefore, moles of B consumed when 0.04 moles of A have been consumed = 0.04 × ½ = 0.02 mole

$\therefore$ [B] = 0.2 – 0.02 = 0.18 mol L^{-1}

Rate = (2.0 × 10^{-6} mol^{-2} L^2 s^{-2}) × (0.06 mol L^{-1}) × (0.18 mol L^{-1})^2

= **3.89 × 10^{-9} mol L^{-1} s^{-1}.**

❑ **Example 16.**

Following reaction takes place in one step :

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

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 reduced volume ?

(A.I.S.B. 2004)

Solution : Before the volume of the reaction vessel is changed, the rate of reaction is expressed as :

$$\text{rate} = k[NO]^2[O_2] \quad ...(i)$$

When the volume is reduced to $\frac{1}{3}$, the concentration of each reactant is increased by 3 times. Therefore, we may write

$$\text{rate}' = k[3NO]^2[3O_2] \quad ...(ii)$$

$$= 27\,k[NO]^2[O_2]$$

$$\therefore \quad \frac{\text{rate}'}{\text{rate}} = 27$$

$\therefore$ Rate will become 27 times.

It is clear from eqn. (*ii*) that the order of reaction remains the same.

Practice Problems

8. The rate of formation of a second order dimerisation reaction is 5.8 × 10^{-6} mol L^{-1} s^{-1} at 0.01 mol L^{-1} monomer concentration. Calculate the rate constant.

9. The gas phase decomposition of $COCl_2$,

$$COCl_2(g) \longrightarrow CO(g) + Cl_2(g)$$

follows the rate law : rate = $k[COCl_2]^{3/2}$

What are the units of its rate constant ?

10. Identify the reaction order for each of the following rate constants :

(*a*) k = 7.6 × 10^{-4} mol $liter^{-1}$ s^{-1} (*b*) k = 5.6 × 10^{-3} mol^{-1} litre s^{-1}

(*c*) k = 7.1 × 10^{-5} s^{-1} (*d*) k = 1.25 × 10^{-2} mol^{-2} $litre^2$ s^{-1}

(*e*) k = 5.0 × 10^{-6} atm^{-1} s^{-1}

11. For a reaction : A + B ⟶ Products,

the rate is given as $k[A]^{1/3}[B]^2$. What are the units of its rate constant ?

12. The rate law for a reaction is found to be :

Rate = k $[NO_2^-][I^-][H^+]^2$

How would the rate of reaction change when

(*i*) concentration of I^- is halved

(*ii*) concentration of H^+ is doubled

(*iii*) concentration of each of NO_2^-, I^- and H^+ are tripled ?

13. For the reaction : 2A ⟶ A_2,

the rate of reaction becomes 27 times when the concentration of A is increased three times. What is the order of the reaction ? *(D.S.B. 2004 C)*

14. For a reaction X ⟶ Y, the rate of reaction increases by a factor of 1.857 when the concentration of X is increased by 1.5 times. What is the order of reaction with respect of X ?

15. The decomposition of N_2O_5 in carbon tetrachloride solution has been found to be first order with respect to N_2O_5 with rate constant, k = 6.2 × 10^{-4} s^{-1}

$$N_2O_5\,(\text{solution}) \longrightarrow 2NO_2\,(\text{solution}) + \tfrac{1}{2}O_2(g)$$

Calculate the rate of the reaction when

(*i*) [N_2O_5] = 2.50 mol L^{-1}

(*ii*) [N_2O_5] = 0.50 mol L^{-1}

(*iii*) What concentration of N_2O_5 would give a rate of 4.2 × 10^{-3} mol L^{-1} s^{-1} ?

16. The rate of a reaction : *(Pb.S.B. 2011, 2015)*

$$2A + B \longrightarrow A_2B$$

has the rate law : rate = $k[A]^2$, with rate constant equal to 0.50 mol^{-1} L s^{-1}. Calculate the rate of the reaction when

(*i*) [A] = 0.60 mol L^{-1}, [B] = 0.05 mol L^{-1} and

(*ii*) when concentration of A and B have been reduced to 1/4. *(Pb.S.B. 2015)*

Answers to Practice Problems

8. 5.8 × 10^{-2} mol L^{-1} s^{-1}

9. $atm^{-1/2}$ s^{-1}

10. (*a*) zero (*b*) second (*c*) first (*d*) third (*e*) second.

11. $mol^{-4/3}$ $L^{4/3}$ s^{-1}.

12. (*i*) halved (*ii*) 4 times (*iii*) 81 times.

13. 3.

14. 1.5.

15. (*i*) 1.55 × 10^{-3} mol L^{-1} s^{-1}, (*ii*) 3.1 × 10^{-4} mol L^{-1} s^{-1}, (*iii*) 6.77 mol L^{-1}.

16. (*i*) 0.18 mol L^{-1} s^{-1}, (*ii*) 0.11 mol L^{-1} s^{-1}.

Hints & Solutions on page 68

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Advanced Level PROBLEMS

Accelerate Your Potential (for JEE Advance)

Problem 1. **Ammonia decomposes as :**

$$2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$$

The rate of reaction can be expressed as :

$$\frac{d[NH_3]}{dt} = k_1[NH_3], \quad \frac{d[N_2]}{dt} = k_2[NH_3] \text{ and}$$

$$\frac{d[H_2]}{dt} = k_3[NH_3]$$

Derive relationship between k_1, k_2 and k_3.

Solution The rate of the reaction is given by

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

Substituting the given values,

$$\frac{1}{2}k_1[NH_3] = k_2[NH_3] = \frac{1}{3}k_3[NH_3]$$

or $\frac{1}{2}k_1 = k_2 = \frac{1}{3}k_3$

if $k_2 = 1$, then $k_1 = 2$ and $k_3 = 3$

$\therefore$ $k_1 : k_2 : k_3 : = 2 : 1 : 3$

add on Conceptual Questions 1

CONCEPTUAL QA

Q. 1. Is there any reaction for which reaction rate does not decrease with time ?

Ans. For a zero order reaction, the reaction rate does not decrease with time because it is independent of concentration of the reactants.

Q. 2. How will rate of a reaction change when $[A]_0$ is doubled and tripled for

(*i*) zero order reaction

(*ii*) second order reaction ?

Ans. When $[A]_0$ is doubled

(*i*) the rate of zero order reaction remains unchanged.

(*ii*) the rate of second order reaction becomes four times.

When $[A]_0$ is tripled.

(*i*) the rate of zero order reaction remains unchanged

(*ii*) the rate of second order reaction becomes 9 times.

Q. 3. Why is the use of instantaneous rate of reaction preferred over average rate of reaction ?

Ans. The rate of reaction continuously decreases with time (except for zero order reaction) and therefore, average rate has no significance for the reaction.

Q. 4. What is the order of a reaction whose rate constant has same units as the rate of the reaction ?

Ans. Zero order reaction. ***(H.P.S.B. 2010)***

Q. 5. State the order with respect to each reactant and overall order for the following reaction:

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

Rate = k [NOBr]^2

What are the units of rate constant? ***(Pb.S.B. 2016)***

Ans. Order w.r.t. NOBr = 2

Overall order = 2

Units of rate constant = $mol^{-1}\ L\ s^{-1}$

Q. 6. A reaction is found to be zero order. Will its molecularity be zero ? ***(H.P.S.B. 2010)***

Ans. No, molecularity of a reaction cannot be zero.

Q. 7. The rate of a reaction is equal to rate constant of the reaction. Mention the order of the reaction. ***(Assam S.B. 2016)***

Ans. Zero order reaction.

Q. 8. How is rate constant related to concentration of the reactants ?

Ans. Rate constant does not depend upon the concentration of the reactants.

Q. 9. For a reaction : $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$

Rate = k

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

(*ii*) Write the unit of k. ***(A.I.S.B. 2016, D.S.B 2016)***

Ans. $2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$

Rate = k

(*i*) Order of reaction : Zero order

Molecularity = 2 (bimolecular)

(*ii*) Unit of k = $mol\ L^{-1}\ s^{-1}$ or $atm\ s^{-1}$

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Q. 10. Identify the order of a reaction from each of the following rate constants : *(H.P.S.B. 2010)*

(*i*) $k = 2.3 \times 10^{-5}$ L mol^{-1} s^{-1} (*ii*) $k = 3.1 \times 10^{-4}$ s^{-1} (*iii*) $k = 9.3 \times 10^{-4}$ mol L^{-1} s^{-1}

Ans. Order can be predicted by the inspection of units of rate constant

(*i*) second order reaction (*ii*) first order reaction (*iii*) zero order reaction

Q. 11. For the reaction : Ester + H^+ $\longrightarrow$ Acid + Alcohol, rate = k [Ester] $[H^+]^0$. Find the order of reaction. *(Pb. S.B. 2005)*

Ans. Order = 1

Q. 12. For the assumed reaction : $X_2 + 2Y_2 \longrightarrow 2XY_2$, write the rate equation in terms of the rate of disappearance of Y_2.

Ans. $\frac{1}{2}\frac{d[Y_2]}{dt} = k\,[X_2]\,[Y_2]^2$; $\frac{d[Y_2]}{dt} = 2k\,[X_2]\,[Y_2]^2$

Q. 13. For the reaction : $Cl_2(g) + 2NO\,(g) \longrightarrow 2NOCl(g)$
The rate law is expressed as rate = $k[NO]^2\,[Cl_2]$
What is the overall order of the reaction ? *(D.S.B. 2007)*

Ans. Overall order = 1 + 2 = 3.

Q. 14. Express the rate of the following reaction in terms of disappearance of hydrogen in the following reaction : $3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$ *(A.I.S.B. 2007)*

Ans. Rate $= -\frac{1}{3}\frac{d[H_2]}{dt}$

Q. 15. The decomposition reaction of ammonia gas on platinum surface has a rate constant, $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}. What is the order of the reaction ? *(C.B.S.E. Sample Paper 2007)*

Ans. According to units of rate constant; it is a zero order reaction.

Q. 16. What is the molecularity of the reaction :

$$Cl \longrightarrow \frac{1}{2}\,Cl_2(g)\ ?$$ *(C.B.S.E. Sample Paper 2007)*

Ans. Unimolecular.

Q. 17. The decomposition of NH_3 on platinum surface, $2NH_3\,(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$ is a zero order reaction with k = 2.5×10^{-4} Ms^{-1}. What are the rates of production of N_2 and H_2 ? *(D.S.B. 2007; 2008)*

Ans. Rate $= -\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = k = 2.5 \times 10^{-4}$ Ms^{-1}

Rate of production of N_2 $\frac{d[N_2]}{dt} = 2.5 \times 10^{-4}$ Ms^{-1}

$\frac{1}{3}\frac{d[H_2]}{dt} = 2.5 \times 10^{-4}$ Ms^{-1}

Rate of production of H_2 $\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4} = 7.5 \times 10^{-4}$ Ms^{-1}

Q. 18. If the concentration be expressed in mol L^{-1} units and time in seconds, what would be units for rate constant, k (*i*) for a zero order reaction (*ii*) for a first order reaction *(D.S.B. 2008)*

Ans. (*i*) For a zero order reaction, Rate $= k[A]^0$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k \times 1 \quad \text{or} \quad k = \text{mol L}^{-1}\,\text{s}^{-1}$$

(*ii*) For a first order reaction, Rate $= k[A]$

$$\frac{\text{mol L}^{-1}}{\text{s}} = k\ \text{mol L}^{-1} \quad \text{or} \quad k = \text{s}^{-1}$$

Q. 19. Identify the order of a reaction if the units of its rate constant are :

(*i*) L^{-1} mol s^{-1} (*ii*) L mol^{-1}s^{-1} *(A.I.S.B.2011)*

Ans. (*i*) Zero order (*ii*) Second order

Q. 20. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half ? What is the unit of rate constant for such a reaction ? *(A.I.S.B. 2011)*

Ans. For a second order reaction, Rate $= k[A]^2$

If the concentration of A is reduced to half, rate will become 1/4 of the original value.

Units of k

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

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

CONCEPTUAL QA

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Q. 21. In the reaction : $aA + bB \longrightarrow$ products; if concentration of A is doubled (keeping B constant), the initial rate becomes four times and if B is doubled (keeping A constant), the rate becomes double. What is the rate law equation and order of the reaction? *(Manipur S.B. 2012)*

Ans. Rate = $k[A]^2 [B]$, Order = 1 + 2 = 3.

Q. 22. The rate constant of a reaction is 3×10^2 min^{-1}. What is the order of reaction ? *(Assam. S.B. 2012)*

Ans. Order = 1 (from units of rate constant).

Q. 23. For a reaction : $A + B \longrightarrow P$, the rate law is given by, $r = k [A]^{1/2} [B]^2$. What is the order of reaction ? *(A.I.S.B. 2013)*

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

Q.24. For a reaction, rate law is give as rate = $k[A] [B]^{1/2}$. Can the reaction be an elementary reaction ? Explain. *(Pb. S.B. 2009)*

Ans. For an elementary reaction, order of a reaction should be equal to molecularity of the reaction and molecularity should be integral. For the given reaction, order of reaction is $\frac{3}{2}\left(1+\frac{1}{2}\right)$. Since molecularity cannot be fractional, therefore, for the given reaction, order is not equal to molecularity. Hence, given reaction cannot be elementary reaction.

Q.25. The rate of formation of a dimer in a second order reaction is 9.5×10^{-5} mol L^{-1} s^{-1} at 0.01 mol L^{-1} monomer concentration. Calculate the rate constant.

Ans. If the monomer is represented by X. Then,

$$2X \longrightarrow (X)_2$$

Since the reaction is of second order, the rate of reaction will be given by:

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

$$\therefore \quad \text{Rate} = -\frac{1}{2}\frac{d[X]}{dt} = +\frac{d[X_2]}{dt} = 9.5 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\therefore \quad 9.5 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1} = k(0.01 \text{ mol L}^{-1})^2$$

$$\therefore \quad k = \frac{9.5 \times 10^{-5}}{(0.01)^2} = 0.95 \text{ L mol}^{-1} \text{ s}^{-1}.$$

INTEGRATED RATE EXPRESSION

We have learnt that for a general reaction:

$$aA + bB \longrightarrow cC + dD$$

rate may be expressed as :

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

This form of equation is called *differential rate equation.* It is not always convenient to measure the instantaneous rate because it is measured by determination of slope of the tangent at point *'t'* in the concentration versus time graph. Therefore, it is difficult to determine the rate law and hence order of the reaction. In order to solve this problem, we can integrate the rate equation and obtain integrated rate equation which gives a relation between directly measured experimental quantities *i.e.,* concentrations at different times and rate constant. The integrated rate equations are different for reactions of different orders.

The integrated rate equations for different order reactions can be derived as given below :

Zero order reaction

A reaction is said to be of zero order, if its rate does not depend on the concentration of any of the reactants. Consider the general zero order reaction :

$$R \longrightarrow \text{Product}$$

Let [R] be the concentration of the reactant R and k is the rate constant for the zero order reaction. For the zero order reaction, the rate of the reaction is proportional to zero power of the concentration of R. Thus,

$$\text{Rate} = -\frac{d[R]}{dt} = k\,[R]^0 = k \times 1 \qquad (\because [R]^0 = 1)$$

$$\text{or} \qquad d[R] = -k.dt \qquad ...(4)$$

Integrating both sides, we get

$$\int d[R] = -k \int dt$$

$$[R] = -kt + I \quad ...(5)$$

where I is the constant of integration. The value of I can be calculated from the initial concentration. For example, the initial concentration of R be $[R]_0$ at $t = 0$. Then equation becomes

$$[R]_0 = -k \times 0 + I$$

or $$I = [R]_0$$

Substituting the value of I in Eqn. (5), we get

$$[R] = -kt + [R]_0 \quad ...(6)$$

Further simplifying the above equation, we get the rate constant, k as

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

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

where $[R]_0$ is the initial concentration of R, [R] is the concentration at time t. From this, rate constant, k can be calculated.

Alternatively, if the initial concentration of R is 'a' moles per litre and let x moles of reactants get changed to products in time t. Then, concentration of R left after time t be $(a - x)$.

$$R \longrightarrow \text{Products}$$
$$a \qquad 0$$
$$a - x \qquad x$$

$\therefore$ $[R]_0 = a$, $[R] = a - x$ so that

$$[R]_0 - [R] = a - (a - x) = x$$

Thus, Eq. 6 becomes

$$k = \frac{x}{t} \quad \text{or} \quad x = kt$$

The above equation is integrated rate equation for zero order reactions. *The amount of the substance reacted is proportional to the time.*

Time taken for a zero order reaction to complete

When the reaction is complete,

$$[R] = 0$$

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

or $$t_{100\%} = \frac{[R]_0}{k}$$

Graphical representation of zero order reactions

(*i*) The differential rate law for zero order reaction is given as

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

The plot of rate versus [R] at different times is a horizontal straight line as shown in Fig. 4.

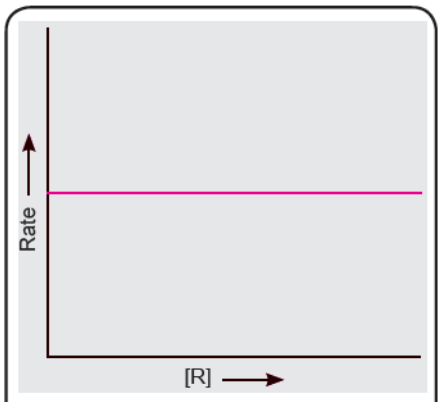

Fig. 4. Plot of rate versus [R] at different times for a zero order reaction.

(*ii*) The integrated rate law for zero order reaction is given by Eqn. 6 as:

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

The equation has the form of linear equation, $y = mx + c$. The plot of [R] versus time (t) is a straight line as shown in Fig. 5. **The slope** of the straight line is equal to $-k$ and **intercept** on [R] axis is $[R]_0$.

In general, the rate of decomposition of ammonia is given as :

$$\text{Rate} = \frac{k_1[NH_3]}{1 + k_2[NH_3]} \quad ...(7)$$

where k_1 and k_2 are constants. When $[NH_3]$ is very low, $k_2[NH_3]$ can be neglected in comparison to unity so that the above equation becomes :

$$\text{Rate} = k_1 [NH_3]$$

This reaction is first order in ammonia.

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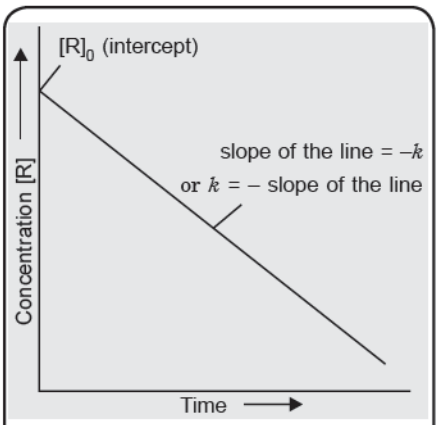

Fig. 5. Variation of concentration of a reactant with time for a zero order reaction.

At higher concentration of ammonia (high pressure), we may neglect 1 as compared to $[NH_3]$ so that the equation 7 becomes :

$$\text{Rate} = \frac{k_1[NH_3]}{k_2[NH_3]} = \frac{k_1}{k_2} = k$$

$\therefore$ Rate = $k\ [NH_3]^0$

This means that rate becomes constant and independent of $[NH_3]$ and therefore, becomes **zero order reaction**.

First order reaction

Consider the general first order reaction

$$R \longrightarrow \text{Products}$$

Let [R] is the concentration of the reactant R and k *is* the rate constant for the first order reaction. For the first order reaction, the rate of the reaction is directly proportional to the concentration of the reactant R. Thus,

$$\text{Rate} = -\frac{d[R]}{dt} = k[R] \qquad ...(8)$$

This form of rate law is known as *differential rate equation*. Rearranging the above equation :

$$\frac{d[R]}{[R]} = -k\,dt \qquad ...(9)$$

Integrating the above equation, we get

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

$$ln\ [R] = -kt + I \qquad ...(10)$$

where I is the constant of integration. The value of I can be calculated from the initial concentration. For example, the initial concentration of R be $[R]_0$ at $t = 0$. Then Eq. (10) becomes

$$ln\ [R]_0 = -k \times 0 + I$$

$$\therefore \quad I = ln\ [R]_0$$

Substituting the value of I in Eqn. (10), we get

$$ln\ [R] = -kt + ln\ [R]_0 \qquad ...(11)$$

Rearranging,

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

or

$$ln\ \frac{[R]_0}{[R]} = kt$$

or

$$k = \frac{1}{t}\, ln\, \frac{[R]_0}{[R]} \qquad ...(12)$$

Eqn. (12) is **integrated rate expression** for the first order reaction.

Changing the above expression to log base 10 ($ln\ x = 2.303 \log x$), we get

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \qquad ...(13)$$

If we perform the experiment at two different times t_1 and t_2 having concentrations $[R]_1$ and $[R]_2$ respectively, then from equation (11)

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$$ln\ [R]_1 = -kt_1 + ln\ [R]_0$$
$$ln\ [R]_2 = -kt_2 + ln\ [R]_0$$

Subtracting we get

$$ln\ [R]_1 - ln\ [R]_2 = -kt_1 - (-kt_2) = k\ (t_2 - t_1)$$

or $$ln \frac{[R]_1}{[R]_2} = k\ (t_2 - t_1)$$

or $$k = \frac{1}{(t_2 - t_1)} ln \frac{[R]_1}{[R]_2}$$

or $$k = \frac{2.303}{(t_2 - t_1)} \log \frac{[R]_1}{[R]_2} \quad ...(14)$$

The equation (12) may also be written in the exponential form as :

$$ln \frac{[R]_0}{[R]} = kt \quad \text{or} \quad ln \frac{[R]}{[R]_0} = -kt$$

Taking antilog of both sides

$$\frac{[R]}{[R]_0} = e^{-kt}$$

$\therefore$ $$[R] = [R]_0\ e^{-kt}$$

The equation (13) may also be written in an alternate form. Let the initial concentration of R is 'a' moles per litre. Suppose in time t, x moles of reactants get changed to products. Then the concentration of R left after time t is $a - x$. Therefore,

$$[R]_0 = a \text{ and } [R] = a - x$$

Thus, Eq. (13) becomes

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \quad ...(15)$$

Significance of Integrated Rate Equation

The integrated rate equation can be used in the following ways :

***(i)* Order of reaction.** All reactions of first order obey the following equation :

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad ...(16)$$

Starting with the known concentration of R, the concentration of the reactant [R], at different intervals of time (t) may be measured. The values of [R] at different time intervals are substituted in the above equation. If the value of k comes out to be constant, then the reaction is of first order.

***(ii)* Calculation of rate constant.** The integrated rate equation can be used to calculate the rate constant of a reaction. If the reaction is known to be of first order, then by substituting the initital concentration of reactant $[R]_0$ and concentrations at different times (t) in Eq. 13, the value of k can be calculated.

The rate constant can also be calculated graphically. The Eq. (13) may be written as

$$\frac{kt}{2.303} = \log \frac{[R]_0}{[R]} \quad ...(17)$$

or $$\frac{kt}{2.303} = \log [R]_0 - \log [R]$$

or $$\log [R] = -\frac{k}{2.303} t + \log [R]_0 \quad ...(18)$$

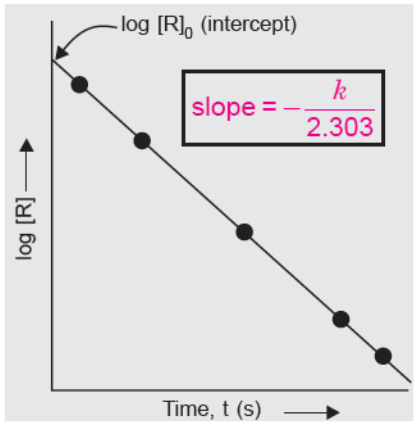

Fig. 6. Plot of t versus log [R] to calculate rate constant for the first order reactions.

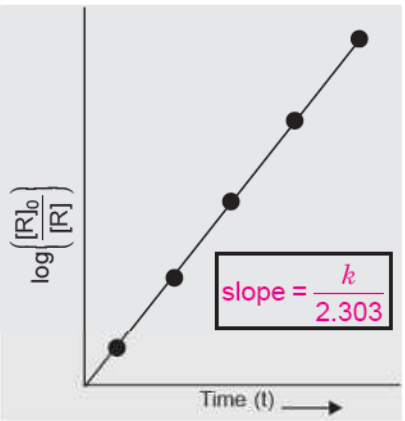

Fig. 7. Plot of log $[R]_0/[R]$ vs t for a first order reaction.

For the **second order** rate law, there are two cases :

(*i*) The reaction is second order in only one reactant :

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

(*ii*) The reaction is first order in two different species :

$$\text{rate} = k\,[A][B]$$

In second order reactions with only one reactant, the integrated rate law is

$$\frac{1}{[R]} = kt + \frac{1}{[R]_0}$$

or

$$k = \frac{1}{t}\left[\frac{1}{[R]} - \frac{1}{[R]_0}\right]$$

This equation is comparable to equation of a straight line ($y = mx + c$). When a graph is plotted between log [R] and time t at different intervals of time we get a straight line. This is shown in Fig. 6.

The slope of this line is equal to

$$\boxed{\text{Slope} = -\frac{k}{2.303}}$$

From this, rate constant k, can be calculated.

Alternatively, if we write the equation (17) as

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

The plot of $\log\frac{[R]_0}{[R]}$ vs t will give a straight line with slope $= \frac{k}{2.303}$

This is shown in Fig. 7.

Hydrogenation of ethene is an example of first order reaction.

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

$$\text{Rate} = k\,[C_2H_4]$$

Decomposition of N_2O_5 and N_2O also follow first order kinetics.

Integrated Rate Equation for a Typical First Order Gas Phase Reaction

Let us consider a typical first order reaction in gaseous phase :

$$A(g) \longrightarrow B(g) + C(g)$$

Let p_i be the initial pressure of A and p_t be the total pressure at time t.

Integrated rate equation may be written as :

$$k = \frac{2.303}{t}\log\frac{p_i}{p_A} \quad \text{...(19)}$$

where p_A is the partial pressure of A at time t. The partial pressure of A can be derived as follows :

Total pressure, p_t will be

$$p_t = p_A + p_B + p_C$$

where p_A, p_B and p_C are the partial pressures of A, B and C respectively. Let the pressure of A decreases by x atm after time t. Since one mole of B and C are formed from 1 mole of A, then increase in pressure of B and C will also be x atm each as :

	$A(g)$	$\longrightarrow B(g)$	$+ \quad C(g)$
At $t = 0$	p_i atm	0	0
At time t	$(p_i - x)$ atm	x atm	x atm

Now, $p_t = (p_i - x) + x + x = p_i + x$

or $x = p_t - p_i$

Now, at time t, $p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$

Substituting in Eqn. (19) we get

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

Knowing the values of p_i and p_t, k can be calculated. However, it may be noted that the relation will depend upon the reaction.

SOLVED EXAMPLES

Example 17.

The rate constant for a reaction of zero order in A is 0.0030 mol $L^{-1}s^{-1}$. How long will it take for the initial concentration of A to fall from 0.10 M to 0.075 M

(D.S.B. 2010)

Solution : For a zero order reaction,

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

$$[A]_o = 0.10 \text{ M}, [A] = 0.075 \text{ M}$$

$$k_0 = \frac{[A]_0 - [A]}{t}$$

$$t = \frac{[A]_0 - [A]}{k} = \frac{0.10 - 0.075}{0.0030} = 8.33 \text{ s.}$$

Example 18.

The decomposition of N_2O_5 at 318 K according to the following equation follows first order reaction :

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2} O_2(g)$$

The initial concentration of N_2O_5 was 1.24×10^{-2} mol L^{-1} and that after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

N.C.E.R.T. *(Meghalaya S.B. 2015)*

Solution : For a first order reaction

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

t = 60 min. $[R]_0 = 1.24 \times 10^{-2}$ mol L^{-1},

$[R] = 0.20 \times 10^{-2}$ mol L^{-1}

$$k = \frac{2.303}{60} \log \frac{1.24 \times 10^{-2} \text{ mol L}^{-1}}{0.20 \times 10^{-2} \text{ mol L}^{-1}}$$

$$= \frac{2.303}{60} \log 6.2 = \frac{2.303}{60} \times 0.7924$$

$$= \mathbf{0.0304\ min^{-1}}$$

Example 19.

The decomposition of a compound is found to follow first order rate law. If it takes 15 minutes for 20 per cent of original material to react, calculate

(i) the specific rate constant

(ii) the time at which 10 per cent of the original material remains unreacted

(iii) the time it takes for the next 20 per cent of the reactant left to react after first 15 minutes.

(D.S.B. 2002)

Solution : (*i*) For the first order reaction :

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

Let $[A]_0 = 100$, $[A] = 100 - 20 = 80$

$$\therefore \quad k = \frac{2.303}{15} \log \frac{100}{80}$$

$$= \frac{2.303}{15} \times 0.0969 = \mathbf{0.0149\ min^{-1}}$$

(*ii*) If $[A]_0 = 100$, and $[A] = 10$, then

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

$$= \frac{2.303}{0.0149} \log \frac{100}{10} = \mathbf{154.6\ min}$$

(*iii*) If $[A]_0 = 80$, $[A] = 80 - \frac{80 \times 20}{100} = 64$

$$t = \frac{2.303}{0.0149} \log \frac{80}{64}$$

$$= \frac{2.303}{0.0149} \times 0.0969 = \mathbf{15.0\ min.}$$

Example 20.

The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at constant volume,

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

S.No.	*Time (s)*	*Total pressure (atm)*
1.	*0*	*0.5*
2.	*100*	*0.512*

Calculate the rate constant. **N.C.E.R.T.**

Solution : Let the pressure of N_2O_5 decreases by $2x$ atm. Since 2 moles of N_2O_5 decompose to give 2 moles of N_2O_4 and 1 mole of O_2, then the pressure of $N_2O_4(g)$ increases by $2x$ atm and that of $O_2(g)$ increases by x atm.

	$2N_2O_5(g)$	$\longrightarrow 2N_2O_4(g)$	$+ \ O_2(g)$
At time, $t = 0$	0.5 atm	0	0
At time t (100 s)	$(0.5 - 2x)$ atm	$2x$ atm	x atm

Total pressure, $p_t = (0.5 - 2x) + 2x + x = 0.5 + x$

or $x = p_t - 0.5$

$t = 100$ s, $p_t = 0.512$ atm

or $x = p_t - 0.5 = 0.512 - 0.5 = 0.012$ atm

Now, $p(N_2O_5) = 0.5 - 2x = 0.5 - 2 \times 0.012 = 0.476$ atm

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{p(N_2O_5)_0}{p(N_2O_5)_t} = \frac{2.303}{100} \log \frac{0.5 \text{ atm}}{0.476 \text{ atm}}$$

$$= \frac{2.303}{100} \log 1.0504 = \frac{2.303}{100} \times 0.0214$$

$$= \mathbf{4.93 \times 10^{-4}\ s^{-1}}$$

Example 21.

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

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Experiment	*Times / s*	*Total pressure / atm*
1	*0*	*0.5*
2	*100*	*0.6*

Calculate the rate of reaction when total pressure is 0.65 atm. *(CBSE Sample Paper 2011)*

Solution : For the decomposition of SO_2Cl_2

	$SO_2Cl_2(g)$	$\longrightarrow SO_2(g)$	$+ \ Cl_2(g)$
At $t = 0$	p_0 atm	0	0
At time t	$(p_0 - x)$atm	x	x

$$p_t = p_0 - x + x + x = p_0 + x$$

or $x = p_t - p_0$

Now at time t, $p(SOCl_2) = p_0 - x = p_0 - (p_t - p_0) = 2p_0 - p_t$

$$\therefore \quad k = \frac{2.303}{t} \log \frac{p_0}{2p_0 - p_t}$$

when $t = 100$ s

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

$$= 2.2316 \times 10^{-3}\ s^{-1}$$

When $p_t = 0.65$ atm *i.e.* $p_0 + p = 0.65$ atm

$p = 0.65 - p_0 = 0.65 - 0.50 = 0.15$ atm

$\therefore$ Pressure of SO_2Cl_2 at time t = 0.50 − 0.15

= 0.35 atm

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

$= \mathbf{7.8 \times 10^{-5}\ atm\ s^{-1}}$

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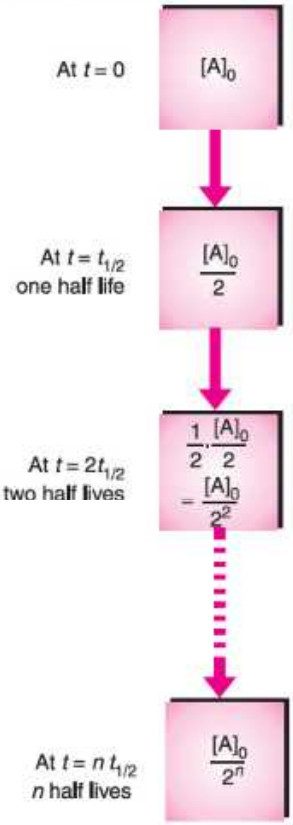
For a first order reaction



REMEMBER

Thus, the time required to reach the concentration values $[A]_0/2$, $[A]_0/4$, $[A]_0/8$, $[A]_0/16$, $[A]_0/32$... are $t_{1/2}$, $2t_{1/2}$, $3t_{1/2}$, $4t_{1/2}$, $5t_{1/2}$... respectively

REMEMBER

It is clear from the above illustration that for a first order reaction: The amount of substance left after ***n* half life periods** is given as :

$$[A] = [A]_0 \left(\frac{1}{2}\right)^n \text{ or } \frac{[A]}{[A]_0} = \left(\frac{1}{2}\right)^n$$

e.g., if half life period of a substance is 10 min, then time taken to reduce its concentration to 1/16 of its original value can be calculated as :

$$\left(\frac{1}{2}\right)^n = \frac{1}{16} \text{ or } \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^4 \text{ or } n = 4$$

i.e., 4 half life periods.

$\therefore$ Time taken = 10 × 4 = 40 min.

Alternatively, if we want to calculate the amount of substance left after 40 min. *i.e.*, 4 half life periods, then

$$\frac{[A]}{[A]_0} = \left(\frac{1}{2}\right)^4 = \frac{1}{16}$$

i.e., its concentration is reduced to $\frac{1}{16}$th of its original value.

HALF LIFE PERIOD OF A REACTION

Half life period of a reaction is defined as

the time during which the concentration of a reactant is reduced to half of its initial concentration.

In other words, it may also be stated as the time in which half of a reaction is completed. It is generally denoted as $t_{1/2}$. The half life period for different order reactions may be calculated as given below :

Half life period for zero order reaction

For a zero order reaction,

$$A \longrightarrow \text{Products}$$

the rate constant is given as

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

Now, half life period corresponds to time during which the initial concentration, $[A]_0$ is reduced to half, i.e.,

At $t = t_{1/2}$, $[A] = [A]_0/2$

$$\therefore \quad k = \frac{[A]_0 - [A]_0/2}{t_{1/2}} = \frac{[A]_0}{2t_{1/2}}$$

$$\text{or} \quad t_{1/2} = \frac{[A]_0}{2k}$$

It is clear that $t_{1/2}$ for a zero order reaction is ***directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.***

Half life period for first order reaction

The first order rate equation for the reaction :

$$A \longrightarrow \text{Products is :}$$

$$kt = 2.303 \log \frac{[A]_0}{[A]}$$

$$\text{or} \quad t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

Now, half life period corresponds to time during which the initial concentration, $[A]_0$ is reduced to half *i.e.*,

$$[A] = [A]_0/2 \text{ at } t = t_{1/2}$$

Then half life period, $t_{1/2}$ becomes

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/2} = \frac{2.303}{k} \log 2$$

$$\text{or} \quad t_{1/2} = \frac{2.303 \times 0.3010}{k} = \frac{0.693}{k} \qquad [\because \log 2 = 0.3010]$$

$$\text{or} \quad \boxed{t_{1/2} = \frac{0.693}{k}} \qquad ...(20)$$

Thus, **half life period of a first order reaction is independent of the initial concentration of the reactant.** Further, it is also clear from the relation that half life period for the first order reaction is inversely proportional to the rate constant.

Similarly, the relation for the time required to reduce the concentration of the reactant to any fraction of the initial concentration can be calculated. For example, for the first order reaction:

(i) time required to complete 1/3 of the reaction will be given as :

$$[A]_0 = a, \; [A] = a - a/3 = 2/3\, a$$

$$\therefore \quad t_{1/3} = \frac{2.303}{k} \log \frac{a}{2/3a} = \frac{2.303}{k} \log \frac{3}{2}$$

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(ii) time required to complete 3/4 of the reaction will be

$$[A]_0 = a,\ [A] = a - 3/4\ a = 1/4\ a$$

$$\therefore \quad t_{3/4} = \frac{2.303}{k}\log\frac{a}{1/4a} = \frac{2.303}{k}\log 4$$

In general, the time required to complete ***n*th fraction** of the first order reaction will be

$$[A]_0 = a,\ [A] = a - \frac{a}{n} = a\left(1-\frac{1}{n}\right)$$

$$\therefore \quad t_{1/n} = \frac{2.303}{k}\log\frac{a}{a\left(1-\frac{1}{n}\right)} = \frac{2.303}{k}\log\frac{1}{\left(1-\frac{1}{n}\right)}$$

Half life period for a second order reaction

The rate equation for second order reaction is

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

For half life period, $t_{1/2}$ = [A] = $[A]_0/2$

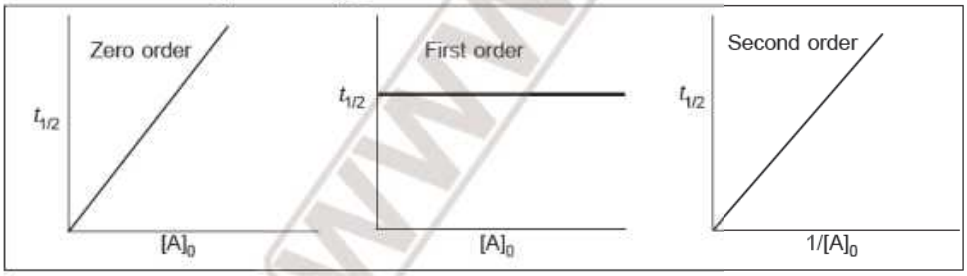
$$\therefore \quad kt_{1/2} = \frac{2}{[A]_0} - \frac{1}{[A]_0} = \frac{1}{[A]_0}$$

$$\therefore \quad \boxed{t_{1/2} = \frac{1}{k[A]_0}}$$

These are summed up below:

Type of reaction	Rate equation	$t_{1/2}$
Zero order	Rate = $k[A]^\circ$	$\frac{[A]_0}{2k}$
First order	Rate = $k[A]$	$\frac{0.693}{k}$
Second order	Rate = $k[A]^2$	$\frac{1}{k[A]_0}$

These results give very interesting observation that only the half life of first order reactions are independent of the concentrations. The half life *vs* concentration $[A]_0$ or $1/[A]_0$ plots are shown below:



Thus we have observed that

For a zero order reaction, $t_{1/2} \propto [A]_0$

For a first order reaction, $t_{1/2} \propto [A]_0^0$

For a second order reaction, $t_{1/2} \propto [A]_0^{-1}$

In general, for a nth order reaction,

In general, for a nth order reaction,

$$t_{1/2} \propto [A]_0^{1-n} \quad \text{or} \quad t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

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Rate of Radioactive Decay

All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics. For example, radium decays as :

$$^{226}_{88}\text{Ra} \longrightarrow ^{222}_{86}\text{Rn} + ^{4}_{2}\text{He}$$

Rate = k[Ra]

Since radioactive decay follows first order kinetics, this means that rate of disintegration is directly proportional to the number of atoms present in the sample at that time.

Suppose a radioactive element A disintegrates to form B,

$$A \longrightarrow B$$

Let N_0 be the number of atoms present in the beginning, at $t = 0$ and N be the number of atoms present at time t, then

$$\lambda = \frac{2.303}{t}\log\frac{N_0}{N}$$

where λ is a constant known as **decay constant or disintegration constant.** Its value depends upon the nature of the decaying element.

Half life period for radioactive decay is

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

The half life period of a radioactive element gives idea about its stability. *If the half life period is small, it means that the element is extremely unstable and will decay in a short period. On the other hand, longer half life periods indicate stability of the radioactive element.* For example, the half life period of Ra-224 is 3.64 days, while the half life period of Ra-228 is 6–7 years and the half life period of Ra-226 is 1596 years. This means that Ra-226 is most stable among the three isotopes of radium while Ra-224 is least stable.

It may be noted that in case of a radioactive substance, the whole of the substance never disintegrates. In other words, the time required for complete disintegration is infinity. Therefore, the term **average life** is used. As faster is the disintegration, smaller is the average life, therefore, average life (expressed as τ, tau) is taken as reciprocal of disintegration constant, λ, ie

$$\tau = \frac{1}{\lambda}$$

But $$t_{1/2} = \frac{0.693}{\lambda}$$

$$\therefore \quad \tau = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693}$$

$$\therefore \quad \tau = 1.44\, t_{1/2}$$

Competition Plus

Radioactive decay of radioactive substances follows first order reaction. The carban dating technique has been developed by Willard Libby to find the age of archaeological object (wood plants or animal fossils). For detail, refer **Compitition File** (Page 94)

SOLVED EXAMPLES

Example 22.

Calculate the half life period of a first order reaction where the specific rate constant is

(a) 200 s^{-1} (b) 2 min^{-1} (c) 4 $year^{-1}$ **N.C.E.R.T.**

Solution : For the first order reaction,

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

(a) $k = 200\ s^{-1}$

$$\therefore \quad t_{1/2} = \frac{0.693}{200} = 3.465 \times 10^{-3}\ s.$$

(b) $k = 2\ min^{-1}$

$$\therefore \quad t_{1/2} = \frac{0.693}{2} = 0.3465\ min.$$

(c) $k = 4\ year^{-1}$

$$\therefore \quad t_{1/2} = \frac{0.693}{4} = 0.1732\ year.$$

Example 23.

A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half life period of the reaction.

N.C.E.R.T. *,(A.I.S.B. 2013)*

Solution : For the first order reaction,

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

$$= \frac{0.693}{5.5 \times 10^{-14} s^{-1}} = \mathbf{1.26 \times 10^{13}\ s.}$$

Example 24.

For a first order reaction, calculate the ratio between the time taken to complete three-fourth of the reaction and the time taken to complete half of the reaction.

Solution : For first order reaction,

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

For 3/4 of a reaction to take place, $t = t_{3/4}$, $[A] = [A]_0 - \frac{3}{4}[A]_0$

$$= \frac{1}{4}[A]_0$$

Thus, $$t_{3/4} = \frac{2.303}{k} \log \frac{[A]_0}{1/4[A]_0} = \frac{2.303}{k} \log 4 \quad ...(i)$$

Now, for half of a reaction to take place,

$$t = t_{1/2};\ [A] = [A]_0 - \frac{1}{2}[A]_0 = \frac{1}{2}[A]_0$$

Thus, $$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/2} = \frac{2.303}{k} \log 2 \quad ...(ii)$$

Dividing eq. (*i*) by eq. (*ii*)

$$\frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{0.6020}{0.3010} = 2$$

Thus, **the time required for 3/4 th of the reaction to occur is two times that required for half of the reaction.**

Practice Problems

17. During the decomposition of N_2O_5 dissolved in carbon tetrachloride at 303 K, the following results were obtained :

Time (min)	0	40	80	120	160	∞
Vol. of O_2 collected (cc)	0	15.6	28.6	38.6	46.8	84.6

Show that the reaction is of first order. Also calculate the rate constant.

18. Diazobenzene chloride decomposes as :

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$

The volume of N_2 evolved at different times was measured and following results were obtained :

Time (min)	0	20	70	∞
Vol. of N_2 (ml)	0	10	33	162

Calculate the (*i*) order of the reaction and (*ii*) rate constant.

19. The rate constant for the decomposition of N_2O_5 is $6.0 \times 10^{-4}\ s^{-1}$. At what time will the initial concentration of 1 M be reduced to 0.2 M if the reaction is of first order ?

20. For the reaction, $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, the initial concentration of N_2O_5 was 1.24×10^{-2} mol L^{-1} at 318 K. The concentration of N_2O_5 after 60 minutes was 0.20×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 318 K.

(Meghalaya S.B. 2013)

21. The decomposition of N_2O_5 in CCl_4 solution follows the first order rate law. The concentration of N_2O_5 measured at different time intervals are given below :

Time in seconds (t)	0	80	160	410	600	1130	1720
$[N_2O_5]$ mol/L	5.5	5.0	4.8	4.0	3.4	2.4	1.6

Calculate the rate constant at t = 410 s and t = 1130 s. What do these results show ?

22. The decomposition of N_2O_5 in CCl_4 at 45°C

$$2N_2O_5 \xrightarrow{CCl_4} 4NO_2 + O_2$$

is first order reaction with $k = 6.32 \times 10^{-4}\ s^{-1}$. Calculate the concentration of N_2O_5 remaining after one hour when the initial concentration of N_2O_5 was 0.40 mol L^{-1}. What percentage of N_2O_5 has reacted ?

Answers to Practice Problems

17. k is almost constant therefore, reaction is of first order. $k = 5.08 \times 10^{-3}\ min^{-1}$.

18. (*i*) order = 1 (*ii*) $3.21 \times 10^{-3}\ min^{-1}$.

19. 2683 s.

20. $3.04 \times 10^{-2}\ min^{-1}$

21. $7.769 \times 10^{-4}\ s^{-1}$, $7.340 \times 10^{-4}\ s^{-1}$.

22. 0.041 mol L^{-1}, 89.75 %

Hints & Solutions on page 68

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EXPERIMENTAL DETERMINATION OF ORDER OF A REACTION

There are a number of methods for determining rate law or order of a reaction. The following methods are commonly used :

1. Graphical Method

This method is used when there is **only one reactant.** It involves the following steps :

1. The concentrations of the reactants are measured by some suitable method.

2. A graph is plotted between concentration and time.

3. The instantaneous rates of the reaction at different times are calculated by finding out the slopes of the tangents corresponding to different times.

4. The rate of reaction (calculated above step 3) is plotted versus concentration, [R] or (concentration)^2, $[R]^2$ and so on.

(*a*) If rate of reaction remains constant in rate versus concentration graph, it means that the rate is independent of the concentration of the reactant, *i.e.*,.

Rate = $k\ [R]^0 = k$

Therefore, the reaction is of **zero order.**

(*b*) If a straight line is obtained in rate versus concentration graph, it means that the rate is directly proportional to concentration of the reactant *i.e.*,

$$\text{Rate} = k[R]$$

Therefore, the reaction is of *first order.*

(*c*) If a straight line is obtained in rate versus (concentration)^2 graph, it means that

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

Therefore, the order of the reaction is two.

(*d*) Similarly, if we get straight line in rate versus (concentration)^3 graph, then

$$\text{Rate} = k[R]^3$$

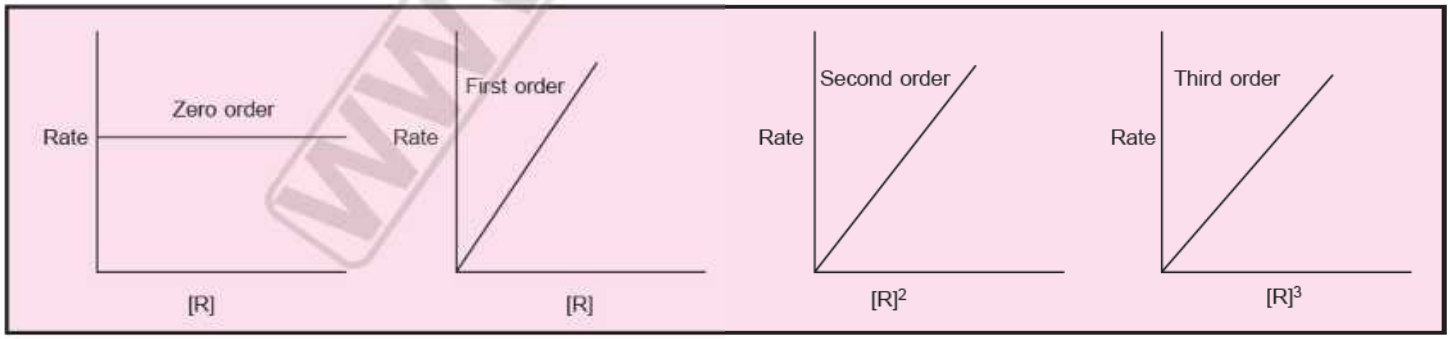
and the order of reaction is 3.

In general, if we get straight line by plotting graph of rate versus (concentration)^n, where n = 1, 2, 3 .... so on, then

$$\text{Rate} = k[R]^n$$

and the order of reaction is n.

These graphs are given below :



Let us illustrate the above method by taking the example of the decomposition of nitrogen pentoxide.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

This reaction involves the gaseous reactants and products. Therefore, the reaction can be easily studied by measuring the increase in pressure of the gaseous mixture at different intervals of time. From the measured values of

total pressure, the partial pressure of N_2O_5 at different times can be calculated. From this, the concentration of N_2O_5 in moles per litre can be calculated. The molar concentrations of N_2O_5 obtained are plotted against time. The rates at different times are obtained by measuring the slopes of the tangents corresponding to these times.

The rate of this reaction at different concentration of N_2O_5 is given in Table 1. The table indicates that the rate of the reaction is proportional to the concentration of N_2O_5 and it may be expressed as :

$$\text{Rate} \propto [N_2O_5]^n \text{ or Rate} = k[N_2O_5]^n$$

Table 1. Rate of reaction corresponding to different concentrations of N_2O_5.

$[N_2O_5]$ (mol L^{-1})	Rate (mol L^{-1} min^{-1})
1.13×10^{-2}	3.4×10^{-4}
0.84×10^{-2}	2.5×10^{-4}
0.62×10^{-2}	1.1×10^{-4}
0.46×10^{-2}	1.3×10^{-4}
0.35×10^{-2}	1.0×10^{-4}
0.26×10^{-2}	0.8×10^{-4}

Now, different graphs are drawn by plotting rate versus $[N_2O_5]$, rate versus $[N_2O_5]^2$, etc. These are given in Fig. 8 and Fig. 9 respectively. We observe that the plot of rate versus $[N_2O_5]$ is a straight line (Fig. 8). This means that the rate of the reaction is directly proportional to the $[N_2O_5]$. Therefore, the rate law is :

$$\text{Rate} = k[N_2O_5]$$

However, we do not get straight line by plotting rate of reaction against $[N_2O_5]^2$. This means that the reaction is not of second order.

Thus, the correct rate law for this reaction is :

$$\text{Rate} = -\frac{dx}{dt} = k[N_2O_5]$$

and order of the reaction is 1.

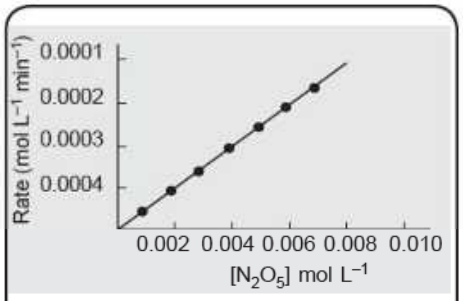


Fig. 8. Rate of decomposition of N_2O_5 as a function of $[N_2O_5]$.

From the above discussion, we notice that the coefficient of N_2O_5 in the balanced equation is 2 while the exponent in the rate law is 1. Thus, *the order of the reaction is not same as the coefficient in the balanced chemical equation.*

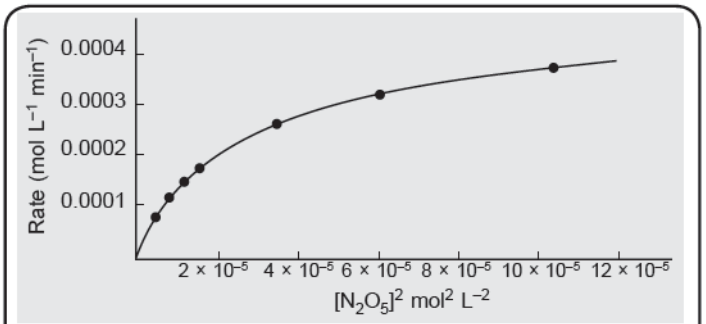


Fig. 9. Rate of decomposition of N_2O_5 as a function of $[N_2O_5]^2$.

Calculation of Rate Constant

The rate constant can be calculated by substituting the values of rate and concentration of N_2O_5 in the rate law expression

$$\text{Rate} = k[N_2O_5]$$

For example, when

$$[N_2O_5] = 1.13 \times 10^{-2} \text{ mol L}^{-1} \text{ and}$$

$$\text{rate} = 3.4 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$$

$$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{3.4 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}}{1.13 \times 10^{-2} \text{ mol L}^{-1}}$$

$$= 3.0 \times 10^{-2} \text{ min}^{-1}$$

2. Use of integrated rate equation

This method is also known as method of trial and error. The kinetic data is fitted to different integrated rate equation. Wherever the data fit with the

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equation for the correct order of the reaction, it will give constant value of rate constant for all data points (concentrations at different times). Alternatively, graphical method can also be applied for integrated rate equation. In the method, appropriate function of concentration is plotted against time. The resulting curve will be straight line only for the case in which the appropriate integrated equations has been used. For a general reaction :

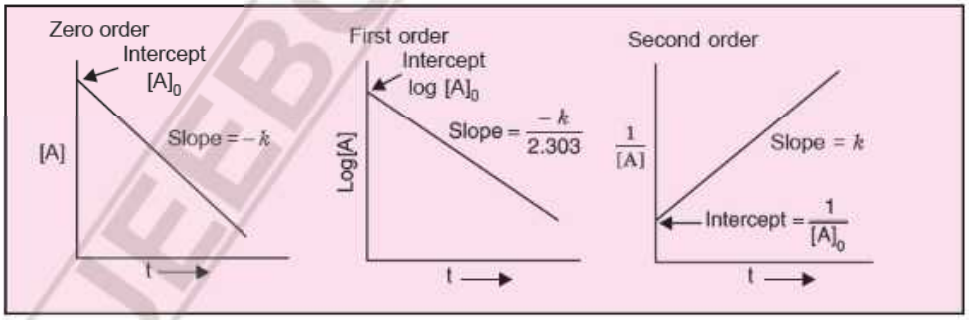
$$A \longrightarrow \text{Products}$$

the integrated rate equation for zero, first and second order reactions are given below :

Type of reaction	Equation corresponding	Linear plot to $y = mx + c$	Slope	Intercept
Zero order (rate = k)	$[A] = -kt + [A]_0$	[A] vs t	$-k$	$[A]_0$
First order (rate = $k[A]$)	$\log [A] = -\frac{kt}{2.303} + \log [A]_0$	log [A] vs t	$-\frac{k}{2.303}$	$\log [A]_0$
Second order (rate = $k[A]^2$)	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{[A]}$ vs t	k	$\frac{1}{[A]_0}$

It is clear from the above relations that the straight lines are obtained for a plot of [A] versus t for a zero order reaction, of log [A] versus t for a first order reaction and of 1/[A] versus t above for second order reaction as shown below:

The plot of ln [A] against t for a first order reaction is a straight line with slope = $-k$.



These curves also help to calculate the value of k from the slope of the straight line.

SOLVED EXAMPLES

Example 25.

The rate of decomposition of hydrogen peroxide at a particular temperature was measured by titrating its solution with acidic $KMnO_4$ solution. Following results were obtained :

Time, t (min)	*0*	*10*	*20*
mol ($KMnO_4$)	*22.8*	*13.8*	*8.3*

(i) Show that the reaction is of first order.

(ii) Calculate the rate constant.

Solution : Volume of $KMnO_4$ used is proportional to the amount of H_2O_2 present. If the reaction is of first order, it must obey the equation,

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

or $$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

Here V_0 = 22.8 and the value of k can be calculted by substituting the concentration of V_t at different times.

t = 10 min, V_t = 13.8

$$\therefore \quad k = \frac{2.303}{10} \log \frac{22.8}{13.8} = 0.05022 \text{ min}^{-1}$$

t = 20 min, V_t = 8.3

$$\therefore \quad k = \frac{2.303}{20} \log \frac{22.8}{8.3} = 0.05053 \text{ min}^{-1}$$

(*i*) Since the value of k comes out to be almost constant, the reaction therefore, is of **first order.**

(*ii*) The mean value of k = **0.05037 min^{-1}.**

❑ Example 26.

The following results were obtained for the decomposition of nitrogen peroxide in an inert solvent :

t (s)	*0*	*300*	*600*	*900*	*∞*
Vol. of O_2 evolved (cm^3)	*0*	*3.42*	*6.30*	*8.95*	*34.75*

Show that the reaction is of first order and also calculate the rate constant.

Solution : The reaction will be of first order, if it obeys the equation,

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

In this reaction, oxygen is liberated and collected at different times. The total volume of oxygen collected at the end of reaction (after infinite time, $t = \infty$) gives a measure of the total concentration of nitrogen peroxide taken initially *i.e.,* a. If V_t is the volume collected after time t and V_∞ is the total volume collected at the end of the reaction, then the concentration of nitrogen peroxide at any time t *i.e.,* $(a - x)$ is $V_\infty - V_t$. Thus,

$$V_\infty = a, \quad V_t \propto x \text{ and } a - x = V_\infty - V_t$$

Thus, the above equation becomes

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

Substituting the values,

$$t = 300 \text{ s}, V_\infty = 34.75, V_t = 3.42$$

$$\therefore \quad k = \frac{2.303}{300} \log \frac{34.75}{34.75 - 3.42}$$

$$= 0.000345$$

$$t = 600 \text{ s}, V_\infty = 34.75, V_t = 6.30$$

$$k = \frac{2.303}{600} \log \frac{34.75}{34.75 - 6.30} = 0.000333$$

$$t = 900 \text{ sec}, V_\infty = 34.75, V_t = 8.95$$

$$k = \frac{2.303}{900} \log \frac{34.75}{34.75 - 8.95} = 0.000331$$

Since the value of k is almost constant, the reaction is of first order. The average value of rate constant is **0.000336**.

❑ Example 27.

The experimental data for decomposition of N_2O_5

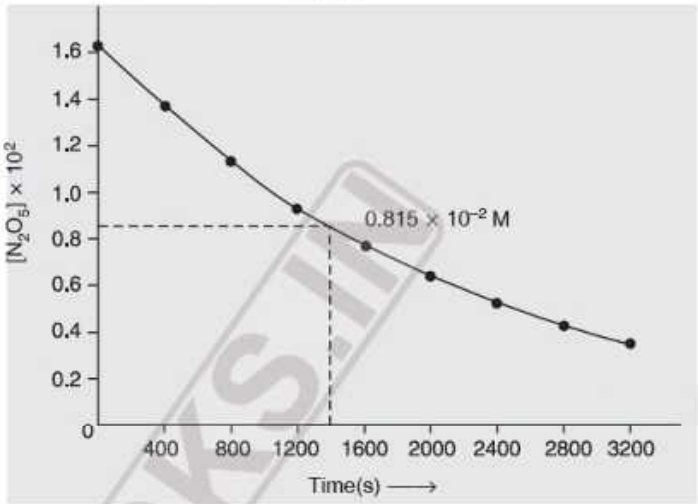
$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

in gas phase at 318K are given below:

t/s	*0*	*400*	*800*	*1200*	*1600*	*2000*	*2400*	*2800*	*3200*
$10^2 \times [N_2O_5]$/ mol L^{-1}	*1.63*	*1.36*	*1.14*	*0.93*	*0.78*	*0.64*	*0.53*	*0.43*	*0.35*

(i) Plot $[N_2O_5]$ against t.
(ii) Find the half-life period for the reaction.
(iii) Draw a graph between log $[N_2O_5]$ and t.
(iv) What is the rate law?
(v) Calculate the rate constant.
(vi) Calculate the half-life period from k and compare it with (b).

Solution. (*i*) The plot of $[N_2O_5]$ versus time is shown below:



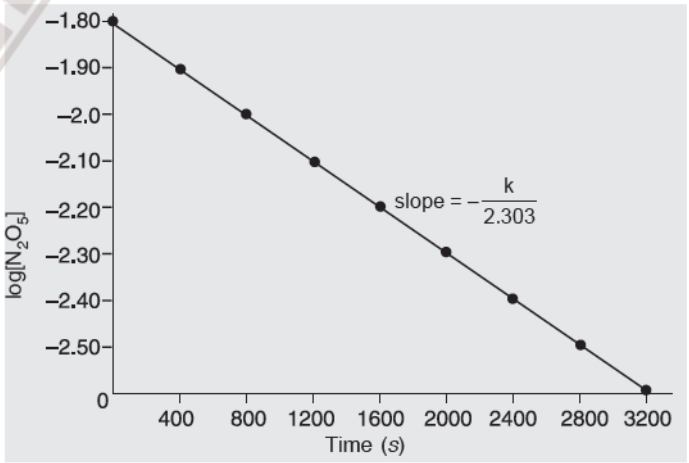
(*ii*) Initial conc. of $N_2O_5 = 1.63 \times 10^{-2}$ M

Half of initial conc. $= 1.63 \times 10^{-2} \times \frac{1}{2}$

$= 0.815 \times 10^{-2}$ M

Time corresponding to half of initial conc. ($t_{1/2}$) from the plot = 1440s

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



(*iv*) Since the graph between $\log[N_2O_5]$ *vs* time is a straight line, the reaction is of first order.

Rate equation :

$$\text{Rate} = k[N_2O_5]$$

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

$$\text{Slope} = -2.10 \times 10^{-4} \text{ (from graph)}$$

$$\therefore \quad k = -2.10 \times 10^{-4} \times (-2.303)$$

$$= 4.84 \times 10^{-4} \text{ s}^{-1}$$

(*vi*) $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.84 \times 10^{-4}} = \mathbf{1432\ s}$$

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3. Initial Rate Method

The graphical methods cannot be applied for the reactions which involve more than one reactants. The rates of such reactions can be determined by *initial rate method*. This method involves the following steps :

1. The initial rate of the reaction *i.e.,* the rate at the beginning of the reaction is measured. This may be taken as the rate over an initial time interval that is short enough so that concentrations of the reactants do not change appreciably from their initial values. This corresponds to slope of the tangent to the concentration versus time graph at $t = 0$.

2. The initial concentration of only one reactant is changed (keeping other concentrations constant) and the rate is determined again. From this the order with respect to that particular reactant is calculated.

3. The procedure is repeated with respect to each reactant until the overall rate law is fully determined.

4. The sum of the individual orders with respect to each reactant gives the order of the reaction.

This method can be illustrated by taking a hypothetical reaction :

$$2A + 2B \longrightarrow \text{Products}$$

The order of this reaction can be experimentally determined by studying the concentration dependence of reactants A and B. Let us assume that we start with 0.01 M concentration of both A and B and the initial rate of the reaction is 0.005 (say). This has been listed in Table 2 in experiment I. In second experiment when the initial concentration of A is doubled (from 0.01 M to 0.02 M), keeping concentration of B constant, the rate becomes four times (i.e., changes from 0.005 to 0.020). This means that the rate of the reaction is proportional to the square of the concentration of A,

$$\text{Rate of reaction} \propto [A]^2$$

In other words, order of the reaction with respect to A is two.

Table 2. Data for the hypothetical reaction, $2A + 2B \longrightarrow$ Product.

Experiment	Concentration(M) [A]	[B]	Rate of reaction
I	0.01	0.01	0.005
II	0.02	0.01	0.020
III	0.02	0.03	0.060

Similarly, the comparison of results of experiments II and III shows that when the concentration of B is tripled (from 0.01 M to 0.03 M) keeping the concentration of A constant, rate becomes triple (from 0.020 to 0.060). The rate of reaction is, therefore, proportional to the concentration of B *i.e.*,

$$\text{Rate} \propto B$$

In other words, order of the reaction with respect to B is one.

The overall rate law equation may be written as :

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

Thus, the overall order of reaction is 2 + 1 = 3. Obviously, the powers of the reactants in rate law expression are different than the coefficients in the overall chemical equation.

Alternative Method

In some cases, it is not easy to compare the rates by simple inspection. Then an alternative mathematical method is used as given below :

Consider a general reaction :

$$aA + bB + cC \longrightarrow \text{Products}$$

The general form of the rate law may be written as :

$$\text{Rate} = k[A]^p\,[B]^q\,[C]^r \qquad ...(i)$$

Then initial rate of the reaction may be given as :

r_0 = Rate = $k\ [A]_0^p\ [B]_0^q\ [C]_0^r$

If [B] and [C] are kept constant, then

$r_0 = k_0\ [A]_0^p$ where $k_0 = k[B]_0^q\ [C]_0^r$

The value of p can be determined by inspecting the rate at different values of [A]. Alternatively, if we know the initial rates at two different concentrations of A, we have :

$$(r_0)_1 = k_0\ [A_0]_1^p \qquad .....(ii)$$

$$(r_0)_2 = k_0\ [A_0]_2^p \qquad ....(iii)$$

where $(r_0)_1$ and $(r_0)_2$ are the initial rates of reaction when the initial concentration of A are $[A_0]_1$ and $[A_0]_2$ respectively. Dividing eqn. (*ii*) by Eq. (*iii*) we get

$$\frac{(r_0)_1}{(r_0)_2} = \left\{\frac{[A_0]_1}{[A_0]_2}\right\}^p$$

Taking log on both sides we get

$$\log \frac{(r_0)_1}{(r_0)_2} = p \log \frac{[A_0]_1}{[A_0]_2}$$

$$\therefore \qquad p = \frac{\log \{(r_0)_1 / (r_0)_2\}}{\log \{[A_0]_1 / [A_0]_2\}}$$

Therefore, the order of reaction with respect to A can be determined. In the same manner, the order of reaction with respect to other reactants can also be determined. The overall order of the reaction is the sum of all the exponents in equation (*i*) as

$$n = p + q + r.$$

This may be illustrated by considering the above reaction :

$$2A + 2B \longrightarrow \text{Product}$$

The general form of the rate law may be written as :

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

Then, the expression for the initial rate is

$$(\text{Rate})_0 = k[A]_0^p\ [B]_0^q$$

where subscript zero denotes initial values. The problem involves the determination *of* p and q.

Consider the experiments I and II (Table 3) and substituting the values we get,

$$(\text{Rate})_1 = k(0.01)^p\ (0.01)^q = 0.005 \qquad ...(i)$$

$$(\text{Rate})_2 = k(0.02)^p\ (0.01)^q = 0.020 \qquad ...(ii)$$

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

$$\frac{(0.02)^p}{(0.01)^p} = \frac{0.020}{0.005}$$

$$(2)^p = 4 \text{ or } (2)^p = 2^2 \qquad \therefore\ p = 2$$

Similarly, comparing experiments II and III

$$(\text{Rate})_2 = k(0.02)^p\ (0.01)^q = 0.020 \qquad ...(iii)$$

$$(\text{Rate})_3 = k(0.02)^p\ (0.03)^q = 0.060 \qquad ...(iv)$$

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

$$\frac{(0.03)^q}{(0.01)^q} = \frac{0.060}{0.020}$$

$$3^q = 3 \quad \text{or} \quad q = 1$$

Therefore, the order with respect to A is 2 and the order with respect to B is 1. Thus, the rate law may be written as :

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

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Example 28.

The following data were obtained for the reaction:

$$2NO(g) + Br_2(g) \longrightarrow 2NOBr(g)$$

Experiment	Initial conc. [NO]	Initial conc. $[Br_2]$	Initial rate (mol L^{-1} min^{-1})
I	0.10	0.10	1.3×10^{-6}
II	0.20	0.10	5.2×10^{-6}
III	0.20	0.30	1.56×10^{-5}

Determine (i) *the orders with respect to NO and Br_2*
(ii) *the rate law and*
(iii) *rate constant.*

Solution : The rate law may be written as :

$$\text{Rate} = k[NO]^p[Br_2]^q$$

The initial rate becomes

$$(\text{Rate})_0 = k[NO]^p[Br_2]^q$$

Comparing experiment I and II, we get

$$(\text{Rate})_1 = k(0.1)^p(0.1)^q = 1.3 \times 10^{-6} \quad ...(i)$$

$$(\text{Rate})_2 = k(0.2)^p(0.1)^q = 5.2 \times 10^{-6} \quad ...(ii)$$

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

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k(0.2)^p(0.1)^q}{k(0.1)^p(0.1)^q} = \frac{5.2 \times 10^{-6}}{1.3 \times 10^{-6}}$$

or $(2)^p = 4$ or $(2)^p = 2^2$

$\therefore$ $p = 2$

Thus, **order with respect to NO is 2.**

Comparing experiments II and III

$$(\text{Rate})_2 = k(0.2)^p(0.1)^q = 5.2 \times 10^{-6} \quad ....(iii)$$

$$(\text{Rate})_3 = k(0.2)^p(0.3)^q = 1.56 \times 10^{-5} \quad ....(iv)$$

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

$$\frac{k(0.2)^p(0.3)^q}{k(0.2)^p(0.1)^q} = \frac{1.56 \times 10^{-5}}{5.2 \times 10^{-6}}$$

or $(3)^q = 3$

or $q = 1$

Thus, **order with respect to Br_2 is 1.**

(ii) The rate law for the reaction

$$\text{Rate} = k[NO]^2[Br_2]$$

(iii) Rate constant can be calculated by substituting the values of rate, [NO] and $[Br_2]$ for any experiment

$$k = \frac{\text{Rate}}{[NO]^2[Br_2]} = \frac{1.3 \times 10^{-6}}{(0.1)^2(0.1)}$$

$$= \mathbf{1.3 \times 10^{-3}\ mol^{-2}\ L^2\ s^{-1}.}$$

Example 29.

The rates of a reaction starting with initial concentrations 2×10^{-3} M and 1×10^{-3} M are equal to 2.40×10^{-4} M s^{-1} and 0.60×10^{-4} M s^{-1} respectively. Calculate the order of the reaction with respect to the reactant and also the rate constant.

Solution : Let the initial rate be :

$$r_0 = k[A_0]^a$$

$$\frac{(r_0)_1}{(r_0)_2} = \left\{\frac{[A_0]_1}{[A_0]_2}\right\}^a$$

or $$a = \frac{\log\{(r_0)_1/(r_0)_2\}}{\log\{[A_0]_1/[A_0]_2\}}$$

$$= \frac{\log(2.40 \times 10^{-4}/0.60 \times 10^{-4})}{\log(2 \times 10^{-3}/1 \times 10^{-3})} = \frac{\log 4}{\log 2} = 2$$

$\therefore$ The order of reaction = 2

Now, Rate $= k[A]^2$

or $$k = \frac{\text{Rate}}{[A]^2} = \frac{2.4 \times 10^{-4}\ \text{mol L}^{-1}\text{s}^{-1}}{(2 \times 10^{-3}\ \text{mol L}^{-1})^2}$$

$$= \mathbf{0.6 \times 10^2\ mol^{-1}\ L\ s^{-1}.}$$

Example 30.

The following data were obtained for the reaction:

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F$$

Experiment	Initial conc. $[NO_2]_0$	Initial conc. $[F_2]_0$	Initial rate mol L^{-1} min^{-1}
1	0.20	0.05	6.0×10^{-3}
2	0.40	0.05	1.2×10^{-2}
3	0.80	0.10	4.8×10^{-2}

Determine (i) *order of reaction*
(ii) *rate law*
(iii) *rate of reaction when $[NO_2] = 0.50$ mol L^{-1} and $[F_2] = 0.60$ mol L^{-1}.*

Solution : The initial rate expression may be written as :

$$(\text{Rate})_0 = k[NO_2]^p[F_2]^q$$

Comparing experiments 1 and 2, we get

$$(\text{Rate})_1 = k(0.2)^q(0.05)^q = 6.0 \times 10^{-3} \quad ...(i)$$

$$(\text{Rate})_2 = k(0.4)^q(0.05)^q = 1.2 \times 10^{-2} \quad ...(ii)$$

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

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{k(0.4)^p(0.05)^q}{k(0.2)^p(0.05)^q} = \frac{1.2 \times 10^{-2}}{6.0 \times 10^{-3}}$$

or $(2)^p = 2$

$\therefore$ $p = 1$

Thus, **order with respect to NO_2 is 1.**

Comparing experiments 2 and 3,

$$(\text{Rate})_2 = k(0.4)^p(0.05)^q = 1.2 \times 10^{-2} \quad ...(iii)$$

$$(\text{Rate})_3 = k(0.8)^p(0.10)^q = 4.8 \times 10^{-2} \quad ...(iv)$$

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

$$\frac{k(0.8)^p(0.10)^q}{k(0.4)^p(0.05)^q} = \frac{4.8 \times 10^{-2}}{1.2 \times 10^{-2}}$$

$$(2)^p(2)^q = 4$$

Now, we have obtained $p = 1$ for the reaction, so that

$$(2)^1(2)^q = 4 \quad \text{or} \quad (2)^q = 2 \quad \text{or} \quad q = 1$$

Thus, **order w.r.t. F_2 is 1**

(i) Order of reaction = 1 + 1 = 2

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(*ii*) Rate law for the reaction is :

$$\text{Rate} = k[NO_2][F_2]$$

(*iii*) Rate of reaction, when $[NO_2] = 0.50$ mol L^{-1} and $[F_2] = 0.60$ mol L^{-1}

Let us first calculate, k from first run.

$$\text{Rate} = k[NO_2][F_2]$$

6.0×10^{-3} mol L^{-1} $min^{-1} = k(0.20$ mol $L^{-1}) \times (0.05$ mol $L^{-1})$

or $$k = \frac{6.0 \times 10^{-3}}{0.20 \times 0.05} = 0.6 \text{ mol}^{-1} \text{ L min}^{-1}$$

Substituting the values of k, $[NO_2]$ and $[F_2]$

$$\text{Rate} = 0.6 \times (0.5) \times (0.60)$$
$$= \mathbf{0.18 \text{ mol L}^{-1} \text{ min}^{-1}}.$$

❑ Example 31.

The initial rate of reaction :

$$A + 5B + 6C \rightleftharpoons 3L + 3M$$

has been determined by measuring the rate of disappearance of A under the following conditions :

Expt. No.	$[A]_0$ *M*	$[B]_0$ *M*	$[C]_0$ *M*	*Initial rate* M/min^{-1}
1.	0.02	0.02	0.02	2.08×10^{-3}
2.	0.01	0.02	0.02	1.04×10^{-3}
3.	0.02	0.04	0.02	4.16×10^{-3}
4.	0.02	0.02	0.04	8.32×10^{-3}

Determine the order of reaction with respect to each reactant and overall order of the reaction. What is the rate constant ?

Calculate the initial rate of the reaction when the concentration of all the reactants is 0.01 M. Calculate the initial rate of change in concentration of B and L.

Solution : Rate law may be written as:

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

The initial rate becomes $(\text{Rate})_0 = k[A_0]^a [B_0]^b[C_0]^c$ ...(*i*)

Comparing experiments 1 and 2

$(\text{Rate})_1 = k(0.02)^a (0.02)^b (0.02)^c = 2.08 \times 10^{-3}$ ...(*ii*)

$(\text{Rate})_2 = k(0.01)^a (0.02)^b (0.02)^c = 1.04 \times 10^{-3}$ ...(*iii*)

Dividing Eq. (*ii*) by Eq. (*iii*) we get

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{(0.02)^a}{(0.01)^a} = \frac{2.08 \times 10^{-3}}{1.04 \times 10^{-3}} = 2$$

or $2^a = 2$

$\therefore$ $a = 1$

Comparing experiment 3 and 1, we get

$(\text{Rate})_1 = k (0.02)^a (0.02)^b (0.02)^c = 2.08 \times 10^{-3}$ ...(*iv*)

$(\text{Rate})_3 = k (0.02)^a (0.04)^b (0.02)^c = 4.16 \times 10^{-3}$ ...(*v*)

Dividing Eqn. (*v*) by Eqn. (*iv*),

$$\frac{(0.04)^b}{(0.02)^b} = \frac{4.16 \times 10^{-3}}{2.08 \times 10^{-3}} = 2$$

$2^b = 2$

$\therefore$ $b = 1$

Comparing experiment 1 and 4, we get

$(\text{Rate})_1 = k(0.02)^a (0.02)^b (0.02)^c = 2.08 \times 10^{-3}$ ...(*vi*)

$(\text{Rate})_4 = k(0.02)^a (0.02)^b (0.04)^c = 8.32 \times 10^{-3}$ ...(*vii*)

Dividing eqn. (*vii*) by eqn. (*vi*), we get

$$\frac{(\text{Rate})_4}{(\text{Rate})_1} = \frac{(0.04)^c}{(0.02)^c} = \frac{8.32 \times 10^{-3}}{2.08 \times 10^{-3}} = 4$$

or $2^c = 2^2$

$\therefore$ $c = 2$

Therefore, the order of the reaction with respect to A, B and C are 1, 1 and 2 respectively and overall order of reaction $= 1 + 1 + 2 = 4$

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

Substituting the values from expt. 1, we get

$2.08 \times 10^{-3} = k \times 0.02 \times 0.02 \times (0.02)^2$

$$\therefore \quad k = \frac{2.08 \times 10^{-3}}{(0.02)^4} = \frac{2.08 \times 10^{-3}}{16 \times 10^{-8}} = \mathbf{1.3 \times 10^4 \text{ M}^{-2} \text{ min}^{-1}}.$$

Rate of reaction when concentration of all reactants = 0.01 M

$$\text{Rate} = 1.3 \times 10^4 \times (0.01) \times (0.01) \times (0.01)^2$$
$$= 1.3 \times 10^{-4} \text{ M min}^{-1}.$$

According to the reaction,

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{5}\frac{d[B]}{dt} = -\frac{1}{6}\frac{d[C]}{dt}$$
$$= \frac{1}{3}\frac{d[C]}{dt} = \frac{1}{3}\frac{d[M]}{dt}$$

Now, $$\text{Rate} = -\frac{1}{5}\frac{d[B]}{dt}$$

or $$\frac{d[B]}{dt} = -5 \times \text{Rate} = -5 \times 1.3 \times 10^{-4} \text{ M min}^{-1}$$
$$= \mathbf{-6.5 \times 10^{-4} \text{ M min}^{-1}}.$$

Similarly,

$$\text{Rate} = \frac{1}{3}\frac{d[L]}{dt}$$

or $$\frac{d[L]}{dt} = 3 \times \text{Rate} = 3 \times 1.3 \times 10^{-4} \text{ M min}^{-1}$$
$$= \mathbf{3.9 \times 10^{-4} \text{ M min}^{-1}}.$$

❑ Example 32.

Nitrogen pentoxide decomposes according to equation :

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

This first order reaction was allowed to proceed at 40°C and the data below were collected :

$[N_2O_5]$ *(M)*	*Time (min)*
0.400	0.00
0.289	20.0
0.209	40.0
0.151	60.0
0.109	80.0

(*a*) *Calculate the rate constant. Include units with your answer.*

(*b*) *What will be the concentration of N_2O_5 after 100 minutes ?*

(*c*) *Calculate the initial rate of reaction. (D.S.B. 2011)*

Solution : (*a*) Since it is a first order reaction.

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

k can be calculated as :

at t = 20 min

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

$$= \frac{2.303}{20} \times 0.141$$

$$= 0.01624 \text{ min}^{-1}$$

at t = 40 min

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

$$= \frac{2.303}{40} \times 0.282$$

$$= 0.01624 \text{ min}^{-1}$$

at t = 60 min

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

$$= \frac{2.303}{60} \times 0.423$$

$$= 0.01624 \text{ min}^{-1}$$

at t = 80 min

$$k = \frac{2.303}{80} \log \frac{0.400}{0.109}$$

$$= \frac{2.303}{80} \times 0.565$$

$$= 0.01626 \text{ min}^{-1}$$

The average value of rate constant,

k = 0.01624 min^{-1} or = **1.624 × 10^{-2} min^{-1}.**

(*b*) Concentration of $[N_2O_5]$ at t = 100 min

$$0.01624 = \frac{2.303}{100} \log \frac{0.400}{[N_2O_5]}$$

$$\frac{0.01624}{2.303} \times 100 = \log \frac{0.400}{[N_2O_5]}$$

or $$\log \frac{0.400}{[N_2O_5]} = 0.7052$$

$$\frac{0.400}{[N_2O_5]} = \text{antilog } (0.7052) = 5.072$$

$$\therefore \quad [N_2O_5] = \frac{0.400}{5.072} = \mathbf{0.0789\ M}$$

(*c*) Initial rate of reaction,

$$\text{rate} = k[N_2O_5]$$

$$= 0.01624 \times 0.400 = \mathbf{6.496 \times 10^{-3}}$$

Practice Problems

23. The following rate data were obtained for the reaction :

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Experiment	Concentration (mol L^{-1}) [NO]	[O_2]	Rate of reaction mol L^{-1} s^{-1}
I	0.30	0.30	0.096
II	0.60	0.30	0.384
III	0.30	0.60	0.192
IV	0.60	0.60	0.768

Determine the rate law expression and order of the reaction.

24. For the reaction :

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g)$$

the following data were collected. All the measurements were taken at 263 K.

Experiment No	Initial [NO] (M)	Initial [Cl_2] (M)	Initial rate of disappearance of Cl_2 (M/min)
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(*a*) Write the expression for rate law.

(*b*) Calculate the value of rate constant and specify its units.

(*c*) What is the initial rate of disappearance of Cl_2 in exp. 4 ? (*D.S.B. 2012*)

25. Fill in the blanks in the following table which treats a reaction of a compound A with a compound B, that is the first order with respect to A and zero order with respect to B.

Answers to Practice Problems

23. Rate = $k[NO]^2[O_2]$, order = 3

24. (*a*) Rate = $k[NO]^2[Cl_2]$

(*b*) 177.8 M^{-2} min^{-1}

(*c*) 2.78 M min^{-1}

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

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

A (M)	0.20	0.20	0.40
B (M)	0.30	0.10	0.05
r_0(Ms^{-1})	8.93×10^{-5}	8.93×10^{-5}	2.53×10^{-4}

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

Answers to Practice Problems

25. 2nd line 0.2, 3rd line 8.0×10^{-2} mol L^{-1} min^{-1}, 4th line 0.1.

26. $n_A = 1.5$, $n_B = 0$.

Hints & Solutions on page 68

4. Ostwald isolation method

This method was introduced by Ostwald in 1902 and is used to find the order of a reaction with respect to one reactant at a time. The total order of the reaction is then equal to the sum of the orders of reaction for individual reactants. This method is based on the principle that if the concentrations of all but one reactant are taken in excess, then during the course of the reaction, the concentration of those reactants taken in excess will remain almost constant and hence variation in rate will correspond to the concentration of that reactant whose concentration is small. This process is repeated with other reactants one by one and order with respect to each reactant is determined. The overall order will be the sum of all these orders. For example, consider the general reaction:

$$aA + bB + cC \longrightarrow \text{Products}$$

Suppose we isolate A by taking B and C in large excess and get order of reaction with respect to A (say p). Similarly, we isolate B by taking A and C in excess and isolate C by taking A and B in excess and get order with respect to B and (say q) and C (say r) respectively.

Overall order of reaction $n = p + q + r$.

5. Half Life Period Method

The order of a reaction can also be determined by half life period method. This method is based on the principle that if a reaction is of the nth order in a reactant, then half life is inversely proportional to $(n-1)$th power of its initial concentration.

For example, if initial concentration of a reactant is C_1 and half life period is $(t_{1/2})_1$, if initial concentration of a reactant is C_2 and half life period is $(t_{1/2})_2$

then $$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{C_2}{C_1}\right)^{n-1}$$

or $$\log(t_{1/2})_1 / (t_{1/2})_2 = (n-1)\log C_2 / C_1$$

or $$n = 1 + \frac{\log(t_{1/2})_1/(t_{1/2})_2}{\log C_2/C_1}$$

From this, n can be calculated.

SOLVED EXAMPLES

❑ **Example 33.**

The reaction :

$CH_3COF + H_2O = CH_3COOH + HF$

has been studied under the following initial conditions:

Experiment I	*Experiment II*
$[H_2O]_0 = 1.00$ M	$[H_2O]_0 = 0.02$ M
$[CH_3COF]_0 = 0.01$ M	$[CH_3COF]_0 = 0.80$ M

Concentrations were measured as a function of time and are given as :

Expt. I		*Expt. II*	
t(min)	*$[CH_3COF]$ (M)*	*t(min)*	*$[H_2O]$ (M)*
0	0.01000	0	0.02000
10	0.00857	10	0.0176
20	0.00735	20	0.0156
40	0.00540	40	0.0122

Calculate the order of the reaction and the rate constant for the reaction.

Solution : Let rate of reaction is

$$\text{Rate} = k[CH_3COF]^a\,[H_2O]^b$$

In the first case, $[H_2O] >> [CH_3COF]$. Therefore, we can determine rate with respect to CH_3COF according to Ostwald isolation method. Since rate of reaction changes with time, the reaction is not of zero order. We can now apply first order equation as :

$$k = \frac{2.303}{t}\log\frac{[CH_3COF]_0}{[CH_3COF]}$$

t (min)	$[CH_3COF]$ (M)	$k[H_2O]^b = \frac{2.303}{t}\log\left(\frac{[CH_3COF]_0}{[CH_3COF]}\right)$ (min^{-1})
0	0.0100	–
10	0.00857	0.0154
20	0.00735	0.0154
40	0.00540	0.0154

$\therefore$ $k\,[H_2O] = 0.0154\ min^{-1}$

$\therefore$ Order of reaction with respect to CH_3COF is 1.

Now let us determine order of reaction with respect to H_2O. Since the concentration of water changes, it is not of zero order. We now apply first order equation as :

t (min)	$[H_2O]$ (M^{-1})	$k[CH_3COF]^a = \frac{2.303}{t}\log\frac{[H_2O]_0}{[H_2O]}$ (min^{-1})
0	0.0200	–
10	0.0176	0.0128
20	0.0156	0.0124
40	0.0122	0.0124

The value of k is almost constant and mean value = 0.0125 min^{-1}.

$\therefore$ The reaction is first order in H_2O and we have $k[CH_3COF]^b = 0.0125\ min^{-1}$.

The rate constant can be calculated as :

$$\text{In case I, } k = \frac{k[H_2O]^b}{[H_2O]} = \frac{0.0154\ min^{-1}}{1.0\ M} = 0.0154\ M^{-1}min^{-1}$$

$$\text{In case II, } k = \frac{k[CH_3COF]^a}{[CH_3COF]} = \frac{0.0125\ min^{-1}}{0.80\ M}$$

$$= 0.0156\ M^{-1}\ min^{-1}$$

$\therefore$ Rate constant = **0.0155 M^{-1} min^{-1}.**

Example 34.

The half life period for the conversion of ammonium cyanate into urea at 303 K, at initial concentrations of ammonium cyanate of 0.1 mol L^{-1} and 0.2 mol L^{-1} are 1152 and 568 min respectively. What is the order of the reaction ?

Solution : For $C_1 = 0.1$ mol L^{-1}, $(t_{1/2})^1 = 1152$ min

For $C_2 = 0.2$ mol L^{-1}, $(t_{1/2})_2 = 568$ min

Since $t_{1/2} \propto \frac{1}{C^{n-1}}$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{C_2}{C_1}\right)^{n-1}$$

$$\frac{1152}{568} = \left(\frac{0.2}{0.1}\right)^{n-1}$$

$$2.02 = (2)^{n-1}$$

or $n - 1 = 1$

$\therefore$ $n = 2$

Thus, order of reaction is 2.

Alternatively, applying the formula

$$n = 1 + \frac{\log (t_{1/2})_1/(t_{1/2})_2}{\log C_2/C_1}$$

$$= 1 + \frac{\log 1152/568}{\log 0.2/0.1} = 1 + \frac{0.3071}{0.3010}$$

$$= 1 + 1 = 2$$

MISCELLANEOUS SOLVED EXAMPLES

Example 35.

A first order reaction has a rate constant of 0.0051 min^{-1}. If we begin with 0.10 M concentration of the reactant, what concentration of reactant will remain in solution after 3 hours ?(D.S.B. 2009; A.I.S.B. 2009)

Solution : For first order reaction,

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

$[A]_0 = 0.10$ M, $k = 0.0051\ min^{-1}$, $t = 3 \times 60 = 180$ min, $[A] = ?$

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

$$\log\frac{0.10}{[A]} = \frac{180 \times 0.0051}{2.303} = 0.3986$$

$$\frac{0.10}{[A]} = 2.504$$

$$\therefore \quad [A] = \frac{0.10}{2.504} = \mathbf{0.04\ M}$$

Example 36.

What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of the reactant is 0.2 mol dm^{-3} ? How much of the reactant will be converted into the products in 200 minutes ?

Solution : Rate constant, $k = 10^{-3}\ min^{-1}$,

$$\text{Initial rate} = k[A]$$

$$= (10^{-3}\ min^{-1}) \times (0.2\ mol\ dm^{-3})$$

$$= 2 \times 10^{-4}\ mol\ dm^{-3}\ min^{-1}$$

Now, the integrated rate equation for the first order reaction is :

$$kt = 2.303 \log\frac{a}{a-x}$$

or $$\log\frac{a}{a-x} = \frac{kt}{2.303}$$

$t = 200$ min, $k = 10^{-3}\ min^{-1}$ so that

$$\log\frac{a}{a-x} = \frac{10^{-3} \times 200}{2.303} = 8.68 \times 10^{-2}$$

or $$\frac{a}{a-x} = 1.22 \qquad (\text{antilog } 8.68 \times 10^{-2} = 1.22)$$

or $a = 1.22a - 1.22x$

or $1.22x = 1.22a - a = 0.22a$

or $x = \frac{0.22a}{1.22} = 0.18a$

$$\% \text{ conversion} = \frac{0.18a \times 100}{a} = \mathbf{18\%}$$

Example 37.

A first order reaction takes 20 minutes for 25% decomposition. Calculate the time when 75% of the reaction will be completed. (A.I.S.B. 2017)

Solution : For the first order reaction :

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

If $[A]_0 = a$, $[A] = a - \frac{a \times 25}{100} = 0.75\,a$, $t = 20$ min

$$\therefore \quad k = \frac{2.303}{20}\log\frac{a}{0.75\,a}$$

$$= \frac{2.303}{20} \times 0.1249 = 0.0144 \text{ min}^{-1}$$

In second case, if $[A]_0 = a$, $[A] = a - \frac{a \times 75}{100} = 0.25\,a$ and time, $t = ?$

Now, $$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]} = \frac{2.303}{0.0144}\log\frac{a}{0.25a}$$

$$= \frac{2.303}{0.0144} \times 0.6021 = \mathbf{96.3\ min.}$$

Example 38.

A first order reaction takes 23.1 minutes for 50% completion. Calculate the time required for 75% completion of this reaction. (log2 = 0.301, log3 = 0.4771, log4 = 0.6021) (A.I.S.B. 2015)

Solution : For a first order reaction,

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

If $[A]_0 = a$, *then* $[A] = a - \frac{a \times 50}{100} = 0.50\,a$, $t = 23.1$ min

$$k = \frac{2.303}{23.1}\log\frac{a}{0.5\,a}$$

$$k = \frac{2.303}{23.1}\log 2$$

$$\frac{2.303}{23.1} \times 0.301 = 0.030 \text{ min}^{-1}$$

Now, if $[A]_0 = a$, and $[A] = a - \frac{a \times 75}{100} = 0.25\,a$

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

$$t = \frac{2.303}{0.030}\log\frac{a}{0.25\,a}$$

$$t = \frac{2.303}{0.030}\log 4$$

$$t = \frac{2.303}{0.030} \times 0.6021 = \mathbf{46.2\ min}$$

Example 39.

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 1/10th of its initial value ?

(A.I.S.B. 2007, H.P.S.B. 2012, Pb. S.B. 2013, 2016, Mizoram S.B. 2013)

Solution : For a first order reaction,

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

$k = 60\ s^{-1}$, $[A] = [A]_0/10$

Now, $$t = \frac{2.303}{60}\log\frac{[A]_0}{[A]_0/10} = \frac{2.303}{60}\log 10$$

$$= 0.038 \text{ s } \mathbf{or\ 3.8 \times 10^{-2}\ s.}$$

Example 40.

The half life period for radioactive decay of ^{14}C is 5730 year. An archaeological artefact contained wood had only 80% the ^{14}C found in a living tree. Estimate the age of the sample.

(H.P.S.B. 2010, Mizoram S.B.2014)

Solution : Decay constant, $k = \frac{0.693}{t_{1/2}}$

$t_{1/2} = 5730$ year

$$\therefore \quad k = \frac{0.693}{5730\,y} = 1.209 \times 10^{-4} \text{ year}^{-1}$$

Since the rate of counts is proportional to the number of ^{14}C atoms in the sample,

$N_0 = 100$, $N = 80$

Now, $$t = \frac{2.303}{k}\log\frac{N_0}{N}$$

$$= \frac{2.303}{1.209 \times 10^{-4}}\log\frac{100}{80}$$

$$= \frac{2.303}{1.209 \times 10^{-4}} \times 0.0969$$

$$= \mathbf{1846\ year.}$$

Example 41.

Calculate two-third life of a first order reaction having $k = 5.48 \times 10^{-14}\ s^{-1}$. (H.P.S.B. 2010, Pb. S.B. 2013)

Solution : For two-third of a reaction,

$[A]_0 = a$, $[A] = a - 2/3\,a = a/3$

$$t_{2/3} = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

$$= \frac{2.303}{k}\log\frac{a}{a/3} = \frac{2.303}{k}\log 3$$

$$\therefore \quad t_{2/3} = \frac{2.303}{5.48 \times 10^{-14}}\log 3 = \mathbf{2.01 \times 10^{13}\ s.}$$

Example 42.

The reaction : $SO_2Cl_2 \xrightarrow{k_1} SO_2 + Cl_2$

is a first order reaction with half life 3.15 × 10^4s at 575 K. What percentage of SO_2Cl_2 would be decomposed on heating at 575 K for 90 minutes? (A.I.S.B. 2003)

Solution : For the first order reaction :

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

Now, $t_{1/2} = 3.15 \times 10^4\ s^{-1}$

$$\therefore \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.15 \times 10^4} = 2.2 \times 10^{-5}\ s^{-1}$$

time, $t = 90$ min $= 90 \times 60 = 5400$ s

$$\therefore \quad 2.2 \times 10^{-5} = \frac{2.303}{5400}\log\frac{[A]_0}{[A]}$$

$$\text{or} \quad \log\frac{[A]_0}{[A]} = \frac{2.2 \times 10^{-5} \times 5400}{2.303} = 0.0516$$

or $\frac{[A]_0}{[A]} = 1.126$

or $\frac{[A]}{[A]_0} = 0.888$

Amount of SO_2Cl_2 decomposed = 1 – 0.888 = 0.112

∴ Percentage of SO_2Cl_2 decomposed = $\frac{0.112}{1} \times 100$ = **11.2%.**

Example 43.

The rate of decomposition of N_2O_5 in CCl_4 solution has been measured at 318 K and the following results were obtained :

t(min)	*0*	*135*	*339*	*689*	*1680*
c (M)	*2.08*	*1.91*	*1.67*	*1.35*	*0.57*

Find the order of reaction and calculate its rate constant. What is its half life period ?

Solution: It is clear that the rate of reaction does not remain constant with time and therefore, it is not a zero order reaction. We try integrated rate equation for first order reaction as :

$$k = \frac{1}{t} ln \frac{(C_0)}{(C)}$$

t (min)	C (M)	$k = \frac{2.303}{t} \log \frac{(C_0)}{(C)}$ min^{-1}
0	2.08	—
135	1.91	$\frac{2.303}{135} \log \frac{2.08}{1.91} = 6.32 \times 10^{-4}$
339	1.68	$\frac{2.303}{339} \log \frac{2.08}{1.68} = 6.30 \times 10^{-4}$
683	1.35	$\frac{2.303}{683} \log \frac{2.08}{1.35} = 6.33 \times 10^{-4}$
1680	0.72	$\frac{2.303}{1680} \log \frac{2.08}{0.72} = 6.31 \times 10^{-4}$

Since value of k remains to be constant, the reaction is of first order.

$k = 6.315 \times 10^{-4}$ min^{-1}

Now, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.315 \times 10^{-4} \text{ min}^{-1}}$

= **1.097×10^3 min.**

Example 44.

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

(Pb.S.B.2010, H.P.S.B. 2012, Mizoram S.B. 2018)

Solution : For the first order reaction :

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

If $[A]_0 = a$, $[A] = a - \frac{a \times 15}{100} = 0.85\,a$, $t = 20$ min

$$k = \frac{2.303}{20} \log \frac{a}{0.85\,a}$$

$$= \frac{2.303}{20} \times 0.0706$$

$$= 8.13 \times 10^{-3} \text{ min}^{-1}$$

In second case, if $[A]_0 = a$, $[A] = a - \frac{a \times 60}{100} = 0.40\,a$ and time, t = ?

Now, $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$

$$= \frac{2.303}{8.13 \times 10^{-3}} \log \frac{a}{0.40\,a}$$

$$= \frac{2.303}{8.13 \times 10^{-3}} \times 0.3979$$

= **112.7 min.**

Example 45.

Show that in case of a first order reaction, the time taken for completion of 99.9% reaction is ten times the time required for half change of the reaction. **N.C.E.R.T.**

Solution : When 99.9% reaction is completed,

$$[R] = [R]_0 - \frac{99.9}{100}[R]_0 = 0.001\,[R]_0$$

$$t_{(99.9\%)} = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$$= \frac{2.303}{k} \log \frac{[R]_0}{0.001[R]_0} = \frac{2.303}{k} \log 10^3$$

$$= \frac{2.303 \times 3}{k} \quad ....(i)$$

When half of the reaction is completed

$$[R] = [R]_0 - 0.5\,[R]_0 = 0.5\,[R]_0$$

$$t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{0.5[R]_0} = \frac{2.303}{k} \log 2$$

$$= \frac{2.303 \times 0.3010}{k} \quad ....(ii)$$

Dividing eq. (*i*) by eq. (*ii*)

$$\frac{t_{(99.9\%)}}{t_{1/2}} = \frac{3}{0.3010} = \textbf{10 times.}$$

Example 46.

The decomposition of phosphine, PH_3, proceeds according to the following equation :

$$4PH_3\,(g) \longrightarrow P_4\,(g) + 6H_2\,(g)$$

It is found that the reaction follows the following rate equation :

$$Rate = k[PH_3].$$

The half-life of PH_3 is 37.9 s at 120° C.

(i) How much time is required for 3/4th of PH_3 to decompose?

(ii) What fraction of the original sample of PH_3 remains behind after 1 minute? (A.I.S.B. 2010)

Solution : Half life period, $t_{1/2} = \frac{0.693}{k}$

or $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{37.9\text{ s}} = 0.0183$ s^{-1}

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

(*i*) For 3/4th of a reaction to decompose,

$$[A] = [A]_0 - \frac{3}{4}[A]_0 = \frac{1}{4}[A]_0$$

$$t = \frac{2.303}{0.0183} \log \frac{[A]_0}{\frac{1}{4}[A]_0} = \frac{2.303}{0.0183} \log 4$$

$$= \frac{2.303}{0.0183} \times 0.6020 = 75.76 \text{ s}$$

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

For $t = 1$ min. = 60 s

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

or $$\log \frac{[A]_0}{[A]} = \frac{0.0183 \times 60}{2.303} = 0.4768$$

or $$\frac{[A]_0}{[A]} = 2.998$$

$$\therefore \quad \frac{[A]}{[A]_0} = 0.33$$

Example 47.

Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law with $t_{1/2}$ = 3 hrs. Calculate the fraction of sucrose which remains after 8 hrs. *(CBSE Sample Paper 2011)*

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

Now, $$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$0.231 = \frac{2.303}{8 \text{ hr}} \log \frac{[A]_0}{[A]}$$

$$\log \frac{[A]_0}{[A]} = \frac{0.231 \times 8}{2.303} = 0.8024$$

$$\frac{[A]_0}{[A]} = 6.345$$

$$\therefore \quad \frac{[A]}{[A]_0} = \mathbf{0.158}$$

Example 48.

The thermal decomposition of HCO_2H is a first order reaction with a rate constant of 2.4×10^{-3} s^{-1} at a certain temperature. Calculate how long will it take for three-fourths of initial quantity of HCO_2H to decompose. (log 0.25 = – 0.6021). *(A.I.S.B. 2011)*

Solution : $$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

If initial conc. of A is a, then

$$[A] = a - \frac{3}{4}a = \frac{1}{4}a$$

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

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

$$= \frac{2.303}{2.4 \times 10^{-3}} \times 0.6021 = \mathbf{578\ s}$$

Example 49.

Starting from 10g of a radioactive element, 0.25 g was left after 5 years. Calculate

(i) Rate constant for the decay of the radioactive element.
(ii) The amount left after one year.
(iii) The time required for half of the element to decay.
(iv) Average life of the element. *(A.I.S.B. 2011)*

Solution : (i) $$k = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$[A]_0 = 10$ g, $[A] = 0.25$ g, $t = 5$ years

$$k = \frac{2.303}{5} \log \frac{10}{0.25}$$

$$= \frac{2.303}{5} \log 40 = 0.7379 \text{ year}^{-1}$$

(ii) Amount left after 1 year

$t = 1$ year, $[A]_0 = 10$ g, $[A] = ?$

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

$$0.7379 = \frac{2.303}{1} \log \frac{10}{[A]}$$

$$\log \frac{10}{[A]} = \frac{0.7379 \times 1}{2.303} = 0.3204$$

$$\frac{10}{[A]} = \text{Antilog } (0.3204) = 2.09$$

$$\therefore \quad [A] = \frac{10}{2.09} = \mathbf{4.785\ g}$$

(iii) Time for decay of half of the element

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.7379} = \mathbf{0.9392\ year}$$

(iv) Average life,

$$\tau = \frac{1}{k} = \frac{1}{0.7379} = \mathbf{1.3552\ year}$$

Practice Problems

27. An acidic solution of sugar was hydrolysed to the extent of 57% after 66 minutes. Assuming the reaction to be of first order, calculate the time taken for 75% hydrolysis.

28. A first order reaction is 20% complete in 10 minutes. Calculate the time taken for the reaction to go to 80% completion. *(Hr.S.B. 2017)*

29. A first order decomposition reaction takes 40 minutes for 30% decomposition. Calculate its $t_{1/2}$ value. *(D.S.B. 2008, 2013)*

30. A first order reaction is 20% complete in 10 minutes. Calculate the time for 75% completion of the reaction.

(Pb.S.B. 2010, H.P.S.B. 2011, 2012, Hr. S.B. 2017)

Answers to Practice Problems

27. 108.4 min.
28. 72.12 min.
29. 77.69 min.
30. 62.18 min

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31. The three-fourth of a first order reaction is completed in 32 minutes. What is the half life period of the reaction ? *(J.K.S.B. 2000, H.P.S.B. 2011, Mizoram S.B. 2017)*

32. The half life period for a reaction of first order is 2.31×10^3 min. How long will it take for 1/5 of the reactant to be left behind ? *(Pb. S.B. 2013)*

33. A reaction is first order with respect to reactant P having rate constant 6 min^{-1}. If we start with [P] = 0.5 mol L^{-1}, when would [P] reach the value of 0.05 mol L^{-1} ? Calculate half life period of the reaction. *(Pb. S.B. 2013)*

34. For a first order reaction half life period is 100 seconds. How long will it take the reaction to complete 75%? *(Uttarakhand S.B. 2013)*

35. The rate constant for a first order reaction is 80 s^{-1}. How much time will it take to reduce the concentration of the reactant to 1/18th of its initial value? *(Pb. S.B. 2016)*

36. The pressure of a gas decomoposing at the surface of a solid catalyst has been measured at different times and the results are given below :

t(s)	0	100	200	300
p(Pa)	4.00×10^3	3.50×10^3	3.00×10^3	2.5×10^3

Determine the order of reaction, its rate constant and half life period.

37. The half life period of a substance is 60 min at a certain initial concentration. When the concentration is reduced to one half of the initial concentration, the half life period is found to be 30 min. Calculate the order of the reaction.

38. The thermal decomposition of a compound is of first order. If 50% of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose ? *(H.P.S.B. 2011, Nagaland S.B. 2018)*

39. A first order reaction takes 69.3 minutes for 50% completion. Calculate the time required for 80% completion of this reaction. *(D.S.B. 2005)*

31. 16 min.
32. 5.36×10^3 min.
33. 0.383 min, 0.1155 min.
34. 200 min.
35. 3.61×10^{-2} s.
36. Order = 0, k = 5 Pa s^{-1}, $t_{1/2}$ = 400s.
37. Zero order.
38. 399 min.
39. 161 min.

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Advanced Level PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 2. The half life time of a first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2\,(aq) \longrightarrow N_2O\,(g) + H_2O\,(l)$$

If 6.2 of NH_2NO_2 is allowed to decompose, calculate
(*i*) time taken for NH_2NO_2 to decompose 99% and
(*ii*) volume of dry N_2O produced at this point measured at S.T.P.

Solution (*i*) For first order reaction.

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

Here $t_{1/2}$ = 2.1 hr

$$\therefore \quad k = \frac{0.693}{2.1} = 0.33\ hr^{-1}$$

Now, $$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$$

If $[A]_0 = a$, $[A] = a - \frac{99\,a}{100} = 0.01\,a$

$$\therefore \quad t = \frac{2.303}{0.33}\log\frac{a}{0.01\,a} = \frac{2.303}{0.33} \times 2 = \mathbf{13.96\ hr}$$

(*ii*) 1 mole of NH_2NO_2 decomposed to give = 1 mole of N_2O

Moles of NH_2NO_2 taken = $\frac{6.2}{62}$ = 0.1 mol (Molecular mass of NH_2NO_2 = 62)

Moles of NH_2NO_2 decomposed = $\frac{0.1 \times 99}{100}$ = 0.099 mole

Moles of N_2O (*g*) produced = 0.099 mole

Now, 1 mole of N_2O (*g*) at S.T.P. = 22.4 L

0.099 mole of N_2O (*g*) at S.T.P. = 22.4 × 0.099

= **2.218 litres.**

Problem 3. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.

(*i*) After 55 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(*ii*) Calculate the pressure of Cl_2O_7 after 100 s of decomposition at this temperature.

Solution For the first order reaction :

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

(*i*) Here, a = 0.062 atm, $(a - x)$ = 0.044 atm, t = 55 s

$$\therefore \quad k = \frac{2.303}{55}\log\frac{0.062}{0.044} = 6.24 \times 10^{-3}\ s^{-1}.$$

(*ii*) To calculate $(a - x)$ when t = 100 s, a = 0.062 atm.

$$6.24 \times 10^{-3} = \frac{2.303}{100}\log\frac{0.062}{(a-x)}$$

or $$\log\frac{0.062}{(a-x)} = \frac{6.24 \times 10^{-3} \times 100}{2.303} = 0.2709$$

or $$\frac{0.062}{(a-x)} = 1.866$$

or $(a - x)$ = **0.033 atm.**

Problem 4. The gas phase decomposition of dimethyl ether (CH_3OCH_3) follows first order kinetics.

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 775 K and has a half life of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 min? Assume ideal gas behaviour.

Solution

	$CH_3OCH_3(g)$	$\longrightarrow CH_4(g)$	$+ H_2(g)$	$+ CO(g)$
Initial pressure	0.40 atm	–	–	–
Pressure after 12 min	(0.40 – P) atm	P	P	P

Since the reaction is of first order:

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

For ideal behaviour, mole $\propto$ pressure(at constant T and V)

$[R]_0 = 0.40\ atm^{-1}$, $[R] = (0.40 - P)$ atm

$$k = \frac{0.693}{14.5} = 0.0478\ min^{-1}$$

$$\therefore \quad 0.0478 = \frac{2.303}{12}\log\frac{0.40}{(0.40-P)}$$

$$\log\frac{0.40}{(0.40-P)} = \frac{0.0478\times 12}{2.303} = 0.249$$

Taking antilog

$$\frac{0.40}{0.40-P} = 1.774$$

$$0.40 = 1.774 \times 0.40 - 1.774\ P$$

$$1.774\ P = 0.7096 - 0.40 = 0.3096$$

$$\therefore \quad P = \frac{0.3096}{1.774} = 0.175\ atm$$

$\therefore$ Pressure of dimethyl ether decomposed = 0.175 atm

Total pressure = 0.40 – P + P + P + P = 0.40 + 2P

= 0.40 + 2 × 0.175 = **0.75 atm**

Problem 5. A flask contains a mixture of A and B. Both the compounds decompose by first order kinetics. The half lives of A and B are 60 min and 15 min respectively. If the initial concentrations of A and B are equal, how long will it take for the concentration of A to be three times that of B?

Solution Let the initial concentration of both A and B be 1M.

$[A]_0 = 1M$, $[B]_0 = 1M$

Let at time t, [A] = 3[B]

For A, $k_A = \frac{0.693}{60}$. For B, $k_B = \frac{0.693}{15}$

For A after time t,

$$t_A = \frac{2.303}{0.693}\times 60\log\frac{1}{[A]} \quad \text{or} \quad \frac{2.303}{0.693}\times 60\log\frac{1}{3[B]} \quad (i)$$

For B after time t,

$$t_B = \frac{2.303}{0.693}\times 15\log\frac{1}{[B]} \quad (ii)$$

Now $t_A = t_B$

$$\therefore \quad \frac{2.303}{0.693}\times 60\log\frac{1}{3[B]} = \frac{2.303}{0.693}\times 15\log\frac{1}{[B]}$$

$$\text{or} \quad 4 = \frac{\log\frac{1}{[B]}}{\log\frac{1}{3[B]}} = \frac{\log 1 - \log[B]}{\log 1 - \log 3[B]}$$

$$4 = \frac{-\log[B]}{-\log 3[B]} = \frac{\log[B]}{\log 3[B]} \quad (\because \log 1 = 0)$$

$$4 = \frac{\log[B]}{\log 3 + \log[B]}$$

$$4(\log 3 + \log[B]) = \log[B]$$

$$4(0.477 + \log[B]) = \log[B]$$

$$1.908 + 4\log[B] = \log[B]$$

or $3\log[B] = -1.908$

or $\log[B] = -0.636$

$\therefore$ [B] = antilog (–0.636) = 0.231 ...(*iii*)

Substituting the value of B in eqn (*ii*)

$$t = \frac{2.303\times 15}{0.693}\log\frac{1}{0.231}$$

$$= \frac{2.303\times 15}{0.693}\times 0.636$$

$$= 31.7\ min$$

PSEUDO CHEMICAL REACTIONS

Some reactions are first order each with respect to two different reactants *i.e.*,

$$A + B \longrightarrow \text{Products}$$

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

However, if one of the reactants is present in high concentration (solvent) then there is very little change in its concentration. In other words, the concentration of that reactant remains practically constant during the reaction. For example, if [A] = 0.01 M and that of solvent water [B] = 55.5 M, the concentration of B changes only from 55.50 to 55.49 M even after the completion of the reaction. Under such conditions, we may write,

Rate = $k_0[A]$ where $k_0 = k[B]$

The reaction, therefore, behaves as a first order reaction in A. Such reactions are called **pseudo first order reactions**.

The reactions which are not truly of first order but under certain conditions become reactions of first order *are called* ***pseudo first order reactions.***

Consider the hydrolysis of ethyl acetate :

$$CH_3COOC_2H_5 + H_2O \xrightleftharpoons{\text{Acid}} CH_3COOH + C_2H_5OH$$

The molecularity of the reaction is **two** because it involves two reacting species, namely ethyl acetate and water. However, the concentration of ethyl acetate changes during the reaction while water is present in **such a large excess** that its concentration remains practically unchanged. Therefore, the rate of the reaction depends only on the concentration of ethyl acetate and hence the order of the reaction is **one**.

$$\text{Rate} = k' [CH_3COOC_2H_5] [H_2O]$$

$[H_2O]$ can be takes as constant so that

$$\text{Rate} = k [CH_3COOC_2H_5]$$

where $k = k' [H_2O]$

Thus, the reaction appears to be second order but follows the first order kinetics. Such reactions which appear to be of higher order but actually follow lower order kinetics are called **pseudo chemical reactions**. For example, the above reaction is called **pseudo first order reaction**. Another important example is the hydrolysis of cane sugar or inversion of cane sugar to give glucose and fructose :

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}} + \underset{\text{Excess}}{H_2O} \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k[C_{12}H_{22}O_{11}]$$

In this case also molecularity is **two** while order is **one**.

SOLVED EXAMPLES

Example 50.

Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentraction of the ester at different times is given below :

t (min)	*0*	*30*	*60*	*90*
c (mol L^{-1})	*0.8500*	*0.8004*	*0.7538*	*0.7096*

Show that it follows a pseudo first order reaction as the concentration of H_2O remains nearly constant (55 mol L^{-1}) during the course of the reaction. What is the value of k in this equation ?

rate = k' [CH_3COOCH_3] [H_2O] **N.C.E.R.T.**

Solution : For pseudo first order reaction, the reaction should be first order with respect to ester because $[H_2O]$ = constant $k = k'[H_2O]$. Let us calculate the value of k for the first order reaction :

t(min)	c(M)	$k = \frac{2.303}{t} \log \frac{C_0}{C}$ (min^{-1})
0	0.8500	—
30	0.8004	$\frac{2.303}{30} \log \frac{0.8500}{0.8004} = 2.004 \times 10^{-3}$
60	0.7538	$\frac{2.303}{60} \log \frac{0.8500}{0.7538} = 2.002 \times 10^{-3}$
90	0.7096	$\frac{2.303}{90} \log \frac{0.8500}{0.7096} = 2.005 \times 10^{-3}$

Since $k[H_2O]$ is constant, it is pseudo first order reaction.

$$k[H_2O] = 2.004 \times 10^{-3} \text{ min}^{-1}$$

$$[H_2O] = 55 \text{ M}$$

$$\therefore \quad k = \frac{2.004 \times 10^{-3}}{55} = \mathbf{3.64 \times 10^{-5} \text{ M}^{-1} \text{ min}^{-1}}.$$

COLLISION THEORY : ENERGY AND ORIENTATION BARRIERS TO REACTIONS

We have learnt that the basic requirement for a reaction to occur is that the reacting species (atoms, molecules or ions) must collide with one another. This is also the basis of **collision theory** for reactions. This theory was put forward by Max Trautz and William Lewis in 1916–18. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other.

The number of collisions that take place per second per unit volume of the reaction mixture is known *as* **collision frequency Z.**

The value of collision frequency is normally very high. For instance, under ordinary conditions of temperature and pressure, in a gaseous system, the collision frequency of binary collisions is of the order of 10^{25} to 10^{28}. If all the collisions are effective in forming the products, the reactions must be completed in a very short time. However, in actual practice, most of the chemical reactions are slow and take much longer time for their completion.

This means that all the collisions among the reacting species at a given temperature are not effective in bringing about the chemical reaction. *The collisions which actually produce the products and therefore, result in the chemical reactions* are called **effective collisions.**

There are two important barriers to a reaction namely

(*i*) *energy barrier* (*ii*) *orientation barrier.*

(*i*) **Energy barrier.** For the reacting species to make effective collisions, they should have sufficient energy to break the chemical bonds in the reacting molecules. *The minimum amount of energy which the colliding molecules must possess is* known as **threshold energy.** This means that only those collisions of reactants will give products which possess energies greater than threshold energy.

(*ii*) **Orientation barrier.** The colliding molecules should also have proper orientation so that the old bonds may break and new bonds are formed.

For example, consider the reaction :

$$NO_2\,(g) + NO_2\,(g) \longrightarrow N_2O_4\,(g)$$

During this reaction, the products are formed only when the colliding molecules have proper orientation at the time of collisions. These are called effective collisions [Fig. 10 (*a*)].

On the other hand, when the molecules do not have proper orientation at the time of collision as shown in Fig. 10 (*b*), they result in ineffective collisions and do not form the products.

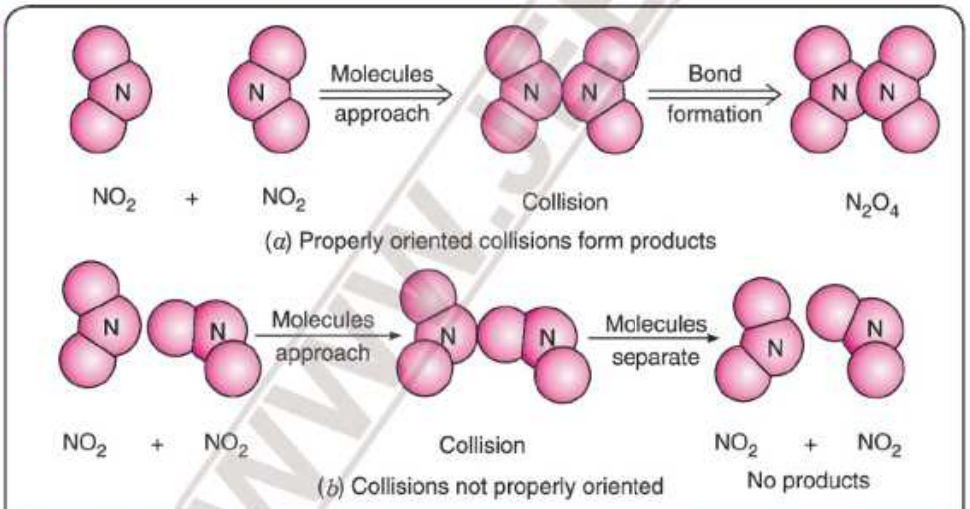
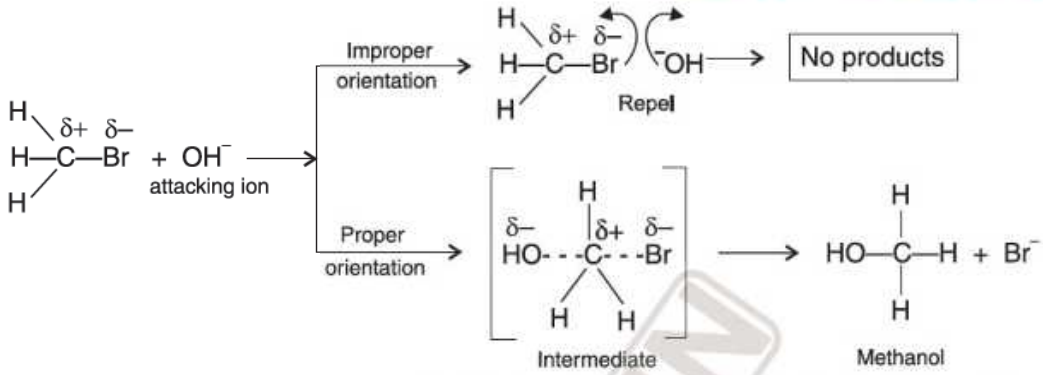


Fig. 10. Illustration of (*a*) effective and (*b*) ineffective collisions between molecules for the reaction.
$NO_2(g) + NO_2(g) \rightleftharpoons N_2O_4(g)$

Similarly, consider the reaction of bromomethane (CH_3Br) with OH^- ions to form methanol. The OH^- ion must attack the positively charged carbon to form an intermediate which changes to product after elimination of Br^- ion. If OH^- does not get proper site for attack, reaction will not occur. It is observed that in this reaction, first an intermediate is formed by the attack of OH^- at the site away form Br^- and finally product is formed as shown below :

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$



It is clear that proper orientation of reactants leads to the bond formation whereas improper orientation simply makes them to bounce back and products are not formed.

Thus, the collisions in which the colliding molecules do not possess the minimum energy for effective collisions (threshold energy) or proper orientation do not form products. In other words, the colliding species rebound unchanged in such cases. Therefore, it follows that *only a small fraction of collisions is effective.*

Thus, the main points of **collision theory** are summed up below :

(*i*) *For a reaction to occur, there must be collisions between the reacting species.*

(*ii*) *Only a certain fraction of the total number of collisions are effective in forming the products.*

(*iii*) *For effective collisions, the molecules should possess sufficient energy as well as orientation.*

The fraction of effective collisions, under ordinary conditions may vary from nearly zero to about one for ordinary reactions.

Thus, the rate of reaction is proportional to

(*a*) the number of collisions per unit volume per second (collision frequency, Z) between the reacting species,

(*b*) the fraction of effective collisions (properly oriented and possessing sufficient energy), f :

$$i.e., \quad \text{Rate} = -\frac{dx}{dt} = f \times Z$$

Table 3. Rate constant for N_2O_5 at different temperatures.

Temperature (K)	k (s^{-1})
273	7.87×10^{-7}
298	3.56×10^{-5}
318	4.98×10^{-4}
338	4.87×10^{-3}

DEPENDENCE OF REACTION RATES ON TEMPERATURE

Temperature has a great influence on reaction rates. In general, an increase in temperature increases the rate of almost all reactions. On the other hand, a decrease in temperature decreases the rate. This effect is observed for exothermic as well as for endothermic reactions. For example, the rate constant for the decomposition of N_2O_5 is 7.87×10^{-7} s^{-1} at 273 K but it becomes 3.56×10^{-5} s^{-1} at 298 K. This means that for a rise of 25° in temperature, the rate constant is increased by about 45 times. Similarly, it has been observed that the time taken for the decomposition of N_2O_5 to half of its original concentration is 10 days at 0°C, 5 hour at 25°C and 12 min at 50°C. You must have observed in practicals that in a mixture of potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$), potassium permanganate gets decolourised faster at a higher temperature than at a lower temperature.

A general **approximate rule** for the effect of temperature on reaction rates is that *the rate of a reaction or rate constant becomes almost double for every 10° rise in temperature.* This is also called **temperature coefficient.** It is *the ratio of rate constants* of the reaction at two temperatures differing by 10°. Thus,

$$\text{Temperature coefficient} = \frac{\text{Rate constant } (T + 10)^\circ C}{\text{Rate constant at } T^\circ C}$$

Explanation for Increase in Rate of Reaction with Rise in Temperature

According to collision theory of chemical reactions, we know that the rate of a reaction depends upon collision frequency (Z) and fraction of the effective collisions (*f*). Obviously, we may think that the increase in rate of a reaction with temperature is brought about by either of the two or a combination of both factors. These are discussed below :

(*i*) Increase in collision frequency. With the increase in temperature, the average kinetic energy of the molecules increases and this leads to an increase in number of collisions per unit time (Z). The average kinetic energy of the molecules is directly proportional to the absolute temperature. This increases only by 3% when the temperature rises from 300 K to 310 K.

This means that if the increase in the collision frequency is the only reason for increase in rate of reaction with temperature, then the reaction rate would have been increased by a factor of only 3%. This is very small in comparison to the experimentally observed factor of 2 or even more in some cases. *Therefore, the increase in rate of a reaction is not simply due to the increase in collision frequency.*

(*ii*) Effective collisions. According to the collision theory, only a small fraction of collisions is effective in bringing about the chemical reaction and the rest of the collisions are ineffective. *For effective collision (to yield products) the colliding molecules must have more than or equal to certain minimum amount of energy called* **threshold energy.** If the energy of the reacting molecules is less than this value, collisions will be ineffective. Thus, the energy of collisions determines the possibility of a reaction.

Now let us consider as to why some collisions should be highly energetic while others are not so. Ludwig Boltzmann and James Clark Maxwell used statistics to predict the behaviour of large number of molecules.

We know that all the molecules in a substance do not possess the same kinetic energy. This is due to collisions between the moving molecules so that their energies are transferred from one molecule to another. Thus, there is a distribution of kinetic energies among reacting molecules. If the energy of molecules are plotted against the corresponding fraction of molecules, N_E/N_T with a given energy (where N_E = number of molecules having kinetic energy E and N_T = total number of molecules), at a particular temperature, a curve of the type shown in Fig. 11, is obtained. This is called *Maxwell's distribution of energies.* From the figure, it is evident that the fraction of molecules having very low or very high energies is very small. Most of the molecules have intermediate kinetic energies as shown by the peak in the graph. This peak corresponds to **most probable kinetic energy** *i.e.*, kinetic energy of maximum fraction of molecules. In the figure, E corresponds to minimum or threshold energy required for effective collisions. The molecules having energy equal to or greater than E will result in the formation of products and this fraction of molecules capable of effective collisions is very small.

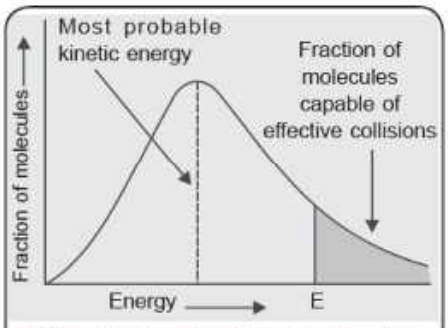


Fig. 11. Distribution of molecular energies.

It may be noted that for reactions having low values of E, there will be larger fraction of colliding molecules which produce effective collisions and hence, rate of the reaction will be **high.** On the other hand, if the value of E for a particular reaction is high, then only a few collisions will be sufficiently energetic to give products while all other collisions will be ineffective. The reaction will proceed very **slowly.**

Let us now consider the **effect of increase in temperature** on the number of effective collisions. Fig. 12 shows the energy distribution of molecules at two different temperatures T_1 and T_2, where $T_2 = T_1 + 10°$.

From the figure, it is evident that the curve at higher temperature gets shifted towards the right indicating that at higher temperature, the molecules have higher energies. Further, the curve at higher temperature is flatter than that at lower temperature which also indicates that the number of molecules with higher energy content have increased.

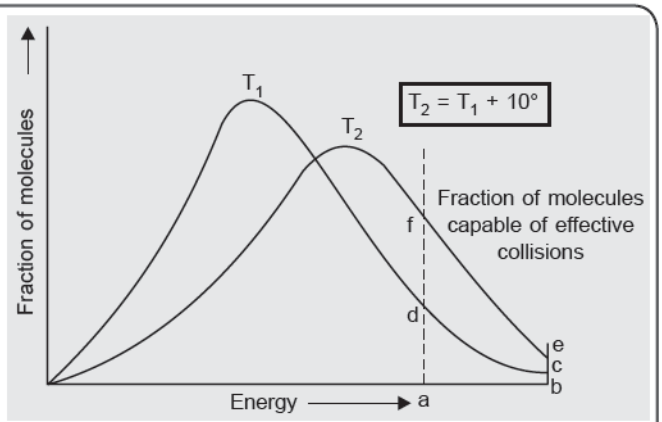


Fig. 12. Distribution of molecular energies at temperatures T_1 and T_2.

The minimum energy required for the effective collisions is also shown in the diagram and the number of molecules possessing energies equal to or greater than E, is proportional to area *abcd* at temperature T_1 and area *abef* at temperature T_2. In the figure, the area *abef is* roughly twice as large as *abcd*. Since the rate of reaction depends upon the number of molecules which possess energies larger than threshold energy (for effective collisions), it may be interpreted that the fraction of molecules possessing threshold energy has increased approximately two times and thereby, increases the rate by two times for a rise of 10 degrees.

Thus, we may conclude that *increase in the rate of reaction with the rise in temperature is mainly due to the increase in number of effective collisions.*

ARRHENIUS EQUATION AND CALCULATION OF ACTIVATION ENERGY

Arrhenius proposed a quantitative relationship between rate constant and temperature as :

$$k = Ae^{-E_a/RT} \qquad ...(21)$$

This equation is called **Arrhenius equation** in which constant A is known as **Arrhenius factor or frequency factor.** It is also called **pre-exponential factor.** It is a constant specific to a particular reaction. This factor is related to how many successfully oriented collisions occur in a particular reaction. E_a is the **activation energy** which represents the minimum energy that the reacting molecules must possess before undergoing a reaction. Both A and E_a are characteristic of the reaction. These are collectively called **Arrhenius parameters.** The factor $e^{-E_a/RT}$ corresponds to the fraction of molecules that have energy greater than E_a. T is the absolute temperature and R is the gas constant.

Taking logarithm, Eqn. (21) may be written as

$$ln\ k = ln\ A - \frac{E_a}{R} \times \frac{1}{T} \qquad [\because ln\ e = 1]$$

Converting to common logarithm (ln X = 2.303 log X), we get

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

Dividing each side by 2.303, we get

$$\log k = \log A - \frac{E_a}{2.303\ RT} \qquad ...(22)$$

It is clear that by **increasing the temperature or decreasing the activation energy will result in an increase in the rate of reaction.**

Calculation of activation energy.

The activation energy can be calculated from Eqn. (22). As is clear the equation is in the form $y = mx + c$ which represents a straight line. When log k is plotted against $\frac{1}{T}$, we get a straight line (Fig. 13). The intercept of this line is equal to log A and slope is equal to $-\frac{E_a}{2.303\ R}$.

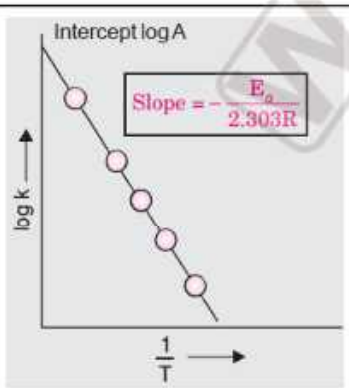


Fig. 13. Plot of log k versus 1/T to calculate activation energy.

Therefore, $$\text{Slope} = -\frac{E_a}{2.303\ R} \qquad ...(23)$$

Knowing the value of slope and gas constant R, activation energy can be calculated as

$$E_a = -2.303\ R \times \text{Slope}$$

Alternatively, E_a and A can be determined by measuring the values of rate constant at two different temperatures. Let k_1 and k_2 are the rate constants for the reaction at two different temperatures T_1 and T_2 respectively. Then,

$$\log k_1 = \log A - \frac{E_a}{2.303\ RT_1} \quad ...(24)$$

and

$$\log k_2 = \log A - \frac{E_a}{2.303\ RT_2} \quad ...(25)$$

Subtracting Eq. (24) from Eqn. (25), we get

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

or

$$\boxed{\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]} \quad ...(26)$$

or

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

Collision Theory and Arrhenius Equation

Though Arrhenius equation is applicable under a wide range of circumstances, collision theory provides a greater insight into the energetics and mechanistic aspects of reactions. For a bimolecular elementary reaction:

$$A + B \longrightarrow \text{Products}$$

rate of reaction may be expressed as

$$\text{Rate} = Z_{AB}\, e^{-E_a/RT} \quad ...(27)$$

where Z_{AB} represents the collision frequency of reactants A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a. Since rate of reaction is directly related to rate constant, k, we can also write

$$k = Z_{AB}\, e^{-E_a/RT} \quad ...(28)$$

This equation predicts the values of rate constants fairly accurately for reactions involving atomic species or simple molecules. However, if reactant molecules are complex, significant deviations are observed. This is because, even if the colliding molecules have energy greater than threshold energy, they may not have proper orientation at the time of collision and therefore, no breaking of bonds between reacting species and formation of new bonds to form products may occur. In other words, besides the requirement of sufficient energy, the molecules must be properly oriented in space also for a collision to be successful resulting effective collisions.

To account for effective collisions, another factor P, called the **orientation factor** or **stearic factor** or **probability factor** is introduced. Hence, eqn. (28) may modified as

$$k = P\, Z_{AB}\, e^{-E_a/RT} \quad (29)$$

if we compare this equation with Arrhenius equation,

$$k = A e^{-E_a/RT}$$

we observe that pre-exponential term, A in Arrhenius equation is

$$A = PZ_{AB}$$

Thus, in collision theory, activation energy and proper orientation of the molecules determine the criteria for an effective collision and hence the rate of a chemical reaction.

It may be noted that collision theory has certain drawbacks. It considers the atoms or molecules to be hard spheres and does not take into account the structural aspects. Some other theories such as 'transition state theory' have been proposed to explain reaction rates. However, their discussion is beyond the scope of present class.

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Solving Numerical Problems

FORMULAE AND UNITS

Arrhenius equation

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

k = rate constant,
A = frequency factor
E_a = Activation energy
R = Gas constant
= 8.314 $JK^{-1}\,mol^{-1}$

For two different temperatures T_1 and T_2,

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

where k_1 and k_2 are rate constants at temperatures T_1 and T_2 respectively.

SOLVED EXAMPLES

Example 51.

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

$k_1 = 2.15\times10^{-8}\ s^{-1}$ *at 650 K*

and $k_2 = 2.39 \times 10^{-7}\ s^{-1}$ *at 700 K.*

Calculate the activation energy for the reaction.

(A.I.S.B. 2009, Pb. S.B. 2014)

Solution : The Arrhenius equation is :

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

$k_1 = 2.15 \times 10^{-8}\ s^{-1}$ $T_1 = 650$ K
$k_2 = 2.39 \times 10^{-7}\ s^{-1}$ $T_2 = 700$ K

Substituting the values,

$$\log \frac{2.39\times10^{-7}}{2.15\times10^{-8}} = \frac{E_a}{2.303\times8.314}\left[\frac{1}{650} - \frac{1}{700}\right]$$

$$1.046 = \frac{E_a}{2.303\times8.314}\left[\frac{700-650}{650\times700}\right]$$

$$E_a = \frac{1.046\times2.303\times8.314\times650\times700}{50}$$

= 182254 J mol^{-1}

or = **182.254 kJ mol^{-1}**

Example 52.

In general, it is observed that the rate of a chemical reaction becomes double with every 10° rise in temperature. If this generalization holds for a reaction in the temperature range 298 to 308 K what would be the value of activation energy for this reaction ? (R = 8.314 $JK^{-1}\,mol^{-1}$)

(D.S.B. 2000, Pb. S.B. 2014)

Solution : Arrhenius equation is :

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

$T_1 = 298$ K, T_2 = 308 K, R = 8.314 $JK^{-1}\,mol^{-1}$

$$\frac{k_2}{k_1} = 2$$

$$\log 2 = \frac{E_a}{2.303\times8.314}\left[\frac{1}{298} - \frac{1}{308}\right]$$

$$0.3010 = \frac{E_a}{2.303\times8.314}\times\frac{10}{298\times308}$$

or $$E_a = \frac{0.3010\times2.303\times8.341\times298\times308}{10}$$

= 52898 J mol^{-1}

= **52.898 kJ mol^{-1}.**

Example 53.

The rate constant of a first order reaction becomes 5 times when the temperature is raised from 350K to 400K. Calculate the activation energy of the reaction. (R = 8.314 JK^{-1}, log 5 = 0.69897).

(Nagaland S.B. 2018)

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

$\frac{k_2}{k_1} = 5$, R = 8.314 $JK^{-1}\,mol^{-1}$, $T_1 = 350$ K, $T_2 = 400$ K

$$\log 5 = \frac{E_a}{2.303\times8.314}\left[\frac{1}{350} - \frac{1}{400}\right]$$

$$0.69897 = \frac{E_a}{2.303\times8.314}\times\left[\frac{400-350}{350\times400}\right]$$

$$\therefore \quad E_a = \frac{0.69897\times2.303\times8.314\times350\times400}{50}$$

or = 37473.2 J mol^{-1} = **37.473 kJ mol^{-1}.**

Example 54.

The rate constants of a reaction at 700 K and 760 K are 0.011 s^{-1} and 0.105 s^{-1} respectively. Calculate the values of Arrhenius parameters.

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

$k_1 = 0.011\ s^{-1}$, $T_1 = 700$ K, $k_2 = 0.015\ s^{-1}$, $T_2 = 760$ K, $R = 8.314\ JK^{-1}\ mol^{-1}$

$$\therefore \quad \log \frac{0.105}{0.011} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{700} - \frac{1}{760}\right]$$

$$\log 9.545 = \frac{E_a}{2.303 \times 8.314}\left[\frac{760 - 700}{700 \times 760}\right]$$

$$0.9798 = \frac{E_a \times 60}{2.303 \times 8.314 \times 700 \times 760}$$

$$\therefore \quad E_a = \frac{0.9798 \times 2.303 \times 8.314 \times 700 \times 760}{60}$$

$$= 166.342 \times 10^3\ J\ mol^{-1}$$

$$= \mathbf{166.342\ kJ\ mol^{-1}}.$$

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

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

$$\log A = \log 0.011 + \frac{166.342 \times 10^3}{2.303 \times 8.314 \times 700}$$

$$= -1.9586 + 12.411$$

$$= 10.4524$$

$$\therefore \quad A = \mathbf{2.834 \times 10^{10}\ s^{-1}}.$$

Example 55.

The first order rate constant for the decomposition of ethyl iodide by the reaction:

$$C_2H_5I(g) \longrightarrow C_2H_4(g) + HI(g)$$

at 600 K is $1.60 \times 10^{-5}\ s^{-1}$. Its energy of activation is 209 kJ mol^{-1}. Calculate the rate constant of the reaction at 700 K. **N.C.E.R.T.** *(Kerala S.B. 2013)*

Solution : $E_a = 209\ kJ\ mol^{-1} = 209 \times 10^3\ J\ mol^{-1}$

$k_1 = 1.60 \times 10^{-5}\ s^{-1}$, $T_1 = 600$ K

$k_2 = ?$ $T_2 = 700$ K

Substituting the values

$$\log \frac{k_2}{1.60 \times 10^{-5}} = \frac{209 \times 10^3}{2.303 \times 8.314}\left[\frac{700 - 600}{700 \times 600}\right]$$

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

$$\frac{k_2}{1.60 \times 10^{-5}} = 397.19$$

$$\therefore \quad k_2 = 397.19 \times 1.60 \times 10^{-5}$$

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

Example 56.

In the Arrhenius equation for a certain reaction, the values of A and E_a are $4 \times 10^{13}\ s^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperture will its half life period be 10 min ?

(H.P.S.B. Sample paper)

Solution : Accroding to Arrhenius equation,

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

or $\log \frac{k}{A} = -\frac{E_a}{RT} \times \frac{1}{2.303}$

Calculation of k

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10 \times 60} = 1.155 \times 10^{-3} s^{-1}$$

$$\therefore \log \frac{1.155 \times 10^{-3}}{4 \times 10^{13}} = -\frac{98.6 \times 10^3}{8.314 \times T \times 2.303}$$

or $-16.54 = -\frac{98600}{8.314 \times 2.303\,T}$

or $T = \frac{98600}{8.314 \times 2.303 \times 16.54} = \mathbf{311.34\ K.}$

Example 57.

A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction.

(Given : log 2 = 0.3010, log 4 = 0.6021, R = 8.314 JK^{-1} mol^{-1}) *(A.I.S.B. 2018)*

Solution : Let us first calculate k_1 and k_2 at temperatures 300 K and 320 K. We know that

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

At 300 K, $t_{1/2} = 40$ min $\quad k_1 = \frac{0.693}{40}$

At 320 K, $t_{1/2} = 20$ min $\quad k_2 = \frac{0.693}{20}$

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

Substituting the values,

$$\log \frac{0.693}{20} \times \frac{40}{0.693} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{320}\right]$$

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left[\frac{320 - 300}{300 \times 320}\right]$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314} \times \frac{20}{300 \times 320}$$

$$\text{or} \quad E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 300 \times 320}{20}$$

$$= 27663.8\ J\ mol^{-1} \text{ or } \mathbf{27.66\ kJ\ mol^{-1}}.$$

Example 58.

The values of rate constant for the decomposition of HI into H_2 and I_2 at different temperatures are given below:

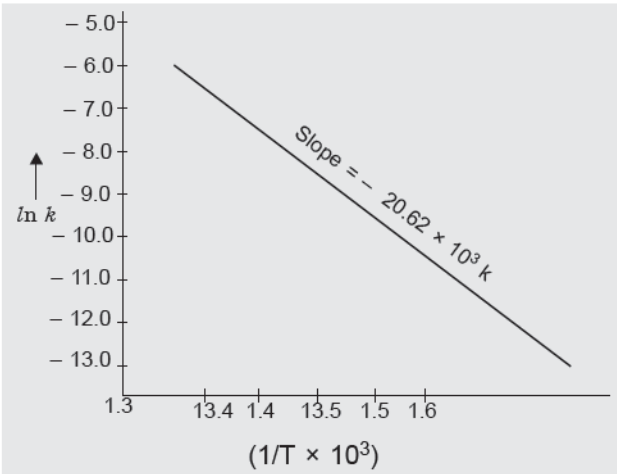
T(K)	*633*	*667*	*710*	*738*
k(s^{-1})	*0.19*	*1.00*	*8.31*	*25.1*

Draw a graph between ln k and 1/T and calculate the values of Arrhenius parameters.

Solution : The values of *ln k* and 1/T at different temperatures are :

T(K)	633	667	710	738
1/T(K^{-1})	1.58×10^{-3}	1.50×10^{-3}	1.41×10^{-3}	1.36×10^{-3}
ln k	– 10.87	– 9.21	– 7.09	– 5.99

The plot of *ln k* against 1/T is shown below :



The slope of the line is -20.62×10^3

$$\therefore \quad E_a = -\text{Slope} \times R$$
$$= -(-20.62 \times 10^3\, k) \times 8.314$$
$$= 171.4 \text{ kJ mol}^{-1}$$

Now, we can calculate A from the value of k at 633 K

$$\ln A = \ln k + \frac{E_a}{RT}$$
$$\ln A = -10.87 + \frac{171400}{8.314 \times 633} = -10.87 + 32.57$$
$$\ln A = 21.7$$
$$\therefore \quad A = \mathbf{2.65 \times 10^9\ s^{-1}}.$$

Example 59.

Rate constant 'k' of a reaction varies with temperature 'T' according to the equation:

$$\log k = \log A - \frac{E_a}{2.303\,R}\left(\frac{1}{T}\right)$$

where E_a is the activation energy. When a graph is plotted for log k vs. $\frac{1}{T}$, a straight line with a slope of – 4250 K is obtained. Calculate 'E_a' for the reaction ($R = 8.314\ JK^{-1}\ mol^{-1}$) *(D.S.B. 2013)*

Solution : $\text{Slope} = -\frac{E_a}{2.303\,R} = -4250 \text{ K}$

$$\therefore \quad E_a = -2.303 \times R \times \text{Slope}$$
$$= -2.303 \times 8.314 \text{ JK}^{-1}\text{ mol}^{-1} \times (-4250 \text{ K})$$
$$= \mathbf{81375.3\ J\ mol^{-1}\ or\ 81.375\ kJ\ mol^{-1}}.$$

Example 60.

The rate constant for a reaction is found to be $1.96 \times 10^{-2}\ s^{-1}$ at 313 K. The activation energy of the reaction is 93.62 kJ mol^{-1}. Calculate the frequency factor, A.

Solution : $\log k = -\frac{E_a}{2.303\,RT} + \log A$

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

$k = 1.96 \times 10^{-2}\ s^{-1}$, $E_a = 93.62 \times 10^3$ J mol^{-1}

$R = 8.314\ JK^{-1}\ mol^{-1}$, T = 313 K

$$\log A = \log(1.96 \times 10^{-2}) + \frac{93.62 \times 10^3}{2.303 \times 8.314 \times 313}$$
$$= -1.708 + 15.621$$
$$= 13.913$$
$$A = \text{antilog}(13.913) = \mathbf{8.185 \times 10^{13}\ s^{-1}}$$

Example 61.

The rate constants of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} respectively. Calculate the values of E_a and A. **N.C.E.R.T.** *(CBSE Sample Paper 2011, Hr. S.B. 2012, Assam S.B. 2013)*

Solution : According to Arrhenius equation,

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

$k_1 = 0.02\ s^{-1}$, $k_2 = 0.07\ s^{-1}$, $T_1 = 500$ K, $T_2 = 700$ K

Substituting the values :

$$\log \frac{0.07}{0.02} = \frac{E_a}{2.303 \times 8.314}\left[\frac{700 - 500}{700 \times 500}\right]$$
$$0.544 = \frac{E_a}{2.303 \times 8.314} \times \frac{200}{3500}$$
$$E_a = \frac{0.544 \times 2.303 \times 8.314 \times 3500}{200}$$
$$= 182281 \text{ J or } 18.228 \text{ kJ}$$

Calculation of A

$$k = Ae^{-E_a/RT}$$
$$\log k = \log A - \frac{E_a}{2.303\,RT}$$

Substituting the values at 500 K

$$\log 0.02 = \log A - \frac{18228}{2.303 \times 8.314 \times 500}$$
$$-1.699 = \log A - 1.904$$
$$\log A = 1.904 - 1.699 = 0.205$$
$$\therefore \quad A = \mathbf{1.603\ s^{-1}}.$$

Example 62.

The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and 50.14 kJ mol^{-1} with a catalyst. How many times will the rate of reaction grow in the presence of the catalyst if the reaction proceeds at 25°C ? ($R = 8.314\ JK^{-1}\ mol^{-1}$) *(A.I.S.B. 2005)*

Solution : According to Arrhenius equation,

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

For uncatalysed reaction,

$$\log k_1 = \log A - \frac{E_a(1)}{2.303\,RT} \quad ...(i)$$

For catalysed reaction,

$$\log k_2 = \log A - \frac{E_a(2)}{2.303\,RT} \quad ...(ii)$$

A is equal for the same reaction.

Subtracting Eqn. (*i*) from Eqn. (*ii*)

$$\log \frac{k_2}{k_1} = \frac{E_a(1) - E_a(2)}{2.303\,RT}$$

$$= \frac{(75.2 - 50.14)\,kJ\,mol^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log \frac{k_2}{k_1} = 4.39$$

$$\frac{k_2}{k_1} = 2.45 \times 10^4$$

∴ Rate of reaction increases by **2.45×10^4 times**.

Example 63.

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

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

Calculate E_a for this reaction and rate constant k if its half-life period be 200 minutes. (Given : R = 8.314 JK^{-1} mol^{-1}) *(D.S.B. 2016, A.I.S.B 2016)*

Solution : According to Arrhenius equation,

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

The given equation is

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

Comparing eq. (*i*) and (*ii*)

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

$$\therefore \quad E_a = 1.0 \times 10^4 \times 2.303 \times 8.314$$

$$= 19.147 \times 10^4\,J\,mol^{-1}$$

$$\text{or} = 191.47\,kJ\,mol^{-1}$$

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

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

$$= \frac{0.693}{200\,min} = \mathbf{3.465 \times 10^{-3}\,min^{-1}}$$

Practice Problems

40. The rate of a reaction becomes four times when the temperature changes from 293 K to 313 K. Calculate the energy of activation (E_a) of the reaction assuming that it does not change with temperature.
[R = 8.314 J K^{-1} mol^{-1}, log 4 = 0.6021] *(A.I.S.B. 2013)*

41. The reaction, $2NO_2 \longrightarrow 2NO + O_2$
has an activation energy of 110 kJ mol^{-1}. At 400°C, the rate constant is 7.8 s^{-1}. What is the value of rate constant at 430°C?

42. The rate constant for the decomposition of nitrogen pentoxide :
$N_2O_5 \longrightarrow N_2O_4 + ½\,O_2$ is 3.46×10^{-5} s^{-1} at 25°C and 4.87×10^{-3} s^{-1} at 65°C. Calculate the energy of activation for the reaction. *(Pb.S.B. 2008)*

43. The rate of a particular reaction triples when temperature changes from 50° C to 100°C. Calculate the activation energy of the reaction.
(log 3 = 0.4771, R = 8.314 JK^{-1} mol^{-1}) *(D.S.B. 2006, H.P.S.B. 2010)*

44. The rate of a reaction doubles when the temperature changes from 27°C to 37°C. Calculate the energy of activation. *(Pb S.B. 2006, Mizoram S.B. 2015)*

45. A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the activation energy of the reaction.

46. The rate constants for a reaction are 2.0 s^{-1} and 32.0 s^{-1} at 700 K and 800 K respectively. Calculate the energy of activation for the reaction.

47. The rate constant for a first order reaction becomes six times when the temperature is raised from 350 to 400 K. Calculate the activation energy for the reaction.
(Gas constant R = 8.314 J K^{-1} mol^{-1}) *(Pb. S.B. 2014)*

48. The rate constant for a reaction is 1.6×10^{-5} s^{-1} and 6.36×10^{-3} s^{-1} at 600 K and 700 K respectively. Calculate the activation energy for the reaction.

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

T(°C)	0	20	40	60	80
$10^5 \times k$ (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°C and 50°C.

50. The rate constant of a reaction is 1.2×10^{-3} s^{-1} at 30°C and 2.1×10^{-3} s^{-1} at 40°C. Calculate the energy of activation of the reaction. *(Pb. S.B. 2004, 2006)*

Answers to Practice Problems

40. 52.86 kJ mol^{-1}
41. 18.0 s^{-1}
42. 103.56 kJ
43. 22.012×10^3 kJ mol^{-1}.
44. 53.6 kJ mol^{-1}.
45. 43.8 kJ mol^{-1}.
46. 129.1 kJ mol^{-1}.
47. 41.7 kJ mol^{-1}.
48. 209.01 kJ mol^{-1}.
49. A = 1.51×10^{13} min,
E_a = 100.67 kJ mol^{-1},
k (30°C) = 6.64×10^{-5} s^{-1},
k (50°C) = 7.93×10^{-4} s^{-1}.
50. 44.1 kJ mol^{-1}.

Hints & Solutions on page 68

51. For the decomposition of ethyl iodide :

$$C_2H_5I \longrightarrow C_2H_4 + HI$$

the rate constants are $1.60 \times 10^{-5}\ s^{-1}$ and $6.36 \times 10^{-3}\ s^{-1}$ at 600 K and 700 K respectively. Calculate the activation energy for the reaction. *(Pb. S.B. 2004, 2008)*

52. The specific rate constant for the combination of H_2 and I_2 to form HI

$$H_2 + I_2 \longrightarrow 2HI$$

is $2.34 \times 10^{-3}\ s^{-1}$ at 673 K and $7.50 \times 10^{-2}\ s^{-1}$ at 773 K. Calculate the activation energy for the reaction.

53. Rate constant, k of a reaction varies with temperature as:

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

where E_a is the activation energy. When a graph is plotted for $\log k$ *vs* 1/T, a straight line with a slope of –6670K is obtained. Calculate the energy of activation for this reaction. ($R = 8.314\ JK^{-1}\ mol^{-1}$) *(D.S.B. 2011)*

54. The activation energy of a first order reaction at 300 K is 60 kJ mol^{-1}. In the presence of a catalyst, the activation energy gets lowered to 50 kJ mol^{-1} at 300 K. How many times the reaction rate changes in the presence of a catalyst at the same temperature ?

55. The decomposition of A into product has value of k as $4.5 \times 10^3\ s^{-1}$ at 10°C and activation energy is 60 kJ mol^{-1}. Calculate the temperature at which the value of k be $1.5 \times 10^4\ s^{-1}$. *(CBSE Sample Paper 2011)*

Answers to Practice Problems

51. 209.1 kJ mol^{-1}.
52. 15.1 kJ mol^{-1}.
53. 127.7 kJ mol^{-1}.
54. 55.08 times
55. 24°C

Hints & Solutions on page 68

Advanced Level PROBLEMS *Accelerate Your Potential (for JEE Advance)*

Problem 6. Two reactions of the same order have equal pre-exponential factors but their activation energies differ by 24.9 kJ mol^{-1}. Calculate the ratio between the rate constants of these reactions at 27°C. (Gas constant, $R = 8.3\ JK^{-1}\ mol^{-1}$).

Solution The Arrhenius equation is :

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

Taking log on both sides, $\log k = \log A - \dfrac{E_a}{2.303\ RT}$

For reaction (*i*), $\log k_1 = \log A - \dfrac{E_a(1)}{2.303\ RT}$

For reaction (*ii*) $\log k_2 = \log A - \dfrac{E_a(2)}{2.303\ RT}$

Subtracting (*i*) from (*ii*) $\log \dfrac{k_2}{k_1} = \dfrac{E_a(1) - E_a(2)}{2.303\ RT}$

$$\log \frac{k_2}{k_1} = \frac{24.9 \times 1000}{2.303 \times 8.3 \times 300} = 4.342$$

$$\therefore \quad \frac{k_2}{k_1} = \mathbf{2.198 \times 10^4.}$$

Problem 7. 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 by 20 kJ mol^{-1}.

Solution According to Arrhenius equation,

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

Let activation energy in the absence of catalyst be E_a and in the presence of catalyst be $E_a(c)$, then

At 500 K, $k = Ae^{-E_a/500R}$

At 400 K, $k = Ae^{-E_a(c)/400R}$

$$e^{-E_a/500R} = e^{-E_a(c)/400R}$$

or $\dfrac{E_a}{500\ R} = \dfrac{E_a(c)}{400\ R}$

or $E_a(c) = \dfrac{4}{5}E_a$

But $E_a - E_a(c) = 20$ kJ

$\therefore \quad E_a - \dfrac{4}{5}E_a = 20$ kJ or $\dfrac{1}{5}E_a = 20$ kJ

$\therefore \quad E_a = 20 \times 5 = 100$ kJ mol^{-1}.

Problem 8. 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 $4 \times 10^{10} s^{-1}$, calculate k at 318 K and E_a.

Solution For 10% completion of the reaction,

$$k(298K) = \frac{2.303}{t}\log\frac{100}{90}$$

For 25% completion of reaction

$$k(308K) = \frac{2.303}{t}\log\frac{100}{75}$$

$$\frac{k(308\ K)}{k(298\ K)} = \frac{\frac{2.303}{t}\log\frac{100}{75}}{\frac{2.303}{t}\log\frac{100}{90}}$$

$$= \frac{0.1249}{0.0458} = 2.73$$

Now, $\log \frac{k(308K)}{k(208K)} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$\log 2.73 = \frac{E_a}{2.303 \times 8.314} \times \frac{(308-298)}{308 \times 298}$$

$$0.436 = \frac{E_a}{2.303 \times 8.314} \times \frac{10}{308 \times 298}$$

$$\therefore \quad E_a = \frac{0.436 \times 2.303 \times 8.314 \times 308 \times 298}{10}$$

$$= 76623 \text{ J mol}^{-1} = 76.623 \text{ kJ mol}^{-1}$$

Now, $\log K = \log A - \frac{E_a}{2.303\,RT}$

$$\log K(318K) = \log 4 \times 10^{10} - \frac{76623}{2.303 \times 8.314 \times 318}$$

$$= 10.6020 - 12.5843$$

$$\log K\,(318) = -1.9823$$

$$K\,(318) = \mathbf{1.042 \times 10^{-2}\ s^{-1}}$$

Problem 9. A first order reaction, A → B requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the per cent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature.

Solution Calculation of k at 25°C (say k_1)

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

$$[A]_0 = a \text{ (say)},\ [A] = a - a \times \frac{25}{100} = 0.75\,a$$

$$k_1 = \frac{2.303}{20}\log\frac{a}{0.75a} = 0.01439 \text{ min}^{-1}$$

Calculation of k_2.

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

$$\log\frac{k_2}{0.01439} = \frac{70000}{2.303 \times 8.314}\left[\frac{1}{298} - \frac{1}{313}\right] = 0.5879$$

or $\frac{k_2}{0.01439} = 3.872$ or $k_2 = 0.0557$ min^{-1}

Calculation of percentage decomposition at 40°C

Let the percentage decompostion in this case = x

$$a = 100,\ a - x = 100 - x$$

$$k_2 = \frac{2.303}{20}\log\frac{100}{100-x}$$

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

$$\log\frac{100}{100-x} = 0.4837$$

$$\frac{100}{100-x} = 3.045 \quad \text{or} \quad x = 67.15$$

Percentage decomposition = **67.15%**

CONCEPT OF ACTIVATION ENERGY AND TRANSITION STATE THEORY

We are quite familiar with chemical reactions such as burning of coal gas in air or combustion of carbon or combination of hydrogen and oxygen gases, which do not occur unless some energy in one form or the other is supplied to reacting system. Thus, some **extra energy** has to be supplied to the reactants to bring their energy equal to the threshold energy.

The excess energy (over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called activation energy, E_a. It is equal to the difference between the threshold energy needed for the reaction and the average kinetic energy of all the reacting molecules. That is,

Activation energy = Threshold energy – Average kinetic energy of the reacting molecules

or E_a = E (threshold) – E (reactants)

Each reaction has definite value of E_a and this decides the fraction of total collisions which are effective. If the activation energy for a reaction is low, large number of molecules can have this energy and the fraction of effective collisions, *f*, will be large. The reaction will proceed at high rate. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction may be quite slow. Thus,

Low activation energies : Fast reactions
High activation energies : Slow reactions

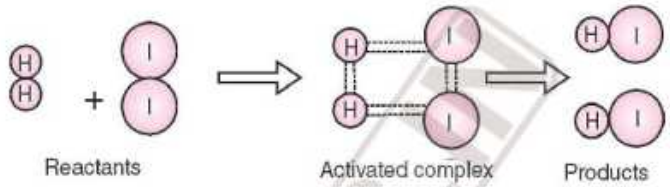
R U Curious...

Combustion of fuels is highly **exothermic reaction** yet these can be safely stored in contact with oxygen or air.

❒ The stability of fuels is due to *high activation energy of these combustion reactions.* As a result of high activation energy, these reactions do not occur at ordinary conditions. When some extra energy (flame) is supplied to the fuel in the presence of air, a portion of reactants absorb energy (equal to activation energy) and the reaction gets initiated. The enormous amount of energy is released during the reaction because the reaction is exothermic. The released energy increases the energy of other molecules in the remaining fuel and therefore, the combustion continues. Explosive reactions have also high activation energy and therefore, can be safely stored for years inspite of the fact that they give enormous amount of energy when they explode. The explosive reactions occur when activation energy is supplied by heating or mechanical energy.

Activated Complex State

When the colliding molecules possess the kinetic energy equal to E_a, the atomic configuration of species formed at this stage is different from the reactants as well as the products. This stage is called the **activated state or transition state** and *specific configuration of this state* is called **activated complex or intermediate.** For example, in the reaction between $H_2(g)$ and $I_2(g)$, activated complex has configuration in which H—H and I—I bonds are breaking and H—I bonds are forming as shown below :



This activated complex state is unstable transitions state of the reacting system which is mid-way between the reactants and the products. It has a very short life span (being highly unstable) and splits into the products to acquire stable state of lower energy.

Progress of a Reaction

According to the concept of activation energy, the reactants do not change directly into the products. The reactants first absorb energy equal to activation energy and thereby form activated complex. At this state, the molecules have energy at least equal to the threshold energy. This means that the reaction involves some energy barrier which must be overcome before products are formed. The energy barrier is known as **activation energy barrier.** In graphical representation of the reaction, the energy barrier is shown as an *energy hump* which has to be crossed before the reactants go to the products (Fig. 14).

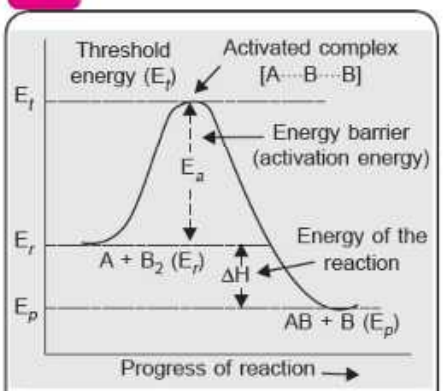


Fig. 14. Progress of a reaction.

As an illustration, consider the general reaction,

$$A(g) + B_2(g) \longrightarrow AB(g) + B(g)$$

The reactants have the average energy, E_r and the products have the energy E_p. The reaction involves the approach of an atom A to a molecule B_2. The reaction cannot occur until the colliding reactants A and B_2 possess sufficient energy to reach the top of the energy barrier and form activated complex. **The energy required to form activated complex is called the activation energy.** The activated complex formed [A....B] has a very short life span and splits into the products. This may be shown as :

$$\underset{\text{Reactants}}{A + B—B} \longrightarrow \underset{\text{Activated complex}}{A\cdots\cdots\cdots B\cdots\cdots\cdots B} \longrightarrow \underset{\text{Products}}{A—B + B}$$

Activation energy plays an **important** role in comparing the rates of reactions. To illustrate this, consider the two reactions, oxidation of NO and CO, which appear to be similar. As already discussed, the oxidation of NO is a fast reaction whereas that of CO is a slow reaction.

$$NO(g) + \frac{1}{2} O_2(g) \longrightarrow NO_2(g) \qquad \text{Fast}$$

$$CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g) \qquad \text{Slow}$$

In the oxidation of NO, the activation energy is small and only the small increase in energy enables the reacting species to cross the energy barrier to form NO_2. Therefore, the reaction is fast at room temperature. However, in the case of oxidation of CO, the activation energy is high, consequently large amount of energy is needed by the reactants to cross the energy barrier. Such a large amount of energy is not available at room temperature. Hence, the reaction is slow at room temperature.

Activation Energies and Reversible Reactions

Consider a reversible reaction :

$$A + B \rightleftharpoons C + D$$

Just as activation energy is required for forward reaction, activation energy is also required for backward reaction. During the progress of the reaction the reactant molecules in the forward reaction and the product molecules in the backward reaction follow the same path and form the same activated complex. However, the activation energies of the two are different. These are represented graphically in Fig. 15 (*a*) and (*b*) for exothermic and endothermic reactions. It is clear from the figure that the reactant molecules in their forward reaction and the product molecules in their backward reaction have to pass through the same transition state even though the activation energies for the forward E_a (forward) and E_a (backward) reactions are different. Mathematically, E_a (forward) and E_a (backward) are related to the overall energy change, ΔH, in the process as :

$$\Delta H = E_a \text{ (forward)} - E_a \text{ (backward)}$$

As evident from Fig. 15 (*a*), for the **exothermic reaction**.

$$\begin{bmatrix}\textbf{Activation energy for}\\ \textbf{the forward reaction}\end{bmatrix} < \begin{bmatrix}\textbf{Activation energy for}\\ \textbf{the backward reaction}\end{bmatrix}$$

$$E_a \text{ (forward)} < E_a \text{ (backward)}$$

Thus, $\Delta H = E_a$ (forward) $- E_a$ (backward) $= -$ve

On the other hand, for the **endothermic reaction**.

$$\begin{bmatrix}\textbf{Activation energy for}\\ \textbf{the forward reaction}\end{bmatrix} > \begin{bmatrix}\textbf{Activation energy for}\\ \textbf{the backward reaction}\end{bmatrix}$$

$$E_a \text{ (forward)} > E_a \text{ (backward)}$$

Thus, $\Delta H = E_a$ (forward) $- E_a$ (backward) $= +$ve

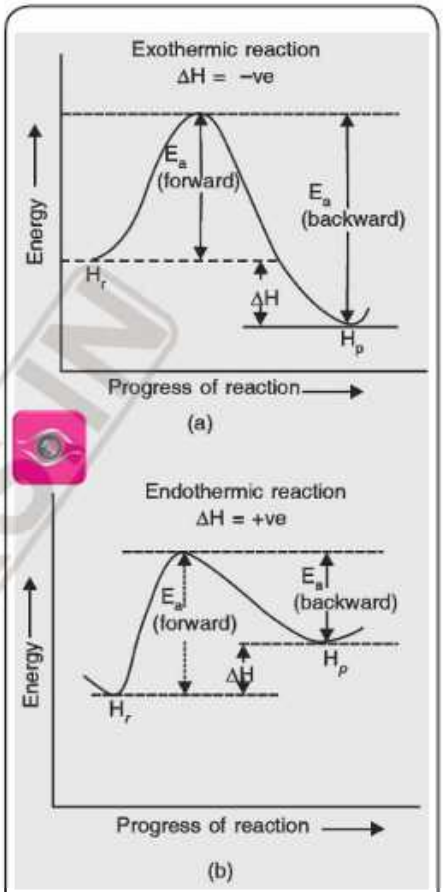


Fig.15. Activation energies for the forward and backward reactions in case of (*a*) exothermic and (*b*) endothermic reactions.

EFFECT OF A CATALYST ON REACTION RATES

A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change.

For example, manganese dioxide (MnO_2), a black powder speeds up the thermal decomposition of potassium chlorate.

$$2KClO_3\,(s) \xrightarrow[\text{heat}]{MnO_2\text{, catalyst}} 2KCl(s) + 3O_2$$

The phenomenon of increasing the rate of a reaction by the use of catalyst is called **catalysis.** It is observed that a catalyst is not consumed in the reaction. Actually, what happens is that in a catalysed reaction the catalyst is used in one step and is regenerated in a subsequent step and thus, it is used up again and again without undergoing any permanent change.

The action of catalyst can be explained by **intermediate complex theory.** According to this theory, a catalyst combines with reactants to form an intermediate activated complex which is short lived. This decomposes to form the products and regenerating the catalyst. The intermediate complex formed has lower potential energy. This means that the activation energy becomes lower for the catalysed reaction than that for uncatalysed reaction. Consequently, the fraction of the total number of collisions possessing lower activation energy is increased and hence, the rate of reaction also increases.

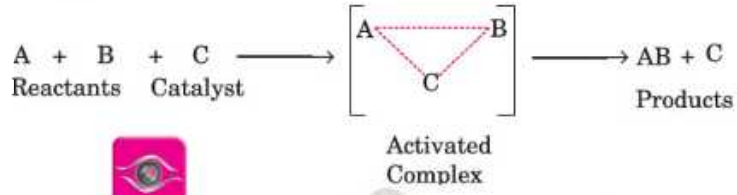
Consider a hypothetical reaction

$$A + B \longrightarrow AB$$

The reaction proceeds through the formation of activated complex as :

$$\underset{\text{Reactants}}{A + B} \longrightarrow \underset{\text{Activated complex}}{[A\cdots\cdots B]} \longrightarrow \underset{\text{Product}}{AB}$$

Addition of a catalyst C result into the formation of new activated complex of lower activation energy.



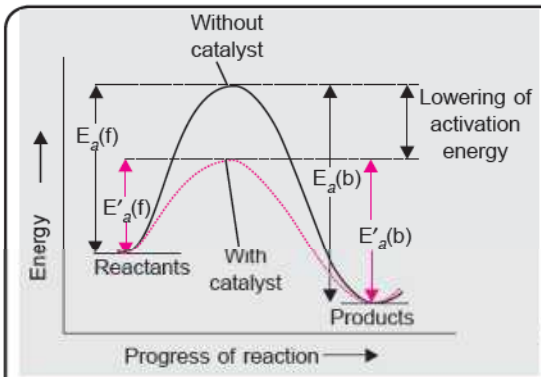


Fig. 16. Progress of an uncatalysed and catalysed reaction. Addition of a catalyst provides a path of lower activation energy (shown dotted).

Thus, *a catalyst provides a new pathway for the reaction of lower activation energy than that of the reaction in the absence of the catalyst.* Because of lower activation energy, the reaction becomes fast and the reactants are converted to products quickly.

Fig. 16 gives an energy diagram which depicts the effect of a catalyst on the energy of activation. The solid line shows the path for uncatalysed reaction and dotted line shows the path adopted by catalysed reaction.

Some Important Characteristics of Catalysts and Catalysed Reactions

(*i*) Only a small amount of catalyst can catalyse a large amount of reactants.

(*ii*) A catalyst cannot initiate a reaction. It can only accelerate the rate of a reaction. It other words, a catalyst cannot catalyse non spontaneous reactions. It catalyses only spontaneous reactions.

It may be noted that some substances reduce the rates of reactions. These are called **inhibitors**.

(*iii*) Catalysts are highly specific in nature. A catalyst which can catalyse one reaction may have no effect on another reaction even, if that reaction is very similar.

(*iv*) A catalyst may undergo intermediate physical changes and it may even form temporary chemical bonds with the reactants but it is recovered unchanged in original form at the end of the reaction.

(*v*) The catalyst does not change ΔE (or ΔH) of the reaction. This is clear from Fig. 16 that the addition of a catalyst does not change the energies of reactants (E_r) and products (E_p) so that ΔE ($E_p - E_r$) remains same.

(*vi*) A catalyst does not change the free energy change (ΔG) of a reaction.

(*vii*) Although a catalyst speeds up the reaction but it does not shift the position of equilibrium. This is due to the fact that the presence of a catalyst reduces the height of barrier by providing an alternative path for the reaction and lowers the activation energy. However, the lowering in activation energy is to the same extent for the forward as well as for the backward reaction. In the figure, it is clear that decrease in activation energy for the forward reaction E_a (forward) — E_a' (forward) is same as for backward reaction, E_a (backward) — E_a' (backward), where E_a' (forward) and E_a' (backward) are the activation energies for the catalysed reaction. As a result, the increase in the rate of the forward and backward reactions is same and hence, the position of equilibrium remains unaltered. However, by increasing the two rates, the equilibrium is attained earlier.

Catalysts are very important for our existence. Catalysts are used in many industrial processes. Many biochemical reactions occurring in living organisms are catalysed by enzymes.

SOLVED EXAMPLES

Example 64.

An exothermic reaction A ⟶ B has an activation energy of 17 kJ per mole of A. The heat of the reaction is 40 kJ. Calculate the activation energy for the reverse reaction B ⟶ A.

Solution : For the reaction A ⟶ B.

Activation energy, E_a = 17 kJ

Since the reaction is exothermic, the energy of the products is less than that of reactants. The potential energy diagram for such a reaction is given in Fig. 17.

From the figure, it is clear that the activation energy for the reverse reaction, B ⟶ A is :

$$E_a \text{ (reverse)} = E_a \text{ (forward)} + \Delta E$$
$$= 17 + 40 = \mathbf{57\ kJ}$$

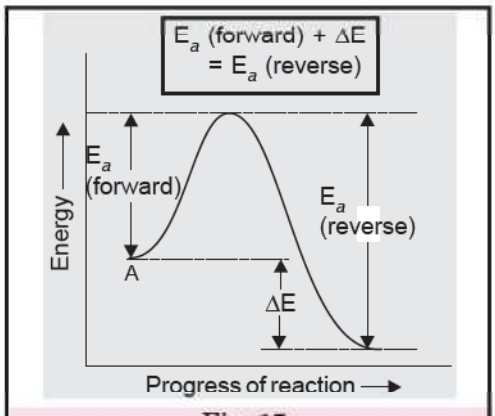


Fig. 17.

Example 65.

Consider the diagram (Fig. 18) for a reaction

$$A_2 + B_2 \rightleftharpoons 2AB$$

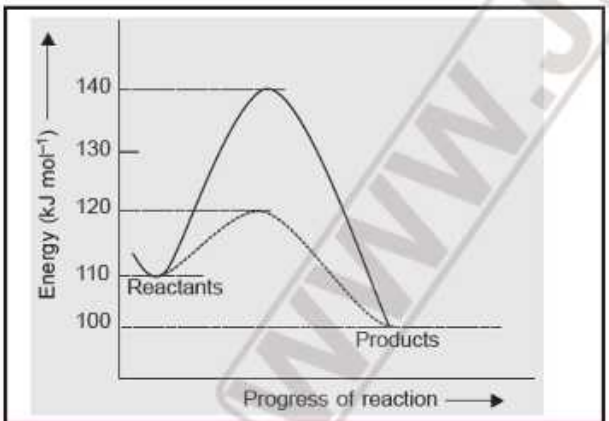


Fig. 18.

(a) Calculate ΔE for the rection.

(b) Calculate the energy of activation for the forward and the backward reactions.

(c) The dotted curve is the reaction path in the presence of the catalyst ? What is the energy of activation for the forward and backward reactions in the presence of the catalyst ? What is the lowering in activation energy in the presence of a catalyst ?

(d) Will the catalyst change the extent of the reaction ?

Solution : (*a*) It is clear from the figure that

Energy of reactants (A_2 and B_2) = 110 kJ mol^{-1}

Energy of products (2AB) = 100 kJ mol^{-1}

$$\therefore \quad \Delta E = E_p - E_r$$
$$= 100 - 110 = \mathbf{-10\ kJ\ mol^{-1}}$$

∴ Reaction is exothermic.

(*b*) Threshold energy = 140 kJ mol^{-1}

Energy of reactants = 110 kJ mol^{-1}

$$E_a \text{ (forward)} = E_t - E_r$$
$$= 140 - 110$$
$$= 30 \text{ kJ mol}^{-1}$$

Energy of products, E_p = 100 kJ mol^{-1}

$$E_a \text{ (backward)} = E_t - E_p$$
$$= 140 - 100 = \mathbf{40\ kJ\ mol^{-1}}$$

(*c*) In the presence of catalyst, threshold energy becomes 120 kJ

$$E_a' \text{ (forward)} = 120 - 110 = 10 \text{ kJ mol}^{-1}$$
$$E_a' \text{ (backward)} = 120 - 100 = 20 \text{ kJ mol}^{-1}$$

Lowering in activation energy = E_t (without catalyst) – E_t (with catalyst)

$$= 140 - 120 = \mathbf{20\ kJ\ mol^{-1}}$$

(*d*) There will be no change in the extent of reaction because activation energy for the forward reaction and the backward reaction have decreased equally.

Advanced Level PROBLEMS

Accelerate Your Potential (for JEE Advance)

Problem 10. The rate constant of a reaction increases by 7% when its temperature is raised from 300 K to 301 K while its equilibrium constant increases by 3%. Calculate the activation energy of forward and reverse reaction.

Solution Let the rate constant at 300 K = k

Increase in rate constant = $k \times \frac{7}{100} = 0.07\,k$

∴ Rate constant at 301 K = $k + 0.07\,k = 1.07\,k$

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Now,

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

$$\log \frac{1.07\,k}{k} = \frac{E_a}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{301}\right]$$

$$\log 1.07 = \frac{E_a}{2.303 \times 8.314} \times \frac{301 - 300}{300 \times 301}$$

$$0.02938 = \frac{E_a}{2.303 \times 8.314} \times \frac{1}{300 \times 301}$$

$$\therefore \quad E_a = 0.02938 \times 2.303 \times 8.314 \times 300 \times 301$$

$$= 50798 \text{ J} = \mathbf{50.8\ kJ\ mol^{-1}}$$

This is activation energy for the forward reaction, *i.e.*,

$$E_a^f = 50.8 \text{ kJ mol}^{-1}$$

Let equilibrium constant at 300 K = K

Increase in equilibrium constant = $\frac{K \times 3}{100}$ = 0.03 K

Equilibrium at 301 K = K + 0.03 K = 1.03 K

Now,

$$\log \frac{K_2}{K_1} = \frac{\Delta_r H^\ominus}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log \frac{1.03\,K}{K} = \frac{\Delta_r H^\ominus}{2.303 \times 8.34}\left[\frac{1}{300} - \frac{1}{301}\right]$$

$$0.01284 = \frac{\Delta_r H^\ominus}{2.303 \times 8.314}\left[\frac{301 - 300}{300 \times 301}\right]$$

$$\therefore \quad \Delta_r H^\ominus = 0.01284 \times 8.314 \times 2.303 \times 300 \times 301$$

$$= 22.19 \text{ kJ mol}^{-1}$$

Since $\Delta_r H^\ominus$ is positive, the reaction is endothermic.

But $\Delta_r H^\ominus = E_a^f - E_a^r$

$$\therefore \quad E_a^r = E_a^f - \Delta_r H^\ominus$$

$$= 50.8 - 22.19 = \mathbf{27.61\ kJ\ mol^{-1}}$$

add on Conceptual Questions 2

CONCEPTUAL QA

Q.1. The half life period of first order reaction is *x* and three-fourth of the same reaction is *y*. How are *x* and *y* related to each other ?

Ans. *y* is twice of *x* because the time required for 3/4th of a reaction to occur is two times that required for half of the reaction.

Q.2. After five half life periods for a first order reaction what fraction of reactant remains ?

Ans. $\frac{1}{32}$.

Q.3. For a first order reaction, time taken for half of the reaction to complete is t_1 and 3/4 of the reaction to complete is t_2. How are t_1 and t_2 related ?

Ans. $t_2 = 2t_1$ because for 3/4th of the reaction to complete, time required is equal to two half lives.

Q.4. A reaction is first order in reactant A and second order in reactant B.
(*i*) Write differential rate equation.
(*ii*) How is the rate affected when concentration of B alone is increased to three times ?
(*iii*) How is the rate affected when concentration of both A and B are doubled ? ***(D.S.B. 2010)***

Ans. (*i*) Rate = $k[A]\,[B]^2$
(*ii*) Rate becomes $(3)^2$ = 9 times
(*iii*) Rate becomes $(2)\,(2)^2$ = 8 times.

Q.5. Express the relation between the half life period of a reactant and its initial concentration for a reaction of *n*th order. ***(A.I.S.B. 2005)***

Ans. $t_{1/2} = \frac{1}{k[A_0]^{n-1}}$.

Q.6. (*a*) For the reaction

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

write :

(*i*) Rate of reaction expression,

(*ii*) Rate law equation,

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(*iii*) Molecularity,

(*iv*) Order of reaction ***(CBSE Sample paper 2011)***

Ans. (*i*)

$$\text{Rate} = -\frac{d[C_{12}H_{22}O_{11}]}{dt} = \frac{-d[H_2O]}{dt}$$

$$= \frac{d[C_6H_{12}O_6]}{dt} = \frac{d[C_6H_{12}O_6]}{dt}$$

(*ii*) Rate law equation :

$$\text{Rate} = k[C_{12}H_{22}O_{11}]$$

(*iii*) Molecularity = 2

(*iv*) Order = 1

Q.7. Consider the decomposition of hydrogen peroxide in alkaline medium which is catalysed by iodide ions.

$$2H_2O_2 \xrightarrow{OH^-/I^-} 2H_2O + O_2$$

This reaction takes place in two steps as given below :

Step - I $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ **(slow)**

Step - II $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ **(fast)**

(*a*) Write the rate law expression and determine the order of reaction w.r.t. H_2O_2.

(*b*) What is the molecularity of each individual step? ***(CBSE Sample paper 2011)***

Ans. (*a*)

$$\text{Rate} = k[H_2O_2][I^-]$$

Order w.r.t. H_2O_2 = 1

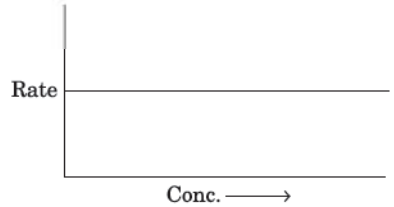
(*b*) Molecularity : Step I = 2, Step II = 2

Q.8. For a chemical reaction variation in rate with conc. is shown :

(*a*) What is the order of the reaction ?

(*b*) What are the units of rate constant *k* for the reaction ?

(CBSE Sample paper 2012)



Ans. (*a*) Order of reaction is zero.

(*b*)Units of rate constant is mol $L^{-1}s^{-1}$.

Q.9. Can activation energy for reactions be zero ?

Ans. In the Arrhenius equation,

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

if E_a is zero then $k = A$

i.e., every collision between molecules leads to the chemical reaction. This is not true. Thus, E_a cannot be zero.

Q.10. What value of *k* is predicted for the rate constant by Arrhenius equation if $T \to \infty$? Is this value physically reasonable ?

Ans. From the equation, $k = Ae^{-E_a/RT}$, if $T \to \infty$; $k \to A$ so that $E_a = 0$. This is not feasible.

Q.11. Why ΔG is positive for photochemical reactions ?

Ans. This is because a part of light energy absorbed by the reactants gets converted into free energy.

Q.12. What is the main difference between a photosensitizer and a catalyst ?

Ans. A catalyst only changes the speed of the reaction, while a photosensitizer only initiates the reaction.

Q.13. Give the damaging effect of photochemistry.

Ans. The colour of fabrics fades away on exposure to sunlight.

Q14. Why does equilibrium constant not change with the presence of a catalyst?

Ans. The catalyst increases the speed of forward and backward reaction to the same extent. Therefore, equilibrium is attained quickly but the position of equilibrium does not change.

CONCEPTUAL QA

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Q15. What is the fraction of molecules having energy equal to or greater than activation energy, E_a ? What is this quantity called ?

Ans. The fraction of molecules having energy equal to or greater than activation energy (E_a) is equal to $e^{-E_a/RT}$ at temperature T. It is called Boltzmann factor.

Q16. For a reaction: A + B ⟶ P, the rate law is given as:

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

(*i*) How is the rate of reaction affected when the concentration of B is doubled?

(*ii*) What is the order of reaction if A is present in large excess. ***(A.I.S.B. 2015)***

Ans. (*i*) Rate becomes four times

(*ii*) Order = 2

Q17. Find out half life time of a first order reaction with rate constant, $k = 2.31 \times 10^{-14}\ s^{-1}$ ***(Assam S. B. 2017)***

Ans. $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.31\times10^{-14}\ s^{-1}} = 3 \times 10^{13}\ s$$

Q18. What is the effect of adding a catalyst on

(*i*) Activation energy (E_a) and

(*ii*) Gibbs free energy (ΔG) of a reaction? ***(A.I.S.B. 2017)***

Ans. (*i*) Activation energy decreases

(*ii*) No effect on ΔG because Gibbs free energies of products and reactants remain the same in the presence of catalyst.

Q19. In the Arrhenius equation, what does the factor $e^{-E_a/RT}$ correspond to ?

(CBSE Sample Paper 2017-18)

Ans. $e^{-E_a/RT}$ corresponds to the fraction of molecules having kinetic energy greater than E_a.

Solution File

Hints & Solutions for Practice Problems

❒ **1.** (*i*) $\text{Rate} = -\frac{1}{2}\frac{d[O_3]}{dt} = \frac{1}{3}\frac{d[O_2]}{dt}$

(*ii*) $\text{Rate} = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{d[Br_2]}{dt} = \frac{1}{2}\frac{d[NOBr]}{dt}$

(*iii*) $\text{Rate} = -\frac{1}{2}\frac{d[ICl]}{dt} = -\frac{d[H_2]}{dt} = \frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HCl]}{dt}$

❒ **2.** $-\frac{\Delta[N_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{1}{2}\times 2.4\times10^{-4}$

$= \mathbf{1.2 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$

$-\frac{\Delta[H_2]}{\Delta t} = \frac{3}{2}\frac{\Delta[NH_3]}{\Delta t} = \frac{3}{2}\times 2.4\times10^{-4}$

$= \mathbf{3.6 \times 10^{-4}\ mol\ L^{-1}s^{-1}}$

❒ **3.** $\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{dt} = \frac{1}{4}\frac{\Delta[NO_2]}{dt}$

$-\frac{\Delta[N_2O_5]}{dt} = \frac{2}{4}\frac{\Delta[NO_2]}{dt} = \frac{1}{2}\times 2.8\times10^{-3}$

$= -1.4 \times 10^{-3}\ Ms^{-1}$

∴ Rate of disappearance of N_2O_5 i.e. $\left(-\frac{\Delta[N_2O_5]}{\Delta t}\right)$

$= \mathbf{1.4 \times 10^{-3}\ Ms^{-1}}$

❒ **4.** $\frac{1}{2}\frac{\Delta[Y]}{\Delta t} = \frac{1}{3}\frac{\Delta[X]}{\Delta t}$

$\frac{\Delta[Y]}{\Delta t} = \frac{2}{3} \times 0.072 = \mathbf{0.048\ mol\ L^{-1}\ s^{-1}}$

$\frac{\Delta[Z]}{\Delta t} = \frac{1}{2}\frac{\Delta[Y]}{\Delta t} = \frac{1}{2} \times 0.048 = \mathbf{0.024\ mol\ L^{-1}\ s^{-1}}$

❒ **5.** $\text{Rate} = -\frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$

(*i*) $\frac{-1}{4}\frac{\Delta[NO_2]}{\Delta t} = -\frac{\Delta[O_2]}{\Delta t}$

∴ $\frac{\Delta[NO_2]}{\Delta t} = 4 \times 0.024 = \mathbf{0.096\ mol\ L^{-1}\ s^{-1}}$

(*ii*) $-\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t}$

∴ $\frac{\Delta[N_2O_5]}{\Delta t} = 2\times -\frac{d[O_2]}{dt} = 2 \times 0.024$

$= \mathbf{0.048\ mol\ L^{-1}\ s^{-1}}$

❒ **6.** $\text{Rate} = -\frac{(0.02-0.03)}{25\ \text{min}} = \mathbf{4.0 \times 10^{-4}\ mol\ L^{-1}min^{-1}}$

or $= \frac{4\times10^{-4}\ \text{mol L}^{-1}}{60\ s} = \mathbf{6.6 \times 10^{-6}\ mol\ L^{-1}s^{-1}}$

❒ **7.** For the reaction,

$$2A + B \longrightarrow 3C$$

$$\text{rate} = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt}$$

(*i*) Rate of reaction $= \frac{1}{3}\frac{d[C]}{dt} = \frac{1}{3}\times1.30\times10^{-4}$

$= \mathbf{4.33 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}}$

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Solution File

(*ii*) Rate of disappearance of A

$$= -\frac{d[A]}{dt} = \frac{2}{3}\frac{d[C]}{dt}$$

$$= \frac{2}{3} \times 1.3 \times 10^{-4}$$

$$= \mathbf{8.67 \times 10^{-5}\ mol\ L^{-1}s^{-1}}$$

❒ **8.** Rate = $k[A]^2$ or $k = \frac{5.8 \times 10^{-6}}{(0.01)^2}$

$$= \mathbf{5.8 \times 10^{-2}\ mol\ L^{-1}s^{-1}}$$

❒ **9.** Rate = $k[COCl_2]^{3/2}$

$$\frac{atm}{sec} = k\,(atm)^{3/2} \qquad \therefore k = \mathbf{atm^{-1/2}\ s^{-1}}$$

❒ **10.** The order can be predicted by the inspection of units of rate constants.

❒ **11.** $\frac{mol\ L^{-1}}{s} = k\left(\frac{mol}{L}\right)^{1/3}\left(\frac{mol}{L}\right)^2$

$\therefore \quad k = \mathbf{mol^{-4/3}\ L^{4/3}\ s^{-1}}$

❒ **12.** Let the initial concentrations are :

$[NO_2^-] = a$ mol L^{-1}, $[I^-] = b$ mol L^{-1}, $[H^+] = c$ mol L^{-1}

$\therefore$ rate = $k\,abc^2$

(*i*) When $[I^-] = \frac{b}{2}$; rate′ = $ka\left(\frac{b}{2}\right)c^2 = \frac{1}{2}abc^2$ *i.e.*, rate of reaction is **halved.**

(*ii*) When $[H^+] = 2c$

rate″ = $k\,ab\,(2c)^2 = 4\,k\,abc^2$ *i.e.*, rate becomes **4 times.**

(*iii*) When $[NO_2^-] = 3a$, $[I^-] = 3b$ and $[H^+] = 3c$

rate‴ = $k\,(3a)\,(3b)\,(3c)^2 = 81\,kabc^2$ *i.e.*, rate becomes **81 times.**

❒ **13.** $r = k[X]^n$ ...(*i*)

$27\,r = k[3X]^n$ ...(*ii*)

Dividing eq. (*ii*) by eq. (*i*), $27 = 3^n$ or $\boldsymbol{n = 3}$

❒ **14.** $r = k[X]^n$ ...(*i*)

$1.837\,r = k[1.5X]^n$ ...(*ii*)

Dividing eq. (*ii*) by eq. (*i*), $1.837 = (1.5)^n$

Taking log on both sides

$\log 1.837 = n \log 1.5$

$\therefore \quad n = \frac{\log 1.837}{\log 1.5} = \mathbf{1.5}$

❒ **15.** Rate = $k[N_2O_5]$

(*ii*) Rate = $(6.2 \times 10^{-4}\ s^{-1}) \times (2.50\ mol\ L^{-1})$

$$= \mathbf{1.55 \times 10^{-3}\ mol\ L^{-1}s^{-1}}$$

(*ii*) Rate = $(6.2 \times 10^{-4}\ s^{-1}) \times (0.50\ mol\ L^{-1})$

$$= \mathbf{3.1 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

(*iii*) 4.2×10^{-3} mol L^{-1} s^{-1} = $(6.2 \times 10^{-4}\ s^{-1})\ [N_2O_5]$

$\therefore\ [N_2O_5] = \frac{4.2 \times 10^{-3}}{6.2 \times 10^{-4}} = \mathbf{6.77\ mol\ L^{-1}}$

❒ **16.** Rate = $k[A]^2$

(*i*) Rate = $(0.50\ mol^{-1}\ L\ s^{-1}) \times (0.60\ mol\ L^{-1})^2$

$$= \mathbf{0.18\ mol\ L^{-1}s^{-1}}$$

(*ii*) Rate = $(0.50\ mol^{-1}L\ s^{-1}) \times (0.15\ mol\ L^{-1})^2$

$$= \mathbf{0.11\ mol\ L^{-1}\ s^{-1}}$$

❒ **17.** $k = \frac{2.303}{t}\log\frac{a}{a-x}$

Volume of O_2 liberated is collected at different time intervals :

$V_t = x$, $V_\infty = a$

$$k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$$

Substituting the values of V_t and V_∞, k comes out to be almost constant (k = **5.08 × 10⁻³**).

❒ **18.** $k = \frac{2.303}{t}\log\frac{V_\infty}{V_\infty - V_t}$

Time	V_t	$V_\infty - V_t$	k
20	10	162 – 10	$\frac{2.303}{20}\log\frac{162}{152} = 3.19 \times 10^{-3}\ min^{-1}$
70	33	162 – 33	$\frac{2.303}{70}\log\frac{162}{129} = 3.25 \times 10^{-3} min^{-1}$

(*i*) Since k is constant, it is a first order reaction.

(*ii*) k (average) = $\mathbf{3.21 \times 10^{-3}\ min^{-1}}$

❒ **19.** $t = \frac{2.303}{6.0 \times 10^4}\log\frac{1.0}{0.2} = \mathbf{2683\ s}$

❒ **20.** $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$

t = 60 min, $[A]_0 = 1.2 \times 10^{-2}$ mol L^{-1}

$[A] = 0.20 \times 10^{-2}$ mol L^{-1}

$$k = \frac{2.303}{60}\log\frac{1.24 \times 10^{-2}}{0.20 \times 10^{-2}}$$

$$= \frac{2.303}{60} \times 0.7924$$

$$= \mathbf{3.04 \times 10^{-2}\ min^{-1}}$$

❒ **21.** At 410 s, $k = \frac{2.303}{410}\log\frac{5.5}{4.0} = \mathbf{7.769 \times 10^{-4}s^{-1}}$

At 1130 s, $k = \frac{2.303}{1130}\log\frac{5.5}{2.4} = \mathbf{7.34 \times 10^{-4}s^{-1}}$

Since k is almost constant, it is first order reaction.

❒ **22.** $6.32 \times 10^{-4} = \frac{2.303}{3600}\log\frac{0.40}{[A]}$

$\log\frac{0.40}{[A]} = 0.9879$ or $[A] = \mathbf{0.041}$

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Amount of N_2O_5 reacted $= 0.40 - 0.041 = 0.359$

% N_2O_5 reacted $= \frac{0.359}{0.40} \times 100 =$ **89.75%**

❒ **23.** The initial rate is

$$(\text{Rate})_0 = k[NO]_0^p\ [O_2]_0^q$$

Comparing experiments I and II and substituting the values we get

$$(\text{Rate})_1 = k(0.30)^p\ (0.30)^q = 0.096 \quad ...(i)$$

$$(\text{Rate})_2 = k(0.60)^p\ (0.30)^q = 0.384 \quad ...(ii)$$

Dividing eq. (*ii*) by eq. (*i*) we get

$$\frac{(0.60)^p}{(0.30)^p} = \frac{0.384}{0.096} = 4$$

$$(2)^p = 4 \quad \text{or} \quad (2)^p = 2^2 \quad \therefore \quad p = 2$$

Similarly, comparing experiments I and III and substituting the values, we get

$$(\text{Rate})_1 = k\ (0.30)^p\ (0.30)^q = 0.096 \quad ...(i)$$

$$(\text{Rate})_3 = k\ (0.30)^p\ (0.60)^q = 0.192 \quad ...(iii)$$

Dividing eqn. (*iii*) by (*i*), we get

$$\frac{(0.60)^q}{(0.30)^q} = \frac{0.192}{0.096} = 2 \quad \text{or} \quad 2^q = 2 \quad \therefore \quad q = 1$$

Thus, the overall rate low expression is

Rate = $k[NO]^2\ [O_2]$

❒ **24.** Let the rate law may be expressed as :

$$\text{rate} = k[NO]^p\ [Cl_2]^q$$

The initial rate becomes

$$(\text{rate})_0 = k\ [NO]^p\ [Cl_2]^q$$

Comparing experiment 1 and 2, we get

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

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

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

$$\frac{(\text{rate})_2}{(\text{rate})_1} = \frac{(0.30)^q}{(0.15)^q} = 2 \quad \text{or} \quad 2^q = 2^1 \quad \therefore \quad q = 1$$

Thus, order with respect to Cl_2 is 1.

Comparing experiment 1 and 3, we get

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

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

Dividing eq. (*iv*) by eq. (*iii*)

$$\frac{(0.30)^p}{(0.15)^p} = 4$$

or $\quad 2^p = 2^2 \quad \therefore \quad p = 2$

Thus, order w.r.t. NO is 2.

(*a*) Rate law expression :

$$\text{Rate} = k\ [NO]^2\ [Cl_2]$$

(*b*) According to experiment 1,

$$[NO] = 0.15\ M\ ;\ [Cl_2] = 0.15\ M$$

$$\text{Rate} = 0.6\ M/min$$

$$\text{Rate} = k[NO]^2\ [Cl_2]$$

$$0.6\ M/min = k\ (0.15\ M)^2\ (0.15\ M)$$

$$k = 177.8\ M^{-2}\ min^{-1}$$

$\therefore$ Units of k are $M^{-2}\ min^{-1}$ or $mol^{-2}\ L^{-2}\ min^{-1}$

(*c*) In experiment 4, $[NO] = 0.25\ M\ [Cl_2] = 0.25M$

$$k = 177.8\ M^{-2}\ min^{-1}$$

$$\text{Rate} = k\ [NO]^2\ [Cl_2]$$

$$= 177.8\ M^{-2}\ min^{-1} \times (0.25\ M)^2 \times (0.25\ M)$$

$$= \mathbf{2.78\ M\ min^{-1}}$$

❒ **25.** Rate $= k[A][B]^0$

$2.0 \times 10^{-2} = k\ [0.1]$ or $k = 0.2$

2nd line : $4.0 \times 10^{-2} = 0.2\ [A]$

or $[A] =$ **0.2**

3rd line : Rate $= 0.2 \times 0.4 =$ **8.0×10^{-2}**

4th line : $2.0 \times 10^{-2} = 0.2[A]$ or $[A] =$ **0.1**

❒ **26.**

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

$$\text{Rate}_1 = k(0.20)^p\ (0.30)^q = 8.93 \times 10^{-5}$$

$$\text{Rate}_2 = k(0.20)^p\ (0.10)^q = 8.93 \times 10^{-5}$$

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{(0.30)^q}{(0.10)^q} = 1$$

or $3^q = 3^0$ or $\quad q =$ **0**

$$\text{Rate}_3 = k(0.40)^p\ (0.05)^q = 2.53 \times 10^{-4}$$

$$\text{Rate}_2 = k(0.20)^p\ (0.10)^q = 8.93 \times 10^{-5}$$

$$\frac{\text{Rate}_3}{\text{Rate}_2} = \left(\frac{0.40}{0.20}\right)^p \left(\frac{0.05}{0.10}\right)^q = 2.83$$

$$2^p \left(\frac{1}{2}\right)^q = 2.83$$

$$2^p \left(\frac{1}{2}\right)^0 = 2.83$$

$$2^p = 2.83$$

$$p\ \log 2 = \log 2.83 = 0.452$$

$$p(0.3010) = 0.452$$

$$p = \mathbf{1.5}$$

❒ **27.** $k = \frac{2.303}{66} \log \frac{100}{43} = 0.01279\ min^{-1}$

When $[A] = 100 - 75 = 25$

$$t = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \mathbf{108.4\ min}$$

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❒ **28.** $k = \frac{2.303}{10}\log\frac{a}{0.8a} = 0.0223\ \text{min}^{-1}$

$t = \frac{2.303}{0.0223}\log\frac{a}{0.2a} =$ **72.12 min**

❒ **29.** Let initial conc. = a

Conc. after 40 min = 0.70 a

$$k = \frac{2.303}{40}\log\frac{a}{0.70a} = 8.92 \times 10^{-3}\ \text{min}^{-1}$$

$$t_{1/2} = \frac{0.693}{8.92\times10^{-3}} = \textbf{77.7 min.}$$

❒ **30.** $k = \frac{2.303}{t} = \log\frac{[A]_0}{[A]}$

If $[A]_0 = a$, $[A] = a - \frac{a\times20}{100} = 0.80\ a$, $t = 10$ min

$k = \frac{2.303}{10}\log\frac{a}{0.80a} = 0.0223\ \text{min}^{-1}$

In second case, if $[A]_0 = a$, $[A] = a - \frac{a\times75}{100} = 0.25a$

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

$$= \frac{2.303}{0.0223}\times\log\frac{a}{0.25a} = \textbf{62.18 min}$$

❒ **31.** $k = \frac{2.303}{32}\log\frac{a}{1/4a} = 0.0433$

$t_{1/2} = \frac{0.693}{0.0433} =$ **16 min.**

❒ **32.** $k = \frac{0.693}{2.31\times10^3} = 3.0 \times 10^{-4}\ \text{min}^{-1}$

$t = \frac{2.303}{3.0\times10^{-4}}\log\frac{a}{1/5a} = \textbf{5.366 × 10}^{\textbf{3}}$ **min.**

❒ **33.** $t = \frac{2.303}{6}\log\frac{0.5}{0.05} =$ **0.383 min.**

$t_{1/2} = \frac{0.693}{6} =$ **0.1155 min.**

❒ **34.** $t_{1/2} = 100\ s$

$$k = \frac{0.693}{100} = 6.93 \times 10^{-3}$$

If $[A]_0 = a$

For 75% completion, $[A] = a - \frac{75a}{100} = 0.25\ a$

$$t = \frac{2.303}{6.93\times10^{-3}}\log\frac{a}{0.25a}$$

$=$ **200 min.**

❒ **35.** $t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$

$[A] = [A]_0/18$, $k = 80\ \text{s}^{-1}$

$$t = \frac{2.303}{80}\log\frac{[A]_0}{[A]_0/18}$$

$$= \frac{2.303}{80}\times\log 18$$

$$= \frac{2.303}{80} \times 1.255 = \textbf{3.61 × 10}^{\textbf{-2}}\ \textbf{s}$$

❒ **36.** Between 0 – 100 s, rate $= -\frac{(3.50-4.00)\times10^3}{100}$

$= \textbf{5 Pa s}^{\textbf{-1}}$

Calculate rate between 100 – 200 s and 200 – 300 s, it comes out to be 5 Pa s^{-1}.

Since rate remains constant, it is **zero order reaction.**

$$t_{1/2} = \frac{4.00\times10^3\text{Pa}}{2\times5\ \text{Pa s}^{-1}} = \textbf{400 s.}$$

❒ **37.** Let initial conc. is a, then

$[A]_0 = a$, $(t_{1/2})_1 = 60$ min, when $[A]_0 = a/2$, $(t_{1/2})_2 = 30$ min

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a/2}{a}\right)^{n-1}$$

$$\frac{60}{30} = \left(\frac{1}{2}\right)^{n-1}$$

or $\quad 2 = \left(\frac{1}{2}\right)^{n-1}$

or $\quad 2 = 2^{1-n}$

or $\quad 1 = 1 - n$

$\therefore \quad n = \textbf{1 – 1 = 0}$

❒ **38.** $\therefore \quad k = \frac{0.693}{120\ \text{min}} = 5.77 \times 10^{-3}\ \text{min}^{-1}$

Now, for the first order reaction,

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

If $[A]_0 = a$, then $[A] = a - a \times 0.90 = 0.10a$.

$$\therefore \quad t = \frac{2.303}{5.77\times10^{-3}}\log\frac{a}{0.1a}$$

$$= \frac{2.303}{5.77\times10^{-3}}\log 10$$

$= \textbf{399 min.} \qquad (\because \log 10 = 1)$

❒ **39.** $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 0.01\ \text{min}^{-1}$

Now, $\quad t = \frac{2.303}{k}\log\frac{[A]_0}{[A]}$

For 80% completion, let initial conc. $[A]_0 = a$

then $\quad [A] = a - \frac{a\times80}{100} = 0.20\ a$

$$t = \frac{2.303}{0.01}\log\frac{a}{0.20a} = \textbf{161 min.}$$

❒ **40.** $\log 4 = \frac{E_a}{2.303\times8.314}\left[\frac{1}{293} - \frac{1}{313}\right]$

$$0.6021 = \frac{E_a}{2.303\times8.314}\times\left[\frac{313-293}{293\times313}\right]$$

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Solution File

$\therefore \quad E_a = \dfrac{2.303 \times 8.314 \times 0.6021 \times 293 \times 313}{20}$

or $\quad = 52863.3 \text{ J mol}^{-1} = \mathbf{52.86 \text{ kJ mol}^{-1}}$.

❒ **41.** $\log \dfrac{k_2}{7.8} = \dfrac{110 \times 10^3}{2.303 \times 8.314}\left[\dfrac{1}{673} - \dfrac{1}{703}\right]$

$\log \dfrac{k_2}{7.8} = \dfrac{110 \times 10^3 \times (703 - 673)}{2.303 \times 8.314 \times 673 \times 703}$

$\log \dfrac{k_2}{7.8} = 0.3643$ or $\dfrac{k_2}{7.8} = 2.31$

or $k_2 = 2.31 \times 7.8 = \mathbf{18 \text{ s}^{-1}}$.

❒ **42.** $\log \dfrac{4.87 \times 10^{-3}}{3.46 \times 10^{-5}} = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{338 - 298}{338 \times 298}\right]$

$E_a = \mathbf{103.56 \text{ kJ mol}^{-1}}$

❒ **43.** $k_2/k_1 = 3$

$\log 3 = \dfrac{E_a}{2.303 \times 8.314} \log\left(\dfrac{373 - 323}{373 \times 273}\right)$

$E_a = \mathbf{22.012 \times 10^3 \text{ kJ mol}^{-1}}$

❒ **44.** $\dfrac{k_2}{k_1} = 2$

$\log 2 = \dfrac{E_a}{2.303 \times 8.314} \times \left(\dfrac{310 - 310}{300 \times 310}\right)$

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

❒ **45.** $t_{1/2} = \dfrac{0.693}{k}$

or $\quad k = \dfrac{0.693}{t_{1/2}}$

At 27°C, $t_{1/2} = 30$ min; $k_1 = \dfrac{0.963}{30} = 0.0231$

At 47°C, $t_{1/2} = 10$ min; $k_2 = \dfrac{0.963}{10} = 0.0693$

$\log \dfrac{0.0693}{0.0231} = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{1}{300} - \dfrac{1}{320}\right]$

$0.4771 = \dfrac{E_a \times 20}{2.303 \times 8.314 \times 300 \times 320}$

$= \mathbf{43.8 \text{ kJ mol}^{-1}}$.

❒ **46.** $\log \dfrac{32.0}{2.0} = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{800 - 700}{700 \times 800}\right]$

$E_a = \mathbf{129.1 \text{ kJ mol}^{-1}}$.

❒ **47.**

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

or $\quad \dfrac{k_2}{k_1} = 6$, $T_1 = 350$ K, $T_2 = 400$ K

$\log 6 = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{400 - 350}{400 \times 350}\right]$

$0.7782 = \dfrac{E_a}{2.303 \times 8.314} \times \dfrac{50}{400 \times 350}$

or $\quad E_a = \dfrac{0.7782 \times 2.303 \times 8.314 \times 400 \times 350}{50}$

$= 41721 \text{ J mol}^{-1} = \mathbf{41.7 \text{ kJ mol}^{-1}}$.

❒ **48.** $\log \dfrac{6.36 \times 10^{-3}}{1.6 \times 10^{-5}} = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{700 - 600}{600 \times 700}\right]$

$E_a = \mathbf{209.01 \text{ kJ mol}^{-1}}$.

❒ **49.** The plot of in k vs 1/T comes out be straight line with slope = – 12.109 × 10^3

$\text{Slope} = -\dfrac{E_a}{R}$

or $E_a = -(-12.109 \times 10^3) \times 8.314 = 100.67 \text{ kJ mol}^{-1}$

$\ln A = \ln k + \dfrac{E_a}{RT}$

$= -10.98 + \dfrac{100.67 \times 10^3}{8.314 \times 293} = 30.34$

or A = antilog (30.34) = 1.51×10^{13} min

Now, $\quad 30.34 = \ln k + \dfrac{100.67 \times 10^3}{8.314 \times 303}$

In $\quad \ln k = 30.34 - 39.96 = -9.62$

$k = \mathbf{6.64 \times 10^{-5} \text{ s}^{-1}}$

Similarly at 50°C, $k = \mathbf{7.93 \times 10^{-4} \text{ s}^{-1}}$

❒ **50.** $\log \dfrac{2.1 \times 10^{-3}}{1.2 \times 10^{-3}} = \dfrac{E_a}{2.303 \times 8.314}\left[\dfrac{313 - 303}{303 \times 313}\right]$

$\therefore \quad E_a = \mathbf{44.126 \text{ kJ mol}^{-1}}$.

❒ **51.** $\log \dfrac{6.36 \times 10^{-3}}{1.60 \times 10^{-5}} = \dfrac{E_a}{2.303 \times 8.314} \log\left(\dfrac{700 - 600}{700 \times 600}\right)$

$E_a = \mathbf{209.1 \text{ kJ mol}^{-1}}$

❒ **52.** $\log \dfrac{7.50 \times 10^{-2}}{2.34 \times 10^{-3}} = \dfrac{E_a}{2.303 R}\left(\dfrac{1}{673} - \dfrac{1}{773}\right)$

$E_a = 1.51 \times 10^4 \text{ J mol}^{-1} = \mathbf{15.1 \text{ kJ mol}^{-1}}$.

❒ **53.** Slope of the line $= -\dfrac{E_a}{2.303 R} = -6670$ K

$\therefore \quad E_a = 2.303 \times 8.314 \text{ (Jmol}^{-1}\text{K}^{-1}) \times 6670 \text{ K}$

$= 127711.4 \text{ J mol}^{-1} = \mathbf{127.7 \textit{ kJ} \text{ mol}^{-1}}$

❒ **54.** $k = Ae^{-E_a/RT}$

$k_2 = Ae^{-E_a(c)/RT}$

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$$\log \frac{k_2}{k_1} = \frac{E_a - E_a(c)}{2.303\ RT}$$

$$\log \frac{k_2}{k_1} = \frac{6000-5000}{2.303 \times 8.314 \times 300} = 1.741$$

$$\therefore \quad \frac{k_2}{k_1} = 55.08$$

$\therefore$ **The reaction rate increases by 55.08 times.**

❒ **55.** $$\log \frac{k_2}{k_1} = \frac{E_a}{2.303}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log \frac{1.5\times10^4}{4.5\times10^3} = \frac{60\times10^3}{2.303\times8.314}\left[\frac{T_2-283}{283\ T_2}\right]$$

$$\log 3.33 = \frac{60\times10^3}{2.303\times8.314}\left[\frac{T_2-283}{283\ T_2}\right]$$

$$0.523 = \frac{60\times10^3}{2.303\times8.314}\left[\frac{T_2-283}{283\ T_2}\right]$$

$$\left[\frac{T_2-283}{283\ T_2}\right] = \frac{0.523\times2.303\times8.314}{60000} = 1.66 \times 10^{-4}$$

$$T_2 - 283 = 0.047\ T_2$$

or $$0.953\ T_2 = 283$$

$$T_2 = \frac{283}{0.953} = 297\ K$$

or $$T_2 = 297 - 273 = \mathbf{24°C}$$

Chapter Summary

Key Terms & Laws

- **Rate of a reaction.** It is the change of concentration of any one of the reactants or products per unit time.
- **Rate constant.** It is the rate of a reaction when the molar concentration of each of the reactants is unity.
- **Order of a reaction.** The sum of the powers to which the concentration terms are raised in the rate law equation to express the observed rate of the reaction.
- **Molecularity of a reaction.** The number of reacting species (atoms, ions or molecules) which collide simultaneously to bring about a chemical reaction.
- **Elementary steps.** The reaction steps which contribute to the overall reaction.
- **Half life period or time.** The time during which the concentration of a reactant is reduced to half of its initial concentration.
- **Pseudo first order reaction.** The reaction which appears to be of higher order but actually follow lower order (first order) kinetics.
- **Activation energy.** The excess energy (over and above the average energy of reactants) which must be supplied to the reactants to undergo a chemical reaction.
- **Law of mass action.** The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is directly proportional to the product of the active masses of the reactants.
- **Rate law:** The mathematical expression which denotes the observed or actual rate of a reaction in terms of the molar concentration of the reacting species which influences the rate of the reaction.

QUICK CHAPTER ROUND UP

Rate of reaction

For a reaction,

$aA + bB \rightleftharpoons cC + dD$

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

▶ −ve sign is used for conc. of reactants.

Dependence of rate of reaction on concentration for a reaction

$aA + bB \rightleftharpoons cC + dD$

Law of mass action
rate $= k[A]^a[B]^b$

Rate law expression
rate $= k[A]^x[B]^y$

⇒ x and y are experimentally determined
⇒ x and y may or may not be equal to a and b

Order of a reaction

Rate $= k[A]^\alpha[B]^\beta[C]^\gamma$ Order $= \alpha + \beta + \gamma$

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Order of a reaction
- Sun of the powers to which the conc. terms are raised.
- can be fractional
- can be zero
- experimentally determined

Molecularity
- Number of reacting species which collide simultaneously
- always whole number
- cannot be zero
- theoretical concept

⇒ For elementary reactions, order and molecularity are same
⇒ In a multi-step reaction, slowest step determines order of reaction

Order		Units of k		Integrated rate equation		Half life period		
Zero	⇒	$mol\ L^{-1}\ s^{-1}$	⇒	$[A] = -kt + [A]_0$	⇒	$[A]_0/2k$		Amount left after n-half lives
First	⇒	s^{-1}	⇒	$\log [A] = -\frac{kt}{2.303} + \log[A]_0$	⇒	$\frac{0.693}{k}$	=	$\frac{[A]_0}{2^n}$
Second	⇒	$L\ mol^{-1}\ s^{-1}$	⇒	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	⇒	$\frac{1}{[A]_0}$		

For nth order, units of $k = (mol\ L^{-1})^{1-n}\ s^{-1}$

For nth order $t_{1/2} = \frac{1}{[A]_0^{n-1}}$

Arrhenius Equation

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

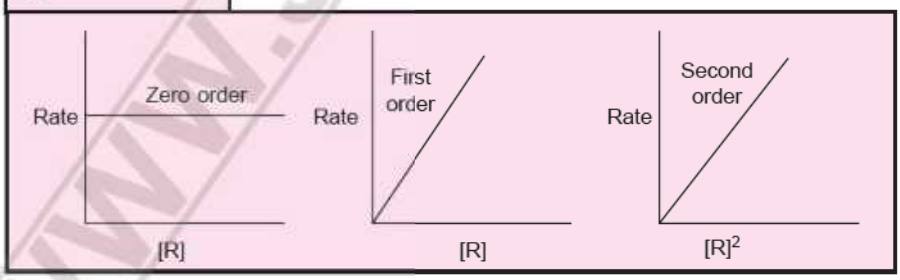
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$\Delta H = E_a$ (forward) $- E_a$(backward)
Low $E_a \Rightarrow$ Fast reactions
High $E_a \Rightarrow$ Slow reactions
E_a (catalysed) < E_a uncatalysed

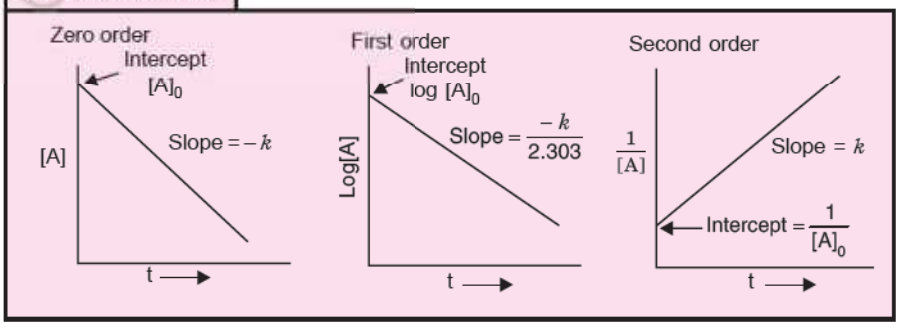
- A catalyst speeds up a reaction usually by lowering the value of E_a.
- A catalyst can be recovered unchanged at the end of the reaction.
- A catalyst does not change ΔH of a reaction.

Important Graphs

- Rate vs conc.



- Conc. vs time



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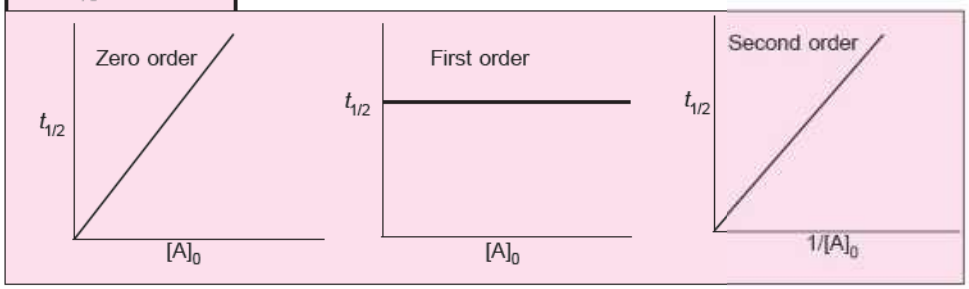
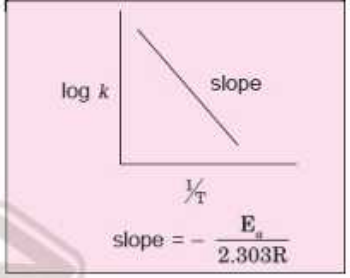
❑ $t_{1/2}$ vs conc.



❑ log k vs $\frac{1}{T}$ for **first order**



NCERT FILE Solved

NCERT In-text Questions

Q.1. For the reaction R ⟶ 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. Average rate $= -\frac{\Delta[R]}{\Delta t}$

$$= -\frac{(0.02 - 0.03)\text{ mol L}^{-1}}{25\text{ min}}$$

$$= \mathbf{4 \times 10^{-4}\ mol\ L^{-1}\ min^{-1}}$$

Time = 25 min = 25 × 60s

$$\text{Rate} = -\frac{(0.02 - 0.03)\text{ mol L}^{-1}}{25 \times 60\text{s}}$$

$$= \mathbf{6.67 \times 10^{-6}\ mol\ L^{-1}s^{-1}}$$

Q.2. In a reaction 2A ⟶ 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 time interval.

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

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

$$= \mathbf{5 \times 10^{-3}\ mol\ L^{-1}\ min^{-1}}$$

Q.3. For a reaction, A + B → Product, the rate is given by,

$$r = k[A]^{1/2}[B]^2.$$

What is the order of the reaction?

Ans. Order $= \frac{1}{2} + 2 = \frac{5}{2} = \mathbf{2.5}$

Q.4. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased three times how will it affect rate of formation of Y?

Ans. Rate $= k[A]^2$ or ka^2

When conc. of A is increased 3 times, then

$$[A] = 3a$$

$$\therefore \quad \text{Rate} = k\,(3a)^2 = k9a^2$$

Rate of formation will become nine times.

Q.5. A first order reaction has a rate constant 1.15 × 10⁻³ s⁻¹. How long will 5g of this reactant take to reduce to 3g? ***(Hr. S.B. 2017)***

Ans. For a first order reaction:

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

$[A]_0$ = 5g/M, [A] = 3g/M, $k = 1.15 \times 10^{-3}\ s^{-1}$

where M is molar mass

$$t = \frac{2.303}{1.15 \times 10^{-3}}\log\frac{5/M}{3/M}$$

$$= \frac{2.303}{1.15 \times 10^{-3}}\log\frac{5}{3}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2218 = \mathbf{444\ s}$$

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Q.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. $t_{1/2}$ = 60 min = 60 × 60 s

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

Q.7. What will be the effect of temperature on rate constant?

Ans. The rate constant of a reaction increases with increase in temperature. *For detail refer Text, page 52.*

Q.8. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a.

Ans.
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

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

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

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

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

$$= \mathbf{52.898\ kJ}$$

Q.9. The activation energy for the reaction

$$2HI\,(g) \longrightarrow H_2(g) + I_2(g)$$

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

Ans. The fraction of molecules having energy equal to or greater than activation energy,

$$\text{Fraction of molecules} = e^{-E_a/RT} = e^{-\frac{209.5 \times 1000}{8.314 \times 581}}$$

$$= e^{-43.37} = \mathbf{1.461 \times 10^{-19}}$$

NCERT Textbook Exercises

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

(*i*) $3NO(g) \rightarrow N_2O(g)$ Rate = $k[NO]^2$

(*ii*) $H_2O_2(aq) + 3I^-(aq) + 2H^+ \rightarrow 2H_2O(l) + I_3^-$ Rate = $k[H_2O_2]\,[I^-]$

(*iii*) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ Rate = $k[CH_3CHO]^{3/2}$

(*iv*) $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl\,(g)$ Rate = $k[C_2H_5Cl]$

Ans. (*i*) Order = 2

Dimensions of *k*

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

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

(*ii*) Order = 1 + 1 = 2

Dimensions of *k*

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

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

(*iii*) Order = 3/2

Dimensions of *k*

$$\text{mol L}^{-1}\text{ s}^{-1} = k\,(\text{mol L}^{-1})^{3/2}$$

$$\therefore \quad k = \text{mol}^{-1/2}\text{ L}^{1/2}\text{ s}^{-1}$$

(*iv*) Order = 1

Dimensions of *k*

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

$$\therefore \quad k = \text{s}^{-1}$$

Q.2. For the reaction :

$2A + B \rightarrow A_2B$

the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6}$ mol^{-2} L^2 s^{-1}.

Calculate the initial rate of the reaction when [A] = 0.1 mol L^{-1}, [B] = 0.2 mol L^{-1}. Calculate the rate of reaction after [A] is reduced to 0.06 mol L^{-1}.

Ans. (*i*) Rate = k[A] $[B]^2$

When [A] = 0.1 mol L^{-1}, B = 0.2 mol L^{-1}

$$\text{Rate} = 2.0 \times 10^{-6} \times (0.1) \times (0.2)^2$$

$$= \mathbf{8.0 \times 10^{-9}\ L\ mol^{-1}\ s^{-1}}$$

(*ii*) When [A] = 0.06 mol L^{-1}

$\therefore$ A reacted = 0.1 − 0.06 = 0.04

B reacted = 0.02

$\therefore$ [B] = 0.2 − 0.02 = 0.18 mol L^{-1}

$$\text{Rate} = 2.0 \times 10^{-6} \times (0.06) \times (0.18)^2$$

$$= \mathbf{3.89 \times 10^{-9}\ L\ mol^{-1}\ s^{-1}}$$

Q.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 $k = 2.5 \times 10^{-4}$ mol^{-1} Ls^{-1}.

(*D.S.B. 2008*)

Ans. $$2\ NH_3 \longrightarrow N_2 + 3\ H_2$$

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

For a zero order reaction

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

$$\text{Rate of production of } N_2 = \frac{d[N_2]}{dt} = 2.5 \times 10^{-4}$$

$$= \mathbf{2.5 \times 10^{-4}\ M\ s^{-1}}$$

$$\text{Rate of production } H_2 = \frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4}$$

$$= \mathbf{7.5 \times 10^{-4}\ M\ s^{-1}}$$

Q.4. The decomposition of dimethyl ether leads to the formation of CH_4, H_2 and CO and the reaction rate is given by

Rate = $k[CH_3OCH_3]^{3/2}$

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.*, Rate = $k(p_{CH_3OCH_3})^{3/2}$

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

Ans. $$\text{Rate} = \frac{\text{bar}}{\text{min}} = \text{bar min}^{-1}$$

$$\text{Rate} = k(pCH_3OCH_3)^{3/2}$$

$$\text{bar min}^{-1} = k(\text{bar})^{3/2}$$

$$k = \frac{\text{bar min}^{-1}}{(\text{bar})^{3/2}} = \mathbf{bar^{-1/2}\ min^{-1}}$$

Q.5. Mention the factors that effect the rate of a chemical reaction.

Ans. *Refer Text Page 9.*

Q.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(*A.I.S.B. 2012*) (*i*) doubled (*ii*) reduced to half?

Ans. *Refer Solved Example 13 (page 20)*

Q.7. What is the effect of temperature on the rate constant of reaction ? How can this temperature effect on rate constant be represented quantitatively?

Ans. *Refer Text Page 52 — 53.*

Q.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*) $$r_{av} = \frac{0.17 - 0.31}{60 - 30}$$

$$= \mathbf{4.67 \times 10^{-3}\ s^{-1}}$$

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

At t = 30 s

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

$$= \frac{2.303}{30} \times 0.249 = \mathbf{1.91 \times 10^{-2}\ s^{-1}}$$

At t = 60 s

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

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

At t = 90 s

$$k = \frac{2.303}{90}\log\frac{0.55}{0.085}$$

$$= \frac{2.303}{90} \times 0.8109 = \mathbf{2.07 \times 10^{-2}\ s^{-1}}$$

Average value of k = **1.98×10^{-2} s**

Q.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 ?

Ans. (*i*) Rate = k[A] $[B]^2$

(*ii*) Rate becomes 9 times

(*iii*) Rate becomes 8 times

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

$$\text{Rate}_1 = (0.20)^p\ (0.30)^q = 5.07 \times 10^{-5} \quad ...(i)$$

$$\text{Rate}_2 = (0.20)^p\ (0.10)^q = 5.07 \times 10^{-5} \quad ...(ii)$$

$$\frac{(\text{Rate})_1}{(\text{Rate})_2} = \frac{(0.30)^q}{(0.10)^q} = 1$$

$3^q = 1$ or $3^q = 3^0$ $\therefore q = 0$

$$\text{Rate}_3 = (0.40)^p\ (0.05)^q = 1.43 \times 10^{-4} \quad ...(iii)$$

Dividing (*iii*) by (*ii*)

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{(0.40)^p\ (0.05)^q}{(0.20)^p\ (0.10)^q} = \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}}$$

$$2^p \times \frac{1}{2^0} = 2.8$$

Since $q = 0$

$$2^p \times \frac{1}{2^0} = 2.8$$

$$2^p = 2.8$$

Taking log on both sides

$$p \log 2 = \log 2.8$$

or $$p = \frac{\log 2.8}{\log 2} = \frac{0.45}{0.3010} = 1.5$$

Order of reaction w.r.t. A = 1.5,

order of reaction w.r.t. B = 0.

Q.11. The following results have been obtained during the kinetic studies of the reaction :

$2A + B \longrightarrow C + D$

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. The initial rate is

$$(\text{rate})_0 = k[A]_0^p\ [B_0]^q$$

Comparing experiments I and IV and substituting the values we get

$$(\text{rate})_1 = k(0.1)^p\ (0.1)^q = 6.0 \times 10^{-3} \quad ...(i)$$

$$(\text{rate})_4 = k(0.4)^p\ (0.1)^q = 2.40 \times 10^{-2} \quad ...(ii)$$

Dividing eq. (*ii*) by eq. (*i*), we get

$$\frac{(0.4)^p}{(0.1)^p} = \frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = 4$$

$$4^p = 4 \text{ or } (4)^1$$

or $$p = 1$$

Similarly, comparing experiments II and III and substituting the values we get

$$(\text{rate})_2 = k(0.3)^p\ (0.2)^q = 7.2 \times 10^{-2} \quad ...(iii)$$

$$(\text{rate})_3 = k(0.3)^p\ (0.4)^q = 2.88 \times 10^{-1} \quad ...(iv)$$

Dividing eq. (*iv*) by eq.(*iii*), we get

$$\frac{(0.4)^q}{(0.2)^q} = \frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = 4$$

$$(2)^q = 4 \quad \text{or} \quad 2^2$$

$\therefore$ $$q = 2$$

Thus the overall rate law expression is:

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

Substituting the values from (*i*), we get

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

or $$k = \frac{6.0 \times 10^{-3}}{(0.1)(0.1)^2} = \mathbf{6.0\ mol^{-2}\ L^2\ min^{-1}}.$$

Q.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. *Refer Solution of Practice Problem 25 (Page 70).*

Q.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. *Refer Solved Example 22. (Page 32)*

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

Ans. *Refer Solved Example 40. (Page 45)*

Q.15. The experimental data for decomposition of N_2O_5

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

in gas phase at 318K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5]$/ mol L^{-1}	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(*i*) Plot $[N_2O_5]$ against *t*.

(*ii*) Find the half-life period for the reaction.

(*iii*) Draw a graph between log $[N_2O_5]$ and *t*.

(*iv*) What is the rate law?

(*v*) Calculate the rate constant.

(*vi*) Calculate the half-life period from *k* and compare it with (*b*).

Ans. *Refer Solved Example 27. (Page 37)*

Q.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 1/16th value ? ***(Pb.S.B. 2016)***

Ans. Let initial concentration, $[A]_0 = a$

Final concentration = $[A] = \frac{1}{16}a$

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

$$= \frac{2.303}{60} \log \frac{a}{a/16}$$

$$= \frac{2.303}{60} \log 16$$

$$= \frac{2.303}{60} \times 1.204 = 0.046 \text{ sec}$$

$$= \mathbf{4.6 \times 10^{-2}\ seconds.}$$

Q.17. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If 1 μg of ^{90}Sr was absorbed in the bones of a 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. $$k = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = 28.1 \text{ years}$$

$$k = \frac{0.693}{28.1} = 0.0247 \text{ years}^{-1}$$

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

Initial concentration of ^{90}Sr = 1μg

Let concentration of ^{90}Sr after 10 years = x μg

$$0.0247 = \frac{2.303}{10 \text{ years}}\log\frac{1\mu g}{x\mu g}$$

$$\log\frac{1}{x} = \frac{0.0247 \times 10}{2.303} = 0.1072$$

or $$\frac{1}{x} = 1.280$$

∴ $$x = 0.782 \ \mu g$$

Concentration of ^{90}Sr after 10 years = 0.782 μg

Let concentration of ^{90}Sr after 60 years = y μg

$$0.0247 = \frac{2.303}{60}\log\frac{1\mu g}{y\mu g}$$

$$\log\frac{1}{y} = \frac{0.0247 \times 60}{2.303} = 0.6435$$

or $$\frac{1}{y} = 4.40$$

∴ $$y = 0.228 \ \mu g$$

Concentration of ^{90}Sr after 60 years = **0.228 μg.**

Q.18. Show that time required for 99% completion is twice the time required for the completion of 90% reaction. ***(D.S.B. 2013, H.P.S.B. 2014)***

Ans. For a first order reaction

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

Let initial concentration, $[A]_0 = a$

For 99% completion of reaction,

$$[A] = a - \frac{a \times 99}{100} = 0.01\,a$$

$$t_{(99\%)} = \frac{2.303}{k}\log\frac{a}{0.01a}$$

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

$$= \frac{2.303 \times 2}{k} \quad ...(i)$$

For 90% completion of reaction,

$$[A] = a - \frac{a \times 90}{100} = 0.1a$$

$$t_{(90\%)} = \frac{2.303}{k}\log\frac{a}{0.1a}$$

$$= \frac{2.303}{k} \times 1 \quad ...(ii)$$

Dividing equation (*i*) by (*ii*)

$$\frac{t_{(99\%)}}{t_{(90\%)}} = 2$$

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

Q.19. A first order reaction takes 40 min for 30% decomposition. Calculate $t_{1/2}$.
(D.S.B. 2008, Mizoram S.B.2014, H.P.S.B. 2014)

Ans. Let initial conc. = a

Conc. after 40 min = $a - a \times \frac{30}{100} = 0.70\,a$

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

$$= \frac{2.303}{t}\log\frac{a}{0.70a}$$

$$= \frac{2.303}{40} \times 0.1549$$

∴ $$k = 8.92 \times 10^{-3} \text{ min}^{-1}$$

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

$$= \frac{0.693}{8.92 \times 10^{-3} \text{ min}^{-1}} = \mathbf{77.7 \text{ min.}}$$

Q.20. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data is obtained.

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

Calculate the rate constant.

Ans. Let initial pressure of azoisopropane = p_i

Let x atm of azoisopropane decreases at time t so that

$$(CH_3)_2CHNH = NHCH(CH_3)_2 \longrightarrow N_2 + C_6H_{14}$$

At $t = 0$	p_i	0	0
At time = t	$(p_i - x)$ atm	x atm	x atm

$$p_t = p_i - x + x + x = p_i + x$$

or $$x = p_t - p_i$$

$$p \text{ (azoisopropane)} = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$$

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

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

At time 360 s

$$k = \frac{2.303}{360}\log\frac{35.0}{(2 \times 35.0 - 54)}$$

$$= \frac{2.303}{360}\log\frac{35.0}{16}$$

$$= \frac{2.303}{360} \times 0.3399$$

$$= 2.17 \times 10^{-3}\text{s}^{-1}$$

At time 720 s

$$k = \frac{2.303}{720}\log\frac{35.0}{(2 \times 35.0 - 63.0)}$$

$$= \frac{2.303}{720}\log\frac{35.0}{7} = \frac{2.303}{720} \times 0.699$$

$$= 2.24 \times 10^{-3}\text{s}^{-1}$$

Mean value of k = $$\frac{2.17 \times 10^{-3} + 2.24 \times 10^{-3}}{2}$$

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

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Q.21. The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$$SO_2Cl_2\,(g) \longrightarrow SO_2(g) + Cl_2(g)$$

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. ***(CBSE Sample Paper 2010)***

Ans.
$$k = \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)} \text{ (same as for Q.20)}$$
$$= \frac{2.303}{100}\log\frac{0.5}{(2\times 0.5 - 0.6)} = \frac{2.303}{100}\log\frac{0.5}{0.4}$$
$$= \frac{2.303}{100}\times 0.0969 = 2.23\times 10^{-23}\text{s}^{-1}$$

Now, rate $= p\,SO_2Cl_2$

Pressure of SO_2Cl_2 when total pressure = 0.65 atm

$$p\,SO_2Cl_2 = 2p_i - p_t$$
$$= 2\times 0.5 - 0.65 = 0.35 \text{ atm}$$
$$\therefore \quad \text{Rate} = 2.23\times 10^{-3}\times 0.35$$
$$= \mathbf{7.805\times 10^{-4}\ atm\ s^{-1}}$$

Q.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/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. Please try yourself (similar to Solved Example 58 page 57) by plotting graph between ln k vs 1/T. This will give slope = $-E_a$

Q.23. The rate constant for the decomposition of hydrocarbons is 2.418×10^{-5} 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.
$$\log k = \log A - \frac{E_a}{2.303\,RT}$$
$$\log A = \log k + \frac{E_a}{2.303\,RT}$$
$$= \log 2.418\times 10^{-5} + \frac{179.9\times 10^3}{2.303\times 8.314\times 546}$$
$$= -4.616 + 17.208$$
$$= 12.592$$
$$\therefore \quad \mathbf{A = 3.90\times 10^{12}\ s^{-1}}$$

Q.24. Consider a certain reaction A → Products with $k = 2.0\times 10^{-2}$s^{-1}. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L^{-1}.

Ans.
$$k = 2.0\times 10^{-2}\ \text{s}^{-1}$$
$$t_1 = 0,\ [A]_0 = 1.0\ \text{M}$$
$$t_2 = 100\text{s},\ [A] = ?$$
$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$
$$2.0\times 10^{-2} = \frac{2.303}{t}\log\frac{1.0}{[A]}$$
$$\log\frac{1.0}{[A]} = \frac{2.0\times 10^{-2}\times 100}{2.303} = 0.868$$
$$\frac{1.0}{[A]} = 7.379$$
$$\therefore \quad [A] = \frac{1}{7.379} = \mathbf{0.135\ M.}$$

Q.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 sample of sucrose remains after 8 hours ?

Ans.
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.0} = 0.231\ \text{hr}^{-1}$$

Let initial conc. of sucrose = 1 M

Conc. after 8 hr. = $(1 - x)$ where x is the amount of sucrose decomposed.

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$
$$0.231 = \frac{2.303}{8}\log\frac{1}{1-x}$$
$$\log\frac{1}{1-x} = \frac{0.231\times 8}{2.303} = 0.8024$$
$$\frac{1}{1-x} = 6.345$$
$$1 = 6.345 - 6.345\,x$$
$$\therefore \quad x = \frac{5.345}{6.345} = 0.842$$

Conc. of sucrose left after 8 hr

$$= 1 - 0.842$$
$$= \mathbf{0.158\ M}$$

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

Comparing the equation with Arrhenius equation

$$k = A\,e^{-E_a/RT}$$
$$-\frac{E_a}{R} = -28000\text{K}$$
$$\therefore \quad E_a = 28000\times 8.314$$
$$= 232792\ \text{J mol}^{-1}$$
$$= \mathbf{232.792\ k\ J\ mol^{-1}}$$

Q.27. The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

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

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

Ans. According to Arrhenius equation,

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

The given equation is,

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

Comparing eqn. (*i*) and eq. (*ii*),

$$\frac{E_a}{2.303\,R} = 1.25 \times 10^4$$

$$\therefore \quad E_a = 1.25 \times 10^4 \times 2.303 \times 8.314$$

$$= 23.934 \times 10^4\ J\ mol^{-1}.$$

or $= 239.34\ kJ\ mol^{-1}$

Half life period,

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

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

$$k = \frac{0.693}{256\ min} = 4.51 \times 10^{-5}\ s^{-1}$$

Substituting the values in Eqn. (*ii*),

$$\log 4.51 \times 10^{-5} = 14.34 - \frac{125 \times 10^4}{T}$$

$$-4.3458 = 14.34 - \frac{125 \times 10^4}{T}$$

$$T = \frac{125 \times 10^4}{18.6858} = \mathbf{669\ K}.$$

Q.28. The decomposition of A product has value of *k* as $4.5 \times 10^3\ s^{-1}$ at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature would *k* be $1.5 \times 10^4\ s^{-1}$?

Ans.

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

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60 \times 10^3}{2.303 \times 8.314}\left[\frac{T_2 - 283}{283 \times T_2}\right]$$

$$\log 3.333 = 3133.62\left(\frac{T_2 - 283}{283 \times T_2}\right)$$

$$0.5228 = 3132.62\left(\frac{T_2 - 283}{283 \times T_2}\right)$$

$$\frac{T_2 - 283}{283 \times T_2} = \frac{0.5228}{3132.62}$$

$$T_2 - 283 = 0.0472\ T_2$$

$$0.9528\ T_2 = 283$$

$$\therefore \quad T_2 = \frac{283}{0.9528} = 297.02$$

$$= 297.02 - 273 = \mathbf{24.02°C}$$

Q.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 $4 \times 10^{10} s^{-1}$, calculate *k* at 318 K and E_a.

Ans. *Advanced Level Problem 8 (Page 60)*

Q.30. The rate of 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. ***(A.I.S.B. 2013)***

Ans. *Refer Solved Example 53 (page 56).*

NCERT Exemplar Problems

Subjective Questions

Note: *Objective Questions from Exemplar Problems are given in Competition File, page 112.*

Short Answer Type Questions

1. State a condition under which a bimolecular reaction is kinetically first order reaction.

Ans. Bimolecular reaction becomes kinetically first order when one of the reactants is in excess.

2. Write the rate equation for the reaction 2A + B ⟶ C if the order of the reaction is zero.

Ans. Rate = $k\ [A]^0[B]^0$ or Rate = k

3. How can you determine the rate law of the following reaction?

$$2NO(g) + O_2(g) \longrightarrow 2NO_2\ (g)$$

Ans. The rate law can be determined by measuring the rate of this reaction as a function of initial concentration by keeping the concentration of one of the reactants constant and changing the concentration of other reactant or by changing the concentration of both the reactants. From the concentration dependance of rate, rate law can be determined.

4. For which type of reactions, order and molecularity have the same value?

Ans. For elementary reaction, order and molecularity have the same value.

5. In a reaction if the concentration of reactant A is tripled, the rate of reaction becomes twenty seven times. What is the order of the reaction?

Ans. Order is 3 because

$k = [A]^3$

6. Derive an expression to calculate time required for completion of zero order reaction.

Ans. For a zero order reaction,

$R = [R]_0 - kt$

For completion of the reaction, [R] = 0

$\therefore\ kt = [R]_0$

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

7. For a reaction A + B ⟶ Products, the rate law is : Rate = $k[A][B]^{3/2}$.

Can the reaction be an elementary reaction? Explain.

Ans. The reaction is not elementary because order of the reaction is fractional $1 + \frac{3}{2} = \frac{5}{2}$

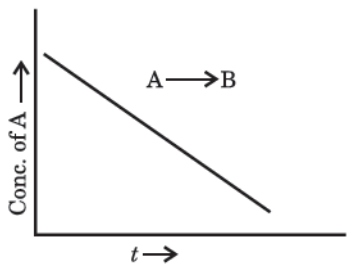
8. For a certain reaction large fraction of molecules has energy more than the threshold energy, yet the rate of reaction is very slow. Why?

Ans. Though the reacting molecules may be having energy more than threshold energy, yet they may not be effective due to lack of proper orientation.

9. For a zero order reaction will the molecularity be equal to zero? Explain.

Ans. Molecularity can never be zero or a fractional number.

10. For a general reaction A ⟶ B, plot of concentration of A vs time is given in figure below. Answer the following question on the basis of this graph.



(*i*) What is the order of the reaction?

(*ii*) What is the slope of the curve?

(*iii*) What are the units of rate constant?

Ans. (*i*) zero order reaction

(*ii*) $[R] = [R_0] - kt$

$\therefore$ Slope $= -k$

(*iii*) $\frac{mol^{-1}L}{s^{-1}} = k[A]^0$ or $k = mol^{-1}\ L\ s^{-1}$

11. The reaction between $H_2(g)$ and $O_2(g)$ is highly feasible yet allowing the gases to stand at room temperature in the same vessel does not lead to the formation of water. Explain.

Ans. This is because activation energy for the reaction is very high at room temperature.

12. Why does the rate of a reaction increase with rise in temperature?

Ans. At higher temperatures, larger fraction of colliding particles can cross the energy barrier (*i.e.* the activation energy), which leads to faster rate. For detail *refer text*.

13. Oxygen is available in plenty in air yet fuels do not burn by themselves at room temperature. Explain.

Ans. The activation energy for combustion reactions of fuels is very high at room temperature therefore they do not burn by themselves.

14. Why is the probability of reaction with molecularity higher than three very rare?

Ans. The probability of more than three molecules colliding simultaneously is very small. Therefore, the possibility of molecularity being three is very low.

15. Why does the rate of any reaction generally decreases during the course of the reaction?

Ans. The rate of a reaction depends on the concentration of reactants. As the reaction progresses, the concentration of reactant decreases because the reactants start getting converted to products. Hence the rate decreases.

16. Thermodynamic feasibility of the reaction alone cannot decide the rate of the reaction. Explain with the help of one example.

Ans. Thermodynamic feasibility (–ve ΔG) cannot alone decide the rate of reaction because the reaction may be feasible but its rate may be very very slow because of very high activation energy. For example, conversion of diamond to graphite is highly feasible but this reaction is very slow because it has high activation energy.

17. Why in the redox titration of $KMnO_4$ vs oxalic acid, we heat oxalic acid solution before starting the titration?

Ans. The reaction between $KMnO_4$ and oxalic acid is very slow. By raising the temperature we can increase the rate of reaction.

18. Why can't molecularity of any reaction be equal to zero?

Ans. Molecularity is the number of molecules taking part in an elementary step. For this we require at least a single molecule leading to the value of minimum molecularity of one.

19. Why molecularity is applicable only for elementary reactions and order is applicable for elementary as well as complex reactions?

Ans. A complex reaction occurs through several elementary reactions. Numbers of molecules involved in each elementary reaction may be different *i.e.*, the molecularity of each step may be different. Therefore, the molecularity of overall complex reaction is meaningless. On the other hand, order of a complex reaction is experimentally determined by the slowest step in its mechanism and is therefore, applicable even in the case of complex reactions.

20. Why can we not determine the order of a reaction by taking into consideration the balanced chemical equation?

Ans. Balanced chemical equation often leads to incorrect order or rate law. For example, the following reaction appears to be a tenth order reaction.

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow KCl + 3H_2O + 3Fe_2(SO_4)_3$$

However, this is actually a second order reaction. Actually the reaction is complex and occurs in several steps. The order of such reaction is determined by the slowest step in the reaction mechanism. Order is determined experimentally and gives the actual dependence of observed rate of reaction on the concentration of reactants.

QUICK MEMORY TEST

A. Say True or False

1. The units of rate constant of a zero order reaction are same as the units of rate of a reaction.
2. For a particular reaction, the rate constant is independent of concentration.
3. In general, for nth order gaseous reaction, the units of rate constant are $(atm)^{n-1}\ s^{-1}$.
4. The rate of a multistep reaction is determined by the fastest step in the sequence.
5. For the second order reaction with respect to a reactant rate becomes 8 times when its concentration is tripled.
6. For a zero order reaction, rate becomes 1/2 times on doubling its concentration.
7. The half life period for a first order reaction is independent of its initial concentration.
8. If $[A]_0$ is the initial concentration of a reactant following first order reaction, then after three half lives its concentration becomes $\frac{[A]_0}{3^2}$.
9. The molecularity of a reaction is always greater than order of the reaction.
10. Higher the activation energy of a reaction, faster is the reaction.
11. Order of a reaction may be fractional but molecularity is never fractional.
12. For a first order reaction, plot of $ln([A]_0/[A])$ versus time has a positive slope whose value is equal to the rate constant of the reaction.
13. The time taken for $3/4^{th}$ of a first order reaction to complete is 1.5 times the half life period.
14. For a zero order reaction, plot of [A] vs t is a horizontal line.
15. Average life period for a first order reaction is equal to reciprocal of disintegration constant.

B. Complete the missing links

1. Rate constant and rate of a reaction have the same units for reactions of ..... order.
2. Hydrolysis of ethyl acetate in an aqueous solution is of ..... order.
3. The order of a reaction whose rate law is rate = $k[A]^{3/4}\ [B]^{1/2}$ is ..... .
4. The difference in energy between the energy of activated complex and the average energy of reactants is called ..... .
5. The factor $e^{-Ea/RT}$ in Arrhenius equation is called ..... factor.
6. The units of rate constant for a second order gaseous reaction are ..... .
7. The rate of a reaction when the concentration of each reactant is taken as unity is called ..... .
8. A catalyst provides a path of ..... activation energy.
9. For a first order reaction, half life period is equal to ..... .
10. If the rate of reaction : $N_2 + 3H_2 \longrightarrow 2NH_3$ measured as $\Delta[NH_3]/\Delta t$ was found to be 3.6×10^{-4} mol $L^{-1}\ s^{-1}$, then rate of reaction expressed as $\Delta[H_2]\ /\ \Delta t$ is ..... .
11. The sum of powers to which concentration terms are raised in the rate law expression is called ..... of the reaction.
12. For a reaction : $A + B \longrightarrow$ Products, the rate is given as $k[A]^{1/3}B^2$. The units of its rate constant are ..... .
13. When the concentration of a reactant of a second order is tripled, then rate will become ..... times.
14. If half life period of a first order reaction is 32 min, then the time taken for concentration to be reduced to $1/16^{th}$ is ..... .
15. If rate constant for a first order reaction has been found to be $2.31 \times 10^{-3}\ s^{-1}$, then its half life period is ..... .

C. Choose the correct alternative

1. For a zero order reaction, a plot of [A] vs t is linear with slope equal to *– k / k.*
2. Half life period for a second order reaction is *$t_{1/2} = [A]_0/2k$* or *$1/k[A]_0$.*
3. Average life time is *more/less* than half life time for a first order reaction.
4. For fast reactions, activation energy is *low / high.*
5. The molecularity of hydrolysis of cane sugar is *two/one.*
6. Increase in rate of reaction with rise in temperature is mainly due to increase in *collision frequency/effective collisions.*
7. For an endothermic reaction, activation energy for the forward reaction is *more/less* than activation energy for the backward reaction.
8. For exothermic reaction, E_a (forward) – E_a (backward) is *+ve / –ve.*
9. For a second order reaction, when the concentration of the reactant is tripled rate becomes *nine/eight* times.
10. The units of zero order reaction are *$molL^{-1}s^{-1}$ / $mol^{-1}Ls^{-1}$.*

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Answers QUICK MEMORY TEST

A. Say True or False

1. True. 2. True.
3. **False.** The units are $(atm)^{1-n}\ s^{-1}$.
4. **False.** Slowest step is the rate determining step.
5. **False.** It becomes 9 times.
6. **False.** It remains unchanged.
7. True.
8. **False.** Concentration becomes $[A]_0 / 2^3$
9. **False.** Molecularity may be equal also.
10. **False.** Higher the activation energy, slower is the reaction.
11. True.
12. True.
13. **False.** $t_{3/4} = 2t_{1/2}$
14. **False.** Plot of rate *vs* t is a horizontal line but a plot of [A] *vs* t will be linear.
15. True.

B. Complete the missing links

1. zero 2. first 3. 2
4. activation energy 5. Boltzmann 6. $atm^{-1}s^{-1}$
7. rate constant 8. low 9. $0.693/k$
10. 5.4×10^{-4} mol $L^{-1}s^{-1}$ 11. order 12. $mol^{-4/3}L^{4/3}s^{-1}$
13. 9 14. 128 min 15. 300s

C. Choose the correct alternative

1. $-k$ 2. $1/k[A]_0$ 3. more 4. low
5. two 6. effective collisions 7. more
8. –ve 9. nine 10. mol $L^{-1}s^{-1}$

HOTS Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

Q.1. Derive the rate law expression for the reaction:

$$2P + Q \longrightarrow \text{Products}$$

if the first step is the reversible dimerization of P, followed by reaction of P_2 with Q in a bimolecular rate controlling step. Assume that the equilibrium concentration of P_2 is very small as compared to [P].

Ans.

$$2P \overset{K}{\rightleftharpoons} P_2 \quad ...(i)$$

$$P_2 + Q \xrightarrow{\text{Slow}} \text{Products} \quad ...(ii)$$

From eqn. (*i*)

$$K = \frac{P_2}{[P]^2} \quad \text{or} \quad [P_2] = K[P]^2$$

Since step 2 is rate controlling,

$$\text{Rate} = k\,[P_2]\,[Q]$$
$$= k(K[P]^2)\,[Q]$$
$$= k'\,[P]^2\,[Q] \qquad (k' = kK)$$

Q.2. The $t_{1/2}$ of a reaction is halved as the initial concentration of the reactant is doubled. What is the order of the reaction?

Ans.

$$t_{1/2} \propto \frac{1}{C^{n-1}}$$

Let initial conc. = a, $(t_{1/2})_1 = t$

Initial conc. = $2a$, $(t_{1/2})_2 = t/2$

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{C_2}{C_1}\right)^{n-1}$$

$$\frac{t}{t/2} = \left(\frac{2a}{a}\right)^{n-1}$$

$$2 = 2^{n-1}$$

or $n - 1 = 1$

$\therefore$ $n = 2$

The reaction is second order.

Q.3. For a zero order reaction, starting with initial concentration C_0, how long will it take for the reaction to go to completion ?

Ans. For a zero order reaction :

$$k = \frac{1}{t}[C_0 - C] \quad \text{or} \quad t = \frac{1}{k}[C_0 - C]$$

where C = concentration of the reactant at time t.

For the reaction to go to completion C=0.

$$\therefore \quad t = \frac{C_0}{k}$$

Q.4. The probable mechanism for the reaction :

$$Hg_2^{2+} + Tl^{3+} \longrightarrow 2Hg^{2+} + Tl^{+}$$

is

$$Hg_2^{2+} \overset{K}{\rightleftharpoons} Hg^{2+} + Hg$$

$$Hg + Tl^{3+} \xrightarrow{k'} Hg^{2+} + Tl^{+}$$

Derive the rate law.

Ans.

$$Hg_2^{2+} \overset{K}{\rightleftharpoons} Hg^{2+} + Hg \quad ...(i)$$

$$Hg + Tl^{3+} \xrightarrow{k'} Hg^{2+} + Tl \quad ...(ii)$$

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From eqn. (*ii*)

$$\text{rate} = k'[Hg][Tl^{3+}] \quad ...(iii)$$

From eqn. (*i*)

$$K = \frac{[Hg^{2+}][Hg]}{[Hg_2^{2+}]}$$

or

$$[Hg] = K\frac{[Hg_2^{2+}]}{[Hg^{2+}]}$$

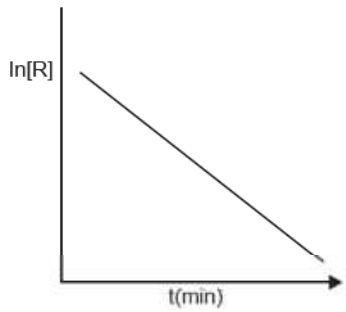
Substituting the value of [Hg] in eqn. (*iii*)

$$\text{rate} = k'K\frac{[Hg_2^{2+}]}{[Hg^{2+}]}\times[Tl^{3+}]$$

or

$$= k\frac{[Hg_2^{2+}]\times[Tl^{3+}]}{[Hg^{2+}]} \quad (k = k'\,K)$$

Q.5. For a certain chemical reaction, variation in the concentration, ln[R] vs time (min) plot is shown below:



For this reaction

(*i*) What is the order of the reaction ?

(*ii*) What are the units of rate constant, *k* for this reaction ?

(*iii*) Give the relationship between *k* and $t_{1/2}$ of this reaction.

(*iv*) If initial concentration for this reaction becomes half, how will $t_{1/2}$ vary?

(*v*) What does the slope of this line indicate ?

(*vi*) Draw the plot of log $[R]_0/[R]$ vs time (*s*).

Ans. (*i*) Reaction is of first order because for the first order reaction :

$$\ln[R] = -kt + \ln[R]_0$$

The plot of ln[R] vs t is a straight line with slope = – *k* and intercept $\ln[R]_0$.

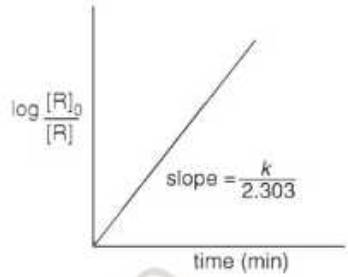
(*ii*) Units of rate constant : min^{-1}

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

(*iv*) No change in $t_{1/2}$ because half life period is independent of initial concentration.

(*v*) Slope of line is equal to – *k*.

(*vi*) The plot of log $[R]_0/R$ vs time (min) is



Q.6. The rate of decomposition of ammonia is found to depend upon the concentration of ammonia as :

$$-\frac{d[NH_3]}{dt} = \frac{k_1[NH_3]}{1+k_2[NH_3]}$$

what will be the order of reaction when :

(*i*) concentration of NH_3 is very high ?

(*ii*) concentration of ammonia is very low ?

Ans. The rate law expression is

$$-\frac{d[NH_3]}{dt} = \frac{k_1[NH_3]}{1+k_2[NH_3]} = \frac{k_1}{1/[NH_3]+k_2}$$

(*i*) when $[NH_3]$ is very high, $\frac{1}{[NH_3]}$ becomes negligible

$$\therefore \quad -\frac{d[NH_3]}{dt} = \frac{k_1}{k_2} = k$$

i.e., rate becomes independent of concentration and hence it is of **zero order.**

(*ii*) when $[NH_3]$ is very small, $\frac{1}{[NH_3]}$ will be very large so that k_2 can be neglected in comparison to $\frac{1}{[NH_3]}$. Hence,

$$-\frac{d[NH_3]}{dt} = \frac{k_1}{1/[NH_3]} = k_1[NH_3]$$

Thus, the reaction is of **1st order.**

Q.7. For a reaction A $\xrightarrow{k}$ product, the reaction occurs as :

$$A \xrightarrow{k_1} A^* \xrightarrow{k_2} B^* \xrightarrow{k_3} \text{product}$$

The overall rate constant *k* is given as :

$$k = 2k_1\left(\frac{k_2}{k_3}\right)^{2/3}$$

If E_{a_1}, E_{a_2} and E_{a_3} are the activation energies of these steps, then what is the relation between overall activation energy E_a and the activation energies of these steps.

Ans. Rate constant is related to activation energy as

$$k = Ae^{-Ea/RT} \text{ so that}$$

$$k_1 = Ae_1^{-Ea_1/RT},\ k_2 = A_2e^{-Ea_2/RT} \text{ and } k_3 = A_3e^{-Ea_3/RT}$$

Now

$$k = 2k_1\left(\frac{k_2}{k_3}\right)^{2/3}$$

$$Ae^{-Ea/RT} = 2A_1e^{-Ea_1/RT}\left[\frac{A_2e^{-Ea_2/RT}}{A_3e^{-Ea_3/RT}}\right]^{2/3}$$

$$Ae^{-Ea/RT} = 2A_1\left(\frac{A_2}{A_3}\right)^{2/3} e^{-Ea_1/RT} \times \left(\frac{e^{-Ea_2/RT}}{e^{-Ea_3/RT}}\right)^{2/3}$$

$$Ae^{-Ea/RT} = 2A_1\left(\frac{A_2}{A_3}\right)^{2/3} e^{\frac{-Ea_1 - \frac{2}{3}Ea_2 + \frac{2}{3}Ea_3}{RT}}$$

$$\therefore \quad -E_a = -E_{a_1} - \frac{2}{3}E_{a_2} + \frac{2}{3}E_{a_3}$$

or $$E_a = E_{a_1} + \frac{2}{3}E_{a_2} - \frac{2}{3}E_{a_3}$$

Q.8. For a reversible reaction

$$H_2(g) + I_2(g) \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2HI$$

derive an expression for the formation of HI.

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

$= k_1[H_2][I_2] - k_2[HI]^2$

$\therefore$ Rate of formation of HI,

$$\frac{d[HI]}{dt} = 2k_1[H_2][I_2] - 2k_2[HI]^2$$

Q.9. The decomposition of N_2O_5 according to the equation,

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$

is a first order reaction. After 30 min from the start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

Ans. $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$

2 mol of gaseous N_2O_5 on complete decomposition gives 5 mol of gaseous product (4 mol NO_2 and 1 mol O_2). Therefore,

initial pressure of N_2O_5, $p_0 = 584.5 \times \frac{2}{5}$

$= 233.8$ mm Hg.

Let x be the amount of N_2O_5 decomposed after 30 min. Therefore,

Pressure due to $N_2O_5 = 233.8 - x$

Pressure due to $NO_2 = 2x$

Pressure due to $O_2 = x/2$

Total pressure after 30 min = 284.5 mm Hg

$\therefore \quad 233.8 - x + 2x + \frac{x}{2} = 284.5$

or $\quad x = 33.8$ mm Hg

Pressure of N_2O_5 after 30 min $= 233.8 - 33.8$

$= 200$ mm Hg

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

Using the partial pressure for concentrations :

$$k = \frac{2.303}{30}\log\frac{233.8}{200} = \mathbf{5.2 \times 10^{-3}\ min^{-1}}.$$

Q.10. The half life for the reaction :

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

is 2.4 hours at 30°C

(*a*) Starting with 100 g of N_2O_5, how many grams will remain after a period of 9.6 hours ?

(*b*) What time would be required to reduce 5×10^{10} molecules of N_2O_5 to 10^8 molecules ?

Ans. $k = \frac{0.693}{t_{1/2}}$ or $k = \frac{0.693}{2.4} = 0.289\ hr^{-1}$

(*i*) For the first order reaction :

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

$$[A]_0 = \frac{100}{M}, [A] = (x/M), t = 9.6 \text{ hr}$$

M = Molecular weight (x = amount of N_2O_5 left in gram)

$$0.289 = \frac{2.303}{9.6}\log\frac{100/M}{x/M}$$

$$\log\frac{100}{x} = \frac{0.289 \times 9.6}{2.303} = 1.2047$$

or $$\frac{100}{x} = 16.02 \text{ or } x = \frac{100}{16.02} = 6.24 \text{ g}$$

(*ii*) $[A]_0 = 5 \times 10^{10}/N_0$, $[A] = 10^8/N_0$

where N_0 is Avogadro number,

$$t = \frac{2.303}{k}\log\frac{5 \times 10^{10}/N_0}{10^8/N_0} = \mathbf{21.51\ hr.}$$

Revision Exercises

Very Short Answer Questions *carrying 1 mark*

1. Define half life period. *(Jammu S.B. 2016)*
2. Can order of a reaction be fractional ? Explain.
3. The specific rate of a reaction is 6.2×10^{-3} mol L^{-1} s^{-1}. What is the order of the reaction ?
4. Is it possible for a reaction to have identical values for molecularity and order ?
5. A reaction is found to be zero order reaction, will its molecularity be also zero ?
6. For a first order reaction, $k = 2.5 \times 10^{-4}\ s^{-1}$, what is the rate of reaction, when the initial concentration of the reactant is 0.1 mol L^{-1} ?
7. Define pseudounimolecular reaction with an example. *(Hr. S.B. 2018)*
8. What are the units of rate constant for first order reaction? *(Pb. S.B. 2018, H.P.S.B. 2018)*
9. For a reaction rate law expression is:
   Rate $= k[A]^{1/2}[B]^2$
   Can the reaction be an elementary? Explain. *(Pb. S.B. 2018)*

10. The rate law for the reaction

$CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4 + HCl$

is rate = $k\,[CHCl_3][Cl_2]^{1/2}$.

What is the order of reaction ?

11. What is the order of reaction whose rate constant has same unit as the rate of reaction? *(H.P.S.B. 2010)*

12. If the units of rate constant of a reaction is $mol^{-1}\,L\,s^{-1}$, then mention its order. *(Karnataka S.B. 2018)*

13. Define order of the reaction. *(H.P.S.B. 2018)*

14. Rate of reaction = $k[H_2]^0[Cl_2]^0$, according to rate law equation. Predict the order of reaction. *(H.P.S.B. 2018)*

15. A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14}\,s^{-1}$. Find the half-life of the reaction. *(Karnataka S.B. 2018)*

16. In a reaction, $2A \longrightarrow$ 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. *(Meghalaya S.B. 2013)*

17. The rate constant of a reaction is $3 \times 10^2\,min^{-1}$. What is the order of reaction? *(Assam S.B. 2012)*

18. What is instantaneous rate of reaction? *(H.P.S.B. 2016, Nagaland S.B. 2018)*

19. Give the definition of collision frequency *(H.P.S.B 2006, Assam S.B. 2016)*

20. For a reaction $R \rightarrow P$, half life ($t_{1/2}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction? *(D.S.B. 2017)*

21. Identify the order of reaction if the unit of rate constant is mol $L^{-1}s^{-1}$. *(Kerala S.B. 2018)*

CBSE QUESTIONS

22. Is there any reaction for which the rate does not decrease with time? *(A.I.S.B. 2006)*

23. Express the rate of the following reaction in terms of disappearance of hydrogen in the reaction :

$$3H_{2(g)} + N_{2(g)} \longrightarrow 2NH_{3(g)}$$ *(A.I.S.B. 2007)*

24. The reaction: $A + 2B \longrightarrow C$ obeys rate equation.

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

What is the order of this reaction? *(A.I.S.B. 2007)*

25. Define order of a reaction. *(A.I.S.B. 2011, D.S.B. 2011, Nagaland S.B. 2015, H.P.S.B. 2014, 2018)*

26. Define activation energy of a reaction *(A.I.S.B. 2011, H.P.S.B. 2016)*

27. What is the effect of adding a catalyst on

(a) Activation energy (E_a) and

(b) Gibbs energy (ΔG) of a reaction *(A.I.S.B. 2017)*

MCQs from State Boards' Examinations

28. A first order reaction has a half life period of 34.65 seconds. Its rate constant is

(*a*) $2 \times 10^{-2}\,s^{-1}$ (*b*) $4 \times 10^{-4}\,s^{-1}$

(*c*) $20\,s^{-1}$ (*d*) $2 \times 10^{-4}\,s^{-1}$

(Jharkhand S.B. 2012)

29. If a graph is plotted between ln k and 1/T for the first order reaction, the slope of the straight line so obtained is given by

(*a*) $-\frac{E_a}{R}$ (*b*) $-\frac{E_a}{2.303\,R}$

(*c*) $-\frac{2.303}{E_a.R}$ (*d*) $-\frac{E_a}{2.303}$

(Jharkhand S.B. 2012)

30. The unit of rate constant for a zero order reaction is

(*a*) mol $L^{-1}s^{-1}$ (b) s^{-1}

(*c*) L $mol^{-1}s^{-1}$ (d) $L^2mol^{-2}s^{-1}$

(Mizoram S.B. 2014, Hr. S.B. 2017)

31. A catalyst increases the speed of a chemical reaction by

(*a*) increasing activation energy

(*b*) decreasing activation energy

(*c*) increasing reactant energy

(*d*) decreasing threshold energy *(Mizoram S.B. 2014)*

32. The units of the rate constant for the second order reaction are:

(*a*) mol^{-1} litre s^{-1} (*b*) mol $litre^{-2}\,s^{-1}$

(*c*) s^{-1} (*d*) mol $litre^{-1}\,s^{-1}$

(H.P.S.B. 2015, Mizoram S.B. 2017)

33. The value of k for a reaction is $2.96 \times 10^{-30}\,s^{-1}$. What is the order of the reaction?

(*a*) Zero (*b*) 3

(*c*) 2 (*d*) 1 *(H.P.S.B. 2015)*

34. A reaction is found to be of second order with respect to concentration of carbon monoxide. If concentration of carbon monoxide is doubled, the rate of reaction will

(*a*) triple (*b*) increase by a factor of 4

(*c*) double (*d*) remain unchanged

(H.P.S.B. 2015)

35. If the concentrations are expressed in mol $litre^{-1}$ and time in s, then the units of rate constant for the first-order reactions are

(*a*) mol $litre^{-1}\,s^{-1}$ (*b*) mol^{-1} litre s^{-1}

(*c*) s^{-1} (*d*) mol^2 $litre^{-2}\,s^{-1}$

(H.P.S.B. 2017, Hr. S.B. 2018)

36. The half life of a first order reaction having rate constant 200 s^{-1} is

(*a*) 3.465×10^{-2} s (*b*) 3.465×10^{-3} s

(*c*) 1.150×10^{-2} s (*d*) 1.150×10^{-3} s

(Mizoram S.B. 2015)

37. The rate of a reaction is $1.209 \times 10^{-4} L^2\,mol^{-2}\,s^{-1}$. The order of the reaction is:

(*a*) zero (*b*) first

(*c*) second (*d*) third *(Mizoram S.B. 2016)*

38. A catalyst increases the rate of a reaction by

(*a*) increasing threshold energy

(*b*) increasing activation energy

(*c*) activating the reactants

(*d*) lowering activation energy *(Mizoram S.B. 2018)*

39. Time required for 100% completion of a zero order reaction is:

(*a*) $t_{100\%} = a/k$ (*b*) $t_{100\%} = a.k$

(*c*) $t_{100\%} = a/2k$ (*d*) None of these *(Hr. S.B. 2017)*

40. Arrhenius equation is represented by :
(*a*) $k = Ae^{Ea/RT}$ (*b*) $k = Ae^{-Ea/RT}$
(*c*) $t_{½} = 0.693/k$ (*d*) None of these (*Hr. S.B. 2017*)

41. The overall order of a reaction, which has the rate expression: Rate = $k[A]^{1/2}[B]^{3/2}$ is:
(*a*) First order (*b*) Second order
(*c*) Third order (*d*) Zero order
(*Mizoram S.B. 2018*)

42. If half life period of a first order reaction is 100 seconds. Then rate constant will be:
(*a*) 6.93×10^{-3} second (*b*) 6.93×10^{-2} second
(*c*) 0.693 second (*d*) 6.93 second (*Hr. S.B. 2018*)

43. If rate constant for a reaction is mole litre^{-1} second^{-1}, then order of reaction is:
(*a*) Zero order (*b*) First order
(*c*) Second order (*d*) None of these
(*Hr. S.B. 2018*)

44. Identify the order of reaction from the given rate constant $k = 2.6 \times 10^{-4}$ L mol^{-1} s^{-1}
(*a*) First (*b*) Zero
(*c*) Second (*d*) None of these
(*Hr. S.B. 2018*)

45. For a reaction: $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction with respect to NH_3 will be:
(*a*) $-\frac{d[NH_3]}{dt}$ (*b*) $-\frac{d[NH_3]^2}{dt}$
(*c*) $+\frac{1}{2}\frac{d[NH_3]}{dt}$ (*d*) $-\frac{1}{2}\frac{d[NH_3]}{dt}$ (*Hr. S.B. 2018*)

46. Half life period of a first order reaction depends upon:
(*a*) Concentration of reactants
(*b*) Concentration of products
(*c*) Rate constant of reaction
(*d*) None of these (*Hr. S.B. 2018*)

47. Half life period of a first order reaction is:
(*a*) directly proportional to the initial concentration of the reactant
(*b*) half of the rate constant
(*c*) same for all reactions
(*d*) independent of the initial concentration of the reactants (*Mizoram S.B. 2018*)

Short Answer Questions *carrying 2 or 3 marks*

1. What is rate of a reaction ? Discuss briefly the various factors which influence the rate of a chemical reaction.
(*Jammu S.Z. 2018*)

2. What is meant by order of a chemical reaction ? The reaction :

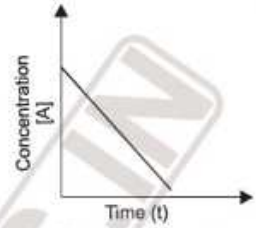
$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

has been found to be first order with respect to NO_2 and with respect to F_2.
(*i*) Write the rate law equation for the reaction.
(*ii*) What is the overall order of the reaction ?
(*iii*) Suggest a suitable mechanism for the reaction.

3. Explain with examples the meaning of the terms average rate and instantaneous rate of the reaction.
(*H.P.S.B. 2007*)

4. Consider the rate equation
Rate = $k[A]^n$
What is the change of rate that occurs on doubling the concentration of A, when
(*i*) $n = 0$ (*ii*) $n = 1$ (*iii*) $n = 2$?

5. Consider the reaction $A \xrightarrow{k} P$. 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.
(*C.B.S.E. Sample Paper 2007*)

6. What is meant by the rate constant, '*k*' of a reaction? If the concentration be expressed in mol L^{-1} units and time in seconds, what would be the units for *k*
(*i*) for a zero order reaction and
(*ii*) for a first order reaction? (*D.S.B. 2008*)

7. Derive the following relation :

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$ (*H.P.S.B. 2010*)

8. Starting from the integrated law of a zeroth order reaction, R→P, show that half-life time of a reaction is directly proportional to the initial molar concentration of the reactant. (*Assam S.B. 2018*)

9. Discuss the effect of temperature on the rate of a reaction.
(*Pb.S.B. 2011, Hr.S.B. 2015, Jammu S.B. 2015*)

10. Distinguish between rate expression and rate constant of a reaction. (*D.S.B. 2011*)

11. (*a*) What is the order of reaction whose rate constant has the same unit as the rate of reaction?
(*b*) Calculate the overall order of a reaction which has the rate expression

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

(*c*) What is the rate determining step of a reaction?
(*Meghalaya S.B. 2018*)

12. Derive the integrated form of rate equation for the first order reaction. (*Pb.S.B. 2012, H.P.S.B. 2012, 2015, 2016*)

13. (*a*) Define pseudo unimolecular reactions.
(*b*) What are zero order reactions ? Derive integrated rate equation for zero order reaction.
(*H.P.S.B. 2012, H.P.S.B 2007)*

14. How you differentiate between reaction rate and reaction rate constant ? (*J.K.S.B 2011, 2015*)

15. (*a*) Define activation energy of a reaction.
(*b*) How does the nature of a reactant affect the rate of a chemical reaction? (*J.K S.B. 2013*)

16. (*a*) Reaction between NO_2 and F_2 to give NO_2F takes place by the following mechanism:

$$NO_2(g) + F_2(g) \xrightarrow{\text{Slow}} NO_2F(g) + F(g)$$

$NO_2(g) + F(g) \xrightarrow{Fast} NO_2F(g)$

Write the rate expression and order of the reaction

(*b*) Calculate two-third life of a first order reaction having $k = 5.48 \times 10^{-14}\ s^{-1}$. *(Pb S.B. 2013)*

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

(*i*) Write differential rate equation.

(*ii*) How is rate affected on increasing concentration of B three times? *(Hr. S.B. 2013)*

18. (*a*) Give four differences between molecularity and order of a reaction. *(H.P. S.B. 2018)*

(*b*) Write units of rate constant for second order reaction.

(*c*) Give an example of first order reaction. *(H.P. S.B. 2013)*

19. (*a*) What is activation energy?

(*b*) What are the units of rate constant for second order reaction?

(c) Write Arrhenius equation. *(H.P. S.B. 2018)*

20. (*a*) Define molecularity of a reaction.

(*b*) Define activation energy.

(*c*) For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction. *(H.P. S.B. 2014)*

21. Write two differences between 'order of reaction' and 'molecularity of a reaction'. *(D.S.B. 2014, Meghalaya S.B. 2017)*

22. (*a*) What are pseudo order reaction?

(*b*) What is half life period? Show that half life period for a first order reaction is independent of the initial concentration of the reactant. *(H.P. S.B. 2015)*

23. The reaction : $2A + B \longrightarrow C + D$ has the rate equation as :

rate = $k\ [A]^x\ [B]^y$

(*i*) What is the molecularity of the reaction?

(*ii*) Order of the reaction when B is present in large excess. *(H.P. S.B. 2015)*

24. (*a*) What is the effect of catalyst on the activation energy of a reaction? *(H.P. S.B. 2015)*

(*b*) Derive integrated rate equation for a zero order reaction. *(Hr. S.B. 2015)*

25. Define the following terms:

(*i*) Half life period of a reaction.

(*ii*) Collision frequency

(*iii*) Activation energy *(Hr. S.B. 2018)*

26. (*a*) Give one example of pseudo first order reaction.

(*b*) A reaction is second order with respect to a reactant. How does the rate of the reaction be affected if the concentration of the reactant is reduced to half?

Or

Show that the time required for completion of 3/4th of a first order reaction is twice the time required for the completion of 1/2 of the reaction. *(Assam S.B. 2016)*

27. What is meant by zero order reaction? Give an example of such a reaction. Establish the integrated rate equation for a zero order reaction involving a single reactant. How can the rate constant be determined using this equation? *(Kolkata S.B. 2016)*

28. What is half life of a reaction? If the half life of a first order reaction in A is 2 minutes, how long will it take to reach 25% of initial concentration? *(Nagaland S.B. 2016)*

29. (*i*) Define order of reaction.

(*ii*) Identify the reaction order from each of the following units of reaction rate constant.

(*a*) $mol\ L^{-1}\ s^{-1}$

(*b*) $L\ mol^{-1}\ s^{-1}$ *(Tripura S.B. 2016)*

30. (*a*) Give an example of a pseudo first order reaction.

(*b*) Write Arrhenius equation which relates the rate constant with temperature.

(*c*) A first order reaction takes 40 minutes for 30 % decomposition. Calculate $t_{1/2}$ for this reaction. *(Tripura S.B. 2016, Meghalaya S.B. 2017)*

31. Derive the integrated rate equation for the first order reaction. Hence prove that half-life period for it is independent of initial concentration. *(Meghalaya S.B. 2016, Jammu S.Z. 2018)*

32. (*i*) For the reaction:

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{HI} C_6H_{12}O_6 + C_6H_{12}O_6$

Write (*a*) Rate of reaction expression

(*b*) Molecularity

(*ii*) Give the units of rate constant for a zero order reaction. *(H.P.S.B 2016)*

33. (*i*) The rate constant for a chemical reaction at a given temperature is $2.3 \times 10^{-5}\ L\ mol^{-1}\ s^{-1}$. What is the order of the reaction?

(*ii*) Show that for a 1st order reaction, time required for completion of 99.9% is 10 times of half time of the reaction. *(Assam S.B. 2018)*

34. (*a*) The molecularity of the reaction $2NO + O_2 \rightarrow 2NO_2$ is,

(*i*) 5 (*ii*) 2

(*iii*) 3 (*iv*) 0

(*b*) (*i*) What do you mean by rate of a reaction?

(*ii*) What will be the effect of temperature on rate of a reaction?

(*c*) A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}\ s^{-1}$. Find out the half-life of the reaction. *(Kerala S.B. 2016)*

35. (*a*) Derive integrated rate law equation for first order reaction.

(*b*) What are the units of rate constant for 3rd order reaction? *(H.P.S.B. 2018)*

36. Define the following terms:

(*a*) Activation Energy (*b*) Molecularity

(*c*) Rate constant *(Hr.S.B 2017)*

37. (a) Derive an integrated rate equation for rate constant of a first order reaction.

(b) Draw a graph of potential energy vs reaction co-ordinates showing the effect of catalyst on activation energy (E_a) of a reaction. *(Karnataka S.B. 2018)*

38. (*a*) The thermal decomposition of a compound is of first order. If 50% of the compound is decomposed in 120 minutes, how long will it take for 90% of the compound to decompose?

Or

(*b*) The three-fourths of a first order reaction is completed in 32 minutes. What is the half-life period of the reaction? (*Mizoram S.B. 2017*)

39. Show that slope of the plot of *ln k* against $\frac{1}{T}$ is $-\frac{E_a}{R}$. Give the graphical representation of the plot. (*Assam S.B. 2017*)

CBSE QUESTIONS

40. For a reaction at 500 K,

$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$

the proposed mechanism is as given below :

(*i*) $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ (slow)

(*ii*) $NO_3(g) + CO(g) \longrightarrow CO_2(g) + NO_2(g)$ (fast)

What is rate law for the reaction ? (*A.I.S.B. 2003, Pb.S.B. 2007*)

41. (*a*) Derive the general form of the expression for the half life of a first order reaction.

(*b*) List the factors on which the rate of a chemical reaction depends. (*A.I.S.B. 2008, D.S.B. 2008*)

42. Define the following :

(*i*) Elementary step in a reaction

(*ii*) Rate of a reaction. (*A.I.S.B. 2009*)

43. Define the following:

(*i*) Order of a reaction

(*ii*) Activation energy (*A.I.S.B. 2009*)

44. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reaction is reduced to half? What is the unit of rate constant for such a reaction? (*A.I.S.B. 2011*)

45. What do you understand by the rate law and rate constant of a reaction ? Identify the order of reaction if the units of its rate constant are:

(*i*) L^{-1} mol s^{-1}

(*ii*) L mol^{-1} s^{-1} (*A.I.S.B. 2011*)

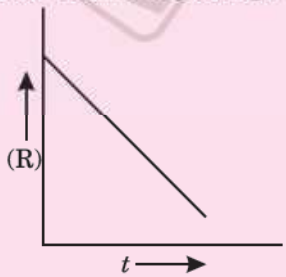
46. A reaction is of second order with respect to a reactant. How is its rate affected if the concentration of the reactant is (i) doubled (*ii*) reduced to half ? (*A.I.S.B. 2012*)

47. (*a*) For a reaction A + B → P, the rate law is given by, $r = k[A]^{1/2}[B]^2$

What is the order of this reaction ?

(*b*) A first order reaction is found to have a rate constant $k = 5.5 \times 10^{-14}\ s^{-1}$. Find the half life of the reaction. (*A.I. S.B. 2013*)

48. For a chemical reaction R → P, the variation in the concentration (R) vs. time (*t*) plot is given as



(*i*) Predict the order of the reaction.

(*ii*) What is the slope of the curve ? (*A.I.S.B. 2014*)

49. For the reaction

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$,

the rate of formation of $NO_2(g)$ is $2.8 \times 10^{-3}\ Ms^{-1}$. Calculate the rate of disappearance of $N_2O_5(g)$. (*A.I.S.B. 2018*)

50. A first order reaction is 50% completed in 40 minutes at 300 K and in 20 minutes at 320 K. Calculate the activation energy of the reaction.

(Given: log 2 = 0.3010, log 4 = 0.6021, R = 8.314 JK^{-1} mol^{-1}) (*A.I.S.B. 2018*)

Long Answer Questions *carrying 5 marks*

1. (*a*) Derive activation energy by Arrhenius equation. Write differences between order and molecularity of a reaction.

(*b*) What is the effect of catalyst on rate of a reaction ? A first order reaction has rate constant $1.15 \times 10^{-3}\ sec^{-1}$. How long will 5g of this reactant take to reduce to 3g ? (*Hr. S.B. 2012, 2015*)

2. (*a*) Write down the unit of rate constant for zero order reaction.

(*b*) Derive the rate equation :

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

for first order reaction and establish the relationship between half life period and its rate constant.

Or

(*i*) What is the difference between molecularity and order of reaction?

(*ii*) For a first order reaction, half life period ($t_{1/2}$) is 100 seconds. How long will it take for the reaction to complete 75%? (*Uttarakhand S.B. 2013*)

3. (*a*) A reaction is second order in A and first order in B.

(*i*) Write the differential rate equation.

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

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

(*b*) A first order reaction takes 40 minutes for 30% decomposition. Calculate t½ for this reaction.

(Given log 1.428 = 0.1548)

Or

(*a*) For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

(*b*) Rate constant '*k*' of a reaction varies with temperature 'T' according to the equation:

$$\log k = \log A - \frac{E_a}{2.303\,R}\left(\frac{1}{T}\right)$$

Where E_a is the activation energy. When a graph is plotted for log *k* vs. $\frac{1}{T}$, a straight line with a slope of – 4250 K is obtained. Calculate 'E_a' for the reaction (R = 8.314 JK^{-1} mol^{-1}) (*D.S.B. 2013*)

4. (*a*) Derive the integrated rate equation for first order reaction.

(*b*) Differentiate between order and molecularity of a chemical reaction. (*Uttarakhand S.B. 2015*)

5. For the hydrolysis of methyl acetate in aqueous solution, the following results were observed:

t/s	0	30	60
$[CH_3COOCH_3]$ mol L^{-1}	0.60	0.30	0.15

(*i*) Show that it follows pseudo first order reaction, as the concentration of water remains constant.

(*ii*) Calculate the average rate of reaction between the time interval 30 to 60 seconds. (Given log 2 = 0.3010, log 4 = 0.6021)

Or

(*a*) For a reaction A + B $\longrightarrow$ P, the rate is given by Rate = $k[A][B]^2$

(*i*) How is rate of reaction affected if the concentration of B is doubled ?

(*ii*) What is the overall order of reaction if A is present in large excess ?

(*b*) A first order reaction takes 30 minutes for 50% completion. Calculate the time required for 90% completion of this reaction (log 2 = 0.3010)

(D.S.B. 2015)

6. (*a*) What is activation energy of a reaction?

(*b*) The rate of a reaction increases in the presence of catalyst. Explain the statement by plotting a curve between reaction coordinate and energy.

(*c*) For a reaction, the initial concentration of a reactant is 0.4M and rate constant is 2.5×10^{-4} s^{-1}. Calculate the half life period of the reaction. *(Manipur S.B. 2017)*

7. (*a*) Plot a graph showing variation in the concentration of reactants against time for zero order reaction.

(*b*) What do you mean by zero order reaction?

(*c*) The initial concentration of 1st order reaction,

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

was 1.24×10^{-2} mol L^{-1} at 300K. The concentration of N_2O_5 after 1 hour was 0.2×10^{-2} mol L^{-1}. Calculate the rate constant of the reaction at 300K.

(Kerala S.B. 2017)

CBSE QUESTIONS

8. (*a*) Explain the following terms :

(*i*) Rate of a reaction

(*ii*) Activation energy of a reaction.

(*b*) The decomposition of phosphine, PH_3, proceeds according to the following equation :

$$4\,PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

It is found that the reaction follows the following rate equation :

$$\text{Rate} = k\,[PH_3].$$

The half-life of PH_3 is 37.9 s at 120°C.

(*i*) How much time is required for 3/4th of PH_3 to decompose ?

(*ii*) What fraction of the original sample of PH_3 remains behind after 1 minute ? *(A.I.S.B. 2010)*

9. (*a*) What is rate of reaction? Write two factors that affect the rate of reaction.

(*b*) The rate constant of a first order reaction increases from 4×10^{-2} to 8×10^{-2} when the temperature changes from 27°C to 37°C. Calculate the energy of activation (E_a).

(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

Or

(*a*) For a reaction A + B $\longrightarrow$ P, the rate is given by 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 reaction if A is present in large excess?

(*b*) A first order reaction takes 23.1 minutes for 50% completion. Calculate the time required for 75% completion of this reaction.

(log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021)

(A.I.S.B. 2015)

NUMERICAL PROBLEMS

1. The decomposition of sulphuryl chloride to SO_2 and Cl_2 is a first order reaction whose half life is 30 minutes. What percentage of the reactant will be decomposed in 2 hours ?

[**Ans.** 93.75%]

2. The activation energy of a first order reaction at 300 K is 60 kJ mol^{-1}. In the presence of a catalyst, the activation energy gets lowered to 50 kJ mol^{-1} at 300 K. How many times the reaction rate changes in the presence of a catalyst at the same temperature ? [**Ans.** 55.08 times]

3. The rate constant for a first order reaction is 5.70×10^{-5} and 1.64×10^{-4} s^{-1} at 25°C and 40°C respectively. Calculate the activation energy and the Arrhenius frequency factor.

[**Ans.** 54.6 kJ mol^{-1}, 2.17×10^5]

4. A first order reaction has $k = 1.5 \times 10^{-6}$ s^{-1} at 200°C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed into the product ? What is the half life period of the reaction ?

[**Ans.** 5.2%, 4.62×10^5 s]

5. A first order reaction is 20% complete in 10 minutes. Calculate

(*i*) the time taken for the reaction to go to 75% complete

(*ii*) specific rate constant of the reaction. *(J. K. S. B. 2014)*

[**Ans.** (*i*) 62.12 min (*ii*) 0.02232 min^{-1}]

6. The rate constants for the decomposition of HI at 283°C and 508°C are 3.517×10^{-7} s^{-1} and 3.954×10^{-2} s^{-1} respectively. Calculate the frequency factor at 283°C and energy of activation of the reaction. [**Ans.** 1.206×10^{11}, 186.68 kJ]

7. The catalytic decomposition of hydrogen peroxide was studied by liberating it at different intervals with $KMnO_4$ solution. Calculate the rate constant from the following data assuming the reaction to be of the first order :

t (seconds)	0	600	1200
$KMnO_4$ (mL)	22.8	13.8	8.2

[**Ans.** 0.000845 s^{-1}]

8. A first order reaction is 40% complete in 50 minutes. How long will it take to 80% complete? (Given log 1.6667 = 0.2220 and log 5 = 0.6990) *(Pb.S.B. 2010)*

[**Ans.** 157.5 min]

9. In a hydrolysis reaction, 5g ethyl acetate is hydrolyzed in presence of dilute HCl in 300 minutes. If the reaction is of first order and the initial concentration of ethyl acetate is 22 g/L, calculate the rate constant of the reaction.

(CBSE Sample Paper 2010)

[**Ans.** 8.60×10^{-4} min^{-1}]

10. The half life period of a first order reaction is 3 minutes. Calculate the time taken to complete 75% of the initial concentration. *(Mizoram S.B. 2014)*

[**Ans.** 6 minutes]

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

$SO_2Cl_2\,(g) \longrightarrow SO_2(g) + Cl_2\,(g)$

Experiment	Time/s^{-1}	Total Pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant. (Given : log 4 = 0.6021, log 2 = 0.3010) *(A.I.S.B. 2014)*

[**Ans.** 1.38×10^{-2} s^{-1}]

12. A first order reaction is 75% complete in 60 minutes. Find the half life period of the reaction. (Given log 4 = 0.6021) *(Nagaland S.B. 2015)* [**Ans.** 30 min]

13. A first order reaction takes 40 minutes for 20% completion. Calculate its half life period. *(Assam S.B. 2015)*

[**Ans.** 1.24×10^2 min]

14. 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}? *(Meghalaya S.B. 2016)*

15. For a reaction $2A \rightarrow 4B + C$, the concentration of B is increased by 5.0×10^{-3} mol L^{-1} in 10 seconds. Calculate the rate of disappearance of A. *(Assam S.B. 2017)*

16. Calculate the time required for the completion of 90% of a reaction of first order kinetics; $t_{½}$ = 44.1 minutes. *(Pb. S.B. 2017)*

17. Following data are obtained for the reaction:

$N_2O_5 \rightarrow 2NO_2 + ½O_2$

t/s	0	300	600
$[N_2O_5]$/mol L^{-1}	1.6×10^{-2}	0.8×10^{-2}	0.4×10^{-2}

(a) Show that it follows first order reaction.

(b) Calculate the half-life.

(Given log 2 = 0.3010, log 4 = 0.6021) *(D.S.B. 2017)*

18. For hydrolysis of methyl acetate in aqueous solution, the following results were observed:

t/s	0	30	60
CH_3COOCH_3 c/mol L^{-1}	0.60	0.30	0.15

Show that it follows pseudo first order reaction as the concentration of water remains constant. *(Kerala S.B. 2018)*

Hints & Answers *for* Revision Exercises

Very Short Answer Questions

2. Yes *e.g.*, order of the reaction for decomposition of acetaldehyde is 3/2.

3. It is zero order reaction. This can be decided on the basis of units of rate constant (for zero order reactions, units of rate constant are mol L^{-1} s^{-1}).

4. Yes, for reaction proceeding in a single step.

5. No

6. Rate = k [conc.] = $(2.5 \times 10^{-4}\ s^{-1}) \times (0.1\ mol\ L^{-1})$
$= 2.5 \times 10^{-5}$ mol L^{-1} s^{-1}.

8. s^{-1}

9. No, because order with respect to A cannot be fractional for an elementary reaction.

10. $1\frac{1}{2}$ **11.** zero order reaction

12. second order **14.** zero order

15. 1.26×10^{13} s **16.** 1×10^{-2} mol L^{-1} min^{-1}

17. First order **20.** First order

21. Zero order reaction. **22.** Zero order reaction

23. Rate $= -\frac{1}{3}\frac{d[H_2]}{dt}$ **24.** Order $= \frac{1}{2} + \frac{3}{2} = 2$

27. *(a)* decreases *(b)* no effect

28. *(a)* **29.** *(a)* **30.** *(a)* **31.** *(b)*

32. *(a)* **33.** *(d)* **34.** *(b)* **35.** *(c)*

36. *(b)* **37.** *(d)* **38.** *(a)* **39.** *(d)*

40. *(b)* **41.** *(b)* **42.** *(a)* **43.** *(a)*

44. *(c)* **45.** *(c)* **46.** *(c)* **47.** *(d)*

Short Answer Questions

2. *(i)* Rate = $k\,[NO_2][F_2]$

(ii) two

(iii) $NO_2 + F_2 \longrightarrow NO_2F + F$ (slow)

$NO_2 + F \longrightarrow NO_2F$ (fast)

4. *(i)* No change *(ii)* rate becomes double

(iii) Rate becomes nine times.

5. *(i)* zero order reaction.

6. *(i)* mol L^{-1} s^{-1} *(ii)* s^{-1}

Numerical Problems

◆ **1.** $k = \frac{0.693}{30} = 0.0231\ min^{-1}$

$$0.0231 = \frac{2.303}{120}\log\frac{a}{a-x}$$

Calculate $\frac{a}{a-x} = 15.98$ and

$x = 0.9375\,a$ or **93.75%** decomposed.

◆ **2.** $\log \frac{k_2}{k_1} = \frac{E_a - E'_a}{2.303\,RT}$

$\log \frac{k_2}{k_1} = \frac{60000 - 50000}{2.303 \times 8.314 \times 300} = 1.741$

$\log \frac{k_2}{k_1} = 55.08.$

Rate increases by **55.08 times.**

◆ **3.** $\log \frac{1.64 \times 10^4}{5.70 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314} \log \left[\frac{313 - 298}{313 \times 298}\right]$

E_a = **54.6 kJ mol^{-1}**

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

$= \log (5.70 \times 10^{-5}) + \frac{54.6 \times 10^3}{2.303 \times 8.314 \times 298}$

$= 5.336$ and A = **2.17×10^5**

◆ **4.** $k = \frac{2.303}{36000} \log \frac{a}{a - x}$

$1.5 \times 10^{-6} = \frac{2.303}{36000} \log \frac{a}{a - x}$

Solving $x = 0.052\,a$

% of initial conc. changed = 5.2%

$t_{1/2} = \frac{0.693}{1.5 \times 10^{-6}}$ = **4.62×10^5 s**

◆ **5.** $k = \frac{2.303}{10} \log \frac{a}{0.8a} = 0.02232 \text{ min}^{-1}$

$t = \frac{2.303}{0.02232} \log \frac{a}{2.25a}$ = **62.12 min.**

◆ **6.** $\log \frac{3.954 \times 10^{-2}}{3.517 \times 10^{-7}} = \frac{E_a}{2.303 \times 8.314} \left[\frac{781 - 556}{556 \times 781}\right]$

$E_a = 186.68$ kJ

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

$= \log 3.517 \times 10^{-7} + \frac{186.68 \times 10^3}{2.303 \times 8.314 \times 556}$

$= 11.0816$ or A = **1.206×10^{11}**

◆ **7.** Calculate k at different times,

mean k = **0.000845 s^{-1}**

◆ **8.** Let $[A]_0 = a$, $[A] = a - \frac{40}{100}a = 0.6a$

$k = \frac{2.303}{50} \log \frac{a}{0.6a} = 1.022 \times 10^{-2} \text{ min}^{-1}$

For 80% completion, $[A] = a - \frac{a \times 80}{100} = 0.2a$

$t = \frac{2.303}{1.022 \times 10^{-2}} \log \frac{a}{0.2a}$ = **157.5 min**

◆ **9.** $[A]_0 = \frac{22}{88}$ mol L^{-1}

$[A] = \frac{22 - 5}{88} = \frac{17}{88}$ mol L^{-1}

$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{22}{17}$

$= \frac{2.303}{300} \times 0.112$ = **8.60×10^{-4} min^{-1}**

◆ **10.** $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{3} = 0.231 \text{ min}^{-1}$

For 75% completion, if $[A]_o = a$, $[A] = a - \frac{a \times 75}{100} = 0.25a$

$t = \frac{2.303}{k} \log \frac{[A]_o}{[A]}$

$= \frac{2.303}{0.231} \log \frac{a}{0.25\,a}$

$= \frac{2.303}{0.231} \times 0.6020 = 6.0$ min

◆ **11.** *Similar to Solved Example 21 (Page 29)*

◆ **12.** $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

$[A]_0 = a$, $[A] = a - \frac{a \times 75}{100} = 0.25\,a$, $t = 60$ min

$k = \frac{2.303}{60} \log \frac{a}{0.25\,a} = 0.0231$

$\therefore \quad t_{1/2} = \frac{0.693}{0.0231}$ = **30 min**

◆ **13.** $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

$[A]_0 = a$, $[A] = a - \frac{a \times 75}{100} = 0.80\,a$, $t = 40$ min

$k = \frac{2.303}{40} \log \frac{a}{0.80\,a} = 5.58 \times 10^{-3}$

$\therefore \quad t_{1/2} = \frac{0.693}{5.58 \times 10^{-3}}$ = **1.24×10^2 min**

◆ **14.** $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

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

$= \frac{2.303}{5} \times 0.176 = 0.0811 \text{ min}^{-1}$

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

$= \frac{2.303}{0.0811} \log \frac{0.6}{0.3}$

$= \frac{2.303}{0.0811} \times 0.3010$ = **8.55 min**

◆ **15.** Rate $= -\frac{1}{2}\frac{d[A]}{dt} = \frac{1}{4}\frac{d[B]}{dt} = \frac{d[C]}{dt}$

$\frac{d[B]}{dt} = \frac{5.0 \times 10^{-3}}{10} = 5.0 \times 10^{-2}$ mol L^{-1}s^{-1}

Rate of disappearance of A

$-\frac{d[A]}{dt} = \frac{2}{4}\frac{d[B]}{dt}$

$= \frac{1}{2} \times 5.0 \times 10^{-2}$ = **2.5×10^{-2} mol L^{-1} s^{-1}**

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◆ **16.** $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{44.1} = 1.57 \times 10^{-2}\ \text{min}^{-1}$

$[A]_0 = a,\ [A] = a - \frac{a \times 90}{100} = 0.1a$

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

$$= \frac{2.303}{1.57 \times 10^{-2}} \log \frac{a}{0.1a} = \mathbf{146.7\ min}$$

◆ **17.** (*i*) $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$

At 300 s,

$$k_1 = \frac{2.303}{300} \log \frac{(1.6 \times 10^{-2})}{(0.8 \times 10^{-2})}$$

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

Similarly, at 600 s,

$$k_2 = \frac{2.303}{600} \log \frac{(1.6 \times 10^{-2})}{(0.4 \times 10^{-2})}$$

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

Since k is constant, it follows first order reaction.

(*ii*) $t_{½} = \frac{0.693}{k} = \frac{0.693}{2.3 \times 10^{-3}} = \mathbf{301.3\ s}$

◆ **18.**

t(min)	c (M)	$k = \frac{2.303}{t} \log \frac{c_0}{c}$
0	0.60	–
30 s	0.30	$k = \frac{2.303}{30} \log \frac{0.60}{0.30}$ $= 2.31 \times 10^{-2}\ \text{s}^{-1}$
60 s	0.15	$k = \frac{2.303}{30} \log \frac{0.60}{0.15}$ $= 2.31 \times 10^{-2}\ \text{s}^{-1}$

Since $k[H_2O]$ is constant, it is pseudo first order reaction.

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Additional Useful Information and Objective Questions

ADDITIONAL USEFUL INFORMATION

▶ CARBON DATING TECHNIQUE TO FIND AGE OF ARCHAEOLOGICAL OBJECTS

The principle of carbon dating is based on the fact that all living matter contain a definite amount of radioactive isotope C-14 formed in the upper atmosphere by the bombardment of N-14 with cosmic rays.

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

A plant or any other living being during its life time maintains a reasonable balance of C–14 in its tissues. The death of the plant brings an end to its tendency to take up C-14. Apart from that, the C-14 contents of the plants slowly decrease because it decays as:

$$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e$$

The half life period of C–14 is 5770 years. This means that after 5770 years, half of the C-14 content remains and after 11540 years (5770 × 2) only 25% of the initial concentration of C–14 remains and so on. A comparison of β-activity of the dead matter with that of carbon still in circulation helps to measure the period of isolation of the material from the living cycle. Thus, by knowing the equilibrium concentration of C–14 in the living plant and the concentration of C–14 in the piece of dead material at a particular time, the age of the material can be determined. This method is illustrated by the following examples:

❑ **Example 1.** *A piece of wood from an archaeological source has a ^{14}C activity which is 60% of the activity found in fresh wood today. Calculate the age of the archaeological sample (the half life period of C–14 is 5770 years).*

Solution : Decay constant, $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = 1.2 \times 10^{-4}\ \text{year}^{-1}$

Since the activity is proportional to the number of C–14 atoms in the sample,

$$N_0 = 100,\ N = 60$$

Now, $t = \frac{2.303}{\lambda} \log \frac{N_0}{N} = \frac{2.303}{1.2 \times 10^{-4}} \log \frac{100}{60} = \mathbf{4258\ years}$

❑ **Example 2.** *A sample of carbon from a wooden article is found to give 7.6 C-14 counts per minute per gram of carbon. If the freshly cut wood gives a count of 15.8 counts per minute per gram, calculate how old is the wood piece? ($t_{1/2}$ of C-14 = 5770 years).*

Solution : Decay constant, $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = 1.2 \times 10^{-4}\ \text{year}^{-1}$

$N_0 \propto$ counts observed for fresh wood = 15.8

$N \propto$ counts observed for wooden article = 7.6

$$\therefore \quad t = \frac{2.303}{\lambda}\log\frac{N_0}{N}$$

$$\text{or} \quad t = \frac{2.303}{1.2\times10^{-4}}\log\frac{15.8}{7.6}$$

$$t = \frac{2.303\times0.3178}{1.2\times10^{-4}} = \mathbf{6094\ years.}$$

❑ **Example 3.** *The β-activity of a sample of CO_2 prepared from a contemporary wood gave a count rate of 25.5 counts per minute (c.p.m). The same mass of CO_2 from an ancient wooden statue gave a count rate of 20.5 c.p.m. in the same counter conditions. Calculate its age to the nearest 50 years taking $t_{1/2}$ for ^{14}C as 5770 years. What would be the expected count rate of an identical mass of CO_2 from a sample which is 4000 years old?*

Solution :

$$\lambda = \frac{0.693}{t_{1/2}}; \quad t_{1/2} = 5770 \text{ years}$$

$$\lambda = \frac{0.693}{5770} = 1.2\times10^{-4}\ \text{year}^{-1}$$

Since rate of counts is proportional to the number of ^{14}C atoms in the sample,

$$N_0 = 25.5,\ N = 20.5$$

$$\therefore \quad t = \frac{2.303}{\lambda}\log\frac{N_0}{N} = \frac{2.303}{1.2\times10^{-4}}\log\frac{25.5}{20.5}$$

$$= \frac{2.303}{1.2\times10^{-4}}\times0.0948 = \mathbf{1819\ years}$$

Now, t for another sample = 4000 years

$$t = \frac{2.303}{\lambda}\log\frac{N_0}{N},\ N = ?$$

$$4000 = \frac{2.303}{1.2\times10^{-4}}\log\frac{25.5}{N}$$

$$\log\frac{25.5}{N} = \frac{4000\times1.2\times10^{-4}}{2.303} = 0.2084$$

$$\frac{25.5}{N} = \text{Antilog } 0.2084 = 1.616$$

$$N = \frac{25.5}{1.616} = \mathbf{15.78\ counts\ per\ min.}$$

▶ MECHANISM OF TYPICAL REACTIONS

1. Reaction involving two first order consecutive reactions. In such reactions, the reactants form a stable intermediate compound before they are finally converted into the products. For example, reactants (R) are first converted to intermediate (I) which is then converted to product (P) as :

$$R \xrightarrow{k_1} I \xrightarrow{k_2} P$$

Therefore, the reaction takes place in two steps, both of which are first order *i.e.,*

Step I $\quad R \xrightarrow{k_1} I$

Step II $\quad I \xrightarrow{k_2} P$

This means that I is produced by step I and consumed by step II. In these reactions, each stage will have its own rate and rate constant.

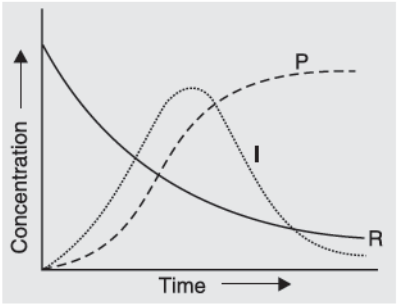

Fig. 19. Concentration profile of reactants (R), intermediate (I) and products (P) as a function of time.

When we start with pure R, its concentration will decrease with time. The concentration of the intermediate I will first increase as it accumulates and reaches a maximum value. After attaining maximum value, it decreases and decays to zero concentration and is converted to the final product. The concentration of the product, P will always increase. These results are shown in Figure 19.

2. Reactions involving slow step. When a reaction occurs by a sequence of steps and one of the steps is slow, then the rate determining step is the slow step. For example, in the reaction :

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$$R \xrightarrow{k_1} I$$
$$I \xrightarrow{k_2} P$$

If $k_1 << k_2$, then I is converted into products as soon as it is formed. We can say that

$$-\frac{d[R]}{dt} = \frac{d[P]}{dt} = k_1[R]$$

This has already been learnt in complex reactions.

3. Reversible reactions. For reversible reactions such as

$$H_2 + I_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2HI$$

$$\text{Rate} = \frac{1}{2}\frac{d[HI]}{dt} = k_1[H_2][I_2] - k_2[HI]^2$$

4. Parallel Reactions. In such reactions, the reactants are consumed by two or more reactions, which may have different orders of the reactions taking place simultaneously. For example, in a system containing NO_2 and SO_2, NO_2 is consumed in the following two reactions :

$$2NO_2 \xrightarrow{k_1} N_2O_4$$
$$NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$$

The rate of disappearance of NO_2 will be sum of the rates of the two reactions, *i.e.*,

$$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 + k_2[NO_2][SO_2]$$

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions *M. C. Q.*

A Topicwise MULTIPLE CHOICE QUESTIONS *with only one correct answer*

Rate of Reaction, Order and Molecularity

A1. Which of the following statement is not correct for the reaction

$$4A + B \longrightarrow 2C + 2D$$

(*a*) the rate of disappearance of B is one–fourth the rate of disappearance of A

(*b*) the rate of appearance of C is one–half the rate of disappearance of B.

(*c*) the rate of formation of D is one–half the rate of consumption of A.

(*d*) the rate of formation of C and D are equal.

A2. Nitrogen tetraoxide (N_2O_4) decomposes as

$$N_2O_4(g) \longrightarrow 2NO_2(g)$$

If the pressure of N_2O_4 fall from 0.50 atm to 0.32 atm is 30 minutes, the rate of appearance of $NO_2(g)$ is:

(*a*) 0.006 atm min^{-1} (*b*) 0.003 atm min^{-1}

(*c*) 0.012 atm min^{-1} (*d*) 0.024 atm min^{-1}

A3. If the concentrations are expressed in mol $litre^{-1}$ and time in s, then the units of the rate constant for the first order reaction are :

(*a*) mol $litre^{-1}$ s^{-1} (*b*) mol^{-1} litre s^{-1}

(*c*) s^{-1} (*d*) mol^2 $litre^{-2}$ s^{-1}

A4. The rate of a first order reaction is 1.8×10^{-3} mol L^{-1} min^{-1} when the initial concentration is 0.3 mol L^{-1}. The rate constant in the units of second is :

(*a*) 1×10^{-2} s^{-1} (*b*) 1×10^{-4} s^{-1}

(*c*) 6×10^{-2} s^{-1} (*d*) 6×10^{-2} s.

A5. The rate constant of a reaction is 1.2×10^{-5} mol^{-2} $litre^2$ s^{-1}. The order of the reaction is :

(*a*) zero (*b*) 1

(*c*) 2 (*d*) 3.

Answers

A1. (*b*) **A2.** (*c*) **A3.** (*c*) **A4.** (*b*) **A5.** (*d*)

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A6. For a reaction, $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$
Rate = $k[NO]^2[O_2]$. If the volume of the reaction vessel is doubled, the rate of the reaction :
(*a*) will diminish to 1/4 of initial value
(*b*) will diminish to 1/8 of initial value
(*c*) will grow 4 times
(*d*) will grow 8 times.

A7. For the reaction :
$2N_2O_5 \longrightarrow 4NO_2 + O_2$ rate and rate constant are 1.22×10^{-4} s^{-1} and 3.4×10^{-5} s^{-1} respectively, then the concentration of N_2O_5 at that time will be :
(*a*) 1.732 (*b*) 3.6
(*c*) 1.02×10^{-4} (*d*) 3.4×10^5.

A8. The reaction :
N_2O_5 (in CCl_4) $\longrightarrow 2NO_2 + \frac{1}{2}O_2$ (*g*) is first order in N_2O_5 with rate constant 6.2×10^{-4} s^{-1}. What is the value of rate of reaction when $[N_2O_5] = 1.25$ mol L^{-1} ?
(*a*) 7.75×10^{-4} mol L^{-1} s^{-1}
(*b*) 6.35×10^{-3} mol L^{-1} s^{-1}
(*c*) 5.15×10^{-5} mol L^{-1} s^{-1}
(*d*) 3.85×10^{-4} mol L^{-1} s^{-1}

Integrated Rate of Equation and Half-life Period

A9. The half life period for a first order reaction is 69.3 s. Its rate constant is :
(*a*) 10^{-2} s^{-1} (*b*) 10^{-4} s^{-1}
(*c*) 10 s^{-1} (*d*) 10^2 s^{-1}.

A10. Half life period of any first order reaction is
(*a*) directly proportional to the initial concentration of the reactant
(*b*) half of the rate constant
(*c*) same for all reactions
(*d*) independent of initial concentration of reactants.

A11. For the reaction; $A \longrightarrow C$, it is found that the rate of the reaction quadruples when the concentration of A is doubled. The rate for the reaction is.
Rate = $[A]^n$ where the value of n is :
(*a*) 1 (*b*) 2
(*c*) zero (*d*) 3.

A12. For a chemical reaction $A + B \longrightarrow C$, the following data were found :

Initial conc. of A (mol litre^{-1})	Initial Conc. of B (mol litre^{-1})	Rate (mol litre^{-1} sec^{-1})
2.0	3.0	0.10
6.0	3.0	0.90
6.0	6.0	0.90

The correct rate expression from these data is :
(*a*) $r = k[A]^2[B]^2$ (*b*) $r = k[A]\,[B]$
(*c*) $r = k[A]^2$ (*d*) $r = k[A]\,[B]^2$.

A13. The rate for the first order reaction is 0.69×10^{-2} mol L^{-1} min^{-1} and the initial concentration is 0.2 mol L^{-1}. The half life period is :
(*a*) 1205 s (*b*) 330 s
(*c*) 600 s (*d*) 1 s.

A14. For the first order reaction, the half life period is (if k is rate constant and a is initial concentration),
(*a*) $\frac{ln\,2}{k}$ (*b*) $\frac{1}{ka}$
(*c*) $\frac{ln\,k}{2}$ (*d*) $\frac{\log k}{2}$

A15. The following rate data were obtained at 303 K for the following reaction :
$2A + B \longrightarrow C + D$

Experiment	[A]	[B]	Initial rate of formation of D
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	2.4×10^{-2}

The order of the reaction is :
(*a*) 2 (*b*) 3
(*c*) 1 (*d*) 4.

A16. For reaction $A \rightarrow B$, the rate of reaction increases by a factor of 1.857 when the concentration of A is increased by 1.5 times. The order of reaction with respect to A is
(*a*) 1 (*b*) 1.5
(*c*) 2 (*d*) 2.5.

A17. For the first order reaction, time required for 99% completion is :
(*a*) half the time required for completion of 90% of reaction
(*b*) thrice the time required for 90% completion of reaction
(*c*) twice the time required for 90% completion of reaction
(*d*) none of these.

A18. For zero order reaction, the integrated rate equation is :
(*a*) $kt = \frac{[A]}{[A]_0}$ (*b*) $kt = [A] - [A]_0$
(*c*) $[A] = -kt + [A]_0$ (*d*) $[A] = kt - [A]_0$.

A19. For a first order reaction involving decomposition of N_2O_5, the following information is available :
$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ Rate = $k\,[N_2O_5]$
$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ Rate = $k'\,[N_2O_5]$.
Which of the following expressions is true ?
(*a*) $k = k'$ (*b*) $k' = 2k$
(*c*) $k' = 1/2k$ (*d*) $k > k'$.

Answers

A6. (*b*) **A7** (*b*) **A8.** (*a*) **A9.** (*a*) **A10.** (*d*) **A11.** (*b*) **A12.** (*c*) **A13.** (*a*) **A14.** (*a*) **A15.** (*b*)
A16. (*b*) **A17.** (*c*) **A18.** (*c*) **A19.** (*b*)

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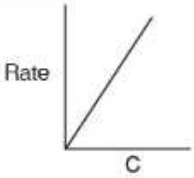
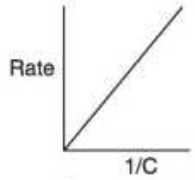
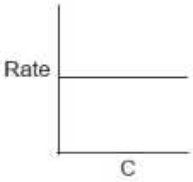
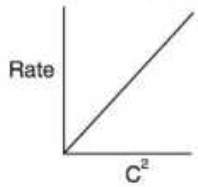
A20. Which of the following graphs correspond to first order reaction ?

(*a*) 

(*b*) 

(*c*) 

(*d*) 

A21. Which of the following relation is correct for zero order reaction ?

(*a*) $t_{3/4} = 2t_{1/2}$ (*b*) $t_{3/4} = 1.5\ t_{1/2}$

(*c*) $t_{3/4} = \frac{1}{2}t_{1/2}$ (*d*) $t_{3/4} = \frac{1}{3}t_{1/2}$.

A22. The half life period for a zero order reaction is equal to :

(*a*) $2k/[A]_0$ (*b*) $\frac{[A]_0}{2k}$

(*c*) $\frac{0.693}{k}$ (*d*) $\frac{0.693}{k[A]_0}$

A23. For a second order reaction rate at a particular time is x. If the initial concentration is tripled, the rate will become:

(*a*) $3x$ (*b*) $9x^2$

(*c*) $9x$ (*d*) $27x$.

A24. For a zero order reaction, linear plot was obtained for [A] *vs* t. The slope of the line is equal to :

(*a*) k_0 (*b*) $-k_0$

(*c*) $\frac{0.693}{k_0}$ (*d*) $-\frac{k_0}{2.303}$.

A25. For a reaction having rate law expression :
Rate = $k[A]^{3/2}\ [B]^{-1/2}$
If the concentration of both A and B become four times, the rate of reaction

(*a*) becomes four times
(*b*) becomes 16 times
(*c*) decreases four times
(*d*) remains same.

A26. For a chemical reaction, A $\longrightarrow$ B, it is observed that the rate of reaction doubles when the concentration of A is increased four times. The order of reaction in A is :

(*a*) Two (*b*) One

(*c*) Half (*d*) Zero

A27. The conversion of A $\longrightarrow$ B follows second order kinetics. Doubling the concentration of A will increase the rate of formation of B by a factor of

(*a*) $\frac{1}{4}$ (*b*) 2

(*c*) $\frac{1}{2}$ (*d*) 4

A28. A reaction is 50% complete in 2 hours and 75% complete in 4 hours. The order of reaction is

(*a*) 0 (*b*) 1

(*c*) 2 (*d*) 3

A29. The reaction : A $\longrightarrow$ B follows first order kinetics. The time taken for 0.8 mol of A to produce 0.6 mol of B is 1 hour. What is the time taken for conversion of 0.9 mol of A to produce 0.675 mol of B ?

(*a*) 1 hour (*b*) 0.5 hour

(*c*) 0.25 hour (*d*) 2 hour

A30. The time taken for 90% of a first order reaction to complete is approximately

(*a*) 1.1 times that of half life
(*b*) 2.2 times that of half life
(*c*) 3.3 times that of half life
(*d*) 4.4 times that of half life

A31. The rate law for a reaction between the substances A and B is given by

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

On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of reaction will be

(*a*) $m + n$ (*b*) $n - m$

(*c*) $2^{(n-m)}$ (*d*) $\frac{1}{2^{m+n}}$.

A32. In a first order reaction, the concentration of the reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of the reaction in sec^{-1} is

(*a*) 2×10^4 (*b*) 3.45×10^{-5}

(*c*) 1.386×10^{-4} (*d*) 2×10^{-4}.

A33. The rate of a first order reaction is
1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half life of the reaction is :

(*a*) 23.1 min (*b*) 8.73 min

(*c*) 7.53 min (*d*) 0.383 min.

A34. The rate equation for the reaction :
2A + B $\longrightarrow$ C is found to be rate = k[A] [B]. The correct statement in relation to this reaction is that the

(*a*) units of k must be s^{-1}
(*b*) $t_{1/2}$ is constant
(*c*) rate of formation of C is twice the rate of disappearance of A
(*d*) value of k is independent of the initial concentration of A and B.

Answers

A20. (*a*)	**A21.** (*b*)	**A22.** (*b*)	**A23.** (*c*)	**A24.** (*b*)	**A25.** (*a*)	**A26.** (*c*)	**A27.** (*d*)	**A28.** (*b*)	**A29.** (*a*)
A30. (*c*)	**A31.** (*c*)	**A32.** (*c*)	**A33.** (*a*)	**A34.** (*d*)					

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Effect of Temperature on Rate of Reaction

A35. On increasing temperature of the reacting system by 10 degrees the rate of reaction almost doubles. The most appropriate reason for this is :

(*a*) Collision frequency increases

(*b*) Activation energy decreases by increase in temperature

(*c*) The fraction of molecules having energy equal to threshold energy or more increases

(*d*) The value of threshold energy decreases.

A36. If k_1 and k_2 are rate constants at temperatures T_1 and T_2 respectively, then according to Arrhenius equation,

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

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

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

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

A37. In the reversible reaction, $2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$, the rate of

disappearance of NO_2 is equal to :

(*a*) $\frac{2k_1}{k_2}[NO_2]^2$ (*b*) $2k_1\,[NO_2] - 2k_2[N_2O_4]$

(*c*) $2k_1[NO_2]^2 - 2k_2[N_2O_4]$ (*d*) $(2k_1 - k_2)\,[NO_2]$.

A38. When *ln k* is plotted against 1/T, the slope was found to be -10.7×10^3 K, activation energy for the reaction would be :

(*a*) -78.9 kJ mol^{-1} (*b*) 2.26 kJ mol^{-1}

(*c*) 88.9 kJ mol^{-1} (*d*) 10.7 kJ mol^{-1}.

A39. A reactant (A) forms two products :

$A \xrightarrow{k_1} B$, Activation energy, E_{a_1}

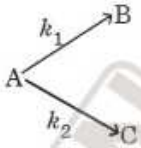
$A \xrightarrow{k_2} C$, Activation energy, E_{a_2}

If $E_{a_2} = 2\,E_{a_1}$, then k_1 and k_2 are related as

(*a*) $k_2 = k_1 e^{E_{a_1}/RT}$ (*b*) $k_2 = k_1 e^{E_{a_2}/RT}$

(*c*) $k_1 = Ak_2 e^{E_{a_1}/RT}$ (*d*) $k_1 = 2k_2 e^{E_{a_2}/RT}$

A40. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :



$k_1 = 1.26 \times 10^{-4}\ s^{-1}$

$k_2 = 3.8 \times 10^{-5}\ s^{-1}$

The percentage distribution of B and C are

(*a*) 75% B and 25% C (*b*) 80% B and 20% C

(*c*) 60% B and 40% C (*d*) 76.83% B and 23.17% C

A41. Milk turns sour at 40°C three times faster than it does at 0°C. This shows that the activation energy of souring of milk in (kJ mol^{-1}) is (R = 8.3 JK^{-1} mol^{-1})

(*a*) $\frac{2.303 \times 8.3 \times 273 \times 313}{40}\log 3$

(*b*) $\frac{2.303 \times 8.3 \times 273 \times 313}{40}\log \frac{1}{3}$

(*c*) $\frac{2.303 \times 8.3 \times 40}{273 \times 313}\log 3$

(*d*) $\frac{2.303 \times 273 \times 313}{40}\log 3$

A42. The activation energy of a reaction is 56.2 kJ/mol. The ratio of rate constants at 300 K and 305 K is (R = 8 J mol^{-1} K^{-1}) about:

(*a*) 1.25 (*b*) 1.47

(*c*) 1.10 (*d*) 1.60

A43. An exothermic reaction A → B has an activation energy of 17 kJ per mole of A. The heat of reaction is 40 kJ. The activation energy for the reverse reaction B → A is:

(*a*) 23 kJ (*b*) 97 kJ

(*c*) 57 kJ (*d*) 17 kJ

A44. Which of the following statement is true?

(*a*) The reaction is fast if the activation energy is low.

(*b*) The activation energy of forward reaction can never be greater than that of the backward reaction.

(*c*) A catalyst increases the rate of a reaction by decreasing the rate of backward reaction.

(*d*) Reaction rates increase with temperature because the activation energy decreases at high temperature.

Answers

A35. (*c*) **A36.** (*b*) **A37.** (*c*) **A38.** (*c*) **A39.** (*c*) **A40.** (*d*) **A41.** (*a*) **A42.** (*b*) **A43.** (*c*) **A44.** (*a*)

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B MULTIPLE CHOICE QUESTIONS *from Competitive Examinations*

AIPMT & Other State Boards' Medical Entrance

B1. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in approximately :

(*a*) 45 minutes (*b*) 60 minutes
(*c*) 40 minutes (*d*) 50 minutes

(log 4 = 0.60, log 5 = 0.69) *(C.B.S.E. P.M.T. 2007)*

B2. The bromination of acetone that occurs in acid solution is represented by the equation

$$CH_3COCH_3(aq) + Br_2(aq) \longrightarrow CH_3COCH_2Br(aq) + H^+(aq) + Br^-(aq)$$

These kinetic data were obtained for given reaction concentrations.

Initial concentrations, M

$[CH_3COCH_3]$	$[Br_2]$	$[H^+]$	Initial Rate, disappearance of Br_2, Ms^{-1}
0.30	0.05	0.05	5.7×10^{-5}
0.30	0.10	0.05	5.7×10^{-5}
0.30	0.10	0.10	1.2×10^{-4}
0.40	0.05	0.20	3.1×10^{-4}

Based on these data, the rate of reaction is :

(*a*) rate = $k[CH_3COCH_3]\ [Br_2]$
(*b*) rate = $k[CH_3COCH_3]\ [Br_2]\ [H^+]^2$
(*c*) rate = $k[CH_3\ COCH_3]\ [Br_2]\ [H^+]$
(*d*) rate = $k[CH_3\ COCH_3]\ [H^+]$ *(C.B.S.E. P.M.T. 2008)*

B3. The rate constants k_1 and k_2 for two different reactions are $10^{16}.e^{-2000/T}$ and $10^{15}.e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is

(*a*) $\frac{2000}{2.303}$K (*b*) 2000K
(*c*) $\frac{1000}{2.303}$K (*d*) 1000K

(C.B.S.E. P.M.T. 2008)

B4. For the reaction A + B → product, it is observed that

(*i*) on doubling the concentration of A only, the rate of reaction is also doubled.
(*ii*) on doubling the initial concentration of both A and B, there is change by a factor of 8 in the rate of reaction. The rate of reaction is given by

(*a*) Rate = $k[A]\ [B]^2$ (*b*) Rate = $k[A]^2\ [B]^2$
(*c*) Rate = $k[A]\ [B]$ (*d*) Rate = $k[A]^2\ [B]$

(C.B.S.E. Med. 2009)

B5. Half life period of a first order reaction is 1386 seconds. The specific rate constant of the reaction is

(*a*) $0.5 \times 10^{-2}\ s^{-1}$ (*b*) $0.5 \times 10^{-3}\ s^{-1}$
(*c*) $5.0 \times 10^{-2}\ s^{-1}$ (*d*) $5.0 \times 10^{-3}\ s^{-1}$

(C.B.S.E. Med. 2009)

B6. For the reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$, if $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol/L/s, the value of $-\frac{d[H_2]}{dt}$ would be

(*a*) 4×10^{-4} mol/L/s (*b*) 6×10^{-4} mol/L/s
(*c*) 1×10^{-4} mol/L/s (*d*) 3×10^{-4} mol/L/s

(C.B.S.E. Med. 2009)

B7. In the reaction

$$BrO_3^-(aq) + 5Br^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

the rate of appearance of bromine is related to the rate of disappearance of bromide ions as

(*a*) $\frac{d[Br_2]}{dt} = -\frac{5}{3}\frac{d[Br^-]}{dt}$ (*b*) $\frac{d[Br_2]}{dt} = \frac{5}{3}\frac{d[Br^-]}{dt}$
(*c*) $\frac{d[Br_2]}{dt} = \frac{3}{5}\frac{d[Br^-]}{dt}$ (*d*) $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

(C.B.S.E. Med. 2009)

B8. During the kinetic study of the reaction.
2A + B ⟶ C + D, following results were obtained :

Based on the above data which one of the following is correct?

Run	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate of formation of D/mol L^{-1} min^{-1}
I	0.1	0.1	6.01×10^{-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}

Based on the above data which one of the following is correct?

(*a*) rate = $k[A]^2\ [B]^2$ (*b*) rate = $k[A]\ [B]^2$
(*c*) rate = $k[A]^2\ [B]$ (*d*) rate = $k[A]\ [B]$.

(C.B.S.E. P.M.T. 2010)

B9. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ the value of rate of disappearance of N_2O_5 is given as 6.25×10^{-3} mol L^{-1} s^{-1}. The rate of formation of NO_2 and O_2 is given respectively as :

(*a*) 6.25×10^{-3} mol L^{-1} s^{-1} and 3.125×10^{-3} mol L^{-1} s^{-1}
(*b*) 6.25×10^{-3} mol L^{-1} s^{-1} and 6.25×10^{-3} mol L^{-1} s^{-1}
(*c*) 6.25×10^{-3} mol L^{-1} s^{-1} and 6.25×10^{-3} mol L^{-1} s^{-1}
(*d*) 1.25×10^{-2} mol L^{-1} s^{-1} and 3.125×10^{-3} mol L^{-1} s^{-1}

(C.B.S.E. P.M.T. 2010)

Answers

B1. (*a*) **B2.** (*d*) **B3.** (*c*) **B4.** (*a*) **B5.** (*b*) **B6.** (*d*) **B7.** (*d*) **B8.** (*b*) **B9.** (*d*)

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B10. In a reaction, A + B → Product, rate is doubled when the concentration of B is doubled, and rate increases by a factor of 8 when the concentration of both the reactants (A and B) are doubled. Rate law for the reaction can be written as

(*a*) rate = $k[A][B]^2$ (*b*) rate = $k[A]^2[B]^2$
(*c*) rate = $k[A][B]$ (*d*) rate = $k[A]^2[B]$

(A.I.P.M.T. 2012)

B11. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become

(*a*) 256 times (*b*) 512 times
(*c*) 64 times (*d*) 128 times

(A.I.P.M.T. 2012)

B12. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C ? (R = 8.314 J mol^{-1} K^{-1})

(*a*) 34.7 kJ mol^{-1} (*b*) 15.1 kJ mol^{-1}
(*c*) 342 kJ mol^{-1} (*d*) 269 kJ mol^{-1}

(NEET 2013)

B13. The rate constant of the reaction A ⟶ B is 0.6×10^{-3} mole per second. If the concentration of A is 5 M, then concentration of B after 20 minutes is:

(*a*) 0.36 M (*b*) 0.72 M
(*c*) 1.08 M (*d*) 3.60 M *(AIPMT 2015)*

B14. The activation energy of a reaction can be determined from the slope of which of the following graphs?

(*a*) $\ln k$ vs. $\frac{1}{T}$ (*b*) $\frac{T}{\ln k}$ vs. $\frac{1}{T}$
(*c*) $\ln k$ vs. T (*d*) $\frac{\ln k}{T}$ vs. T *(AIPMT 2015)*

B15. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is

(*a*) second
(*b*) more than zero but less than first
(*c*) zero
(*d*) first *(AIPMT 2015)*

B16. The addition of a catalyst during a chemical reaction alters which of the following quantities?

(*a*) Enthalpy (*b*) Activation energy
(*c*) Entropy (*d*) Internal energy

(NEET 2016)

B17. The rate of first-order reaction is 0.04 mol L^{-1} s^{-1} at 10 seconds and 0.03 mol L^{-1} s^{-1} at 20 seconds after initiation of the reaction. The half-life period of the reaction is?

(*a*) 44.1 s (*b*) 54.1 s
(*c*) 24.1 s (*d*) 34.1 s

(NEET 2016)

B18. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first order reaction. It is because the

(*a*) rate is proportional to the surface coverage
(*b*) rate is inversely proportional to the surface coverage
(*c*) rate is independent of the surface coverage
(*d*) rate of decomposition is very slow

(NEET 2016)

B19. Mechanism of a hypothetical reaction $X_2 + Y_2 \rightarrow 2XY$, is given below:

(*i*) $X_2 \rightarrow X + X$ (fast) (*ii*) $X + Y_2 \rightarrow XY + Y$ (slow)
(*iii*) $X + Y \rightarrow XY$ (fast)

The overall order of the reaction will be

(*a*) 2 (*b*) 0
(*c*) 1.5 (*d*) 1 *(NEET 2017)*

B20. A first order reation has a specific reaction rate of 10^{-2} sec^{-1}. How much time will it take for 20 g of the reactant to reduce to 5 g?

(*a*) 138.6 sec (*b*) 346.5 sec
(*c*) 693.0 sec (*d*) 238.6 sec *(NEET 2017)*

B21. The correct difference between first and second order reaction is that

(*a*) the rate of a first-order reaction does not depend on reactant concentrations; the rate of a second-order reaction does depend on reactant concentrations
(*b*) the half-life of a first-order reaction does not depend on $[A]_0$; the half-life of a second-order reaction does depend on $[A]_0$
(*c*) a first-order reaction can be catalysed; a second-order reaction cannot be catalysed
(*d*) the rate of a first-order reaction does depend on reactant concentration; the rate of a second-order reaction does not depend on reactant concentrations.

(NEET 2018)

B22. When initial concentration of the reactant is doubled, the half-life period of a zero order reaction

(*a*) is halved (*b*) is doubled
(*c*) is tripled (*d*) remains unchanged.

(NEET 2018)

B23. If the initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then order of the reaction is

(*a*) zero (*b*) fraction
(*c*) three (*d*) one
(*e*) two *(Kerala P.M.T. 2007)*

B24. For a reaction taking place in three steps, the rate constants are k_1, k_2 and k_3. The overall rate constant $k = \frac{k_1 k_2}{k_3}$. If the energy of activation values for the first, second and third stages are respectively 40, 50 and 60 kJ mol^{-1}, then the overall energy of activation in kJ mol^{-1} is

(*a*) 30 (*b*) 40
(*c*) 60 (*d*) 50
(*e*) 150 *(Kerala P.M.T. 2008)*

Answers

B10. (*d*)	**B11.** (*b*)	**B12.** (*a*)	**B13.** (*b*)	**B14.** (*a*)	**B15.** (*d*)	**B16.** (*b*)	**B17.** (*c*)	**B18.** (*a*)	**B19.** (*c*)
B20. (*a*)	**B21.** (*b*)	**B22.** (*b*)	**B23.** (*a*)	**B24.** (*a*)					

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B25. For a zero order reaction, the plot of concentration of reactant vs time is (intercept refers to concentration axis)
(*a*) linear with +ve slope and zero intercept
(*b*) linear with –ve slope and zero intercept
(*c*) linear with –ve slope and non-zero intercept
(*d*) linear with +ve slope and non-zero intercept
(*e*) a curve asymptotic to concentration axis
(Kerala P.M.T. 2008)

B26. Consider the decomposition of N_2O_5 as

$$N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$$

The rate of reaction is given by

$$-\frac{d[N_2O_5]}{dt} = \frac{1}{2}\frac{d[NO_2]}{dt} = 2\frac{d[O_2]}{dt} = k_1[N_2O_5]$$

Therefore, $-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$

$$+\frac{d[NO_2]}{dt} = 2k_1[N_2O_5] = k_1'[N_2O_5]$$

$$+\frac{d[O_2]}{dt} = \frac{1}{2}k_1[N_2O_5] = k_1'[N_2O_5]$$

Choose the correct option :
(*a*) $k_1 = k_1' = k_1''$ (*b*) $k_1 = 2k_1' = k_1''$
(*c*) $2k_1 = k_1' = 4k_1''$ (*b*) $4k_1 = 2k_1' = k_1''$
(A.M.U. Med 2010, 2011)

B27. Consider the following statements :
(*i*) increase in concentration of reactant increases the rate of a zero order reaction
(*ii*) rate constant k is equal to collision frequency A if $E_a = 0$.
(*iii*) rate constant k is equal to collision frequency A if $E_a = \infty$.
(*iv*) ln k vs T is a straight line.
(*v*) ln k vs 1/T is a straight line.
Correct statements are
(*a*) (*i*) and (*iv*) (*b*) (*ii*) and (*v*)
(*c*) (*iii*) and (*iv*) (*d*) (*ii*) and (*iii*)
(*e*) (*i*) and (*v*) *(Kerala PMT 2010)*

B28. The initial rates of reaction
$3A + 2B + C \longrightarrow$ Products, at different initial concentrations are given below

Initial rate, Ms^{-1}	$[A]_0$, M	$[B]_0$, M	$[C]_0$, M
5.0×10^{-3}	0.010	0.005	0.010
5.0×10^{-3}	0.010	0.005	0.015
1.0×10^{-2}	0.010	0.010	0.010
1.25×10^{-3}	0.005	0.005	0.010

The order with respect to the reactants, A, B and C are respectively
(*a*) 3, 2, 0 (*b*) 3, 2, 1
(*c*) 2, 2, 0 (*d*) 2, 2, 1
(*e*) 2, 1, 0 *(Kerala PMT 2011)*

B29. For a reaction $A + B \longrightarrow C + 2D$, experimental results were collected for three trials and the data obtained are given below :

Trial	[A], M	[B], M	Initial Rate, Ms^{-1}
1	0.40	0.20	5.5×10^{-4}
2	0.80	0.20	5.5×10^{-4}
3	0.40	0.40	2.2×10^{-3}

The correct rate law of the reaction is
(*a*) rate = $k[A]^0 [B]^2$ (*b*) rate = $k[A] [B]^2$
(*c*) rate = $k[A] [B]$ (*d*) rate = $k[A] [B]^0$
(*e*) rate = $k[A]^0 [B]$ *(Kerala P.M.T. 2012)*

B30. In a first order reaction, the concentration of the reactant is reduced to 1/8 of the initial concentration in 75 minutes at 298 K. What is the half-life period of the reaction in minutes ?
(*a*) 50 (*b*) 15
(*c*) 45 (*d*) 25
(*e*) 30 *(Kerala P.M.T. 2012)*

B31. In the Arrhenius plot of ln k vs $\frac{1}{T}$, a linear plot is obtained with a slope of -2×10^4 K. The energy of a activation of the reaction (in kJ mol^{-1}) is
(R value is 8.3 JK^{-1} mol^{-1})
(*a*) 83 (*b*) 166
(*c*) 249 (*d*) 332
(*e*) 830 *(Kerala P.M.T. 2012)*

B32. The decomposition of ammonia on tungsten surface at 500 K follows zero order kinetics. The half-life period of this reaction is 45 minutes when the initial pressure is 4 bar. The half life period (minutes) of the reaction when the initial pressure is 16 bar at the same temperature is
(*a*) 120 (*b*) 60
(*c*) 240 (*d*) 180
(*e*) 300 *(Kerala P.M.T. 2012)*

B33. The rate constant of a first order reaction is doubled when the temperature is increased from 20°C to 25°C. How many times the rate constant will increase if the temperature is raised from 20°C to 40°C ?
(*a*) 4 (*b*) 8
(*c*) 16 (*d*) 32
(*e*) 64 *(Kerala P.M.T. 2012)*

B34. The rate of a reaction is given by rate, $r = k\ [H^+]^n$
If the rate becomes 100 times when the pH changes from 2 to 1, the order of the reaction is
(*a*) 0 (*b*) 1
(*c*) 2 (*d*) 3 *(A.M.U.Med. 2013)*

Answers

B25. (*c*) **B26.** (*c*) **B27.** (*b*) **B28.** (*e*) **B29.** (*a*) **B30.** (*d*) **B31.** (*b*) **B32.** (*d*) **B33.** (*c*) **B34.** (*c*)

Competition File

B35. In a first order reaction, 80% of the reactant at an instant was reduced to 8% in 4606 seconds. The rate constant of the reaction is

(*a*) $2.303 \times 10^{-4}\ s^{-1}$ (*b*) $4.606 \times 10^{-3}\ s^{-1}$
(*c*) $5.000 \times 10^{-3}\ s^{-1}$ (*d*) $5.000 \times 10^{-4}\ s^{-1}$
(*e*) $4.606 \times 10^{-4}\ s^{-1}$ *(Kerala PMT 2015)*

B36. The decomposition of N_2O_5 in CCl_4 at 318 K is studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.4 mol L^{-1} and after 200 minutes, it is reduced to 2.00 mol L^{-1}. What is the rate of production of NO_2 during this period in mol L^{-1} min^{-1} ?

(*a*) 4×10^{-3} (*b*) 2×10^{-3}
(*c*) 1×10^{-3} (*d*) 2×10^{-4}
(*e*) 5×10^{-3} *(Kerala PMT 2015)*

B37. In a first order reaction, the concentration of the reactant decreases from 0.6 M to 0.3 M in 30 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is

(*a*) 60 min (*b*) 30 min
(*c*) 15 min (*d*) 50 min
(*e*) 90 min *(Kerala PMT 2015)*

JEE (Main) & Other State Boards' Engineering Entrance

B38. The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301)

(*a*) 230.3 minutes (*b*) 23.03 minutes
(c) 46.06 mintues (d) 460.6 minutes
(A.I.E.E.E. 2009)

B39. The time for half life period of a certain reaction A $\longrightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A' is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction?

(*a*) 0.25 h (*b*) 1 h (*c*) 4 h (*d*) 0.5 h.
(A.I.E.E.E. 2010)

B40. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about

(*a*) 10 times (*b*) 24 times
(*c*) 32 times (*d*) 64 times
(A.I.E.E.E. 2011

B41. For a first order reaction, (A) $\rightarrow$ Products, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes The rate of reaction when the concentration of A is 0.01 M is

(*a*) 3.47×10^{-4} M/min (*b*) 3.47×10^{-5} M/min
(*c*) 1.73×10^{-4} M/min (*d*) 1.73×10^{-5} M/min
(A.I.E.E.E. 2012)

B42. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be

(R = 8.314 JK^{-1} mol^{-1} and log 2 = 0.301)

(*a*) 60.5 kJ mol–1 (*b*) 53.6 kJ mol–1
(*c*) 48.6 kJ mol–1 (*d*) 58.5 kJ mol–1
(JEE Main 2013)

B43. For the non-stoichiometric reaction:
$2A + B \longrightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

Initial concentration [A]	Initial concentration [B]	Initial rate of formation of C (mol $L^{-1}s^{-1}$)
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

(*a*) $\frac{dC}{dt} = k[A]$ (*b*) $\frac{dC}{dt} = k[A][B]$
(*c*) $\frac{dC}{dt} = k[A]^2[B]$ (*d*) $\frac{dC}{dt} = k[A][B]^2$
(JEE Main 2014)

B44. Higher order (> 3) reactions are rare due to

(*a*) shifting of equilibrium towards reactants due to elastic collisions
(*b*) loss of active species on collision
(*c*) low probability of simultaneous collision of all the reacting species
(*d*) increase in entropy and activation energy as more molecules are involved. *(JEE Main 2015)*

B45. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes, the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be

(*a*) 6.93×10^{-2} mol min^{-1}
(*b*) 6.93×10^{-4} mol L^{-1} min^{-1}
(*c*) 2.66 L min^{-1} at STP
(*d*) 1.34×10^{-2} mol min^{-1} *(JEE Main 2016)*

B46. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 kJ mol^{-1}. If k_1 and k_2 are rate constants for reactions R_1 and R_2 respectively at 300 K, then $\ln(k_2/k_1)$ is equal to : (R = 8.314 J $mol^{-1}K^{-1}$)

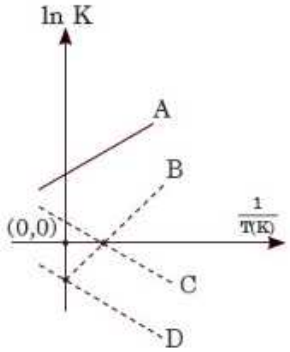
(*a*) 8 (*b*) 12
(*c*) 6 (*d*) 4 *(JEE Main 2017)*

Answers

B35. (*d*) **B36.** (*a*) **B37.** (*a*) **B38.** (*c*) **B39.** (*a*) **B40.** (*c*) **B41.** (*a*) **B42.** (*b*) **B43.** (*a*) **B44.** (*c*) **B45.** (*b*) **B46.** (*d*)

Competition File

B47. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction?



(*a*) A and B (*b*) B and C
(*c*) C and D (*d*) A and D *(JEE Main 2018)*

B48. At 518°C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 torr, was 1.00 torr s^{-1} when 5% had reacted and 0.5 torr s^{-1} when 33% had reacted. The order of the reaction is:

(*a*) 2 (*b*) 3
(*c*) 1 (*d*) 0 *(JEE Main 2018)*

B49. At 500 K, the half life period of a gaseous reaction at an initial pressure of 80 *k*Pa is 350 sec. When the pressure is 40 *k*Pa, the half life period is 175 sec. The order of the reaction is

(*a*) zero (*b*) one
(*c*) two (*d*) three
(*e*) half *(Kerala C.E.T. 2007)*

B50. For the two gaseous reactions, following data are given:

$A \longrightarrow B;\ k_1 = 10^{10}\, e^{-20000/T}$

$C \longrightarrow D;\ k_2 = 10^{12}\, e^{-24606/T}$

The temperature at which k_1 becomes equal to k_2 is

(*a*) 400 K (*b*) 1000 K
(*c*) 800 K (*d*) 1500 K
(*c*) 500 K *(Kerala P.E.T. 2008)*

B51. The activation energies of two reactions are E_1 and E_2 ($E_1 > E_2$). If the temperature of the system is increased from T_1 to T_2, the rate constant of the reaction changes from k_1 to k_1' in the first reaction and k_2 to k_2' in second reaction, predict which of the following expression is correct?

(*a*) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2}$ (*b*) $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$

(*c*) $\frac{k_1'}{k_1} < \frac{k_2'}{k_2}$ (*d*) $\frac{k_1'}{k_1} = \frac{k_2'}{k_2} = 0$

(Kerala C.E.T. 2009)

B52. The activation energy for a reaction at the temperature T K was found to be 2.303 RT J mol^{-1}. The ratio of the rate constant to Arrhenius factor is

(*a*) 10^{-1} (*b*) 10^{-2}
(*c*) 2×10^{-3} (*d*) 2×10^{-2}

(Karnataka CET 2010)

B53. Half lives of a first order and a zero order reactions are same. Then the ratio of the initial rates of first order reaction to that of the zero order reaction is

(*a*) $\frac{1}{0.693}$ (*b*) 2×0.693
(*c*) 0.693 (*d*) $\frac{2}{0.693}$
(*e*) 6.93 *(Kerala PET 2010)*

B54. If the activation energy for the forward reaction is 150 kJ mol^{-1} and that of the reverse reaction is 260 kJ mol^{-1}, what is the enthalpy change for the reaction?

(*a*) 410 kJ mol^{-1} (*b*) –110 kJ mol^{-1}
(*c*) 110 kJ mol^{-1} (*d*) –410 kJ mol^{-1}
(*e*) 90 kJ mol^{-1} *(Kerala PET 2010)*

B55. A first order reaction is 50% complete in 69.3 minutes. Time required for 90% completion for this reaction is

(*a*) 100 minutes (*b*) 230 minutes
(*c*) 2303 minutes (*d*) 125 minutes

(Odisha JEE 2010)

B56. The following data were obtained during the first order decomposition of $2A(g) \longrightarrow B(g) + C(s)$ at a constant volume and at a particular temperature.

S.No.	Time	Total pressure in Pascal
1	At the end of 10 min	300
2	After completion	200

The rate constant in min^{-1} is

(*a*) 0.0693 (*b*) 69.3
(*c*) 6.93 (*d*) 6.93×10^{-4}

(Karnataka CET 2011)

B57. The rate of the reaction A → Products, at the initial concentration of 3.24×10^{-2} M is nine times its rate at another initial concentration of 1.2×10^{-3} M. The order of the reaction is

(*a*) $\frac{1}{2}$ (*b*) $\frac{3}{4}$
(*c*) $\frac{3}{2}$ (*d*) $\frac{2}{3}$
(*e*) $\frac{1}{3}$ *(Kerala PET 2011)*

Answers

B47. (*a*) **B48.** (*a*) **B49.** (*a*) **B50.** (*b*) **B51.** (*b*) **B52.** (*a*) **B53.** (*b*) **B54.** (*b*) **B55.** (*b*) **B56.** (*a*) **B57.** (*d*)

Competition File

B58. A given sample of milk turns sour at room temperature (27°C) in 5 hours. In a refrigerator at –3°C, it can be stored 10 times longer.
The energy of activation for the souring of milk is
(*a*) $2.303 \times 10R$ kJ. mol^{-1} (*b*) 2.303×5 R kJ. mol^{-1}
(*c*) 2.303×3 R kJ. mol^{-1} (*d*) 2.303×2.7 R kJ. mol^{-1}
(Karnataka C.E.T. 2012)

B59. At 300 K, a gaseous reaction : A → B + C was found to follow first order kinetics. Starting with pressure A, the total pressure at the end of 20 minutes was 100 mm of Hg. The total pressure after the completion of the reaction is 180 mm of Hg. The partial pressure of A (in mm of Hg) is
(*a*) 100 (*b*) 90
(*c*) 180 (*d*) 80
(Karnataka C.E.T. 2012)

B60. The half-life for decay of 14C by β-emission is 5730 years. The fraction of 14C decays, in a sample that is 22,920 years old, would be
(*a*) 1/8 (*b*) 1/16
(*c*) 7/8 (*d*) 15/16
(W.B.JEE Engg. 2013)

B61. For a chemical reaction at 27°C, the activation energy is 600 R. The ratio of the rate constants at 327°C to that of at 27°C will be
(*a*) 2 (*b*) 40
(*c*) e (*d*) e^2
(W.B.JEE Engg. 2013)

B62. If 50% of the reactant is converted into a product in a first order reaction in 25 minutes, how much of it would react in 100 minutes ?
(*a*) 93.75% (*b*) 87.5%
(*c*) 75% (*d*) 100%
(Karnataka CET 2013)

B63. The reaction A + B → Products is first order with respect to A and second order with respect to B. When 1.0 mol each of A and B were taken in one litre flask, the initial rate of the reaction is 1.0×10^{-2} mol L^{-1} s^{-1}. The rate of the reaction when 50% of the reactants have been converted into products is
(*a*) 1.00×10^{-3} mol L^{-1} s^{-1} (*b*) 0.05×10^{-2} mol L^{-1} s^{-1}
(*c*) 1.25×10^{-3} mol L^{-1} s^{-1} (*d*) 4.00×10^{-2} mol L^{-1} s^{-1}
(*e*) 2.00×10^{-3} mol L^{-1} s^{-1} *(Kerala P.E.T. 2013)*

B64. A piece of wood from an archaeological sample has 5.0 counts min^{-1} per gram of C-14, while a fresh sample of wood has a count of 15.0 min^{-1} gram^{-1}. If half-life of C-14 is 5770 years, the age of the archaeological sample is
(*a*) 8,500 years (*b*) 9,200 years
(*c*) 10,000 years (*d*) 11,000 years
(W.B. JEE 2014)

B65. Ammonium ion (NH_4^+) reacts with nitrite ion (NO_2^-) in aqueous solution according to the equation:
$NH_4^+{}_{(aq)} + NO_2^-{}_{(aq)} \longrightarrow N_{2(g)} + 2H_2O_{(l)}$
The following initial rates of reaction have been measured for the given reactant concentrations.

Expt. No.	$[NH_4^+]$, (M)	$[NO_2^-]$, (M)	Rate (M/hr)
1	0.010	0.020	0.020
2	0.015	0.020	0.030
3	0.010	0.010	0.005

Which of the following is the rate law for this reaction?
(*a*) rate = $k\,[NH_4^+]\,[NO_2^-]^4$ (*b*) rate = $k\,[NH_4^+]\,[NO_2]$
(*c*) rate = $k\,[NH_4^+]\,[NO_2^-]^2$ (*d*) rate = $k\,[NH_4^+]^2\,[NO_2]$
(*e*) rate = $k\,[NH_4^+]^{1/2}\,[NO_2]^{1/4}$ *(Kerala PET 2014)*

B66. For the reaction A + 2B ⟶ C, the reaction rate is doubled if the concentration of A is doubled. The rate is increased by four times when concentrations of both A and B are increased by four times. The order of the reaction is
(*a*) 3 (*b*) 0
(*c*) 1 (*d*) 2 *(W.B. JEE 2015)*

B67. The relationship between rate constant and half life period of zero order reaction is given by
(*a*) $t_{\frac{1}{2}} = [A]_0\,2k$ (*b*) $t_{\frac{1}{2}} = \frac{0.693}{k}$
(*c*) $t_{\frac{1}{2}} = \frac{[A]_0}{2k}$ (*d*) $t_{\frac{1}{2}} = \frac{2[A]_0}{k}$
(MH-CET 2015)

B68. For the reaction $O_{3(g)} + O_{(g)} \longrightarrow 2O_{2(g)}$, if the rate law expression is, rate = $k[O_3]\,[O]$, the molecularity and order of the reaction are respectively
(*a*) 2 and 2 (*b*) 2 and 1.33
(*c*) 2 and 1 (*d*) 1 and 2 *(MH-CET 2015)*

B69. In the reversible reaction:
$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$, the rate of disappearance of NO_2 is equal to
(*a*) $\frac{2k_1}{k_2}[NO_2]^2$ (*b*) $2k_1[NO_2] - 2k_2[N_2O_4]$
(*c*) $2k_1[NO_2]^2 - 2k_2[N_2O_4]$
(*d*) $(2k_1 - k_2)\,[NO_2]$ *(A.M.U. Engg 2015)*

B70. The reaction takes place in two steps as:
(*i*) $NO_2Cl(g) \xrightarrow{k_1} NO_2(g) + Cl(g)$
(*ii*) $NO_2Cl(g) + Cl(g) \xrightarrow{k_2} NO_2(g) + Cl_2(g)$
Identify the reaction intermediate
(*a*) $NO_2Cl(g)$ (*b*) $NO_2(g)$
(*c*) $Cl_2(g)$ (*d*) $Cl(g)$ *(MH-CET 2016)*

Answers

B58. (*d*) **B59.** (*d*) **B60.** (*d*) **B61.** (*c*) **B62.** (*a*) **B63.** (*c*) **B64.** (*b*) **B65.** (*c*) **B66.** (*c*) **B67.** (*c*)
B68. (*a*) **B69.** (*c*) **B70.** (*d*)

Competition File

B71. The rate constant of the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ at 300 K is 3×10^{-5} s^{-1}. If the rate of the reaction at the same temperature is 2.4×10^{-5} mol dm^{-3} s^{-1}, then the molar concentration of N_2O_5 is
(*a*) 0.4 M (*b*) 0.8 M
(*c*) 0.04 M (*d*) 0.08 M
(*e*) 0.6 M (*Kerala PET 2016*)

B72. In the reaction A → Products, when the concentration of A was reduced from 2.4×10^{-2} M to 1.2×10^{-2} M, the rate decreased 8 times at the same temperature. The order of the reaction is
(*a*) 0 (*b*) 1
(*c*) 2 (*d*) 3
(*e*) 0.5 (*Kerala PET 2016*)

B73. The activation energy of a chemical reaction can be determined by
(*a*) evaluating rate constants at two different temperatures
(*b*) changing the concentration of reactants
(*c*) evaluating the concentration of reactants at two different temperatures
(*d*) evaluating rate constant at standard temperature
(*Karnataka C.E.T. 2016*)

B74. The half-life period of a first order reaction is 60 minutes. What percentage will be left over after 240 minutes?
(*a*) 6.25% (*b*) 4.25%
(*c*) 5% (*d*) 6%(*Karnataka C.E.T. 2016*)

B75. Which of the following statement is incorrect?
(*a*) Molecularity is only applicable for elementary reaction.
(*b*) The rate law for any reaction cannot be determined experimentally.
(*c*) Biomolecular reactions involve simultaneous collision between two species.
(*d*) Complex reactions have fractional order.
(*Karnataka CET 2017*)

B76. Which of the following is not true about a catalyst?
(*a*) Mechanism of the reaction in presence and absence of catalyst could be different.
(*b*) Enthalpy of the reaction does not change with catalysts.
(*c*) Catalyst enhances both forward and backward reaction at equal rate.
(*d*) Catalyst participates in the reaction, but not consumed in the process.
(*e*) Use of catalyst cannot change the order of the reaction. (*Kerala PET 2017*)

B77. What will be the correct unit of rate constant *k* for a reaction whose order is three?
(*a*) $mole^{-1}$ litre sec^{-1} (*b*) $mole^2$ litre sec^{-1}
(*c*) sec^{-1} (*d*) $mole^{-2}$ $litre^2$ sec^{-1}
(*J. K. CET 2018*)

B78. The following equation is the Arrhenius equation, $k = Ae^{-E_a/RT}$, where E_a is the minimum energy molecules must possess in order to react to form a product, *k* is the rate constant, A is the frequency factor, R is the gas constant and T is the Kelvin temperature. Under normal circumstances, the Arrhenius plot is obtained by plotting
(*a*) logarithm of the inverse of rate constant 1/*k*, versus the inverse temperature 1/T
(*b*) logarithm of the rate constant *k*, versus the temperature T
(*c*) logarithm of the rate constant *k*, versus the inverse temperature 1/T
(*d*) logarithm of the inverse of rate constant 1/*k*, versus the temperature T
(*J. K. CET 2018*)

B79. The half-life of C^{14} is 5760 year. For a 200 mg sample of C^{14}, the time taken to change to 25 mg is
(*a*) 11520 years (*b*) 23040 years
(*c*) 5760 years (*d*) 17280 years
(*WB. JEE 2018*)

B80. The temperature coefficient of a reaction is 2. When the temperature is increased from 30°C to 90°C, the rate of reaction is increased by
(*a*) 150 times (*b*) 410 times
(*c*) 72 times (*d*) 64 times
(*Karnataka CET 2018*)

B81. The value of rate constant of pseudo first order reaction
(*a*) depends only on temperature
(*b*) depends on the concentration of reactants present in small amounts
(*c*) depends on the concentration of reactants present in excess
(*d*) is independent of the concentration of reactants.
(*Karnataka CET 2018*)

B82. For the reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the rate of disappearance of O_2 is 2×10^{-4} mol L^{-1} s^{-1}. The rate of appearance of SO_3 is
(*a*) 2×10^{-4} mol L^{-1} s^{-1}
(*b*) 4×10^{-4} mol L^{-1} s^{-1}
(*c*) 1×10^{-1} mol L^{-1} s^{-1}
(*d*) 6×10^{-4} mol L^{-1} s^{-1} (*Karnataka CET 2018*)

Answers

B71. (*b*) **B72.** (*d*) **B73.** (*a*) **B74.** (*a*) **B75.** (*b*) **B76.** (*e*) **B77.** (*d*) **B78.** (*c*) **B79.** (*d*) **B80.** (*d*) **B81.** (*a*) **B82.** (*b*)

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B83. The data given below are for the reaction of A and D_2 to form product at 295 K. Find the correct rate expression for this reaction.

D_2/mol L^{-1}	A/mol L^{-1}	Initial rate/mol L^{-1} s^{-1}
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(*a*) $k[D_2]^1 [A]^2$ (*b*) $k[D_2]^2 [A]^1$
(*c*) $k[D_2]^1 [A]^1$ (*d*) $k[D_2]^2 [A]^2$
(*e*) $k[D_2]^1 [A]^0$ (*Kerala PET 2018*)

B84. Find the unit of the rate constant of a reaction represented with a rate equation, rate = $k[A]^{1/2} [B]^{3/2}$
(*a*) $mol^{-1} L s^{-1}$ (*b*) s^{-1}
(*c*) $mol L^{-1} s^{-1}$ (*d*) $mol^{-2} L^2 s^{-1}$
(*e*) $mol^{-3} L^3 s^{-1}$ (*Kerala PET 2018*)

B85. Under what condition the order of reaction,

$$2HI(g) \xrightarrow{\Delta,\ catalyst} H_2(g) + I_2(g)$$ is zero?

(*a*) At high temperature
(*b*) At high partial pressure of HI
(*c*) At low partial pressure of HI
(*d*) At high partial pressure of I_2
(*e*) At high partial pressure of H_2 (*Kerala PET 2018*)

JEE (Advance) for IIT Entrance

B86. The reaction :

$$X \longrightarrow Product$$

follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M is
(*a*) 1.73×10^{-4} M min^{-1} (*b*) 3.47×10^{-5} M min^{-1}
(*c*) 3.47×10^{-4} M min^{-1} (*d*) 1.73×10^{-5} M min^{-1}.
(*I.I.T. 2004*)

B87. Consider a reaction, $aG + bH \longrightarrow$ Products.
When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when the concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is :
(*a*) 0 (*b*) 1
(*c*) 2 (*d*) 3 (*I.I.T. 2007*)

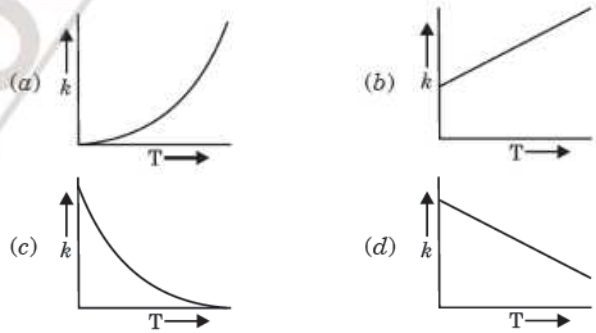
B88. Under the same conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics respectively. Ratio $\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reaction is
(*a*) 0.5 mol^{-1} dm^3 (*b*) 1.0 mol^{-1} dm^{-3}
(*c*) 1.5 mol dm^{-3} (*d*) 2.0 mol^{-1} dm^{-3} (*I.I.T. 2008*)

B89. For a first order reaction, $A \longrightarrow P$, the temperature dependent rate constant (k) was found to follow the equation :

$$\log k = -(2000)/T + 6.0$$

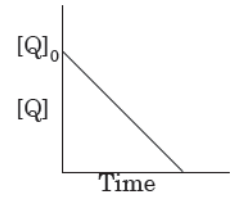
The pre-exponential factor A and the activation energy E_a, respectively are :
(*a*) 1.0×10^6 s^{-1} and 9.2 kJ mol^{-1}
(*b*) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(*c*) 1.0×10^6 s^{-1} and 16.6 kJ mol^{-1}
(*d*) 1.0×10^6 s^{-1} and 38.3 kJ mol^{-1} (*I.I.T. 2009*)

B90. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follow Arrhenius equation is



(*I.I.T. 2010*)

B91. In the reaction, $P + Q \longrightarrow R + S$, the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is



(*a*) 2 (*b*) 3
(*c*) 0 (*d*) 1 (*JEE Advance 2013*)

B92. The initial rate of hydrolysis of methyl acetate (1M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is
(*a*) 1×10^{-4} (*b*) 1×10^{-5}
(*c*) 1×10^{-6} (*d*) 1×10^{-3}
(*JEE Advance 2013*)

B93. For the elementary reaction $M \longrightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is
(*a*) 4 (*b*) 3
(*c*) 2 (*d*) 1 (*JEE Advance 2014*)

Answers

B83. (*a*) **B84.** (*a*) **B85.** (*b*) **B86.** (*c*) **B87.** (*d*) **B88.** (*a*) **B89.** (*d*) **B90.** (*a*) **B91.** (*d*) **B92.** (*a*) **B93.** (*b*)

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C MULTIPLE CHOICE QUESTIONS
with more than one correct answers

C1. Consider the rate law expression for a reaction :

rate = $k[NO_2^-]\ [I^-]\ [H^+]^2$

Which of the following is/are not correct ?

(*a*) When concentration of both NO_2^- and I^- are doubled rate becomes 4 times.

(*b*) When concentration of H^+ is tripled, rate becomes nine times.

(*c*) When concentration of each of H^+, NO_2^- and I^- are tripled, rate becomes nine times.

(*d*) When concentration of NO_2^- is doubled, of I^- is halved and of H^+ is doubled rate becomes 16 times.

C2. For a first order reaction :

(*a*) The degree of dissociation is equal to $1 - e^{-kt}$

(*b*) A plot of reciprocal of concentration of reactant *vs* time gives a straight line.

(*c*) The time taken the completion of 75% of reaction is thrice the $t_{1/2}$ of the reaction.

(*d*) The pre-exponential factor in the Arrhenius equation has the dimensions of time^{-1}.

C3. In acidic medium, the rate of reaction between BrO_3^- and Br^- is given by the expression :

$$-\frac{d[BrO_3]}{dt} = k\,[BrO_3^-]\,[Br^-]\,[H^+]^2$$

which of the following statements are correct ?

(*a*) Rate of reaction is independent of the concentration of acid added.

(*b*) Rate of reaction is affected by change in pH of the solution.

(*c*) Doubling the concentration of H^+ ions increases the reaction rate by 4 times.

(*d*) This is an example of pseudo second order reaction.

C4. The rate law for the reaction :

$$RCl + NaOH \longrightarrow ROH + NaCl$$

is given as : rate = k[RCl].

The rate of this reaction :

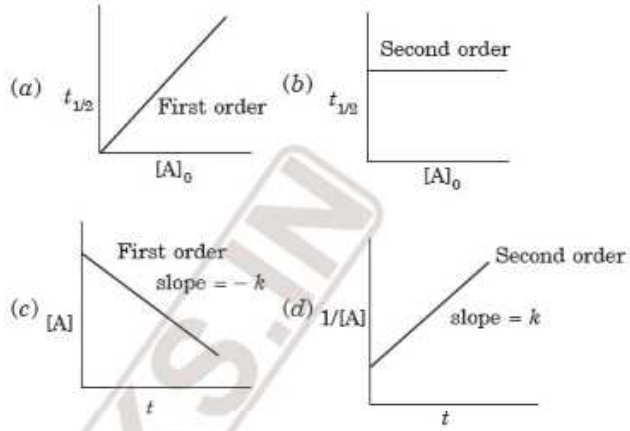
(*a*) is doubled by doubling the concentration of NaOH.

(*b*) is halved by reducing the concentration of RCl by one half.

(*c*) is increased by increasing the temperature of the reaction.

(*d*) is unaffected by change in temperature.

C5. Which of the following plots are not correct ?



C6. For the first order reaction

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$

(*a*) the concentration of the reactant decreases exponentially with time.

(*b*) the half-life of the reaction decreases with increasing temperature.

(*c*) the half-life of the reaction depends on the initial concentration of the reactant.

(*d*) the reaction proceeds to 99.6% completion in eight half-life duration. *(I.I.T. 2011)*

C7. According to the Arrhenius equation,

(*a*) a high activation energy usually implies a fast reaction.

(*b*) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy.

(*c*) higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant.

(*d*) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy. *(JEE Advance 2016)*

C8. Which of the following statements is in accordance with the Arrhenius equation?

(*a*) Rate of a reaction increases with increase in temperature.

(*b*) Rate of reaction does not change with increase in activation energy.

(*c*) Rate constant decreases exponentially with increase in temperature.

(*d*) Rate of a reaction increases with decrease in activation energy. *(Karnataka CET 2017)*

Answers

C1. (*a, b*) **C2.** (*a, d*) **C3.** (*b, c*) **C4.** (*b, c*) **C5.** (*a, b*) **C6.** (*a, b, d*) **C7.** (*b, c, d*) **C8.** (*a, d*)

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C9. In a biomolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are)

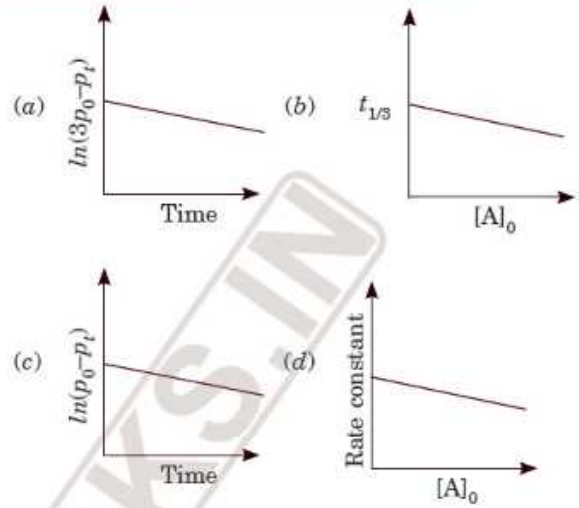
(*a*) experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation

(*b*) the value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(*c*) the activation energy of the reaction is unaffected by the value of steric factor

(*d*) since P = 4.5, the reaction will not proceed unless an effective catalyst is used. *(JEE Advance 2017)*

C10. For a first order reaction $A(g) \longrightarrow 2B(g) + C(g)$ at constant volume and 300 K, the total pressure at the beginning ($t = 0$) and at time t are P_0 and P_t, respectively. Initially, only A is present with concentration $[A]_0$, and $t_{1/3}$ is the time required for the partial pressure of A to reach 1/3rd of its initial value. The correct option(s) is (are) (assume that all these gases behave as ideal gases):



(JEE Advance 2018)

Answers

C9. (*a, c*) **C10.** (*a, d*)

D MULTIPLE CHOICE QUESTIONS

based on the given passage/comprehension

Passage I.

The integrated rate equations can be fitted with kinetic data to determine the order of a reaction. The integrated rate equations for zero, first and second order reactions are :

Zero order : $[A] = -kt + [A]_0$

First order : $\log [A] = -\frac{kt}{2.303} + \log [A]_0$

Second order : $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

These equations can also be used to calculate the half life periods of different reactions, which give the time during which the concentration of a reactant is reduced to half of its initial concentration, *i.e.*, at time $t_{1/2}$; $[A] = [A]_0/2$

Answer the following questions :

D1. The decomposition of nitrogen pentoxide :

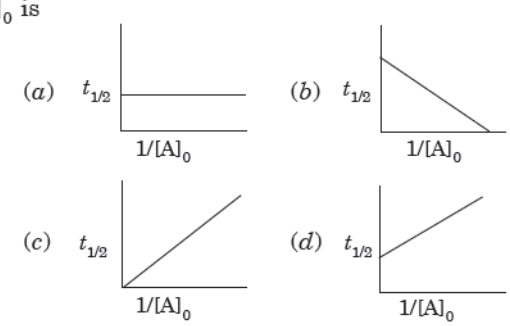
$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

is a first order reaction. The plot of log $[N_2O_5]$ vs time (min) has slope = – 0.01389. The rate constant k is

(*a*) 1.389×10^{-2} min^{-1} (*b*) 3.2×10^{-2} min^{-1}

(*c*) 6.03×10^{-3} min^{-1} (*d*) 71.99 min^{-1}

D2. For a second order reaction, the correct plot of $t_{1/2}$ vs. $1/[A]_0$ is



D3. For a second order reaction, rate at a particular time is x. If the initial concentration is tripled, the rate will become

(*a*) $9x^2$ (*b*) $27x$

(*c*) $9x$ (*d*) $3x$

D4. The rate for the first order reaction is 0.0069 mol L^{-1} min^{-1} and the initial concentration is 0.2 mol L^{-1}. The half life period is

(*a*) 636 s (*b*) 0.635 s

(*c*) 690 s (*d*) 1205 s

D5. The plot of [A] versus t for zero order reaction gives slope

(*a*) $-\frac{k}{2.303}$ (*b*) $\frac{k}{2.303}$

(*c*) $2.303\,k$ (*d*) $-k$

Answers

Passage I. **D1.** (*b*) **D2.** (*c*) **D3.** (*c*) **D4.** (*d*) **D5.** (*d*)

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Passage II.

According to collision theory of chemical reactions, rate of a reaction depends upon collision frequency and fraction of effective collisions. The rate of a reaction generally increases with rise in temperature mainly because of increase in number of effective collisions. Arrhenius proposed a quantitative relation between rate constant and temperature as

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

where E_a is activation energy. It is equal to the difference between threshold energy and average kinetic energy of reacting molecules.

Answer the following questions :

D6. Which of the following plot will be linear ?
(*a*) *ln k* versus T with –ve slope
(*b*) *ln k* versus 1/T with –ve slope
(*c*) *ln k* versus 1/T with +ve slope
(*d*) *k* versus 1/T with –ve slope.

D7. For a first order reaction, the plot of log K versus 1/T gives straight line. The slope of the line has been found to be a -8.95×10^{-3} K. The activation energy for the reaction is
(*a*) 74.4 *k*J mol^{-1} (*b*) – 171.4 *k*J mol^{-1}
(*c*) 171.4 *k*J mol^{-1} (*d*) 20.61 *k*J mol^{-1}

D8. The pre-expotential factor in Arrhenius equation of a second order reaction has the units
(*a*) mol L^{-1} s^{-1} (*b*) s^{-1}
(*c*) L mol^{-1} s^{-1} (*d*) dimensionless

D9. At 27°C in the presence of a catalyst, the activation energy of a reaction is lowered by 10 *k*J mol^{-1}. The ratio of log *k* (catalyst)/*k* (uncatalysed) is
(*a*) 1.741 (*b*) 191.47
(*c*) 0.034 (*d*) 0.0145

D10. The rate of a chemical reaction becomes double for every 10°C rise in temperature. If this generalisation holds for a reaction in the temperature range 290 K to 300 K, what would be the approximate value of E_a for the reaction ?
(*a*) 50 *k*J mol^{-1} (*b*) 25 *k*J mol^{-1}
(*c*) 60 *k*J mol^{-1} (*d*) 40 *k*J mol^{-1}

D11. If activation energy for a reaction is zero and *k* is 1.72×10^5 s^{-1} at 300 K, the rate constant at 310 will be
(*a*) $\frac{310 \times 1.72 \times 10^5}{300}$ (*b*) $\frac{1.72 \times 10^5 \times 300}{310}$
(*c*) 1.72×10^5 (*d*) $\frac{1.72 \times 10^5 \times 10}{300 \times 310}$

D12. If *x* is the fraction of molecules having energy greater than activation energy. E_a then
(*a*) $x = -\frac{E_a}{RT}$ (*b*) $x = e^{E_a/RT}$
(*c*) $\log x = -\frac{E_a}{2.303\,RT}$ (*d*) $x = 10^{-E_a/RT}$

Answers

Passage II. **D6.** (*b*) **D7.** (*c*) **D8.** (*c*) **D9.** (*a*) **D10.** (*a*) **D11.** (*c*) **D12.** (*c*)

Assertion Reason Type Questions

The questions given below consist of an Assertion and Reason. Use the following key to choose the appropriate answer.
(*a*) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
(*b*) If both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
(*c*) If assertion is CORRECT but, reason is INCORRECT.
(*d*) If assertion is INCORRECT but, reason is CORRECT.
(*e*) If both assertion and reason are INCORRECT.

1. Assertion : Rate of reaction increases with increase in temperature.
Reason : Number of collisions increases with increase in temperature.

2. Assertion : Reactions of higher order are rare.
Reason : The chances of simultaneous multimolecular collisions are extremely small.

3. Assertion : The half life period for a first order reaction is independent of initial concentration of reactants.
Reason : For first order reaction, $t_{1/2} = \frac{0.693}{k}$

4. Assertion : For the first order reaction the units of rate constant are time^{-1}.
Reason : The rate of first order reaction remains constant throughout.

5. Assertion : For a second order reaction, graph of [A] vs. *t* is a straight line.
Reason : For second order reaction, $[A] = kt + \frac{1}{[A]_0}$

6. Assertion : For complex reactions molecularity and order are not same.
Reason : Order of a reaction may be zero.

7. Assertion : A catalyst increases the rate of a reaction.
Reason : A catalyst forms an activated complex of lower potential energy.

Answers

1. (*b*) **2.** (*a*) **3.** (*a*) **4.** (*c*) **5.** (*e*)

8. Assertion : The molecularity of the reaction $H_2 + Br_2 \longrightarrow 2HBr$ is 2.

Reason : Order of the reaction is 3/2.

(A.I.I.M.S. 2004)

9. Assertion : For the reaction : RCl + NaOH $(aq) \longrightarrow$ ROH + NaCl, the rate of reaction is reduced to half when the concentration of RCl is reduced to half.

Reason : The rate of reactions is represented by k[RCl] *i.e.*, it is a first order reaction.

10. Assertion : Photochemical reactions always occur in the presence of light.

Reason : Photochemical reactions even with, ΔG = +ve occur.

Answers

6. (*b*) **7.** (*e*) **8.** (*b*) **9.** (*c*) **10.** (*b*)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

	p	q	r	s
A	(p)	(q)	(r)	(s)
B	(p)	(q)	(r)	(s)
C	(p)	(q)	(r)	(s)
D	(p)	(q)	(r)	(s)

If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the units in Column I with the type of reaction in Column II

Column I	Column II
(A) s^{-1}	(*p*) First order reaction
(B) $L^2\ mol^{-2}\ s^{-1}$	(*q*) Second order reaction
(C) $L\ mol^{-1}\ s^{-1}$	(*r*) Third order reaction
(D) $mol\ L^{-1}\ s^{-1}$	(*s*) Zero order reaction

2. Match th e type of reaction in Column I with the property given in Column II.

Column I	Column II
(A) Zero order reaction $A \longrightarrow$ Products	(*p*) Plot of log [A] vs *t* is a linear plot.
(B) First order reaction $A \longrightarrow$ Products	(*q*) Units of *k* are $L\ mol^{-1}s^{-1}$
(C) Second order reaction $A + B \longrightarrow$ Products	(*r*) Doubling conc. of A, rate becomes twice.
(D) Second order reaction $2A \longrightarrow$ Products	(*s*) $t_{1/2} = \frac{[A]_0}{2k}$

Answers

(1) : (A) – (*s*) (B) – (*p*), (*s*) (C) – (*q*), (*s*) (D) – (*r*)

(2) : (A) – (*r*), (*s*) (B) – (*r*) (C) – (*q*) (D) – (*p*)

Integer Type or Numerical Value Type Questions

Integer Type: The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. The concentration of R in the reaction R $\longrightarrow$ P was measured as a function of time and the following data is obtained :

[R] (molar)	1.0	0.75	0.40	0.10
t (min)	0.0	0.05	0.12	0.18

The order of the reaction is .....

(I.I.T. 2010)

2. For a reaction : $2A \longrightarrow A_2$ the rate of reaction becomes 27 times when the concentration of A changes from *x* to 3*x*. The order of reaction is .....

3. The rate of a reaction is expressed as : 3.65×10^{-3} $atm^{-1}\ s^{-1}$. The order of reaction

4. The rate of a reaction of Br^- ions with BrO_3^- ions in the acidic medium is

rate = $k[Br^-][BrO_3^-][H^+]^2$

The order of reaction is .....

5. The order of the following reaction is

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

Answers

1. 0 **2.** 3 **3.** 2 **4.** 4 **5.** 1

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6. An organic compound undergoes first-order decomposition. The time taken for decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of

$\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? (take $\log_{10} 2 = 0.3$) .....

(*I.I.T.J.E.E. 2012*)

7. In dilute aqueous H_2SO_4, the complex diaquodioxalato ferrate (II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is .....

(*JEE Advance 2015*)

Numerical Value Type. Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place).

8. Consider the following reversible reaction,

$$A_{(g)} + B_{(g)} \rightleftharpoons AB_{(g)}$$

The activation energy of the backward reaction exceeds, that of the forward reaction by 2RT (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of $\Delta G°$ (in J mol^{-1}) for the reaction at 300 K is .....

(Given : ln (2) = 0.7, RT = 2500 J mol^{-1} at 300 K and G is the Gibbs energy) (*JEE Advance 2018*)

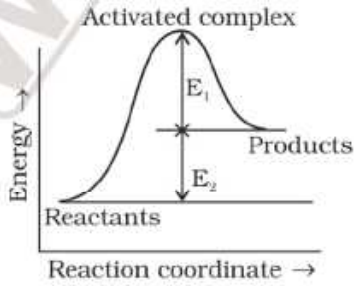
Answers

6. 9 **7.** 8 **8.** 8500

NCERT Exemplar Problems Objective Questions

Multiple Choice Questions (Type-I)

1. The role of a catalyst is to change _____.
   (*a*) gibbs energy of reaction.
   (*b*) enthalpy of reaction.
   (*c*) activation energy of reaction.
   (*d*) equilibrium constant.
2. In the presence of a catalyst, the heat evolved or absorbed during the reaction _____.
   (*a*) increases. (*b*) decreases.
   (*c*) remains unchanged. (*d*) may increase or decrease.
3. Activation energy of a chemical reaction can be determined by _____.
   (*a*) determining the rate constant at standard temperature.
   (*b*) determining the rate constants at two temperatures.
   (*c*) determining probability of collision.
   (*d*) using catalyst.
4. Consider the following figure and mark the correct option.



   (*a*) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant.
   (*b*) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant.
   (*c*) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product.
   (*d*) Activation energy of backward reaction is E_1 and product is more stable than reactant.
5. Consider a first order gas phase decomposition reaction given below :

$$A(g) \longrightarrow B(g) + C(g)$$

The initial pressure of the system before decomposition of A was p_i. After lapse of time 't', total pressure of the system increased by x units and became 'p_t'. The rate constant k for the reaction is given as _____.

(*a*) $\frac{2.303}{t} \log \frac{p_i}{p_i - x}$

(*b*) $\frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$

(*c*) $\frac{2.303}{t} \log \frac{p_i}{p_i - p_t}$

(*d*) $\frac{2.303}{t} \log \frac{p_i}{p_i x}$

Answers

1. (*c*) **2.** (*c*) **3.** (*b*) **4.** (*a*) **5.** (*b*)

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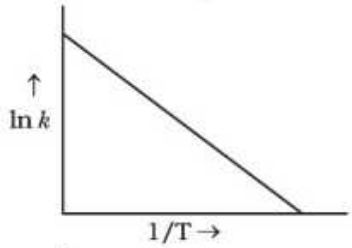
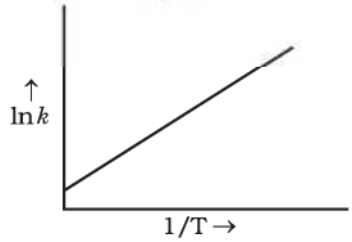
6. According to Arrhenius equation rate constant k is equal to $A\ e^{-Ea/RT}$. Which of the following options represents the graph of $\ln k$ vs $\frac{1}{T}$?

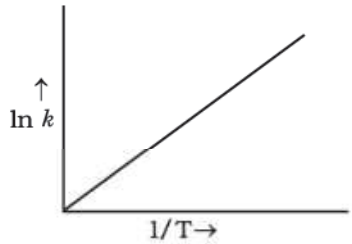
(*a*)



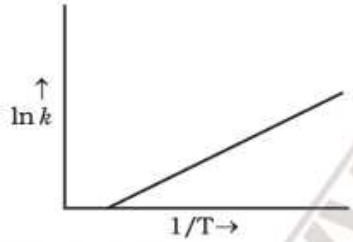
(*b*)



(*c*)



(*d*)



7. Consider the Arrhenius equation given below and mark the correct option. $k = A\ e^{-Ea/RT}$

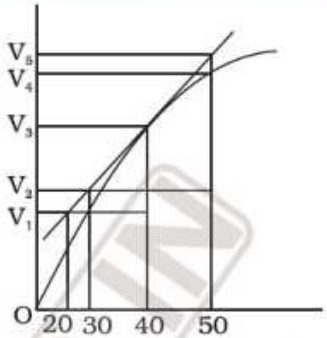
(*a*) Rate constant increases exponentially with increasing activation energy and decreasing temperature.

(*b*) Rate constant decreases exponentially with increasing activation energy and decreasing temperature.

(*c*) Rate constant increases exponentially with decreasing activation energy and decreasing temperature.

(*d*) Rate constant increases exponentially with decreasing activation energy and increasing temperature.

8. A graph of volume of hydrogen released vs time for the reaction between zinc and dil.HCl is given in figure. On the basis of this mark the correct option.



(*a*) Average rate upto 40 seconds $\frac{V_3 - V_2}{40}$

(*b*) Average rate upto 40 seconds is $\frac{V_3 - V_2}{40 - 30}$

(*c*) Average rate upto 40 seconds is $\frac{V_3}{40}$

(*d*) Average rate upto 40 seconds is $\frac{V_3 - V_1}{40 - 20}$

9. Which of the following statements is not correct about order of a reaction ?

(*a*) The order of a reaction can be a fractional number.

(*b*) Order of a reaction is experimentally determined quantity.

(*c*) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction.

(*d*) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression.

10. Consider the graph given in previous question. Which of the following options does not show instantaneous rate of reaction at 40th second ?

(*a*) $\frac{V_5 - V_2}{50 - 30}$ (*b*) $\frac{V_4 - V_2}{50 - 30}$

(*c*) $\frac{V_3 - V_2}{40 - 30}$ (*d*) $\frac{V_3 - V_1}{40 - 20}$

11. Which of the following statements is correct?

(*a*) The rate of a reaction decreases with passage of time as the concentration of reactants decreases.

(*b*) The rate of a reaction is same at any time during the reaction.

(*c*) The rate of a reaction is independent of temperature change.

(*d*) The rate of a reaction decreases with increase in concentration of reactant(s).

Answers

6. (*a*) **7.** (*d*) **8.** (*c*) **9.** (*c*) **10.** (*b*) **11.** (*a*)

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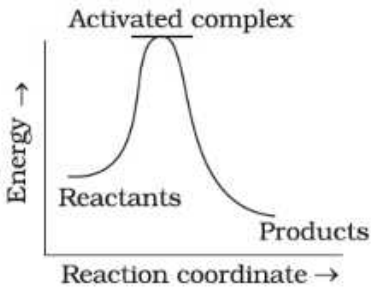
12. Which of the following expressions is correct for the rate of reaction given below?

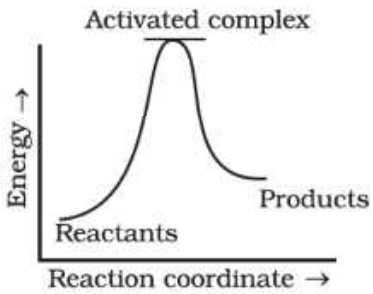
$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

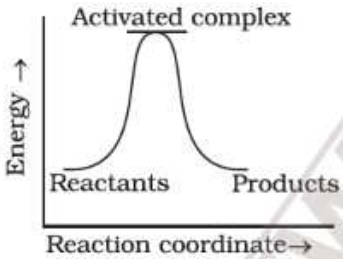
(*a*) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ (*b*) $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{t}$

(*c*) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ (*d*) $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$

13. Which of the following graphs represents exothermic reaction?

(*i*)


(*ii*)


(*iii*)


(*a*) (*i*) only (*b*) (*ii*) only
(*c*) (*iii*) only (*d*) (*i*) and (*ii*)

14. Rate law for the reaction A + 2B ⟶ C is found to be

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

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be _____.

(*a*) the same (*b*) doubled
(*c*) quadrupled (*d*) halved

15. Which of the following statements is incorrect about the collision theory of chemical reaction?

(*a*) It considers reacting molecules or atoms to be hard spheres and ignores their structural features.
(*b*) Number of effective collisions determines the rate of reaction.
(*c*) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation.
(*d*) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

16. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?

(*a*) 1.26×10^{15} s (*b*) 2.52×10^{14} s
(*c*) 2.52×10^{28} s (*d*) infinite

17. Compounds 'A' and 'B' react according to the following chemical equation.

$$A(g) + 2B(g) \longrightarrow 2C(g)$$

Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.

Experiment	Initial concentration of [A]/mol L^{-1}	Initial concentration of [B]/mol L^{-1}	Initial rate of formation of [C]/mol $L^{-1}s^{-1}$
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

(*a*) Rate = $k[A]^2$ [B] (*b*) Rate = k[A] $[B]^2$
(*c*) Rate = k[A] [B] (*d*) Rate = $k[A]^2$ $[B]^0$

18. Which of the following statement is not correct for the catalyst?

(*a*) It catalyses the forward and backward reaction to the same extent.
(*b*) It alters G of the reaction.
(*c*) It is a substance that does not change the equilibrium constant of a reaction.
(*d*) It provides an alternate mechanism by reducing activation energy between reactants and products.

19. The value of rate constant of a pseudo first order reaction _____.

(*a*) depends on the concentration of reactants present in small amount.
(*b*) depends on the concentration of reactants present in excess.
(*c*) is independent of the concentration of reactants.
(*d*) depends only on temperature.

Answers

12. (*c*) **13.** (*a*) **14.** (*b*) **15.** (*c*) **16.** (*d*) **17.** (*b*) **18.** (*b*) **19.** (*b*)

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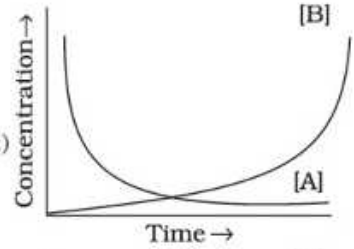
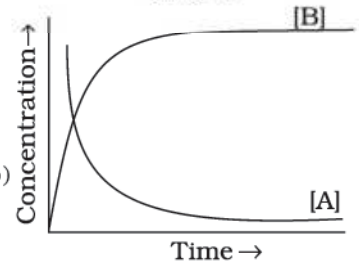
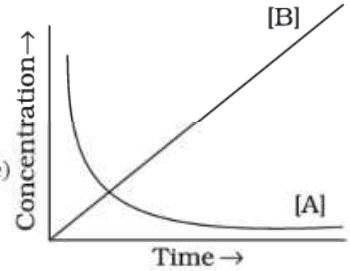
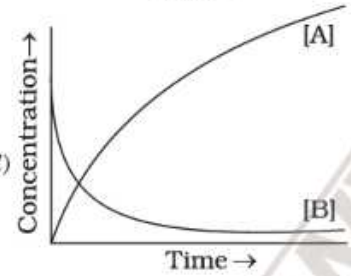
20. Consider the reaction A ⇌ B. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?

(*a*)


(*b*)


(*c*)


(*d*)


Multiple Choice Questions (Type-II)

Note : *In the following questions two or more options may be correct.*

21. Rate law cannot be determined from balanced chemical equation if _____.
(*a*) reverse reaction is involved.
(*b*) it is an elementary reaction.
(*c*) it is a sequence of elementary reactions.
(*d*) any of the reactants is in excess.

22. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?
(*a*) Order is same as molecularity.
(*b*) Order is less than the molecularity.
(*c*) Order is greater than the molecularity.
(*d*) Molecularity can never be zero.

23. In any unimolecular reaction _____.
(*a*) only one reacting species is involved in the rate determining step.
(*b*) the order and the molecularity of slowest step are equal to one.
(*c*) the molecularity of the reaction is one and order is zero.
(*d*) both molecularity and order of the reaction are one.

24. For a complex reaction _____.
(*a*) order of overall reaction is same as molecularity of the slowest step.
(*b*) order of overall reaction is less than the molecularity of the slowest step.
(*c*) order of overall reaction is greater than molecularity of the slowest step.
(*d*) molecularity of the slowest step is never zero or non integer.

25. At high pressure the following reaction is zero order.

$$2NH_3(g) \xrightarrow[\text{Platinum catalyst}]{1130K} N_2(g) + 3H_2(g)$$

Which of the following options are correct for this reaction?
(*a*) Rate of reaction = Rate constant
(*b*) Rate of the reaction depends on concentration of ammonia.
(*c*) Rate of decomposition of ammonia will remain constant until ammonia disappears completely.
(*d*) Further increase in pressure will change the rate of reaction.

26. During decomposition of an activated complex
(*a*) energy is always released
(*b*) energy is always absorbed
(*c*) energy does not change
(*d*) reactants may be formed

27. According to Maxwell Boltzmann distribution of energy, _____.
(*a*) the fraction of molecules with most probable kinetic energy decreases at higher temperatures.
(*b*) the fraction of molecules with most probable kinetic energy increases at higher temperatures.
(*c*) most probable kinetic energy increases at higher temperatures.
(*d*) most probable kinetic energy decreases at higher temperatures.

28. In the graph showing Maxwell Boltzmann distribution of energy, _____.
(*a*) area under the curve must not change with increase in temperature.
(*b*) area under the curve increases with increase in temperature.
(*c*) area under the curve decreases with increase in temperature.
(*d*) with increase in temperature curve broadens and shifts to the right hand side.

Answers

20. (*b*) **21.** (*a, c, d*) **22.** (*a, d*) **23.** (*a, b*) **24.** (*a, d*) **25.** (*a, c, d*) **26.** (*a, d*) **27.** (*a, c*) **28.** (*a, d*)

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29. Which of the following statements are in accordance with the Arrhenius equation?

(*a*) Rate of a reaction increases with increase in temperature.

(*b*) Rate of a reaction increases with decrease in activation energy.

(*c*) Rate constant decreases exponentially with increase in temperature.

(*d*) Rate of reaction decreases with decrease in activation energy.

30. Mark the incorrect statements.

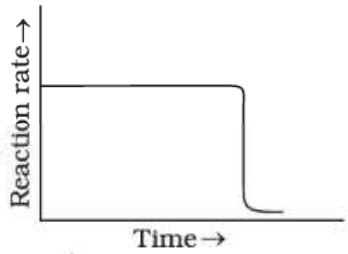
(*a*) Catalyst provides an alternative pathway to reaction mechanism.

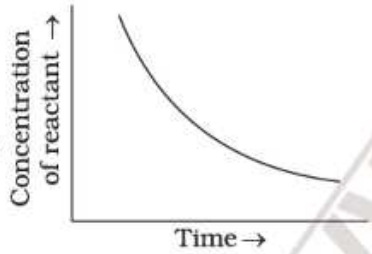
(*b*) Catalyst raises the activation energy.

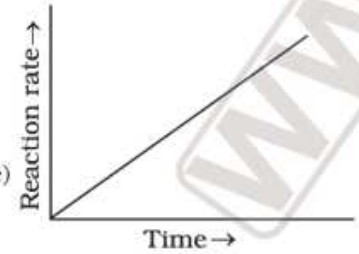
(*c*) Catalyst lowers the activation energy.

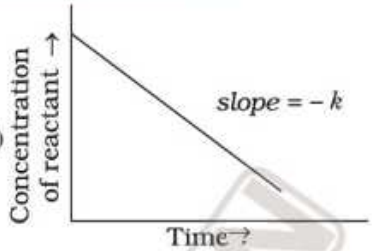
(*d*) Catalyst alters enthalpy change of the reaction.

31. Which of the following graphs is correct for a zero order reaction?

(*a*)


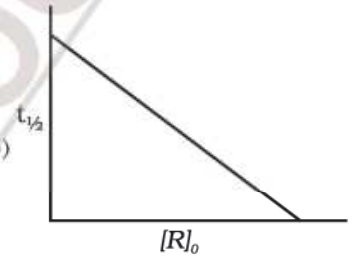
(*b*)


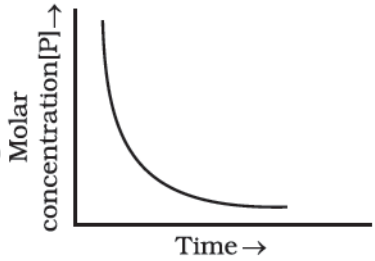
(*c*)


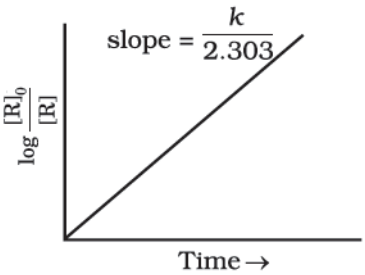
(*d*)


32. Which of the following graphs is correct for a first order reaction?

(*a*)

(*b*)


(*c*)


(*d*)


Answers

29. (*a, b*) **30.** (*b, d*) **31.** (*a, d*) **32.** (*a, d*)

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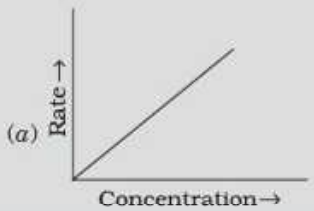
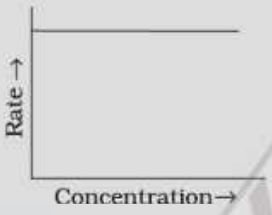
Matching Type Questions

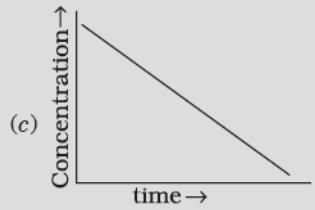
Note : *In the following questions match the items of Column I with appropriate item given in Column II.*

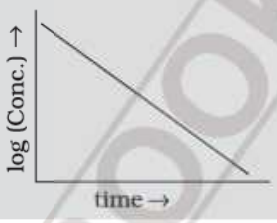
33. Match the graph given in Column I with the order of reaction given in Column II.
More than one item in Column I may link to the same item of Column II.

Column I









Column II

(*i*) Ist order

(*ii*) Zero order

34. Match the statements given in Column I and Column II.

Column I	Column II
(*a*) Catalyst alters the rate of reaction	(*i*) cannot be fraction or zero
(*b*) Molecularity	(*ii*) proper orientation is not there always
(*c*) Second half life of first order reaction	(*iii*) by lowering the activation energy
(*d*) $e^{-Ea/RT}$	(*iv*) is same as the first
(*e*) Energetically favourable reactions are sometimes slow	(*v*) total probability is one
(*f*) Area under the Maxwell Boltzman curve is constant	(*vi*) refers to the fraction of molecules with energy equal to or greater than activation energy

35. Match the items of Column I and Column II.

Column I	Column II
(*a*) Diamond	(*i*) short interval of time
(*b*) Instantaneous rate	(*ii*) ordinarily rate of conversion is imperceptible
(*c*) Average rate	(*iii*) long duration of time

36. Match the items of Column I and Column II.

Column I	Column II
(*a*) Mathematical expression for rate of reaction	(*i*) rate constant
(*b*) Rate of reaction for zero order is equal to	(*ii*) rate law reaction
(*c*) Units of rate constant for zero order reaction is same as that of	(*iii*) order of slowest step
(*d*) Order of a complex reaction is determined by	(*iv*) rate of a reaction

Answers

33. (*a*) — (*i*) ; (*b*) — (*ii*) ; (*c*) — (*ii*) ; (*d*) — (*i*)
34. (*a*) — (*iii*) ; (*b*) — (*i*) ; (*c*) — (*iv*) ; (*d*) — (*vi*) ; (*e*) — (*ii*) ; (*f*) — (*v*)
35. (*a*) — (*ii*) ; (*b*) — (*i*) ; (*c*) — (*iii*)
36. (*a*) — (*ii*) ; (*b*) — (*i*) ; (*c*) — (*iv*) ; (*d*) — (*iii*)

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Assertion and Reason Type Questions

Note: *In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.*

(*a*) Both **assertion** and **reason** are correct and the **reason** is correct explanation of **assertion**.
(*b*) Both **assertion** and **reason** are correct but **reason** does not explain **assertion**.
(*c*) **Assertion** is correct but **reason** is incorrect.
(*d*) Both **assertion** and **reason** are incorrect.
(*e*) **Assertion** is incorrect but **reason** is correct.

37. Assertion : Order of the reaction can be zero or fractional.
Reason : We cannot determine order from balanced chemical equation.

38. Assertion : Order and molecularity are same.
Reason : Order is determined experimentally and molecularity is the sum of the stoichiometric coefficient of rate determining elementary step.

39. Assertion : The enthalpy of reaction remains constant in the presence of a catalyst.
Reason : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

40. Assertion : All collision of reactant molecules lead to product formation.
Reason : Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

41. Assertion : Rate constants determined from Arrhenius equation are fairly accurate for simple as well as complex molecules.
Reason : Reactant molecules undergo chemical change irrespective of their orientation during collision.

Answers

37. (*b*) **38.** (*e*) **39.** (*a*) **40.** (*e*) **41.** (*c*)

Hints & Explanations for *Difficult Objective Type Questions*

A. *mcq with only one correct answer*

A1. (*b*) : The rate of appearance of C is double the rate of disapperance of B; is correct.

A2. (*c*) : Rate of disappearance of N_2O_4

$$= \frac{\Delta[N_2O_4]}{\Delta t} = \frac{0.50 - 0.32}{30}$$

$$= 0.006 \text{ atm min}^{-1}$$

Rate of appearance of NO_2

= Twice rate of disappearance of N_2O_4

$2 \times 0.006 = 0.012$ atm min^{-1}

A3. (*c*) : mol L^{-1} s^{-1} = k mol L^{-1}

∴ units of k is **s^{-1}.**

A4. (*b*) : Rate = k[A]

1.8×10^{-3} mol L^{-1} min^{-1} = k (0.3 mol L^{-1})

$$\therefore \quad k = \frac{1.8 \times 10^{-3}}{0.3} = 6 \times 10^{-3} \text{ min}^{-1} = \frac{6 \times 10^{-3}}{60}$$

$$= \mathbf{1 \times 10^{-4}\ s^{-1}}.$$

A5. (*d*) : The units of k correspond to third order reaction.

A6. (*b*) : On increasing the volume to a twice value, the concentration of each species is reduced by a factor of 2. Therefore,

$$\text{Rate}_1 = k[NO]^2[O_2]$$

$$\text{Rate}_2 = k\left(\frac{[NO]}{2}\right)^2\left(\frac{[O_2]}{2}\right)$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \mathbf{\frac{1}{8}}.$$

A7. (*b*) : Rate = $k[N_2O_5]$

$1.22 \times 10^{-4} = 3.4 \times 10^{-5}[N_2O_5]$

$$\therefore [N_2O_5] = \frac{1.22 \times 10^{-4}}{3.4 \times 10^{-5}} = \mathbf{3.6.}$$

A8. (*a*) : Rate = $k[N_2O_5]$ = $6.2 \times 10^{-4} \times 1.25$

= 7.75×10^{-4} mol L^{-1} s^{-1}

A9. (*a*) : $k = \frac{0.693}{69.3 \text{ s}}$ = **0.01 s^{-1}** or 10^{-2} s^{-1}

A10. (*d*) : Half life period of a first order reaction is independent of the initial concentration of reactants.

A12. (*c*) : Inspection of table shows that by making the conc. of A three times (keeping B constant) rate becomes nine times *i.e.,* Rate ∝ $[A]^2$

By doubling conc. of B (keeping A constant) rate remains same *i.e.,* Rate ∝ $[B]^0$

∴ **Rate = $k[A]^2$.**

A13. (*a*) : Rate = k [A]

$$0.69 \times 10^{-2} = k\ (0.2) \therefore \quad k = \frac{0.69 \times 10^{-2}}{0.2}$$

$$= 3.45 \times 10^{-2} \text{ min}^{-1}$$

$$= \frac{3.45 \times 10^{-2}}{60}$$

$$= 5.75 \times 10^{-4} \text{ s}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.75 \times 10^{-4}} = \mathbf{1205\ s.}$$

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A15. (*b*) : Inspection of table shows that

Rate = k[A] [B]^2 ∴ Order = **3.**

A16. (*b*) : $(1.5)^n = 1.837$

$$n = \frac{\log 1.837}{\log 1.5} = \mathbf{1.5.}$$

A19. (*b*) : $2N_2O_5(g) \longrightarrow 4NO_2 + O_2(g)$

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

$$\text{or Rate} = -\frac{d[N_2O_5]}{dt} = 2k[N_2O_5]$$

For $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

$$-\frac{d[N_2O_5]}{dt} = k'[N_2O_5]$$

$$\text{or Rate} = -\frac{d[N_2O_5]}{dt} = k'[N_2O_5]$$

Since rate must be same, $k' = \mathbf{2k}$.

A23. (*c*) : Rate = $k[A]^2 = x$

If conc. is tripled *i.e.*, A′ = [3A]

Rate′ = $k[3A]^2$ = k.9[A] = x'

∴ $\frac{x'}{x}$ = **9** *i.e.*, becomes nine times (9x).

A24. (*b*) : For a zero order reaction :

$[A] = -k_0t + [A]_0$

∴ Plot of [A] vs. t gives slope = $\mathbf{-k_0}$.

A25. (*a*) : $r_1 = k(a)^{3/2}(b)^{-1/2}$

$r_2 = k(4a)^{3/2}(4b)^{-1/2}$

$\frac{r_2}{r_1} = (4)^{3/2}(4)^{-1/2} = \mathbf{4.}$

A26. (*c*) : Rate = k[A]

$2 = k[4A]^n$ *i.e.*, $4^n = 2$ or $n = \frac{1}{2}$

A28. (*b*) : For a first order reaction, time required to 75% complete is twice the time required to 50% complete.

A29. (*a*) : The fraction of A reacted in each case is same

i.e., $\frac{0.6}{0.8} = \frac{3}{4}$ and $\frac{0.675}{0.90} = \frac{3}{4}$

∴ **Time taken is same.**

A30. (*c*) : $t_{90\%} = \frac{2.303}{k}\log\frac{a}{a-0.9a} = \frac{2.303}{k}\log 10 = \frac{2.303}{k}$

$$t_{1/2} = \frac{2.303}{k}\log\frac{a}{a-0.5a} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{2.303 \times 0.3010}{k}$$

$$\therefore \frac{t_{90\%}}{t_{1/2}} = \frac{1}{0.3010} = 3.3 \quad \therefore t_{90\%} = \mathbf{3.3}t_{1/2}.$$

A31. (*c*) : Earlier rate, rate= $k\,a^nb^m$

$$\text{New rate, rate}' = k(2a)^n\left(\frac{b}{2}\right)^m$$

$$\frac{\text{rate}'}{\text{rate}} = \frac{2^n a^n b^m 2^{-m}}{a^n b^m}$$

$$= 2^n.2^{-m} = \mathbf{2^{n-m}}$$

A32. (*c*) : $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$

$$= \frac{2.303}{2\times10^4}\log\frac{800}{50}$$

or $k = \mathbf{1.38 \times 10^{-4}\ sec^{-1}}$.

A33. (*a*) : Rate = k[C] or $k = \frac{\text{Rate}}{[C]}$

$$k = \frac{1.5\times10^{-2}}{0.5} = 3.0\times10^{-2}$$

$$t_{1/2} = \frac{0.693}{3\times10^{-2}} = \mathbf{23.1\ min.}$$

A37. (*c*) : Rate of reaction $= -\frac{1}{2}\frac{d[NO_2]}{dt}$

$$= k_1[NO_2]^2 - k_2[N_2O_4]$$

Rate of disappearance of NO_2

$$-\frac{d[NO_2]}{dt} = \mathbf{2k_1[NO_2]^2 - 2k_2[N_2O_4]}.$$

A38. (*c*) : Slope = $-E_a = -10.7\times10^3$ R

∴ $E_a = 10.7\times10^3\times8.314 = 88.9\times10^3$

$= \mathbf{88.9\ kJ\ mol^{-1}}$.

A39.(*c*) :

$$k_1 = A_1e^{-E_{a_1}/RT}$$

$$k_2 = A_2e^{-E_{a_2}/RT}$$

$$\frac{k_1}{k_2} = \left(\frac{A_1}{A_2}\right)e^{\frac{-E_{a_1}+E_{a_2}}{RT}}$$

Now, $\frac{A_1}{A_2}$ = constant and $E_{a_2} = E_{a_1}$

$$\frac{k_1}{k_2} = A\,e^{\frac{-E_{a_1}+2E_{a_1}}{RT}}$$

or $\frac{k_1}{k_2} = A\,e^{E_{a_1}/RT}$ or $k_1 = \mathbf{Ak_2e^{E_{a_1}/RT}}$

A40. (*d*) : **% of formation of B** $= \frac{k_1}{k_1+k_2}\times100$

$$= \frac{1.26\times10^{-4}}{1.26\times10^{-4}+3.8\times10^{-5}}\times100$$

$$= \frac{1.26\times10^{-4}}{(1.26+0.38)\times10^{-4}}\times100$$

$= \mathbf{76.83\%}$

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A41. (*a*) : $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$\log 3 = \frac{E_a}{2.303\times 8.3}\times\left[\frac{1}{273} - \frac{1}{313}\right]$$

$$E_a = \frac{2.303\times 8.3\times 273\times 313}{40}\log 3$$

A42. (*b*) : $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$\log\frac{k_2}{k_1} = \frac{56.2\times 10^3}{2.303\times 8}\left[\frac{1}{300} - \frac{1}{305}\right]$$

$$\log\frac{k_2}{k_1} = \frac{56.2\times 10^3}{2.303\times 8}\left(\frac{5}{300\times 305}\right) = 0.167$$

$$\therefore \quad \frac{k_2}{k_1} = 1.47$$

A43. (*c*) : For exothermic reaction,

E_a (backward) = E_a (forward) + ΔH (magnitude)

= 17 + 40 = 57 kJ

B. mcq from Competitive Examinations

B1. (*a*) :

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

Here $[A] = [A]_0 - \frac{60}{100}[A]_0 = 0.4\,[A]_0$

$$\therefore \quad k = \frac{2.303}{60}\log\frac{[A]_0}{0.4[A]_0} = \frac{2.303}{60}\log\frac{10}{4} = \frac{2.303}{60}\times 0.4 = 0.0153$$

Now $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0153} = 45.29 \approx 45$ min.

B2. (*d*) : In expt (1) and (2) rate does not depend on $[Br_2]$.

$\therefore$ Rate expression does not include $[Br_2]$

B3. (*c*) :

$$k_1 = 10^{16}e^{-2000/T}$$
$$k_2 = 10^{15}e^{-1000/T}$$

When $k_1 = k_2$

$$10^{16}e^{-2000/T} = 10^{15}e^{-1000/T}$$
$$10^{16-15} = e^{(-1000+2000)/T}$$
$$10 = e^{1000/T}$$

or $\frac{1000}{T} = 2.303\log 10$

or $T = \frac{1000}{2.303}$ K

B4. (*a*) :

$$\text{Rate} = k[A]^m[B]^n \quad ...(i)$$
$$2\,\text{Rate} = k[2A]^m[B]^n \quad ...(ii)$$
$$8\,\text{Rate} = k[2A]^m[2B]^n \quad ...(iii)$$

From (*i*), (*ii*) and (*iii*)

$m = 1, n = 2$

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

B5. (*b*) : $t_{1/2} = \frac{0.693}{k}$

or $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386} = 0.5\times 10^{-3}\,s^{-1}$

B6. (*d*) :

$$-\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt} = \frac{1}{2}(2\times 10^{-4})\,\text{mol L}^{-1}\text{s}^{-1}$$

$$\therefore \quad \frac{-d[H_2]}{dt} = \frac{3}{2}\times 2\times 10^{-4} = 3\times 10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$$

B7. (*d*) :

$$-\frac{1}{5}\frac{d[Br]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt}$$

or $\frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$

B8. (*b*): Let order w.r.t. A be *a* and order w.r.t. B be *b*

Rate law is Rate = $k[A]^a[B]^b$

Dividing (III) by (II)

$$\frac{(0.3)^a(0.4)^b}{(0.3)^a(0.2)^b} = \frac{2.88\times 10^{-1}}{7.2\times 10^{-2}}$$

$$2^b = 4$$

or $2^b = 2^2$

$\therefore \quad b = 2$

Dividing (IV) by (I)

$$\frac{(0.4)^a(0.1)^b}{(0.1)^a(0.1)^b} = \frac{2.40\times 10^{-2}}{6.01\times 10^{-3}}$$

$$4^a = 4$$

or $4^a = 4^1$

$\therefore \quad a = 1$

Rate law = $k[A][B]^2$

B9. (*d*) : $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$

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

$$\frac{d[NO_2]}{dt} = -\frac{2d[N_2O_5]}{dt} = 2\times 6.25\times 10^{-3} = 1.25\times 10^{-2}\,\text{mol L}^{-1}\,\text{s}^{-1}$$

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$$\frac{d[O_2]}{dt} = -\frac{1}{2}\frac{[N_2O_5]}{dt} = \frac{1}{2}\times 6.25\times 10^{-3}$$

$$= 3.125 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

B10. (*d*) : Let rate $= [A]^p [B]^q = r$ ...(*i*)

rate $= [A]^p [2B]^q = 2r$ ...(*ii*)

Dividing eq. (*ii*) by (*i*)

$2^q = 2$ or $2^q = 2^1$ i.e., $q = 1$

Now, rate $= [2A]^p [2B]^q = 8r$ ...(*iii*)

Dividing eq. (*iii*) by eq. (*i*)

$2^p . 2^q = 8$

or $2^p \times 2 = 8$ or $2^p = 4$ i.e., $2^p = 2^2$ or $p = 2$

rate $= \mathbf{k[A]^2 [B]}$

B11. (*b*): By 10°C rise in temperature rate becomes double For 100°C rise in temperature rate will become $(2)^9$ times i.e., 512 times.

B12. (*a*): $\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$T_1 = 273 + 20 = 293$ K, $T_2 = 273 + 35 = 308$ K

$$\log 2 = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{293} - \frac{1}{308}\right)$$

$$0.3010 = \frac{E_a}{2.303 \times 8.314} \times \frac{15}{293 \times 308}$$

$$E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 293 \times 308}{15}$$

$= 34673$ J mol^{-1} **= 34.7 kJ mol^{-1}.**

B13. (*b*): The units of rate constant indicate that the reaction is a zero order reaction.

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

or $[R]_0 - [R] = kt = 0.6 \times 10^{-3} \times 20 \times 60$

$= 0.72$ mol L^{-1}

Moles of A reacted *i.e.*, $[R]_0 - [R]$ = Moles of B produced

∴ Moles of B produced = **0.72 M**

B14. (*a*): Arrhenius equation is

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

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

so, by plotting ln k vs 1/T, slope is $-E_a/R$ and hence activation energy can be obtained.

B15. (*d*): For a first order reaction, half life is independent of concentration.

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

B16. (*b*): On adding the catalyst, the activation energy of a reaction decreases.

B17. (*c*): $k = \frac{2.303}{20-10}\log\frac{0.04}{0.03}$

$$= \frac{2.303}{10} \times 0.1249$$

$= 0.0287$ s^{-1}

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287} = \mathbf{24.1\ s}$$

B18. (*a*): At low pressure, the decomposition of NH_3 is a first order reaction and the rate is directly proportional to the coverage of surface. However, at high pressure, the decomposition of NH_3 on tungsten surface is a zero order reaction and the rate is independent of the coverage of the surface.

B19. (*c*): Overall order of reaction

= Rate of slowest step (*ii*)

Rate $= k\,[X]\,[Y_2]$ ...(*i*)

Assuming step (*i*) to be reversible,

$X_2 = X + X$

$$K_{eq} = \frac{[X]^2}{[X_2]}$$

or $[X] = (K_{eq}\,[X_2])^{1/2}$ ...(*ii*)

∴ Rate $= k\,K_{eq}^{1/2}\,[X_2]^{1/2}\,[Y_2]$

or $= k'[X_2]^{\frac{1}{2}}[Y_2]$

Order $= \frac{1}{2} + 1 = \frac{3}{2} = 1.5$

B20. (*a*) : $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{10^{-2}} = 69.3$ s

For the reaction of 20 g of reactant to 5 g, two half-life times are required.

∴ $t = 2 \times 69.3 = 138.6$ s

B21. (*b*) : For a first order reaction,

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

$t_{1/2}$ is independent of initial concentration of reactant

For a second order reaction,

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

$t_{1/2}$ depends upon the initial concentration of the reactants.

B22. (*b*) : $t_{1/2}$ (zero order reaction) $= \frac{[A]_0}{2k}$

When the concentration of the reactant is doubled, the half life period of the reaction is also doubled.

B23. (*a*) : For a zero order reaction, if the initial conc. is doubled the half life period is also doubled.

$t_{1/2} = [A]_0^{1-n}$.

B24. (*a*) : According to Arrhenius equation,

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

where E is activation energy

Now $k = \frac{k_1 k_2}{k_3}$

$$Ae^{-E/RT} = \frac{Ae^{-E_1/RT} \cdot e^{-E_2/RT}}{Ae^{-E_3/RT}}$$

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$$e^{-E/RT} = \frac{e^{-E_1/RT} \cdot e^{-E_2/RT}}{e^{-E_3/RT}}$$

$$-\frac{E}{RT} = \frac{-E_1 - E_2 + E_3}{RT}$$

or $E = E_1 + E_2 - E_3 = 40 + 50 - 60$

$= \mathbf{30\ kJ\ mol^{-1}}$.

B25. (*c*) : For a zero order reaction, the plot of conc. of reactant vs time is linear with –ve slope and non-zero intercept.

B26. (*c*)

$$k_1[N_2O_5] = \frac{1}{2}k_1'[N_2O_5]$$

$$k_1[N_2O_5] = 2k''[N_2O_5]$$

Equating $k_1[N_2O_5] = \frac{1}{2}k_1'[N_2O_5] = 2k''[N_2O_5]$

or $2k_1 = k' = 4k''$

B27. (*b*) : The effect of temperature on rate constant is given by Arrhenius equation

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

Here, if $E_a = 0,\ k = A$

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

The plot of ln k vs 1/T is a straight line with slope

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

Hence statements *(ii)* and *(v)* are correct.

B28. (*e*) : Expt. 1 and 2 show that there is no change in rate with the change in concentration of C. So, the order w.r.t. C is zero.

Expt. 4 and 1 show that by only doubling the conc. of A rate becomes four times, so that the order w.r.t. A is 2.

Expt. 1 and 3 show that by only doubling the conc. of B rate becomes double so that the order w.r.t. B is 1.

∴ The order w.r.t A, B and C is 2, 1 and 0 respectively.

B29. (*a*): Let rate $= k\ [A]^x\ [B]^y$

From trial 1 and 2

$k(0.4)^x\ (0.2)^y = 5.5 \times 10^{-4}$

$k(0.8)x\ (0.2)y = 5.5 \times 10^{-4}$

$\left(\frac{0.8}{0.4}\right)^x = 1$ or $2^x = 20$ ∴ $x = 0$

From trial 1 and 3

$k\ (0.4)^x\ (0.20)^y = 5.5 \times 10^{-4}$

$k\ (0.4)^x\ (0.40)^y = 2.2 \times 10^{-3}$

$\left(\frac{0.40}{0.20}\right)^y = 4$ or $2^y = 2^2$ ∴ $y = 2$

∴ The correct rate law is

rate $= k[A]^0\ [B]^2$

B30. (*d*) : $k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{75}\log\frac{1}{1/8}$

$= \frac{2.303}{75}\log 8 = \frac{2.303}{75} \times 0.903\ \text{min}^{-1}$

$t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 75}{2.303 \times 0.903} = 25\ \text{min}$

B31. (*b*) : Slope $= -\frac{E_a}{R}$ or $E_a = -\text{Slope} \times R$

$= -(-2 \times 10^4) \times 8.3$

$= 16.6 \times 10^4\ \text{J mol}^{-1}$

or $= \mathbf{166\ kJ\ mol^{-1}}$

B32. (*d*) : For a zero order reaction :

$t_{1/2} \propto [A]_0$ *i.e.*, initial conc. or initial pressure

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{p_2}{p_1} \text{ or } \frac{(t_{1/2})_2}{45} = \frac{16\ \text{bar}}{4\ \text{bar}}$$

$$\therefore \quad (t_{1/2})_2 = \frac{16}{4} \times 45 = \mathbf{180\ min.}$$

B33. (*c*) : For 5°C rise in temperature, rate constant becomes double.

∴ For 20°C rise in temperature, rate constant becomes $(2)^4$ times *i.e.*, 16 times.

B34. (*c*) : pH = 2, $[H^+] = 10^{-2}$

pH = 1, $[H^+] = 10^{-1}$

Initial rate, $(\text{rate})_0 = k[H^+]^n$

$(\text{rate})_1 = k(10^{-2})^n$

$(\text{rate})_2 = k(10^{-1})^n$

$$\frac{\text{rate}_2}{\text{rate}_1} = 100 = \left(\frac{10^{-1}}{10^{-2}}\right)^n$$

$100 = (10)^n$ or $n = 2$.

B35. (*d*) :

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

$$= \frac{2.303}{4606}\log\frac{80}{8} = \mathbf{5.00 \times 10^{-4}\ s^{-1}}$$

B36. (*a*) : $2N_2O_5 \longrightarrow 4NO_2 + O_2$

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t}$$

$$\frac{\Delta[N_2O_5]}{\Delta t} = \frac{2.0 - 2.4}{200} = -2 \times 10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}$$

$$\frac{\Delta[NO_2]}{\Delta t} = \frac{4}{2}\left(-\frac{\Delta[N_2O_5]}{\Delta t}\right) = 2 \times 2 \times 10^{-3}$$

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

B37. (*a*) :

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

$$= \frac{2.303}{30}\log\frac{0.6}{0.3} = 0.0231\ \text{min}^{-1}$$

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

$$= \frac{2.303}{0.0231}\log\frac{0.1}{0.025} = \mathbf{60\ min}$$

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B38. (*c*) :
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{6.93} = 0.1 \text{ min}^{-1}$$
$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]} = \frac{2.303}{0.1}\log\frac{100}{1}$$
$$= \frac{2.303\times 2}{0.1} = \mathbf{46.06\ min}$$

B39. (*a*) : For zero order reaction
$$t_{1/2} = \frac{[A]_0}{2k}$$
$$k = \frac{[A]_0}{2t_{1/2}} = \frac{2}{2\times 1}$$
$$= 1 \text{ mol L}^{-1}\text{ hr}^{-1}$$
$$k = \frac{[A]_0 - [A]}{t}$$
$$t = \frac{[A]_0 - [A]}{k}$$
$$= \frac{0.50 - 0.25}{1} = \mathbf{0.25\ hr.}$$

B40. (*c*): Increase in reaction rate = $2^5 = 32$ times.

B41. (*a*): For a first order reaction :
$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$
At $t = 40$ min, $[A]_0 = 0.1$M, $[A] = 0.025$ M
$$\therefore \quad k = \frac{2.303}{40}\log\frac{0.1}{0.025}$$
$$\therefore \quad = \frac{2.303}{40}\log 4 = 0.0347 \text{ min}^{-1}$$
Rate = $k[A] = 0.0347 \times 0.01 = 3.47 \times 10^{-4}$ M/min.

B42. (*b*): $\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
$$\log 2 = \frac{E_a}{2.303\times 8.314}\left(\frac{1}{300} - \frac{1}{310}\right)$$
$$0.3010 = \frac{E_a}{2.303\times 8.314}\times\frac{10}{300\times 310}$$
$$E_a = \frac{0.3010\times 2.303\times 8.314\times 300\times 310}{10}$$
$$= 53.6 \text{ kJ mol}^{-1}.$$

B43. (*a*) : Initial rate, $\frac{dc}{dt} = k[A]^x[B]^y$
$$1.2\times 10^{-3} = k\,(0.1)^x\,(0.1)^y \quad ...(i)$$
$$1.2\times 10^{-3} = k\,(0.1)^x\,(0.2)^y \quad ...(ii)$$
Dividing eq. (*ii*) by eq. (*i*)
$$\frac{1.2\times 10^{-3}}{1.2\times 10^{-3}} = \left(\frac{2}{1}\right)^y$$
$$1 = 2^y \text{ or } 2^y = 2^0$$
$$\therefore \quad y = 0$$
Now $\quad 2.4\times 10^{-3} = k\,(0.2)^x\,(0.1)^y \quad ...(iii)$

Dividing eq. (*iii*) by eq. (*i*)
$$\frac{2.4\times 10^{-3}}{1.2\times 10^{-3}} = (2)^x$$
$$2 = 2^x$$
$$\therefore \quad x = 1$$
$$\therefore \quad \text{Rate} = k\,[A]$$
Hence, $\quad \frac{d[C]}{dt} = k\,[A]^1\,[B]^0 = k\,[A]$

B45. (*b*): $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} = \frac{2.303}{50}\log\frac{0.5}{0.125} = \frac{2.303}{50}\log 4$
$= 0.0277 \text{ min}^{-1}$

When $\quad [H_2O_2] = 0.05$ M,

Rate = $k\,[H_2O_2] = 0.0277 \times 0.05$
$= 1.385 \times 10^{-3}$ mol L^{-1} min^{-1}

According to the reaction,
$$H_2O_2 \rightarrow 2H_2O + \frac{1}{2}O_2$$
$$\text{Rate} = \frac{-d[H_2O_2]}{dt} = 2\frac{d[O_2]}{dt}$$
$$\therefore \quad \frac{d[O_2]}{dt} = \frac{1}{2}\times \text{Rate of reaction} = \frac{1}{2}\times 1.385\times 10^{-3}$$
$$= 6.93\times 10^{-4} \text{ mol L}^{-1}\text{ min}^{-1}$$

B46. (*d*) :
$$k_1 = Ae^{-E_{a_1}/RT}$$
$$k_2 = Ae^{-E_{a_2}/RT}$$
$$\frac{k_2}{k_1} = e^{(-E_{a_2} + E_{a_1})/RT}$$
or
$$\frac{k_2}{k_1} = e^{(E_{a_1} - E_{a_2})/RT}$$
$$ln\frac{k_2}{k_1} = \frac{E_{a_1} - E_{a_2}}{RT} = \frac{10\times 10^3}{8.314\times 300} = 4$$

B47. (*a*) : $\Delta G = \Delta H - T\Delta S$
$$-RT\ln k = \Delta H - T\Delta S$$
$$\ln k = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$
The plot of ln k vs. $\frac{1}{T}$ is a straight line with slope $= -\frac{\Delta H}{R}$

Since ΔH is negative (exothermic reaction), slope is positive. Therefore, lines should be A and B.

B48. (*a*) : Rate = $k\,(p)^n$
$$r_1 = k(p_1)^n$$
$$p_1 = 363 - \frac{363\times 5}{100} = 344.85$$
$$r_1 = k(344.85)^n \quad (i)$$
$$r_2 = k(p_2)^n$$
$$p_2 = 363 - \frac{363\times 33}{100} = 243.21$$
$$r_2 = k(243.21)^n \quad (ii)$$
$$\frac{r_1}{r_2} = \left(\frac{344.85}{243.21}\right)^n = (1.41)^n$$

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$$\frac{1}{0.5} = (1.41)^n = (\sqrt{2})^n$$

$$2 = (\sqrt{2})^n \text{ or } (\sqrt{2})^2 = (\sqrt{2})^n \quad \therefore n = 2$$

B49. (*a*) : $p_1 = 80$ *k*Pa, $p_2 = 40$ *k*Pa,
$(t_{1/2})_1 = 350$ sec $(t_{1/2})_2 = 175$ sec

Now $\frac{350}{175} = \frac{80}{40} = 2$

$\therefore \quad \frac{p_1}{p_2} = \frac{(t_{1/2})_1}{(t_{1/2})_2}$

or $\frac{a_1}{a_2} = \frac{(t_{1/2})_1}{(t_{1/2})_2}$ or $t_{1/2} \propto a$

This is true for zero order reaction.

B50. (*b*) : When $k_1 = k_2$

$$10^{10}e^{-20000/T} = 10^{12}\, e^{-24606}$$

$$e^{4606/T} = 100$$

$$\frac{4606}{T} = 2.303 \log 100$$

$$\frac{4606}{T} = 2.303 \times 2$$

$$T = \frac{4606}{2.303 \times 2} = 1000 \text{ K}$$

B51. (*b*) :

$$\log \frac{k_1'}{k_1} = \frac{E_1}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log \frac{k_2'}{k_2} = \frac{E_2}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Since $E_1 > E_2$

$$\frac{\log \frac{k_1'}{k_1}}{\log \frac{k_2'}{k_2}} > 1$$

or $\frac{k_1'}{k_1} > \frac{k_2'}{k_2}$

B52. (*a*) : $2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$

$$E_a = 2.303\ RT$$

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

$$\log k = \log A - 1$$

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

or $\frac{k}{A} = 10^{-1}$

B53. (*b*) : $t_{1/2}$ for zero order reaction $= \frac{[A]_0}{2k}$

$t_{1/2}$ for first order reaction $= \frac{0.693}{k'}$

If initial rate, $[A]_0 = 1$

$$\frac{1}{2k} = \frac{0.693}{k'} \text{ or } \frac{k'}{k} = 2 \times 0.693$$

B54. (*b*): For a reversible reaction

$$\Delta H = E_a \text{(forward)} - E_a \text{(backward)}$$

$$\Delta H = 150 - 260 = -110 \text{ kJ mol}^{-1}$$

B55. (*b*): $k = \frac{0.693}{69.3} = 0.01$

$$t = \frac{2.303}{0.01} \log \frac{100}{10} = \frac{2.303}{0.01} = \mathbf{230.3\ min}$$

B56. (*a*): $2A(g) \longrightarrow B(g) + C(s)$
$\quad 2(1-x)\ x$

At end of the reaction, only 1 mol of gas is present whose pressure is 200 Pa.

$\therefore$ In the beginning of the reaction, when 2 mol of gas were present, pressure would have been $2 \times 200 = 400$ Pa

At the end of 10 min, moles of gas present,

$$2 - 2x + x = 2 - x$$

But pressure of 2 mol of gas = 400 Pa

$\therefore \quad 400 - x = 300$ or $x = 100$

Pressure due to $2 - 2x$ mol of A $= 400 - 2 \times 100 = 200$ Pa

Now, $k = \frac{2.303}{t} \log\left[\frac{a}{a-x}\right]$

$$= \frac{2.303}{10} \log \frac{400}{200} = \frac{2.303}{10} \log 2$$

$$= \frac{2.303}{10} \times 0.3010 = 0.0693 \text{ min}^{-1}$$

B57. (*d*): If rate at conc. 1.2×10^{-2} M is *r*, then

$$r = k(1.2 \times 10^{-3})^a \quad \ldots (i)$$

$$9r = k(3.24 \times 10^{-2})^a \quad \ldots (ii)$$

Dividing eq. (*ii*) by eq. (*i*)

$$9 = \frac{(3.24 \times 10^{-2})^a}{(1.2 \times 10^{-3})^a} = 27^a$$

or $3^2 = 3^{3a}$

$\therefore \quad 3a = 2$ or $a = 2/3$

B58. (*d*): $T_1 = 27°C = 300K$

$$T_2 = -3°C = 270K$$

$$\frac{k_2}{k_1} = \frac{1}{10}$$

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

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$$\log 10^{-1} = \frac{E_a}{2.303R}\left[\frac{1}{300} - \frac{1}{270}\right]$$

$$-1 = \frac{E_a}{2.303R}\left[\frac{270-300}{270\times 300}\right]$$

$$E_a = \frac{2.303R \times 270 \times 300}{30}$$

$$= 2.303R \times 2700 \text{ J mol}^{-1}$$

$$= 2.303 \times 2.7 \text{ R kJ mol}^{-1}$$

B59. (*d*): Let P is the initial pressure of A and p is the decrease in pressure after 20 minutes.

	A	$\longrightarrow$	B	+	C
Initial	P		0		0
at $t = 20$	$P - p$		p		p
At completion	0		P		P

At completion of reaction ($t = \infty$)

$2P = 180$

or $P = 90$

At time = 20 min

Total pressure : $P - p + p + p = 100$

or $P + p = 100$

or $90 + p = 100$

$\therefore$ $p = 10$

$\therefore$ Partial pressure of A at $t = 20$ min

$= P - p = 90 - 10 = 80$ mm.

B60. (*d*): Number of half lives $= \frac{22,920}{5730} = 4$

Amount left after 4 half lives $= \frac{N_0}{2^4} = \frac{N_0}{16}$

The fraction of ^{14}C that decayed $= N_0 - \frac{N_0}{16} = \frac{15}{16} N_0$.

B61. (*c*): $ln\ \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$ln\frac{k_2}{k_1} = \frac{600\ R}{R}\left(\frac{1}{300} - \frac{1}{600}\right)$$

$$ln\frac{k_2}{k_1} = \frac{600\ R}{R}\left(\frac{2-1}{600}\right) = 1$$

or $ln\frac{k_2}{k_1} = \ln e$

or $\frac{k_2}{k_1} = e.$

B62. (*a*): Half life = 25 min.

No. of half lives, $n = \frac{100}{25} = 4$

Amount left $= \frac{[A]_0}{2^n} = \frac{[A]_0}{2^4} = \frac{[A]_0}{16}$

Fraction reacted $= [A]_0 - \frac{[A]_0}{16} = \frac{15}{16}[A]_0$

$= \mathbf{93.75\ \%}$.

B63. (*c*): Rate $= k\ [A]\ [B]^2$

$= 1 \times 10^{-2} \times (0.50)(0.50)^2$

$= 1.25 \times 10^{-3}$ mol L^{-1} s^{-1}.

B64. (*b*): $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = 1.2 \times 10^{-4}$ year^{-1}

Age of sample, $t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$

$= \frac{2.303}{1.2\times 10^{-4}}\log\frac{15}{5}$

$= 9154$ years $\approx$ **9200 years**

B69. (*c*): $2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$

Rate $= -\frac{1}{2}\frac{d[NO_2]}{dt} = k_1[NO_2]^2 - k_2[N_2O_4]$

$\therefore$ Rate of disappearance of NO_2:

$-\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 - 2k_2[N_2O_4]$

B71. (*b*): $k = 3 \times 10^{-5}$ s^{-1}; Rate $= 2.4 \times 10^{-5}$ mol dm^{-3} s^{-1}

$[N_2O_5] = ?$

Rate $= k[N_2O_5]$

$2.4 \times 10^{-5} = 3 \times 10^{-5} \times [N_2O_5]$

$[N_2O_5] = \frac{2.4\times 10^{-5}}{3\times 10^{-5}} = 0.8$ mol dm^{-3} or $= 0.8$ M

B72. (*d*): $\frac{r_1}{r_2} = \left[\frac{2.4\times 10^{-2}}{1.2\times 10^{-2}}\right]^x$

$8 = 2^x$

or $2^3 = 2^x$ $\therefore x = 3$

B74. (*a*): $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60} = 0.0115$ min^{-1}

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

$$240 = \frac{2.303}{0.0115}\log\frac{[R]_0}{[R]}$$

$$\log\frac{[R]_0}{[R]} = \frac{240\times 0.0115}{2.303} = 1.198$$

$\log\frac{[R]}{[R]_0} = -1.198$ or $\frac{[R]}{[R]_0} = \text{Antilog}(-1.198) = 0.063$

Percentage left $= \frac{[R]}{[R]_0} \times 100 = 0.063 \times 100 = \mathbf{6.3\%}$

B75. (*b*): The rate law for any reaction cannot be determined theoretically but it is determined experimentally.

B76. (*e*): A catalyst may change the order of the reaction as the mechanism in presence of catalyst could be different than that in the absence of it.

B77. (*d*): Rate $= k[A]^3$

mol $L^{-1}s^{-1} = k(\text{mol } L^{-1})^3$

$\therefore k =$ mol^{-2} L^2s^{-1}

B78. (*c*): $k = Ae^{-Ea/RT}$

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

log k vs 1/T is a Arrhenius plot.

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B79. (*d*): $[R]_0 = 200$ mg $[R] = 25$ mg

$$\left[\frac{[R]}{[R]_0}\right] = \left(\frac{1}{2}\right)^n \text{ or } \left(\frac{25}{200}\right) = \left(\frac{1}{2}\right)^n$$

$$\frac{1}{8} = \left(\frac{1}{2}\right)^n \text{ or } \left(\frac{1}{2}\right)^3 = \left(\frac{1}{2}\right)^n$$

$\therefore n = 3$

Time taken = 5760 × 3 = **17280 years**

B80. (*d*): Temperature coefficient 2 means that the rate of reaction becomes double for every 10° rise in temperature.

$$\therefore \quad \frac{k(90°C)}{k(30°C)} = 2^6 = 64 \text{ times}$$

B82. (*b*): $\text{Rate} = -\frac{1}{2}\frac{d[SO_2]}{dt} = -\frac{d[O_2]}{dt} = \frac{1}{2}\frac{d[SO_3]}{dt}$

$$\frac{d[O_2]}{dt} = 2 \times 10^{-4}$$

$$\frac{d[SO_3]}{dt} = 2 \times 2 \times 10^{-4} = 4 \times 10^{-4} \text{ mol L}^{-}\text{s}^{-1}$$

B83. (*a*): Rate = $k[D_2]^x[A]^y$

$1 \times 10^{-3} = k\,(0.05)^x\,(0.05)^y$ ... (*i*)

$3 \times 10^{-3} - k\,(0.15)^x\,(0.05)^y$ ... (*ii*)

Dividing eq. (*ii*) by eq. (*i*)

$$\frac{3 \times 10^{-3}}{1 \times 10^{-3}} = \left(\frac{0.15}{0.05}\right) \text{ or } 3 = 3^x \quad \therefore x = 1$$

$9 \times 10^{-3} = k\,(0.05)^x\,(0.15)^y$ ... (*iii*)

Dividing eq. (*iii*) by eq. (*i*)

$$\frac{9 \times 10^{-3}}{1 \times 10^{-3}} = \left(\frac{0.15}{0.05}\right)^y \text{ or } 9 = 3^y \quad \therefore y = 2$$

$\therefore$ Rate law = $\boldsymbol{k[D_2][A]^2}$

B84. (*a*): Rate = $k[A]^{1/2}\,[B]^{3/2}$

$\text{mol L}^{-1}\text{s}^{-1} = k(\text{mol L}^{-1})^{1/2}\,(\text{mol L}^{-1})^{3/2}$

$\text{mol L}^{-1}\text{s}^{-1} = k(\text{mol L}^{-1})^2$

$\therefore \quad k = \text{mol}^{-1}\,\text{L s}^{-1}$

B86. (*c*): For a first order reaction,

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

$$= \frac{2.303}{40}\log\frac{0.1}{0.025}$$

or $$= \frac{2.303}{40}\log 4 = \frac{2.303}{40} \times 0.6020$$

$$= 0.0347 \text{ min}^{-1}$$

Now, at 0.01 M concentration

Rate = $k[A]$

= 0.0347 × 0.01

= **3.47×10^{-4} mol L^{-1} min^{-1}.**

B87. (*d*): If order of reaction w.r.t. G is x and w.r.t. H is *y*, then on doubling [G] and [H], the rate becomes 8 times i.e.,

$2^x 2^y = 8$ or $2^{(x+y)} = 23$

$\therefore x + y = 3$

$\therefore$ Order of reaction **= 3**

B88. (*a*): $$k_1 = \frac{0.693}{40} \text{ min}^{-1}$$

$$k_0 = \frac{1.386}{2 \times 20} = \frac{1.386}{40} \text{ min}^{-1}\text{ mol dm}^{-3}$$

$$\frac{k_1}{k_0} = \frac{0.693}{1.386} = \mathbf{\frac{1}{2}\,mol^{-1}dm^3}$$

B89. (*d*): Arrhenius equation is

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

$$\log k = 6.0 - 2000/T$$

$$\therefore \quad \log A = 6.0$$

$$\therefore \quad A = 10^6\ s^{-1}$$

$$\frac{E_a}{2.303\,R} = 2000$$

$$E_a = 2000 \times 2.303 \times 8.314$$

$$= \mathbf{38.28\ kJ\ mol^{-1}}$$

B90. (*a*): $k = Ae^{-E_a/RT}$

$\therefore$ As T increases, *k* increases exponentially.

B91. (*d*): For P, if $t_{1/2} = x$, then $t_{75\%} = 2x$. This means the order with respect to P is one.

From the graph, concentration of Q decreases linearly with time. So rate with respect to Q remains constant. Therefore, order of reaction with respect to Q is zero

Rate = $k[P]^1\,[Q]^0$ Order = 1 + 0 **= 1**

B92. (*a*): Rate with respect to weak acid,

$$\text{rate}_1 = k[H^+]_{\text{weak acid}}$$

Rate with respect to strong acid

$$\text{rate}_2 = k[H^+]_{\text{strong acid}}$$

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[H^+]_{\text{weak acid}}}{k[H^+]_{\text{strong acid}}} = \frac{1}{100}$$

$$\therefore [H^+]_{\text{weak acid}} = \frac{1}{100} = 0.01 \text{ M}$$

$$HA \rightleftharpoons H^+ + A^-$$

$1 - 0.01$ 0.01 0.01

≈ 1

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.01 \times 0.01}{1} = \mathbf{1 \times 10^{-4}}.$$

C. *mcq more than one correct answer*

C1. (*a, b*): (*c*) rate becomes 81 times.

(*d*) rate becomes 4 times.

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C2. (*a, d*): For a first order reaction, degree of dissociation $= \frac{x}{a}$

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

$$\ln\frac{a}{a-x} = kt \quad \text{or} \quad \frac{a}{a-x} = e^{kt}$$

$$\frac{a-x}{a} = e^{-kt} \quad \text{or} \quad 1-\frac{x}{a} = e^{-kt}$$

$$\frac{x}{a} = 1 - e^{-kt}$$

or degree of dissociation $= 1 - e^{-kt}$

As E_a/RT is dimensionless therefore, A has the dimensions of k, i.e. time^{-1}.

C3. (*b, c*): Since rate depends upon $[H^+]^2$, it is affected by change in *p*H of solution. Doubling the conc. of H^+ increases the rate four times.

C4. (*b, c*): (*a*) is wrong because it is independent of [NaOH]. (*d*) is wrong because all reactions are affected by temperature.

C6. (*a, b, d*) : (*a*) For a reaction, concentration of reactant decreases exponentially with time. It is true.

(*b*) Half life period decreases with increase in concentration because it is inversely proportional to k.

(*d*) $$k = \frac{0.693}{t_{1/2}} \quad ...(i)$$

For 99.6% completion, $a = 100$, $a - x = 100 - 99.6 = 0.4$.

$$k = \frac{2.303}{t_{99.6}} \times \log\frac{100}{0.4}$$

$$= \frac{2.303}{t_{99.6}} \times 2.40 \quad ...(ii)$$

From eq. (*i*) and (*ii*)

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t_{99.6}} \times 2.4$$

$$t_{99.6} = \frac{2.303}{0.693} \times 2.4 \times t_{1/2}$$

$$= 7.976\, t_{1/2} \text{ or } = 8\, t_{1/2}.$$

C8. (*a, d*) : According to Arrhenius equation,

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

On increasing temperature (T) and decreasing activation energy (E_a), rate of reaction increases.

C9. (*a, c*): (*a*) $A = PZ_{AB}$

P = frequency factor, Z_{AB} = collision frequency

A = Arrhenius factor

Assuming Z_{AB} to be same,

$$P = \frac{(A)_{exp}}{(A)_{theo}}$$

Since P = 4.5 i.e P > 1

$(A)_{exp} > (A)_{theo}$

(*c*) The activation energy of the reaction is unaffected by the value of stearic factor.

C10. (*a, d*) : $A(g) \longrightarrow 2B(g) + C(g)$

$t = 0$ $[A]_0$

$t = t$ $[A]_0 - x$ $2x$ x

$[A]_0 \propto p_0$

$[A]_0 - x + 2x + x$ or $[A]_0 + 2x \propto p_t$

$2x \propto p_t - p_0$

$$x \propto \frac{p_t - p_0}{2}$$

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

$$= \frac{1}{k}\ln\frac{p_0}{p_0 - \left(\frac{p_t - p_0}{2}\right)}$$

$$= \frac{1}{k}\ln\frac{2p_0}{2p_0 - p_t + p_0}$$

or $$kt = \ln\frac{2p_0}{3p_0 - p_t} \text{ or } = \ln 2p_0 - \ln(3p_0 - p_t)$$

or $$\ln(3p_0 - p_t) = -kt + 2\,p_0$$

∴ Graph between $\ln(3p_0 - p_t)$ vs t is a straight line with –ve slope. Hence, option (*a*) is correct.

Now $$t_{1/3} = \frac{1}{k}\ln\frac{p_0}{p_0/3} = \frac{1}{k}\ln 3$$

∴ Rate constant is independent of $[A]_0$, hence option (*d*) is correct.

D. mcq based on comprehension

D1. (*b*) : $$\text{Slope} = -\frac{k}{2.303}$$

$$\therefore \quad k = -2.303 \times \text{slope}$$

$$= -2.303 \times 0.01389 = \mathbf{3.2 \times 10^{-2}\ min^{-1}}$$

D4. (*d*) : Rate $= k\,[c]$

$0.0069 = (0.2)\,k$

$$k = \frac{0.0069}{0.2} = \frac{3.45 \times 10^{-2}}{60} = 5.75 \times 10^{-4}\ s^{-1}$$

$$t_{1/2} = \frac{0.693}{5.75 \times 10^{-4}} = \mathbf{1205\ s}$$

D6. (*b*) : $$\ln k = \ln A - \frac{E_a}{RT}$$

Therefore, plot of ln k versus 1/T is linear with

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

D7. (*c*) : $$\text{Slope} = -\frac{E_a}{2.303\,R}$$

$$\therefore \quad E_a = -(-8.95 \times 10^3) \times 2.303 \times 8.314$$

$$= \mathbf{171.4\ kJ\ mol^{-1}}.$$

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D8. (*c*) : The factor A has the same units as those of *k*. For a second order reaction, *k* has the units $L\ mol^{-1}\ s^{-1}$.

D9. (*a*): For uncatalysed reaction :

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

For catalysed reaction (k' is constant)

$$\log k' = \log A - \frac{E_a - 10}{2.303\ RT}$$

or $$\log k' = \log A - \frac{E_a}{2.303\ RT} + \frac{10}{2.303\ RT}$$

Subtracting, $$\log k' - \log k = \frac{10}{2.303\ RT}$$

$$\log \frac{k'}{k} = \frac{10}{2.303 \times 8.314 \times 300} = 1.741$$

D10. (*a*): On solving E_a comes out to be 50 *k*J mol^{-1}.

D11. (*c*): $$E_a = 0$$

$$\log \frac{k_2}{k_1} = 0$$

or $$\frac{k_2}{k_1} = 1 \quad \therefore \quad k_2 = k_1$$

D12. (*c*): Fraction of molecules having energy greater than E_a at any temperature T is given as

$$x = \frac{n}{N} = e^{-E_a/RT} \qquad ln\ x = -\frac{E_a}{RT}$$

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

Integer Type Questions

1. (0): For a zero order reaction,

$$\frac{dx}{dt} = k$$

From 1 to 0.75

$$\frac{0.25}{0.05} = 5$$

From 0.75 to 0.40

$$\frac{0.35}{0.07} = 5$$

From 0.40 to 0.10

$$\frac{0.30}{0.06} = 5$$

Thus, order of reaction is zero.

6. (9): For a first order reaction :

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

At $t_{1/8}$, $[A] = [A]_0/8$

$$t_{1/8} = \frac{2.303}{k} \log \frac{[A]_0}{[A_0]/8}$$

$$= \frac{2.303}{k} \log 8 \qquad ...(i)$$

At $t = t_{1/10}$, $[A] = [A]_0/10$

$$10 = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0/10} = \frac{2.303}{k} \log 10 \qquad ...(ii)$$

From eq. (*i*) and (*ii*)

$$\frac{t_{1/8}}{t_{1/10}} = \frac{\log 8}{\log 10}$$

$$\therefore \quad \frac{t_{1/8}}{t_{1/10}} \times 10 = 10 \times \frac{\log 2^3}{\log 10} = \frac{10 \times 3 \log 2}{\log 10}$$

$$= \frac{10 \times 3 \times 0.3}{1} = \mathbf{9}.$$

7. (8): In the complex $[Fe(C_2O_4)_2(H_2O)_2]^{2-}$

The oxidation state of iron is +2

In acidic medium Fe^{2+} is oxidised to Fe^{3+} as

$$2MnO_4^- + 10Fe^{2+} + 16\ H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$

or $$MnO_4^- + 5Fe^{2+} + 8\ H^+ \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

$$\frac{\text{Rate of change of } [H^+]}{\text{Rate of change of } [MnO_4^-]} = \frac{8}{1} = 8$$

NCERT Exemplar Problems : MCQs Type-I

1. (*c*): A catalyst lowers the activation energy of a reaction.

2. (*c*): In the presence of a catalyst, ΔH does not change.

4. (*a*): The activation energy for the forward reaction is $E_1 + E_2$ and product is stable than reactants.

7. (*d*): Rate constant increases exponentially with decreasing E_{act} and increasing temperature.

9. (*c*): The order of a reaction is not always equal to the sum of the stoichiometric coefficients of the reactants in the balanced chemical equation.

12. (*c*): $$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t}$$

or $$\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$$

13. (*a*): Graph represents (*a*) is exothermic reaction in which $H_{products} < H_{reactants}$.

14. (*b*): Rate will become double.

16. (*d*): It will take infinite time for completion.

17. (*b*): On doubling conc. of B, rate becomes four times (exp. 1 and 2)

$\therefore$ rate $\propto [B]^2$

On doubling conc. of A, rate becomes double (exp. 1 and 3)

$\therefore$ Rate $\propto$ [A]

$\therefore$ Rate $= k[A]\ [B]^2$

18. (*b*): A catalyst does not change ΔG or ΔH of the reaction.

19. (*b*): In pseudo first order reaction, rate constant depends on the concentration of reactant present in excess.

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Unit Practice Test

for Board Examination

Time Allowed : 2 Hrs. Maximum Marks : 35

1. Define activation energy of a reaction. (1)
2. 75% of a radioactive substance disintegrates in 50 s. What is its half-life period? (1)
3. For a chemical reaction $A \longrightarrow B$, the rate increases by a factor of 2.25 when the concentration of A is increased by 1.5. What is the order of the reaction? (1)
4. Can order of a reaction be fractional? Explain. (1)
5. What is the order of a reaction whose rate constant has same units as the rate of the reaction? (1)
6. The decomposition of ammonia on platinum surface is zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}$ mol $L^{-1}s^{-1}$? (2)
7. Show that half life period of a first order reaction does not depend upon the initial concentration of reactants. (2)
8. A first order reaction is 15% complete in 20 minutes. How long will it take to complete 60%? (2)
9. Give differences between rate constant and rate of a reaction. (2)
10. A reaction is of second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is reduced to half? What is the unit of rate constant for such a reaction? (2)
11. The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation for such a reaction. (3)
12. A first order reaction has a 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 ? (3)
13. Explain the following: (3)

    (*i*) pseudo first order reactions

    (*ii*) graphical method for measuring rate of a reaction.
14. Discuss the effect of temperature on the rate of a reaction. How can this temperature effect on rate constant be represented quantitatively ? (3)
15. During nuclear explosion one of the products is ^{90}Sr with half-life of 28.1 years. If 1 μg of ^{90}Sr was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically? (3)
16. (*a*) What is meant by order and molecularity of a reaction? How do these differ?

    (*b*) Derive an expression for the rate constant of a zero order reaction.

    (*c*) A reaction rate is first order in A and second order in B. How is its rate affected on increasing concentrations of A and B two and three times respectively? (5)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part I of the book.

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