

# Chapter-1

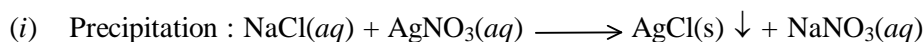
## CHEMICAL KINETICS

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**Chemical kinetics** concerns with the measurements of rates of reactions proceeding under given conditions of temperature, pressure and concentration. The study of this part of chemistry is highly useful in determining the factors which influence the rates of reactions as well as the mechanisms of a number of chemical reactions

There are three main types of reactions

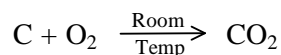
### 1. Instantaneous Reaction:



### 2. Extremely slow reaction

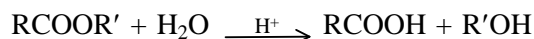
(i) Rusting of Iron

(ii) Reaction between carbon and oxygen at room temperature

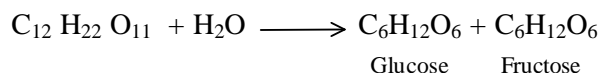


### 3. Moderate Rate Reaction

(i) Hydrolysis of esters



(ii) Inversion of cane sugar



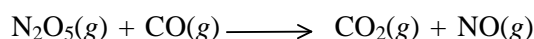
(iii) Oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by  $\text{MnO}_4^-$  in acidic medium



(iv) Oxidation of  $\text{C}_2\text{O}_4^{2-}$  to  $\text{CO}_2$  by  $\text{MnO}_4^-$  in acidic medium



(v) The reaction between nitrogen pentaoxide and carbon monoxide



(vi) Decomposition of dinitrogen pentaoxide



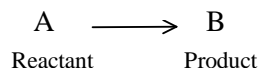
### Rate or Velocity of a Reaction

“The change in the concentration of reactant or product in unit time is called rate or velocity of a chemical reaction”.

Thus,

$$\text{Rate of chemical reaction} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken for the change}}$$

Let us consider a general chemical change



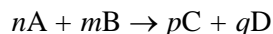
If  $\Delta[\text{A}]$  is the change in concentration of ‘A’ and  $\Delta[\text{B}]$  is the change in concentration of ‘B’ in  $\Delta t$  time, then,

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

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The negative (–) sign shows that the molar concentration of reactant ‘A’ decreases with time while the (+) sign indicates that the molar concentration of product ‘B’ increases with time.

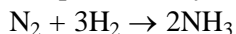
For a general chemical transformation,



the rates of disappearance of reactants and rates of appearance of products are equalized by dividing them with the coefficients in the balanced chemical equation. Thus,

$$-\frac{1}{n} \cdot \frac{\Delta[A]}{\Delta t} = -\frac{1}{m} \cdot \frac{\Delta[B]}{\Delta t} = \frac{1}{p} \cdot \frac{\Delta[C]}{\Delta t} = +\frac{1}{q} \cdot \frac{\Delta[D]}{\Delta t} = \text{Rate of chemical reaction}$$

For example, in the synthesis of ammonia



$$-\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3} \cdot \frac{\Delta[H_2]}{\Delta t} = +\frac{1}{2} \cdot \frac{\Delta[NH_3]}{\Delta t} = \text{Rate of reaction}$$

It can be concluded from these expression that the rate of disappearance of  $H_2$  is  $\frac{3}{2}$  of the rate of appearance of  $NH_3$

### Rates of Disappearance and Appearance

The rate of disappearance of  $H_2$

$$\begin{aligned} \text{also } \frac{-d[H_2]}{dt} &= 3 \times \frac{-d[N_2]}{dt} \\ \frac{-d[H_2]}{dt} &= \frac{3}{2} \times \left\{ +\frac{d[NH_3]}{dt} \right\} \end{aligned}$$

The rate of appearance of Ammonia

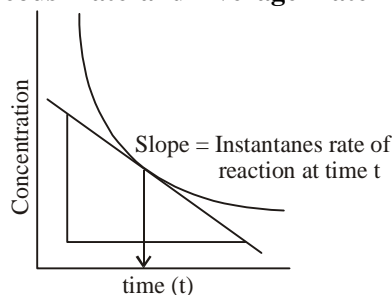
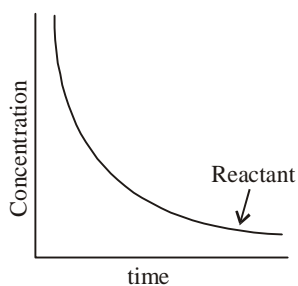
$$\begin{aligned} \frac{d[NH_3]}{dt} &= \frac{2}{3} \times \left[ \frac{-d[H_2]}{dt} \right] \\ &= \frac{2}{3} \times \text{Rate of disappearance of hydrogen} \\ &= 2 \times \left[ \frac{-d[N_2]}{dt} \right] \\ &= 2 \times \text{Rate of disappearance of nitrogen} \end{aligned}$$

**Average rate of reaction :** By dividing the total change in concentration of reactant or product by a time interval, we actually get the average rate of the reaction.

**Instantaneous Rates :** The instantaneous rate is obtained when a very small change in concentration ( $dc$ ) is divided by very small time interval ( $dt$ ). It is assumed that in  $dt$  time, the rate of the reaction remains

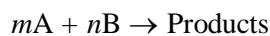
constant. Thus, instantaneous rate =  $\frac{dc}{dt}$

### Graph for Instantaneous Rate and Average Rate



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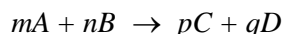
The theoretical rate of a reaction is given by law of mass action. Thus, for the general chemical change



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

**Rate Law or Rate Equation of a Reaction :** The mathematical expression which gives a relation between rate of the reaction and concentrations of reactants is known as rate law equation. The rate law is established by the kinetic study of a reaction experimentally.

Let us consider a general reaction



If it is observed experimentally that the rate of reaction varies directly as the concentration of reactant 'A' raised to the power 'a' and reactant 'B' raised to the power 'b' then,

$$\frac{dx}{dt} \propto [\text{A}]^a \times [\text{B}]^b$$

$$\text{or } \frac{dx}{dt} = k[\text{A}]^a \times [\text{B}]^b$$

This expression is known as the observed rate law of the reaction

1. The reaction is said to be of 'a' order with respect to reactant 'A' and of 'b' order with respect to reactant 'B'.
2. The overall order of the reaction is (a + b).

**Rate constant, velocity constant or specific reaction rate (k):**

The rate constant of a reaction is a measure of its rate of reaction. Fast reactions have higher value of 'k' while for slow reactions 'k' is low. Suppose, in a general chemical change, 'a' is the initial concentration of reactant A.



If 'x' moles of 'A' transform into product 'B' after time 't', the moles of 'A' at time 't' will be (a - x). Since, the rate of reaction is proportional to the concentration of 'A', so the rate of the reaction at time 't' is -

$$\frac{dx}{dt} \propto (a - x)$$

$$\text{or } \frac{dx}{dt} = k(a - x)$$

where k is constant known as rate or velocity constant. When (a - x) = 1.  $\frac{dx}{dt} = k$ .

**Definition of Rate Constant :** At a given temperature, the rate constant is equal to the rate of reaction when the concentration of reactant(s) is unity.

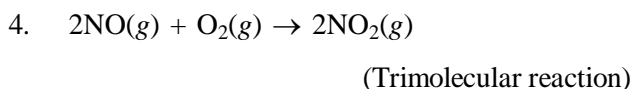
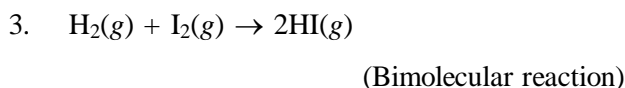
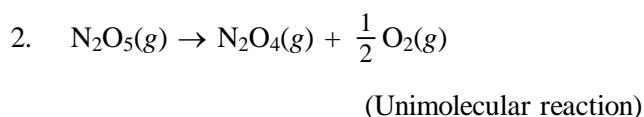
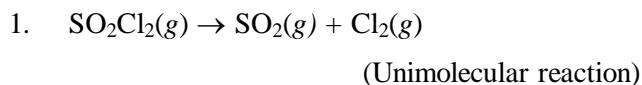
1. Rate constant, k is not affected by the concentration change of reactants, nor does it depend upon the initial concentration of a reactant.
  2. 'k' remains constant throughout the progress of the reaction.
  3. Positive catalyst increases the value of 'k', the rate constant.
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4. Rate constant, 'k' is always increased when temperature rises (for a certain temperature range).
  5. The rate of reaction at any time = Rate constant × Concentrations of reactant(s) at that time.
  6. Unit of 'k' depends upon the order of the reaction.

**Molecularity of a reaction:** It may be defined as, “the total number of atoms, ions or molecules which collide with each other in the rate determining step of a reaction”.

The slow step of the reaction is called rate determining step. Depending upon the number of molecules taking part in the rate determining step, the reactions are divided into unimolecular, bimolecular or trimolecular reactions according as the number of molecules is one, two or three.

**Example**

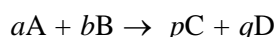


1. Molecularity of a reaction is always a whole number and can never be in fractions.
2. Molecularity of a reaction is never zero (but order can be zero, integral or fractional).
3. Reactions having molecularity more than three are rare. It is because the chances of simultaneous collisions between three or more particles is rare.

**Order of reaction:** The number of reactant molecules whose concentration changes determines the rate of a reaction and is called the order of the reaction.

or

The order of a reaction is the sum of the powers or exponents to which the concentration terms are raised in the rate law expression



If the rate law for this reaction comes out to be

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

the overall order of the reaction is **m + n**.

1. Order of a reaction is experimentally determined quantity
  2. Order of a reaction can not be written from the balanced chemical equation.
  3. Order of a reaction is equal to number of reactant molecules whose concentration changes in a chemical reaction.
  4. Order of a reaction may be zero, whole number, fractional or even negative.
  5. Molecularity and order of a reaction may be the same or different.
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**Zero order Reactions:** The reaction whose rate does not depend upon the concentration of reactants is called a zero order reaction. Consider a zero order reaction :



$$\frac{dx}{dt} = k[A]^0 = k, \text{ a constant}$$

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

or  $k = \frac{dx}{dt} = \frac{\text{Change in concentration}}{\text{Time interval}}$  or

$$k dt = dx$$

on integration we get,

$$kt = x$$

Where  $x$  = concentration of Products/litre of solution

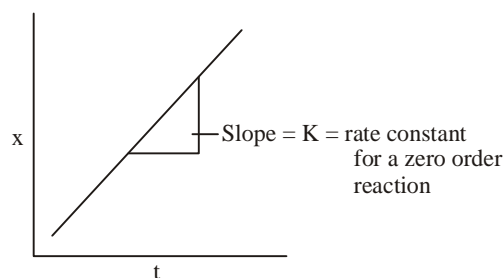
A graph of  $x$  (concentration of products) versus

time should give a straight line

unit of rate constant for a zero order reaction:

$$= \frac{\text{Mol / litre}}{\text{second}}$$

$\therefore$  Unit of  $k$  is  $\text{mole litre}^{-1} \text{sec}^{-1}$ .



**Examples of Zero Order Reaction:**

- (i) Decomposition of hydrogen iodide(g), ammonia (g) on metal surfaces.
- (ii) Combination of hydrogen and chlorine gases in the presence of sun light.

**Characteristics of a Zero Order Reaction :**

1. The concentration of reactant(s) does not vary with time in zero order reaction.
2. The rate of zero order reaction does not change with time.
3. Half life time for a zero order reaction is directly proportional to initial concentration of reactant.
4. Unit of rate constant and rate of reaction are the same ( $\text{mol litre}^{-1} \text{sec}^{-1}$ ) in zero order reactions.

**First order reaction:** When the rate of a reaction is determined by change in one concentration term only, it is called a first order reaction. In such reactions, the rate is directly proportional to the first power of the concentration of the reactant.



follows first order kinetics, then its rate law is,  $\frac{dx}{dt} = k[A]$  ... (i)

where  $k$  is the rate or velocity constant

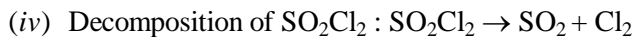
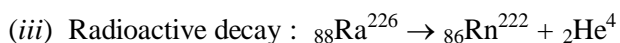
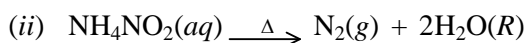
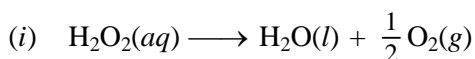
**Unit of first order rate constant :** From expression (i),  $k = \frac{dx}{dt \times [A]}$

$$= \frac{\text{Change in concentration}}{\text{Time interval} \times (\text{concentration of reactant})} = \frac{\text{Mol / litre}}{\text{time} \times \text{Mol / litre}}$$

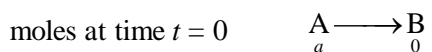
Thus unit of  $k = \text{time}^{-1}$

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### Examples of First Order Reactions:



**First order Kinetic Equation:** Let us consider a hypothetical first order reaction :



Since, the reaction is of first order, its rate at any time is directly proportional to the concentration of 'A'

The rate of reaction at time 't'

$$\frac{dx}{dt} \propto (a - x)$$

$$\text{or} \quad \frac{dx}{dt} = k(a - x) \quad \dots (ii)$$

Rearranging the equation, we get

$$\frac{dx}{(a - x)} = k \cdot dt \quad \dots (iii)$$

On integrating the above equation (ii)

$$\int \frac{dx}{(a - x)} = \int k dt,$$

we get

$$-\ln(a - x) = kt + C \quad \dots (iv)$$

where 'C' is the constant of integration. To evaluate 'C', we apply the conditions,

When  $t = 0, x = 0$

$$\therefore -\ln a = k \times 0 + C$$

$$\text{or} \quad C = -\ln a$$

Substituting, the value of 'C' in (iv)

$$-\ln(a - x) = kt - \ln a$$

$$\text{or} \quad kt = \ln a - \ln(a - x)$$

$$\text{or} \quad k = \frac{1}{t} \ln \frac{a}{(a - x)} \quad \dots (v)$$

On changing the base of logarithm from  $\log_e$  to  $\log_{10}$

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

This expression (vi) is known as **first order kinetic equation**. It gives a relation between the rate constant ( $k$ ), initial concentration of reactant ( $a$ ), concentration of reactant after time 't' and time 't' for which the reaction has proceeded.

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**Half-life period ( $t_{1/2}$ ):** The time in which half of the initial amount of reactant is converted into products or the time taken for the 50% completion of the reaction is known as half-life period.

From first order kinetic equation, (vi)

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

when,  $t = t_{1/2}$                        $x = a/2$

$$\text{So, } k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - \frac{a}{2}}$$

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

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

$$\text{or } t_{1/2} = \frac{0.693}{k} \quad \dots \text{ (vii)}$$

This expression for half-life period does not contain the initial concentration 'a' of the reactant. It indicates that the half-life period of a first order reaction does not depend upon the initial concentration of the reactant.

### Characteristics of First Order Reactions :

- All the first order reactions obey the equation

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

$$\text{or } k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \quad \dots \text{ (viii)}$$

where  $[A]_0$  = Initial concentration of reactant.

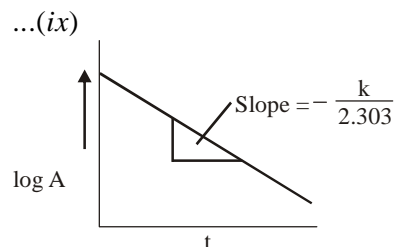
$[A]$  = Concentration of reactant at time 't'

- On rearranging equation (viii) we get

$$\log [A] = \log [A]_0 - \frac{tk}{2.303}$$

If a graph is plotted between time on x-axis and  $\log A$  on y-axis we get a graph as shown below whose

$$\text{slope} = -\frac{k}{2.303}$$



- The value of rate constant, 'k' does not change with the concentration units because  $\frac{a}{(a-x)}$  will have the same value whatever be the units of concentration.
- Time taken for the completion of any fraction of reaction is independent of initial concentration of the reactant.

For example, time taken for  $\frac{2}{3}$  completion of the reaction is  $t_{2/3}$  can be calculated from the 1st order equation.

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

$$\text{when } t = t_{2/3}, x = \frac{2}{3} \times a$$

$$\text{Thus } k = \frac{2.303}{t_{2/3}} \log \frac{a}{a - \frac{2a}{3}}$$

$$\text{or } k = \frac{2.303}{t_{2/3}} \log 3$$

$$\text{or } t_{2/3} = \frac{2.303}{k} \log 3$$

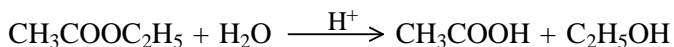
$$\text{or } t_{2/3} = \frac{2.303 \times 0.4771}{k} = \frac{1.098}{k}$$

This expression for  $t_{2/3}$  is also not containing 'a' the initial concentration of the reactant, hence  $t_{2/3}$  is independent of the initial concentration of reactant

**Pseudo-Unimolecular reactions :** Those first order reactions whose molecularity is not one.

**Examples :**

(i) Hydrolysis of an ester :

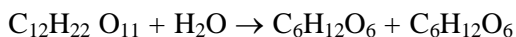


This reaction is bimolecular, but only concentration of the ester is changed because water is present in excess. So, its concentration remains practically constant. The rate equation is

$$\frac{dx}{dt} = k[\text{CH}_3\text{COOC}_2\text{H}_5]$$

So, order of the reaction is one. Hence this is a pseudo unimolecular reaction

(ii) Inversion of sucrose (cane sugar)



Sucrose

Glucose

Fructose

**Second order reactions:** When the rate of a reaction is determined by variation of two concentration terms, the reaction is said to be of second order. For a general reaction,

$A + B \rightarrow$  products, the rate law may be,

$$\frac{dx}{dt} = k [A]^2 [B]^0, \text{ or} \quad \dots (x)$$

$$\frac{dx}{dt} = k [A]^0 [B]^2, \text{ or} \quad \dots (xi)$$

$$\frac{dx}{dt} = k [A] [B] \quad \dots (xii)$$

Thus, the rate of a second order reaction varies directly as the square of the concentration of reactant.

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### Unit of the second order rate constant :

From equation (x) we get

$$k = \frac{dx}{dt \times [A]^2} = \frac{\text{Mol / litre}}{\text{Time interval Mol.}^2/\text{lit.}^2} = \text{lit. mol}^{-1} \text{ time}^{-1}.$$

The unit of second order rate constant involves concentration as well as time.

### Examples of Second Order Reactions :

1. Conversion of ozone into oxygen at 373 K :  $2\text{O}_3 \xrightarrow{373 \text{ K}} 3\text{O}_2$
2. Thermal decomposition of nitrous oxide :  $2\text{N}_2\text{O} \longrightarrow 2\text{N}_2 + \text{O}_2$
3. Alkaline hydrolysis of an ester (saponification) :  $\text{CH}_3 \text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
4. Benzoin condensation,  $\text{C}_6\text{H}_5\text{CHO} + \text{OHC} \cdot \text{C}_6\text{H}_5 \xrightarrow[\text{reflux}]{\text{KCN alc.}} \text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CO} \cdot \text{C}_6\text{H}_5$

**Second order rate equation:** All the second order reactions obey the following kinetic equation,

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \dots \text{ (xiii)}$$

where  $k$  = second order rate constant

$a$  = initial concentration of reactant (s)

$x$  = concentration of reactant converted into products after time ' $t$ '

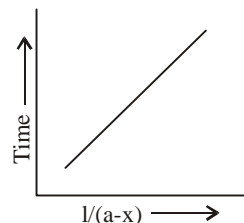
$t$  = time elapsed

### Characteristics of a Second Order Reaction :

- (i) When a graph is plotted between ' $t$ ' and  $\frac{1}{(a-x)}$  a straight line is obtained. On rearranging, equation (xiii).

$$t = \frac{1}{k(a-x)} - \frac{1}{ka} \quad \text{The slope of the line is } \frac{1}{k}.$$

From this ' $k$ ' can be evaluated.



- (ii) The value of second order rate constant depends upon the unit in which concentration of the reactant(s) is expressed, because the value of  $\frac{x}{a(a-x)}$  will be changed when the unit of concentration is changed.
- (iii) The half-life period ( $t_{1/2}$ ) of a second order reaction is inversely proportional to the initial concentration of reactant.

From expression (xiii)

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \dots \text{ (xiii)}$$

when,  $t = t_{1/2}$ ,  $x = a/2$

$$\text{so, } k = \frac{1}{t_{1/2}} \cdot \frac{a/2}{a(a-a/2)}$$

$$\text{or, } t_{1/2} = \frac{1}{ka} \quad \dots \text{ (xv)}$$

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Thus, it is evident from equation (xv) that half life period for a second order reaction is inversely proportional to the initial concentration of reactant.

**Third order reactions:** A chemical reaction is said to be of third order if its rate is determined by the variation of three concentration terms. The rate of a third order reaction is proportional to the third power of concentration of reactants. The rate law for the reaction  $3A \rightarrow \text{products}$ , is:

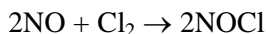
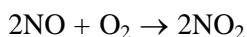
$$\frac{dx}{dt} = k[A]^3.$$

**Unit of third order rate constant :** From the above expression,

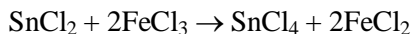
$$k = \frac{dx}{dt \times [A]^3} = \frac{\text{Mol / litre}}{\text{time} \times \text{Mol}^3 / \text{litre}^3} = \text{litre}^2 \text{ mol}^{-2} \text{ time}^{-1}.$$

**Example of third order reactions:**

1. *Gaseous reactions:*



2. *Reaction in solution:*



**Third order kinetic equation:** The following is the kinetic equation obeyed by all the third order reactions

$$k = \frac{1}{2t} \left\{ \frac{1}{(a-x)^2} - \frac{1}{a^2} \right\} \quad \dots \text{ (xvi)}$$

**Characteristics of third order reactions:**

(i) A graph plotted between time 't' and  $\frac{1}{(a-x)^2}$  is straight line. The slope of this straight line is equal to

$$\frac{1}{2k}.$$

(ii) The value of rate constant 'k' depends upon the unit in which the concentration of reactants are expressed.

(iii) The half-life period of the third order reaction is inversely proportional to the initial concentration of reactant raised to the power two *i.e.*,

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

From expression (xvi), it can be derived that

$$t_{1/2} = \frac{1}{2k.a^2}$$

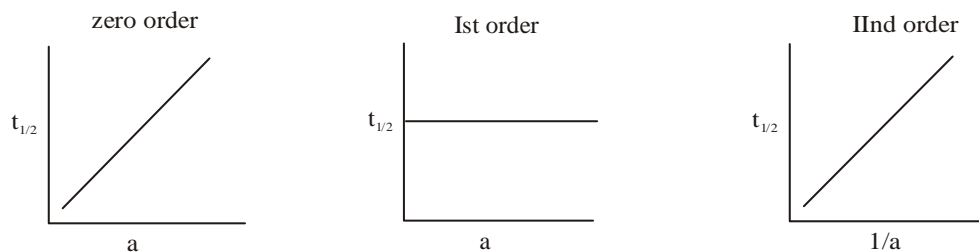
**General expression for  $t_{1/2}$  for any reaction**

In general, the half-life period of any reaction of  $n$ th order is inversely proportional to the initial concentration of the reactant 'a' raised to the power equal to  $(n - 1)$ , *i.e.*, one less than the order of the reaction.

$$\text{i.e.,} \quad t_{1/2} \propto \frac{1}{(a)^{n-1}}$$

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The graphs obtained for different order reactions are

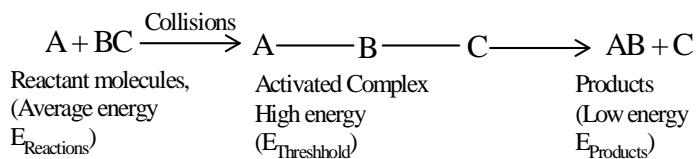


**Collision Theory And Activation Energy :** According to collision theory of reaction rates, the reactant molecules must collide with each other before forming products. Such collisions among reactant molecules which form products, are called effective collisions. All the collisions are not effective collisions. The number of effective collisions is much smaller than the total number of collisions taking place among reactant molecules. Only those collisions result into products in which reactant molecules have energy equal to or excess of a minimum energy known as Threshold Energy.

The reactant molecules which possess energy equal or greater than the threshold energy are called activated molecules. The number of activated molecules is much smaller than the total number of reactant molecules. Since, most of the reactant molecules possess less energy than the threshold energy, therefore reacting molecules require certain energy known as activation energy to reach upto the threshold energy. Thus, the energy of activation may be defined as the energy in excess to the average energy of the reactant molecules which a molecule must be supplied before colliding with one another, so that their collision may result into products.

$\therefore$  Activation energy ( $E_{act}$ ) = Threshold energy – Average energy of reactant molecules,

Thus activation energy is required by the reactant molecules to reach threshold energy so that an activated complex may be formed. An activated complex is unstable arrangement of reacting molecules with high energy. This complex decomposes into products. Thus, there exists an energy barrier between reactants and products. If the reactant molecules possess sufficient energy to cross this energy barrier, their collision will lead to the formation of products. So, reactions having high activation energy proceed slowly and those where activation energy is less, the rate of reaction is very high.



$E_{act}$  = Activation energy for forward reaction

= Threshold energy (Energy of activated complex) –  $E_{\text{Reactants}}$  (Average energy of reactants)

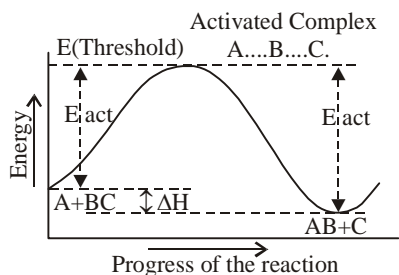
$E_{act}$  = Activation energy for the backward reaction.

=  $E_{act f} + \Delta H$  (where  $E_{act f}$  is activation energy of forward reaction).

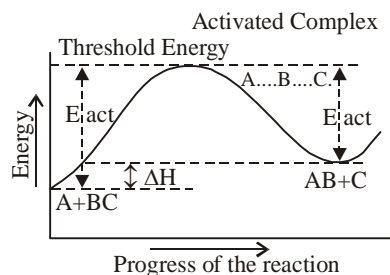
= Activation energy for the forward reaction + heat of reaction.

Heat of reaction =  $E_{\text{Products}} - E_{\text{Reactant}}$

Energy profile for an exothermic reaction



Energy profile for an endothermic reaction



**Factors Affecting Rate of Chemical Reaction:** The reaction rate is influenced by the following factors :

- (i) Concentration of reactants
- (ii) Temperature
- (iii) Nature of reactants and products
- (iv) Presence of a catalyst
- (v) Surface area of solid reactant and
- (vi) Exposure of radiations

(i) **Effect of concentration :** The rate of a reaction is directly proportional to the product of active masses raised to the power equal to their coefficients in a balanced chemical equation, (Law of mass action). Hence, the rate of reaction decreases as the reaction proceeds towards the products because the concentration of reactant(s) decreases.

(ii) **Effect of temperature :** The rate of a reaction always increases on increasing temperature whether the reaction is endothermic or exothermic, because the number of activated molecules increase. In general, the rate of a reaction gets doubled with ten degree increase in temperature.

**Arrhenius Equation :** In order to give a quantitative relation between the rate constant and temperature of a reaction, Arrhenius proposed the following equation which is known as Arrhenius equation after his name.

$$k = Ae^{-E_a/RT} \quad \dots (1)$$

Where  $A$  = Arrhenius factor, pre-exponential factor, collision factor, frequency factor.

$E_a$  = Energy of activation for the reaction

$R$  = Molar gas constant

$T$  = Temperature of the reaction in absolute scale.

On taking logarithm of both sides (1)

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

On multiplying by 2.303 to convert the base of log from  $\log_e$  to  $\log_{10}$

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

On dividing the whole equation by 2.303, we get

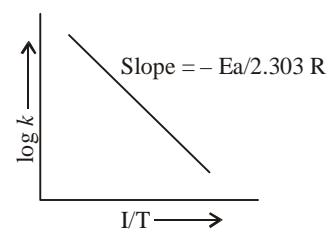
$$\log k = \log A - \frac{E_a}{2.303 RT} \quad \dots (2)$$

Expression (2) is the equation of a straight line, when  $\log k$  is plotted

against  $1/T$ , we get a straight line whose slope is equal to  $-\frac{Ea}{2.303 R}$

If  $k_1$  and  $k_2$  are the rate constant at temperature  $T_1$  and  $T_2$  respectively, then the Arrhenius equation takes the form,

$$\log \left( \frac{k_2}{k_1} \right) = \frac{Ea}{2.303 R} \left( \frac{T_2 - T_1}{T_1 T_2} \right) \quad \dots(3)$$



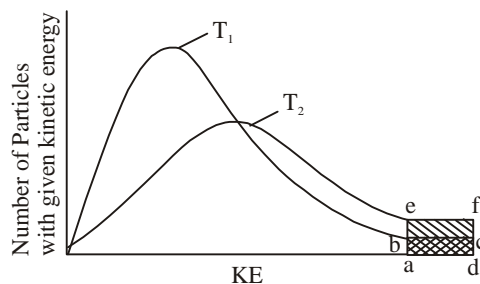
In deriving (3), it has been assumed that 'A' and  $Ea$  are independent of temperature.

In the Arrhenius equation  $k = A e^{-Ea/RT}$ , When the absolute temperature of the reaction becomes infinity, the rate constant of the reaction becomes equal to A, the pre-exponential factor.

$$k = A e^{-Ea/R} \times \infty = A e^0$$

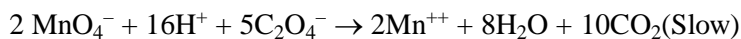
or  $k = A$

When energy of activation  $Ea$  of a reaction is zero, the reaction rate becomes independent of temperature.



If one looks at the graph above then one would observe that as temperature increases from  $T_1$  to  $T_2$  the energy distribution changes

- (1) The number of molecules possessing average kinetic energy decreases?
  - (2) The number of molecules possessing higher kinetic energy increases as observed under the area of shaded portion  $abcd$  and  $aefd$ .
  - (3) When  $T_2 = T_1 + 10$  then the area shaded under the graph  $aefd$  is twice the area shaded under the graph  $abcd$ .
- (iii) **Nature of reactants and products :** Chemical reactions which involve complex molecules as reactants and in which complex molecules are formed as products, proceed at a slower rate. The reason is that, greater number of bond rearrangements are involved in complex reactants and products which makes the reaction slow. Reactions involving lesser number of bond rearrangements are fast reactions. For example, oxidation of  $Fe^{++}$  by  $MnO_4^-$  ion in acidic medium takes place faster than the oxidation of oxalate ion ( $C_2O_4^{--}$ ) under the same condition.



- (iv) **Presence of a catalyst:** Generally, a positive catalyst enhances the rate of a reaction by changing the path of reaction which requires less activation energy. But negative catalyst retards a chemical reaction. Thus, a catalyst alters the rate of reaction.

- 
- (v) **Surface area of solid reactant:** This factor is important for heterogeneous reactions involving a solid as one of the reactants. The rate of such a reaction increases with increasing surface area of solid reactant, *i.e.*,  $\text{Rate of reaction} \propto \text{Surface area of solid reactant}$

**For example :** Wood shavings burn more rapidly than a log of wood of same mass. Coal dust burns at a faster rate than large piece of coal.

- (vi) **Exposure to radiation:** Rates of certain reaction increases by absorption of photons of a particular radiation. Such reactions are called photochemical reactions. For example, Hydrogen and chlorine gases do not combine with each other in dark. But when their mixture is exposed to light, a loud explosion occurs and the chemical combination takes place. Formation of a image on a photographic plate, photosynthesis, fading of colour in sunlight, etc. are other examples of photochemical reactions.

**Temperature Coefficient of Rate Constant :** The ratio of rate constant of a reaction at two temperatures differing by ten degrees is called temperature coefficient of rate constant.

$$\text{Temperature coefficient of rate constant} = \frac{k_{t+10^\circ}}{k_t} = \frac{k_{35^\circ}}{k_{25^\circ}}$$

It has been observed experimentally that for a large number of reactions, the rate increases (rate constant increases) two to three time for a ten degree rise in temperature. Thus,

$$\frac{k_{t+10^\circ}}{k_t} = 2 \text{ to } 3$$

### Determination of Order of Reaction

- (1) *Half-change method* : This method is based on the fact that half-change time is inversely proportional to the initial concentration of reactant raised to the power one less than the order of reaction. *i.e.*,

$$t_{1/2} \propto \frac{1}{(a)^{n-1}}$$

If  $t_1$  and  $t_2$  are the half-life periods of a chemical reaction with different initial concentrations  $a_1$  and  $a_2$  and ' $n$ ' is the order of the reaction, then by using the following relation, order can be determined.

$$t_{1/2 (1)} \propto \frac{1}{(a_1)^{n-1}}$$

$$t_{1/2 (2)} \propto \frac{1}{(a_2)^{n-1}}$$

$$\therefore \frac{t_2}{t_1} = \left[ \frac{a_1}{a_2} \right]^{n-1}$$

- (a) For a zero-order reaction,  $n = 0$

$$\frac{t_2}{t_1} = \left[ \frac{a_1}{a_2} \right]^{0-1} = \frac{a_2}{a_1}$$

or  $\frac{t_1}{a_1} = \frac{t_2}{a_2} = \text{constant.}$

- (b) For a first order reaction,  $n = 1$
-

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$$\frac{t_2}{t_1} = \left[ \frac{a_1}{a_2} \right]^{1-1} = \left[ \frac{a_1}{a_2} \right]^0 = 1$$

or  $t_1 = t_2 = \text{constant}$ .

(c) For a second order reaction,  $n = 2$

$$\frac{t_2}{t_1} = \left[ \frac{a_1}{a_2} \right]^{2-1} = \frac{a_1}{a_2}$$

$$t_1 \times a_1 = t_2 \times a_2 = \text{constant}$$

(d) For third order reaction,  $n = 3$

$$\frac{t_2}{t_1} = \left[ \frac{a_1}{a_2} \right]^{3-1} = \frac{a_1^2}{a_2^2}$$

$$t_1 \times a_1^2 = t_2 \times a_2^2 = \text{constant}.$$

(2) *Differential method* : When the order of a reaction with respect to a particular component is 'n' and  $r_1$  and  $r_2$  are the rates of the reaction at different concentrations  $c_1$  and  $c_2$  of that reactant, then

$$\frac{r_1}{r_2} = \left[ \frac{c_1}{c_2} \right]^n.$$

Thus, order of reaction with respect to individual reactants is determined. The sum of the orders with respect to individual reactants, gives the overall order of the reaction.

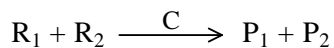
## CATALYST

It is indeed, a fascinating aspect of chemistry that certain reactions which are very slow become very fast when a small quantity of foreign substance is added. These foreign substances increase the rate of the reaction without undergoing any change and can be recovered as such after the completion of the reaction.

The phenomenon of increase in the rate of a reaction with the help of a catalyst is known as catalysis. In certain reactions one of the products itself acts as a catalyst, such catalysts are called Autocatalysts.

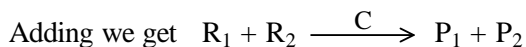
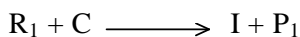
The role of catalyst in increasing the rate is not completely understood, but it is believed to be taking place as follows :

Let us assume a reaction



where  $R_1$  and  $R_2$  are reactants and  $P_1$  and  $P_2$  are products and C is the catalyst.

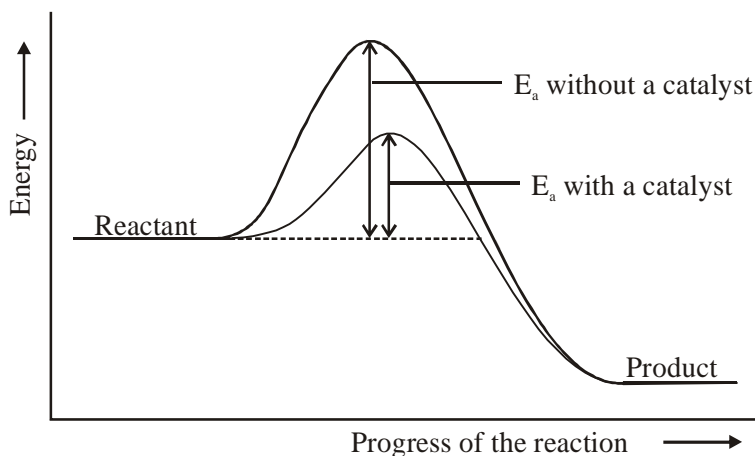
Let us assume that the reaction proceeds in two steps



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A catalyst provides another path for the reaction that has a lower energy of activation  $E_a$ .

This could be explained better by using the activated complex Figure



When one looks at the graph of the free energy of activation it is found that the activation energy is lowered for both the forward and the backward reactions without changing the overall free energy change of the reaction.

This implies that a catalyst changes the rates of both the forward and backward reactions : Since  $\Delta G$  for the reactions is not changed, the equilibrium constant  $K$  remains unchanged in the presence of catalyst.

Hence it follows that a catalyst helps in attaining the equilibrium position rapidly but does not help in changing the relative proportions of reactants and products at equilibrium.

### General Characteristics of Catalytic Reactions

- (1) The catalyst remains unchanged in amount and chemical composition at the end of reactions. However it may undergo a physical change.
  - (2) Only a small quantity of catalyst is generally needed.
  - (3) A catalyst does not alter the positions of equilibrium in reversible reaction
  - (4) A catalyst does not initiate a reaction
  - (5) The catalyst is generally specific in its action
  - (6) The catalyst cannot alter the nature of the products of reactions
-



## SOLVED EXAMPLES

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**Example 1:** Two reactions of same order have equal pre-exponential factors but their activation energies differ by  $24.9 \text{ kJ mol}^{-1}$ . Calculate the ratio between the rate constant of these reactions at  $27^\circ\text{C}$ .

**Solution:** A i.e., (pre-exponential factor) is same.

$$\log k_1 = \log A - \frac{E_{a1}}{2.303RT} \quad \dots (i)$$

$$\log k_2 = \log A - \frac{E_{a2}}{2.303RT} \quad \dots (ii)$$

Subtract equation (i) from (ii)

$$\log k_2 - \log k_1 = \frac{E_{a1} - E_{a2}}{2.303RT}$$

$$\begin{aligned} \text{or} \quad \log \frac{k_2}{k_1} &= \frac{24.9 \times 1000}{2.303 \times 8.314 \times 300} \\ &= 4.334 \end{aligned}$$

$$\text{or} \quad \frac{k_2}{k_1} = \text{Antilog}(4.334)$$

$$\therefore \frac{k_2}{k_1} = 2.162 \times 10^4$$

**Example 2:** The energy of activation for a reaction is  $100 \text{ kJ mole}^{-1}$ . Presence of a catalyst lowers the activation energy by 75%. What will be the effect on rate of reaction at  $20^\circ\text{C}$ ; other things being equal ?

**Solution :** We know,  $k = Ae^{-E_a/RT}$

In the absence of catalyst

$$k_1 = Ae^{-100/RT} \quad \dots (i)$$

In the presence of catalyst

$$k_2 = Ae^{-25/RT} \quad \dots (ii)$$

Dividing equation (1) by (2)

$$\frac{k_1}{k_2} = e^{-75/RT}$$

Taking log

$$\text{or} \quad \ln \frac{k_2}{k_1} = \frac{+75}{RT} \quad (E_a \text{ in kJ})$$

$$\begin{aligned} \text{or} \quad \log \frac{k_2}{k_1} &= \frac{+75}{2.303RT} \\ &= \frac{+75 \times 1000}{2.303 \times 8.314 \times 298 RT} \end{aligned}$$

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$$\frac{k_2}{k_1} = 2.337 \times 10^{13}$$

$$\therefore \frac{r_2}{r_1} = \frac{k_2}{k_1} = 2.35 \times 10^{13}$$

**Example 3:** If in a reaction  $A \rightarrow \text{Products}$ , the concentration of the reaction A is  $C_0, \alpha C_0, \alpha^2 C_0, \alpha^3 C_0 \dots$  after time values  $0, t, 2t, 3t, \dots$  where  $\alpha$  is a constant  $0 < \alpha < 1$ . Show that the reaction is of first order. How is the rate constant  $k$  related to  $a$  and  $t$ ?

**Solution :** We know for first order reaction

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

Here  $a = C_0$

$(a - x) = \alpha C_0, \alpha^2 C_0, \alpha^3 C_0$  etc. at times  $t, 2t, 3t$  etc.

Now, substituting these values in the rate equation

$$k_1 = \frac{2.303}{t} \log \frac{C_0}{C_0 \alpha} = \frac{2.303}{t} \log \alpha^{-1} \quad \dots (1)$$

$$k_2 = \frac{2.303}{2t} \log \frac{C_0}{(C_0 \alpha^2)} = \frac{2.303}{2t} \log \alpha^{-2}$$

$$= \frac{2.303}{2t} \times 2 \log \alpha^{-1} = \frac{2.303}{t} \log \alpha^{-1} \quad \dots (2)$$

Similarly

$$k_3 = \frac{2.303}{3t} \log \frac{C_0}{(C_0 \alpha^3)} = \frac{2.303}{t} \log \alpha^{-3}$$

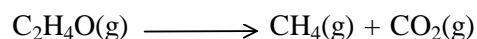
$$\frac{2.303}{3t} \times 3 \log \alpha^{-1} = \frac{2.303}{t} \log \alpha^{-1} \quad \dots (3)$$

Since the value of rate constant,  $k(k_1, k_2, k_3)$  are constant. Hence, the reaction is of first order.

The rate constant  $k$  is related to  $\alpha$  and  $t$  as

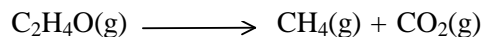
$$k = \frac{2.303}{t} \log \alpha^{-1}$$

**Example 4:** Calculate the half life of the following first order reaction



Given the initial pressure of  $\text{C}_2\text{H}_4\text{O(g)}$  is 84 mm and the total pressure at the end of 16 min is 110 mm.

**Solution :**



Initial conc.  $\qquad\qquad\qquad a \qquad\qquad\qquad 0 \qquad\qquad\qquad 0$

Conc. after 16 min.  $\qquad\qquad\qquad a - x \qquad\qquad\qquad x \qquad\qquad\qquad x$

$a \propto 84$  mm. Total no. of moles after 16 min =  $a - x + x + x = a + x$

$\therefore a + x \propto 110$  mm

$x \propto 26$

$(a - x) \propto 58$

$$\text{or } 16 = \frac{2.303}{t} \log \frac{84}{58} = \frac{2.303}{k} \times 0.1608$$

$$k = \frac{2.303 \times 0.1608}{16} = 0.0231 \text{ min}^{-1}$$

$$\therefore \text{Half life period } t_{1/2} = \frac{0.693}{0.0231 \text{ min}^{-1}} = 30 \text{ min.}$$

**Example 5:** For a reaction  $2A \longrightarrow \text{Product}$ , it is found that the rate of reaction becomes 2.25 when the concentration of A is increased 1.5 times, calculate the order of reaction.

**Solution :** Rate,  $r = k [A]^n$  .... (1)

When concentration is increased 1.5 times, the rate of reaction become 2.25.

$$\therefore 2.25 r = k [1.5A]^n \quad \dots (2)$$

Divide (2) by (1)  $\frac{2.25r}{r} = \frac{k[1.5A]^n}{k[A]^n}$

$$2.25 = (1.5)^n$$

$$(1.5)^2 = (1.5)^n$$

$$n = 2$$

**Example 6:** At  $380^\circ\text{C}$ , the half life period for first order decomposition of  $\text{H}_2\text{O}_2$  is 360 min. The energy of activation of the reaction is  $200 \text{ kJ mol}^{-1}$ . Calculate the time required for 75% decomposition at  $450^\circ\text{C}$ .

**Solution :** At  $380^\circ\text{C}$ , i.e.  $380 + 273 \text{ K} = 653 \text{ K}$  :  $t_{1/2} = 360 \text{ min}$ .

$$\therefore T_1 = 653 \text{ K}, k_1 = \frac{0.693}{360} \text{ min}^{-1}$$

$$= 1.925 \times 10^{-3} \text{ min}^{-1}$$

$$E_a = 2 \times 10^5 \text{ J mol}^{-1}$$

$$T_2 = 450 + 273 = 723 \text{ K}, k_2 = ?$$

$$\therefore \log \frac{k_2}{1.925 \times 10^{-3}} = \frac{2 \times 10^5}{2.303 \times 8.314} \left[ \frac{723 - 653}{653 \times 723} \right]$$

$$= 1.5487$$

$$\text{or } \frac{k_2}{1.925 \times 10^{-3}} = 35.38$$

$$\text{or } k_2 = 35.38 \times 1.925 \times 10^{-3}$$

$$= 6.81 \times 10^{-2} \text{ min}^{-1}$$

For 75% decomposition

$$x = 75\% \text{ of } a = 0.75a$$

$$t = \frac{2.303}{6.81 \times 10^{-2}} \log \frac{1}{0.25}$$

$$= 20.39 \text{ min.}$$

**Example 7 :** The following data are for the reaction  $A + B \rightarrow \text{products}$  :

Conc. A (M)	Conc. B (M)	Initial rate ( $\text{mol L}^{-1} \text{ s}^{-1}$ )
0.1	0.1	$4.0 \times 10^{-4}$
0.2	0.2	$1.6 \times 10^{-3}$
0.5	0.1	$1.0 \times 10^{-2}$
0.5	0.5	$1.0 \times 10^{-2}$

- (a) What is the order with respect to A and B for the reaction ?  
 (b) Calculate the rate constant  
 (c) Determine the reaction rate when the concentration of A and B are 0.2 M and 0.35 M, respectively.

**Solution :**

$$R = K[A]^m [B]^n$$

$$4.0 \times 10^{-4} = K (0.1)^m (0.1)^n \quad \dots (i)$$

$$1.6 \times 10^{-3} = K (0.2)^m (0.2)^n \quad \dots (ii)$$

$$1.0 \times 10^{-2} = K (0.5)^m (0.1)^n \quad \dots (iii)$$

$$1.0 \times 10^{-2} = K (0.5)^m (0.5)^n \quad \dots (iv)$$

- (a) Divide equation (iii) by (iv)

$$\frac{1.0 \times 10^{-2}}{1.0 \times 10^{-2}} = \frac{K(0.5)^m(0.1)^n}{K(0.5)^m(0.5)^n}$$

$$1 = \left(\frac{1}{5}\right)^n$$

$$\therefore n = 0$$

Thus the order of reaction with respect to B is zero.

Divide eq. (i) by (iii)

$$\frac{4.0 \times 10^{-4}}{1.0 \times 10^{-2}} = \frac{K(0.1)^m(0.1)^n}{K(0.5)^m(0.1)^n}$$

$$4 \times 10^{-2} = \left(\frac{1}{5}\right)^m$$

$$(0.2)^m = (0.2)^2$$

$$m = 2$$

Thus the order of reaction with respect to A is two

- (b) Substituting the values of m and n in .....(ii)

$$1.6 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1} = 0.04 \text{ M}^2 \text{ K}$$

$$K = \frac{1.6 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1}}{0.04 \text{ M}^2} = 4.0 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$$

- (c)  $R = K[A]^2[B]^0$

$$= 4 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1} \times 0.04 \text{ M}^2 \times 1 = 1.6 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1}$$

**Example 8 :** The decomposition of hydrogen peroxide in an aqueous solution is a first order reaction. It can be studied by titrating quickly 10 ml. portions of reactions mixture at various times from the  $t = 0$  of reaction against a standard solution of  $\text{KMnO}_4$ . Volume of  $\text{KMnO}_4$  solution used in each case is proportional to the remaining concentration of  $\text{H}_2\text{O}_2$ .

From the following data calculate the rate constant of the reaction.

Time (seconds)	0	600	1200
$\text{KMnO}_4$ solution used (ml)	22.8	13.8	8.2

**Solution :** Here,  $a = 22.8$ ,  $a - x = \text{Vol. of } \text{KMnO}_4 \text{ used at various times } t$ .

At time 600 seconds :

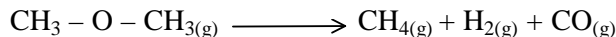
$$K = \frac{2.303}{600} \log \frac{22.8}{13.8} = 0.000837$$

At time 1200 seconds :

$$K = \frac{2.303}{1200} \log \frac{22.8}{8.2} = 0.000852$$

$$\text{Average value of } K = \frac{0.000837 + 0.000852}{2} = 0.000844 \text{ or } 8.44 \times 10^{-4} \text{ sec}^{-1}$$

**Example 9 :** The gas phase decomposition of dimethyl ether follows first order kinetics



The reaction is carried out in a constant volume container at 500°C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minutes? Assume ideal gas behaviour.

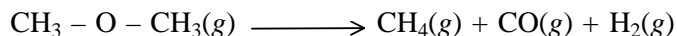
**Solution :** Given  $t_{1/2} = 14.5 \text{ min}$ , initial pressure = 0.40 atm,  $t = 12 \text{ min}$

$$\text{Now, } K = \frac{0.693}{14.5} = 4.78 \times 10^{-2} \text{ min}^{-1}$$

$$4.78 \times 10^{-2} = \frac{2.303}{12 \text{ min}} \log \frac{0.4}{0.4 - x}$$

which gives  $x = 0.175 \text{ atm}$ .

Since volume and temp. are constant, final pressure :

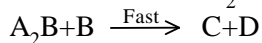
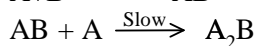
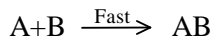


$$\begin{array}{ccccccc} 0.4 & & & & & & \\ 0.4 - 0.175 & & 0.175 & & 0.175 & & 0.175 \end{array}$$

$$\begin{aligned} \text{Hence total pressure} &= 0.4 - 0.175 + 3 \times 0.175 \\ &= \mathbf{0.749 \text{ atm}} \end{aligned}$$

# OBJECTIVE QUESTIONS

1. If a reaction  $A + B \rightarrow C + D$  has the following mechanism

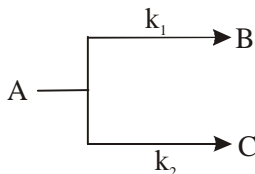


the rate law is

- (a) Rate =  $k[A][B]^2$  (b) Rate =  $k[A]^2[B]$   
(c) Rate =  $k[A][B]$  (d) Rate =  $k[A]^2[B]^2$
2. In a reaction  $A \rightarrow B$ , the rate of reaction increases two times on increasing the concentration of the reactant four times, the order of reaction
- (a) 0 (b) 2 (c) 1/2 (d) 4
3. For a first order reaction  $A \rightarrow B + 2C + 3D$  (A is optically inactive and B, C and D are dextrorotary), the optical rotation at time  $t$  and  $\infty$  are  $r_t$  and  $r_\infty$  respectively, the expression for rate constant is

(a)  $k = \frac{1}{t} \ln \frac{r_t}{r_\infty - r_t}$  (b)  $k = \frac{1}{t} \ln \frac{r_\infty}{r_\infty - r_t}$  (c)  $k = \frac{1}{t} \ln \frac{r_\infty - r_t}{r_t}$  (d) None of these

4. A substance undergoes first order decomposition. The decomposition following two parallel first order reaction as :



$k_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$  and  $k_2 = 3.8 \times 10^{-5} \text{ sec}^{-1}$ .

The percentage distribution of B and C are :

- (a) 80% B and 20% C (b) 76.83% B and 23.17% C  
(c) 90% B and 10% C (d) 60% B and 40% C
5. In a certain reaction, 10% of the reactant decomposes in one hour, 20% in two hours, 30% in three hours and so on. The dimensions of the rate constant is
- (a) Hour<sup>-1</sup> (b) Mol lit<sup>-1</sup> sec<sup>-1</sup> (c) Lit mol<sup>-1</sup> sec<sup>-1</sup> (d) Mol sec<sup>-1</sup>
6. The rate of reaction,  $2NO + O_2 \rightarrow 2NO_2$ , at 25°C is  $0.028 \text{ mol l}^{-1} \text{ s}^{-1}$ . The experimental rate is given by

$$r = k[NO]^2[O_2]$$

If the initial concentrations of the reactants are  $O_2 = 0.040 \text{ mol l}^{-1}$  and  $NO = 0.01 \text{ mol l}^{-1}$ , the rate constant of the reaction is :

- (a)  $7.0 \times 10^{-2} \text{ l}^2 \text{ mol}^2 \text{ s}^{-1}$  (b)  $7.0 \times 10^{-4} \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$   
(c)  $7.0 \times 10^2 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$  (d)  $7.0 \times 10^3 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$
7. The following data are for the decomposition for ammonium nitrite in aqueous solution.

Vol. of $N_2$ in $\text{cm}^3$	6.25	9.0	11.42	13.65	35.02
Tim (min)	10	15	20	25	$\infty$

The order of reaction is :

- (a) 3 (b) 2 (c) 1 (d) 0

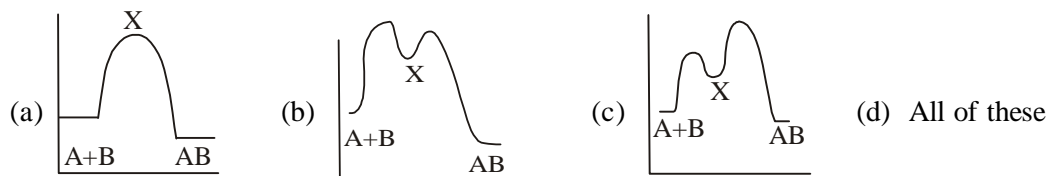
8. The ratio of number of molecules reacting in a given time to number of quanta of light absorbed in the same time is called  
 (a) Activation energy (b) Activated complex (c) Quantum yield (d) None of these
9. The first order reaction is 15% complete in 20 min. The time taken for it to be 60% complete is  
 (a) 112.7 sec. (b) 1.127 sec (c) 1127 sec. (d) None of these
10. The rate constant is numerically same for the three reaction of I order, II order, III order, then the order of rates of reactions will be (A)  $< 1$   
 $r_1 = k[A]^1$ ,  $r_2 = k[A]^2$ ,  $r_3 = k[A]^3$   
 (a)  $r_1 = r_2 = r_3$  (b)  $r_2 > r_1 > r_3$  (c)  $r_3 > r_2 > r_1$  (d) None of these
11. A zero order reaction is one whose rate is independent of  
 (a) Temperature of reaction  
 (b) The concentration of reactant  
 (c) The concentration of the product  
 (d) The material of the vessel in which the reaction is carried out
12. The rate constant of a reaction is  $0.69 \times 10^{-1} \text{ min}^{-1}$  and initial concentration is 0.2 mol/L. The  $t_{1/2}$  is  
 (a) 400 sec (b) 600 sec (c) 800 sec (d) None of these

13. Select the rate law expression that corresponds to the data for the reaction  $A + B \rightarrow \text{H products}$

Exp.	[A]	[B]	Initial rate
1.	0.012	0.035	0.1
2.	0.024	0.070	0.8
3.	0.024	0.035	0.1
4.	0.012	0.070	0.8

- (a) Rate =  $K [B]^3$  (b) Rate =  $K [B]^4$   
 (c) Rate =  $K [A] [B]^3$  (d) Rate =  $K [A]^2 [B]^2$
14. The activation energy for a reaction is  $12.9 \text{ kcal mol}^{-1}$ . The increase in the rate constant when its temperature is increased from 298 K to 308 K is  
 (a) 100% (b) 50% (c) 10% (d) None of these
15. For an exothermic chemical process occurring in two steps as :  
 (i)  $A+B \rightarrow X$  (slow) (ii)  $X \rightarrow AB$  (fast)

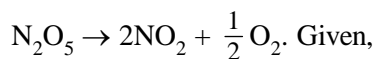
The progress of the reaction can be best described by :



16. In the reversible reaction  $2\text{NO}_2 \xrightleftharpoons[k_2]{k_1} \text{N}_2\text{O}_4$ , the rate of disappearance of  $\text{NO}_2$  is equal to  
 (a)  $k_1 [\text{NO}_2]^2$  (b)  $2k_1 [\text{NO}_2]^2 - 2k_2 [\text{N}_2\text{O}_4]$   
 (c)  $2k_1 [\text{NO}_2]^2 - k_2 [\text{N}_2\text{O}_4]$  (d) None of these

17. For the first order reaction  $A(g) \rightarrow 2B(g) + C(g)$  the initial pressure  $P_A = 90$  mm Hg, the pressure after 10 minute is found to be 180 mm Hg. The rate constant of the reaction is  
 (a)  $1.15 \times 10^{-3} \text{ sec}^{-1}$  (b)  $2.3 \times 10^{-3} \text{ sec}^{-1}$  (c)  $3.45 \times 10^{-3} \text{ sec}^{-1}$  (d) None of these

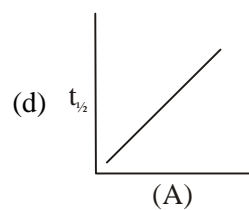
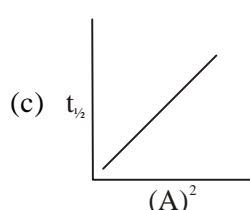
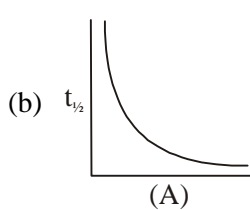
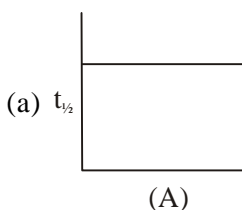
18. For the reaction,



$$-\frac{d[N_2O_5]}{dt} = K_1[N_2O_5], \quad \frac{d[NO_2]}{dt} = K_2[N_2O_5] \text{ and } \frac{d[O_2]}{dt} = K_3[N_2O_5]$$

The relation between  $K_1$ ,  $K_2$  and  $K_3$  :

- (a)  $2K_1 = K_2 = 4K_3$  (b)  $K_1 = K_2 = K_3$  (c)  $2K_1 = 4K_2 = K_3$  (d) None of these
19. In general case when the temperature changes by  $\Delta t^\circ \text{ C}$  the temperature coefficient is given by  
 (a)  $\frac{K_{t+\Delta t}}{K_t}$  (b)  $\frac{K_t}{K_{t+\Delta t}}$  (c) Both of these (d) None of these
20. The graph of  $t_{1/2}$  vs. initial concentration of reactions for a II order reaction is



21. The rate of reaction is expressed in different ways as follows  
 (a) Rate of formation of C = 3 × rate of consumption of B

(b)  $-\frac{1}{3} \frac{d(D)}{dt} = \frac{1}{4} \frac{d(A)}{dt} = -\frac{d(B)}{dt}$

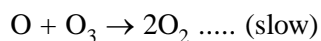
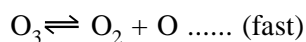
Hence the reaction is

- (a)  $4B + A \rightarrow 2C + 3D$  (b)  $B + 3D \rightarrow 4A + 2C$   
 (c)  $A + B \rightarrow C + D$  (d) None of these
22. In acidic medium the rate of reaction between  $(BrO_3)^-$  and  $Br^-$  ions is given by the expression

$$-\frac{d(BrO_3^-)}{dt} = k[BrO_3^-][Br^-][H^+]^2$$

It means

- (a) Rate constant of overall reaction is  $4 \text{ sec}^{-1}$   
 (b) Rate of reaction is independent of the conc. of  $Br^-$   
 (c) The change in pH of the solution will not affect the rate  
 (d) Doubling the conc. of  $H^+$  ions will increase the reaction rate by 4 times
23. The chemical reaction  $2 O_3 \rightarrow 3O_2$  Proceeds as follows :



The rate law expression should be

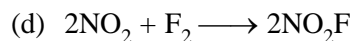
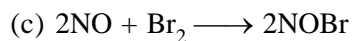
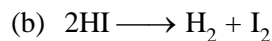
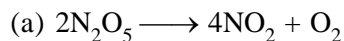
- (a)  $r = k [O_3]^2$  (b)  $r = k [O_3]^2 [O_2]^{-1}$  (c)  $r = k [O_3] [O_2]$  (d) None of these





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31. Reactions of second order among the following



32. For the first order reaction  $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$

(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

33. Which of the following statement(s) about the Arrhenius equation is/are correct?

(a) The pre-exponential factor becomes equal to the rate constant of the reaction at extremely high temperature.

(b) When the activation energy of the reaction is zero, the rate becomes independent of temperature

(c) The term  $e^{-E_a/RT}$  represents the fraction of the molecules having energy in excess of threshold value

(d) On raising temperature, rate constant of the reaction of greater activation energy increases less rapidly than that of the reaction of smaller activation energy.

34. Which of the following statements are correct?

(a) Time required for 75% completion is 1.5 times of half life for zero order reaction

(b) Time needed for a definite fraction of first order reaction does not vary with the initial concentration

(c) Time for 25% reaction is one-third of half-life in second order process

(d) Rate of zero order reaction gets doubled if the concentration of the reactant is increased to a two fold value.

35. Hydrolysis of a sugar is catalysed by  $\text{H}^+$  ion. Half-life of the reaction is independent of initial concentration of sugar at a particular pH. At a constant concentration of sugar rate increases 10 times when pH is decreased by one unit. Pick out the correct statements of the following:

(a) Rate  $\propto$ [sugar]

(b) Rate  $\propto$ [ $\text{H}^+$ ]

(c) Rate law : rate = k[sugar]

(d) Rate law : rate = k[sugar] [ $\text{H}^+$ ]

36. Choose the incorrect statements.

(a) The units of zero order rate constant (k) is that of concentration  $\times$  time<sup>-1</sup>

(b) In zero order reaction the concentration of product increases linearly with time.

(c) The photochemical reaction of  $\text{H}_2$  and  $\text{Cl}_2$  over water surface is of zero order.

(d) The thermal decomposition of HI on gold surface is of zero order.

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# MISCELLANEOUS ASSIGNMENT

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## Comprehension-I

Suppose 50 bacteria are placed in a flask containing nutrients for the bacteria so that they can multiply. A study at 35°C gave the following results

Time (minutes)	0	15	30	45	60
Number of bacteria	100	200	400	800	1600

Then

- This multiplication of bacteria follows a  
(a) zero order reaction (b) 1st order reaction (c) 2nd order reaction (d) 3rd order reaction
- The rate constant for the reaction is  
(a)  $0.0462 \text{ min}^{-1}$  (b)  $0.462 \text{ min}^{-1}$  (c)  $4.62 \text{ min}^{-1}$  (d)  $46.2 \text{ min}^{-1}$
- The rate of the reactions initially is  
(a) 4.62 bacterias per minute (b) 23.1 bacterias per minute  
(c) 23.1 bacterias per sec (d) 0.231 bacterias per sec
- The  $t_{1/2}$  for the reaction is  
(a) 1.5 sec (b) 1.5 min (c) 150 min (d) 15 min
- The expression used for calculating the rate constant value in this experiment is  
(a)  $k = \frac{2.303}{t} \log \frac{a}{a-x}$  (b)  $k = -\frac{2.303}{t} \log \frac{a}{a+x}$   
(c)  $k = \frac{0.693}{t}$  (d)  $k = \frac{x}{t}$

## Comprehension-II

Temperature has a marked effect on the rate of reaction. Quantitatively, the effect of temperature is explained by Arrhenius equation,  $k = Ae^{-E_a/RT}$  in which  $E_a$  represent the activation energy of the reaction. Collision theory explains how the rate of reaction depends upon the energy factor and orientation factor, *i.e.*, for any collision to be effective, the energy of the colliding molecules should be greater than threshold value and should have proper orientation at the time of collision.

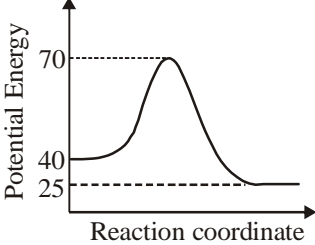
Mathematically, collision theory postulates that  $k = PZ_{AB} e^{-E_a/RT}$ . Another factor which affects the rate of reaction is the addition of a catalyst which increases the speed of forward as well as backward reaction.

- The temperature coefficient of most of the reactions lies between  
(a) 1 and 3 (b) 2 and 3 (c) 1 and 4 (d) 2 and 4
  - When  $\log k$  is plotted against  $1/T$ , where  $k$  is rate constant and  $T$  is temperature, a straight line is obtained with a slope of  $-7000 \text{ K}$ . The energy of activation of the reaction is nearly  
(a)  $11.4 \text{ kJ mol}^{-1}$  (b)  $12.4 \text{ kJ mol}^{-1}$  (c)  $13.4 \text{ kJ mol}^{-1}$  (d)  $14.4 \text{ kJ mol}^{-1}$
-

8. The rate constant is given by the equation  $K = P.Ze^{-E/RT}$ . Which factor should register a decrease for the reaction to proceed more rapidly?
- (a) T                      (b) Z                      (c) E                      (d) P
9. The addition of catalyst to a reaction results in
- (a) decrease in  $\Delta G$  value and no change in  $\Delta H$  value  
 (b) decrease in  $\Delta H$  value and no change in  $\Delta G$  value  
 (c) decrease in  $\Delta H$  as well as  $\Delta G$  value  
 (d) no change in  $\Delta G$  as well as  $\Delta H$  value
10. Radioactive disintegration is a reaction of 1st order. The rate of disintegration
- (a) increases with increase of temperature                      (b) decreases with increase of temperature  
 (c) increases on adding catalyst                      (d) is unaffected by temperature of catalyst

### MATRIX MATCH TYPE QUESTIONS

11. Look at the following diagram and match the entries in the Table below

<b>Column-I</b>	<b>Column-II</b>	
A. Activation energy of forward reaction	(p) $70 \text{ kJ mol}^{-1}$	
B. Threshold energy	(q) $30 \text{ kJ mol}^{-1}$	
C. Activation energy of backward reaction	(r) $15 \text{ kJ mol}^{-1}$	
D. Enthalpy change of the reaction	(s) $45 \text{ kJ mol}^{-1}$	
(a) A-(p); B-(q); C-(s); D-(r)	(b) A-(q); B-(p); C-(r); D-(s)	
(c) A-(r); B-(p); C-(s); D-(q)	(d) A-(q); B-(p); C-(s); D-(r)	

<b>Column-I (Plot)</b>	<b>Column-II (Slope of the line)</b>
A. Concentration vs time for zero order reaction	(p) $k$
B. Half-life period vs initial concentration for zero order reaction	(q) $-k$
C. Reciprocal of concentration vs time for 2 <sup>nd</sup> order reaction	(r) $\frac{1}{2k}$
D. Half-life period vs initial concentration for 1 <sup>st</sup> order reaction	(s) zero
(a) A-(r); B-(q); C-(p); D-(s)	(b) A-(q); B-(r); C-(p); D-(s)
(c) A-(s); B-(r); C-(p); D-(q)	(d) A-(p); B-(q); C-(r); D-(s)

### INTEGER TYPE QUESTIONS

13. The rate of gaseous reaction is halved when the volume of the vessel is doubled. Thus the order of reaction is

- 
14. A reaction  $P \rightarrow Q$  is completed 25% in 25 min. 50% completed in 25 min. if  $[P]$  is halved, 25% complete in 50 min if  $[P]$  is doubled, the order of reaction is
15. For the decomposition of  $N_2O_5$  at  $127^\circ C$ , *i.e.*,  $N_2O_5(s) \longrightarrow N_2O_4(g) + 1/2O_2(g)$ , if the initial pressure is 114 mm and after 25 minutes of the reaction, total pressure of the gaseous mixture is 133 mm, the average rate of reaction is  $10^{-x} \text{ mol L}^{-1} \text{ s}^{-1}$  where  $x$  is.
16. A gaseous reaction is of first order in reactant A and second order in reactant B. If the reaction mixture is compressed to half the volume, the rate of reaction will be..... times
17. The rate constant of a reaction zero order in A is  $3 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$ . The time taken in seconds for the initial concentration of A to fall from 0.10 M to 0.076 M will be
18. For a first order reaction, the number of half-lives required for the initial concentration of the reactant to fall to 3.125% of its initial concentration is
19. For a first order reaction, the ratio of the time taken for  $7/8^{\text{th}}$  of the reaction to complete to that of half of the reaction to complete is
20. After 24 hours, only 0.125 g of the initial quantity of 1 g of a radioactive isotope remains behind. The half-life period of the radioactive isotope in hours is.
21. If the temperature of a reaction is increased from  $20^\circ C$  to  $50^\circ C$ , the rate of reaction will become.....times.
22. 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 reaction is

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# PREVIOUS YEAR QUESTIONS

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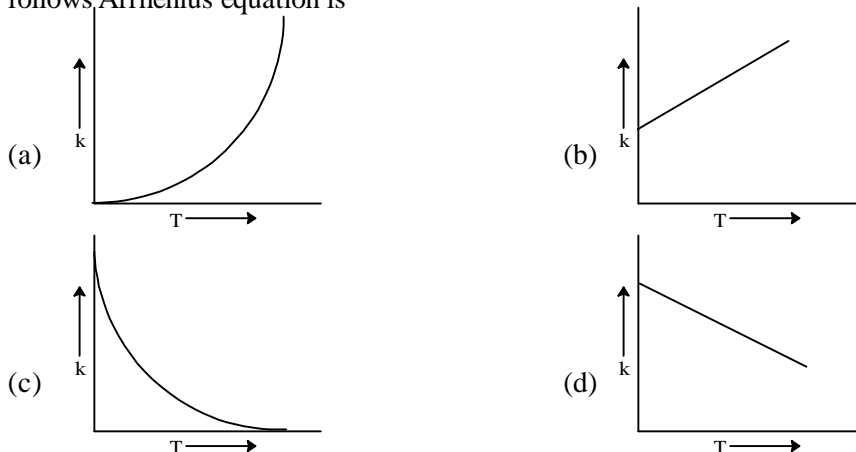
## IIT-JEE/JEE-ADVANCE QUESTIONS

- (A) follows first order reaction.  $A \rightarrow$  product  
Concentration of A, changes from 0.1 M to 0.025 M in 40 minutes. Find the rate of reaction of A when concentration of A is 0.01 M  
(a)  $3.47 \times 10^{-4} \text{ M min}^{-1}$  (b)  $3.47 \times 10^{-5} \text{ M min}^{-1}$   
(c)  $1.73 \times 10^{-4} \text{ M min}^{-1}$  (d)  $1.73 \times 10^{-5} \text{ M min}^{-1}$
  - The rate law for the reaction  
 $\text{RCl} + \text{NaOH (aq)} \longrightarrow \text{ROH} + \text{NaCl}$  is given by  $\text{Rate} = k [\text{RCl}]$ . The rate of the reaction will be  
(a) Doubled on doubling the concentration of sodium hydroxide.  
(b) Halved on reducing the concentration of alkyl halide to one half.  
(c) Decreased on increasing the temperature of the reaction.  
(d) Unaffected by increasing the temperature of the reaction
  - The half-life period of a radioactive element is 140 days. After 560 days, one gram of the element will be reduced to  
(a)  $\frac{1}{2} \text{ g}$  (b)  $\frac{1}{4} \text{ g}$  (c)  $\frac{1}{8} \text{ g}$  (d)  $\frac{1}{16} \text{ g}$
  - Consider the chemical reaction:  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$ . The rate of this reaction can be expressed in terms of time derivative of concentration of  $\text{N}_2(\text{g})$ ,  $\text{H}_2(\text{g})$  or  $\text{NH}_3(\text{g})$ . Identify the correct relationship amongst the rate expressions  
(a)  $\text{Rate} = -d[\text{N}_2]/dt = -1/3d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt$   
(b)  $\text{Rate} = -d[\text{N}_2]/dt = -3d[\text{H}_2]/dt = 2d[\text{NH}_3]/dt$   
(c)  $\text{Rate} = d[\text{N}_2]/dt = 1/3d[\text{H}_2]/dt = 1/2d[\text{NH}_3]/dt$   
(d)  $\text{Rate} = -d[\text{N}_2]/dt = -d[\text{H}_2]/dt = d[\text{NH}_3]/dt$
  - The rate constant for the reaction  $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$ , is  $3.0 \times 10^{-5} \text{ sec}^{-1}$ . If the rate is  $2.40 \times 10^{-5} \text{ mol litre}^{-1}\text{sec}^{-1}$ , then the concentration of  $\text{N}_2\text{O}_5$  (in  $\text{mol litre}^{-1}$ ) is  
(a) 1.4 (b) 1.2 (c) 0.04 (d) 0.8
  - Consider a reaction  $a\text{G} + b\text{H} \longrightarrow$  Products. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when 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
  - Under the same reaction conditions, initial concentration of  $1.386 \text{ mol dm}^{-3}$  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 reactions is  
(a)  $0.5 \text{ mol}^{-1} \text{ dm}^3$  (b)  $1.0 \text{ mol dm}^{-3}$  (c)  $1.5 \text{ mol dm}^{-3}$  (d)  $2.0 \text{ mol}^{-1} \text{ dm}^3$
-

8. For a first order reaction  $A \rightarrow P$ , the temperature ( $T$ ) dependent rate constant ( $k$ ) was found to follow the equation  $\log k = -(2000)\frac{1}{T} + 6.0$ . The pre-exponential factor  $A$  and the activation energy  $E_a$ , respectively are

- (a)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $9.2 \text{ kJ mol}^{-1}$                       (b)  $6.0 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$   
 (c)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $16.6 \text{ kJ mol}^{-1}$                       (d)  $1.0 \times 10^6 \text{ s}^{-1}$  and  $38.3 \text{ kJ mol}^{-1}$

9. Plots showing the variation of the rate constant ( $k$ ) with temperature ( $T$ ) are given below. The plot that follows Arrhenius equation is



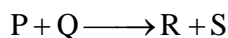
10. The concentration of  $R$  in the reaction  $R \rightarrow P$  was measured as a function of time and the following data is obtained.

[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

11. An organic compound undergoes first-order decomposition. The time taken for its 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  $\log_{10} 2 = 0.3$ )

12. In the reaction,

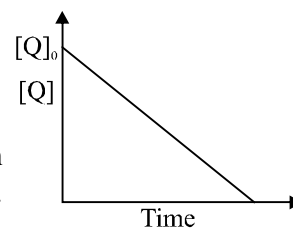


the time taken for 75% reaction of  $P$  is twice the time taken for 50% reaction of  $P$ . The concentration of  $Q$  varies with reaction time as shown in the figure.

The overall order of the reaction is

[JEE-Advance 2013]

- (a) 2                      (b) 3                      (c) 0                      (d) 1



13. For the elementary reaction  $M \rightarrow N$ , 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

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**DCE QUESTIONS**

1. The rate constant of a reaction is  $15 \times 10^{-3}$  at  $25^\circ\text{C}$  and  $2.1 \times 10^{-2}$  at  $60^\circ\text{C}$ . The activation energy is
- (a)  $\frac{35}{333} R \ln \frac{2.1 \times 10^{-2}}{1.5 \times 10^{-2}}$  (b)  $\frac{298 \times 333}{35} R \ln \left( \frac{21}{1.5} \right)$
- (c)  $\frac{290 \times 33}{35} R \ln 2.1$  (d) None of these
2.  $\text{Rx}'' 2\text{N}_2\text{O}_4 \longrightarrow 4 \text{NO}_2$  and given that  $-d/dt (\text{N}_2\text{O}_4) = K$  and  $d/dt (\text{NO}_2) = K'$ , then
- (a)  $K' = 2K$  (b)  $K' = K$  (c)  $2K' = K$  (d) None of these
3.  $1/16^{\text{th}}$  of a radioactive sample decays in 40 days half life of the sample is
- (a) 100 days (b) 10 days (c) 1 day (d)  $\log_e 2$  days
4. What is the order of a reaction which has a rate? Expression rate =  $K[\text{A}]^{3/2} [\text{B}]^{-1}$
- (a)  $3/2$  (b)  $1/2$  (c) 0 (d) None of these
5. For a given reaction  $3\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$ , the rate of reaction can be represented by
- (a)  $-\frac{1}{3} \frac{d[\text{A}]}{dt} = \frac{-d[\text{B}]}{dt} = \frac{+d[\text{C}]}{dt} = \frac{+d[\text{D}]}{dt}$
- (b)  $-\frac{1}{3} \frac{d[\text{A}]}{dt} = \frac{d[\text{C}]}{dt} = K[\text{A}]^m[\text{B}]^n$
- (c)  $+\frac{1}{3} \frac{d[\text{A}]}{dt} = \frac{-d[\text{C}]}{dt} K[\text{A}]^n[\text{B}]^m$
- (d) None of these
6. Which of the following expression is correct for first order reaction? (CO) refers to initial concentration of reactant.
- (a)  $t_{1/2} \propto \text{CO}$  (b)  $t_{1/2} \propto \text{CO}^{-1}$  (c)  $t_{1/2} \propto \text{CO}^{-2}$  (d)  $t_{1/2} \propto \text{CO}^0$
7. 8 gms of a radioactive substance is reduced to 0.5 g after 1 hour. The  $t_{1/2}$  of the radioactive substance is
- (a) 15 min (b) 30 min (c) 45 min (d) 10 min
8. Rate of a reaction can be expressed by following rate expression  
Rate =  $k[\text{A}]^2 [\text{B}]$  if concentration of A is increased by 3 times and concentration of B is increased by 2 times how many times rate of reaction increases
- (a) 9 times (b) 27 times (c) 18 times (d) 8 times
-



9. Rate of a reaction can be expressed by following rate expression  
 Rate =  $k[A]^2 [B]$  if concentration of A is reduced by half by what times concentration of B is to be increased to have same rate of reaction  
 (a) 4 times (b) 2 times (c) 1/4 times (d) 8 times
10. Half life of radioactive element is 16 hrs what time it will take for 75% disintegration.  
 (a) 32 days (b) 32 hrs (c) 48 hrs (d) 16 hrs
11. Which one is *not correct*  
 (a) rate of zero order reaction depends upon initial concentration of reactant  
 (b) rate of zero order reaction does not depend upon initial concentration of reactant  
 (c)  $t_{1/2}$  of first order reaction is independent of initial concentration of reactant  
 (d)  $t_{1/2}$  of zero order reaction is dependent of initial concentration of reactant
12. Which expression is wrong for first order reaction  
 (a)  $k = \frac{2.303}{t} \log \left( \frac{A_0}{A_t} \right)$  (b)  $k = \frac{t}{2.303} \log \left( \frac{A_0}{A_t} \right)$   
 (c)  $-k = \frac{t}{2.303} \log \left( \frac{A_t}{A_0} \right)$  (d) rate =  $k [A]$

**AIEEE/JEE-MAINS QUESTIONS**

1. Consider an endothermic reaction  $X \rightarrow Y$  with the activation energies  $E_b$  and  $E_f$  for the backward and forward reactions, respectively. In general  
 (a)  $E_b < E_f$   
 (b)  $E_b > E_f$   
 (c)  $E_b = E_f$   
 (d) there is no definite relation between  $E_b$  and  $E_f$

2. A schematic plot of  $\ln K_{eq}$  versus inverse of temperature for a reaction is shown below

[AIEEE 2005]

The reaction must be

- (a) exothermic (b) endothermic  
 (c) one with negligible enthalpy change (d) highly spontaneous at ordinary temperature
3.  $t_{\frac{1}{4}}$  can be taken as the time taken for the concentration of a reactant to drop to  $\frac{3}{4}$  of its initial value. If the rate constant for a first order reaction is K, the  $t_{\frac{1}{4}}$  can be written as  
 (a)  $0.10 / K$  (b)  $0.29 / K$  (c)  $0.69 / K$  (d)  $0.75 / K$

4. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in

- 
- 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is
- (a) 7.5 minutes            (b) 15 minutes            (c) 30 minutes            (d) 60 minutes
5. The rate equation for the reaction  $2A + B \rightarrow C$  is found to be: rate =  $k[A][B]$ . The correct statement is relation to this reaction is that the
- (a) rate of formation of C is twice the rate of disappearance of A  
(b)  $t_{1/2}$  is constant  
(c) unit of  $k$  must be  $s^{-1}$   
(d) value of  $k$  is independent of the initial concentrations of A and B
6. The half-life of a radioisotope is four hours. If the initial mass of the isotope was 200 g, the mass remaining after 24 hours undecayed is
- (a) 3.125 g            (b) 2.084 g            (c) 1.042 g            (d) 4.167 g
7. Units of rate constant for first and zero order reactions in terms of molarity M and time in seconds are respectively
- (a)  $sec^{-1}$ , M  $sec^{-1}$             (b)  $sec^{-1}$ , M            (c) M  $sec^{-1}$ ,  $sec^{-1}$             (d) M,  $sec^{-1}$
8. In respect of the equation  $k = Ae^{-E_a/RT}$  in chemical kinetics, which one of the following statements is correct?
- (a) A is adsorption factor            (b)  $E_a$  is energy of activation  
(c) R is Rydberg constant            (d)  $k$  is equilibrium constant
9. For the reaction system  $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$  the volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to  $O_2$  and second order with respect to NO, the rate of reaction will be
- (a) diminish to one-eighth of its initial value  
(b) increase to eight times of its initial value  
(c) increase to four times its initial value  
(d) diminish to one-fourth of its initial value
10. The rate law for a reaction between the substances A and B is given by 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 the reaction will be as
- (a)  $m + n$             (b)  $(n - m)$             (c)  $2(n + m)$             (d)  $1/2^{(m + n)}$
11. The half-life a radioactive isotope is three hours. If the initial mass of the isotope were 256 g, the mass of it remaining undecayed after 18 hours would be
- (a) 8.0 g            (b) 12.0 g            (c) 16.0 g            (d) 4.0 g
12. A reaction was found to be second order with respect to the concentration of carbon monoxide. If the
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concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will

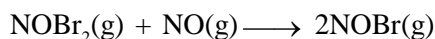
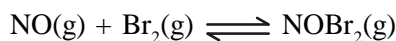
- (a) double (b) remain unchanged  
(c) triple (d) increase by a factor of 4

13. Rate of a reaction can be expressed by Arrhenius equations as

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

In this equation, E represents

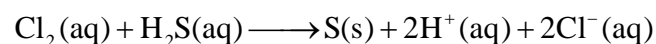
- (a) the fraction of molecules with energy greater than the activation energy of the reaction  
(b) the energy above which all the colliding molecules will react  
(c) the energy below which colliding molecules will not react  
(d) the total energy of the reacting molecules at a temperature T.
14. The following mechanism has been proposed for the reaction of NO with Br<sub>2</sub> to form NOBr



If the second step is the rate determining step, the order of the reaction with respect to NO(g) is

- (a) 2 (b) 1 (c) 0 (d) 3
15. Consider the reaction,  $2A + B \rightarrow \text{Products}$   
When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is
- (a) mol L<sup>-1</sup>s<sup>-1</sup> (b) s<sup>-1</sup> (c) L mol<sup>-1</sup>s<sup>-1</sup> (d) no unit
16. 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) 23.03 minutes (b) 46.06 minutes (c) 460.6 minutes (d) 230.3 minutes
17. The time for half life period of a certain reaction  $A \rightarrow \text{Products}$  is 1 hour. When the initial concentration of the reactant 'A', is 2.0 mol L<sup>-1</sup>, how much time does it take for its concentration to come from 0.50 to 0.25 mol L<sup>-1</sup> if it is zero order reaction?
- (a) 0.25 h (b) 1 h (c) 4 h (d) 0.5 H

18. Consider the reaction:



The rate equation for this reaction is rate = k[Cl<sub>2</sub>][H<sub>2</sub>S]

Which of these mechanisms is/are consistent with this rate equation?

- A.  $\text{Cl}_2 + \text{H}_2\text{S} \longrightarrow \text{H}^+ + \text{Cl}^- + \text{Cl}^+ + \text{HS}^-$  (slow)     $\text{Cl}^+ + \text{HS}^- \longrightarrow \text{H}^+ + \text{Cl}^- + \text{S}$  (fast)  
B.  $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$  (fast equilibrium)     $\text{Cl}_2 + \text{HS}^- \longrightarrow 2\text{Cl}^- + \text{H}^+ + \text{S}$  (slow)
- (a) Neither A nor B (b) A only (c) B only (d) Both A and B

19. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is
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raised by 50°C, the rate of the reaction increases by about:

- (a) 10 times                      (b) 24 times                      (c) 32 times                      (d) 64 times
20. For a first order reaction  $A \rightarrow \text{products}$ , the concentration of A changes from 0.1M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01M is:
- (a)  $1.73 \times 10^{-5} \text{ M/min}$    (b)  $3.47 \times 10^{-4} \text{ M/min}$    (c)  $3.47 \times 10^{-5} \text{ M/min}$    (d)  $1.73 \times 10^{-4} \text{ M/min}$
21. The rate of a reaction double when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be: ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $\log 2 = 0.031$ )
- (a)  $58.5 \text{ kJ mol}^{-1}$                       (b)  $60.5 \text{ kJ mol}^{-1}$                       (c)  $53.6 \text{ kJ mol}^{-1}$                       (d)  $48.6 \text{ kJ mol}^{-1}$
22. For the non-stoichiometre reaction  $2A + B \rightarrow C + D$ , the following kinetic data were obtained in three separated experiments, all at 298 K

Initial Concentration (A)	Initial Concentration (B)	Initial rate of formation of C ( $\text{mol L}^{-1} \text{ S}^{-1}$ )
0.1 M	0.1 M	$1.2 \times 10^{-3}$
0.1 M	0.2 M	$1.2 \times 10^{-3}$
0.2 M	0.1 M	$2.4 \times 10^{-3}$

The rate law for the formation of C is

- (a)  $\frac{dc}{dt} = k[A][B]^2$                       (b)  $\frac{dc}{dt} = k[A]$                       (c)  $\frac{dc}{dt} = k[A][B]$                       (d)  $\frac{dc}{dt} = k[A]^2[B]$
23. Higher order ( $> 3$ ) reactions are rare due to :
- (a) low probability of simultaneous collision of all the reacting species
- (b) increase in entropy and activation energy as more molecules are involved
- (c) shifting of equilibrium towards reactants due to elastic collisions
- (d) loss of active species on collision
-

# SUBJECTIVE PROBLEMS

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1. A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion.
2. The specific rate constant for a reaction increases by a factor 4, if the temperature is changed from 27°C to 47°C. Find, the activation energy for the reaction

3. The reaction

$2A + B + C \rightarrow D + 2E$  is of first order with respect to A, of second order with respect to B and is of zero order with respect to C

- (i) Write down the rate law for the reaction
  - (ii) What will be the effect of doubling concentration of A, B and C.
4. For the reaction  $A \rightarrow B + C$ , the data given below are obtained. Prove that the reaction is of first order  

t	0	90	180
[A]	50.8	19.7	7.62
  5. At 900°C and 200 mm initial pressure, catalytic dissociation of  $N_2O$  in presence of gold is 50% after 53 minutes and 73% after 100 minutes
    - (a) Find out the order of reaction
    - (b) What will be dissociation of  $N_2O$  after 100 minutes at the same temperature and 600 mm initial pressure ?

6. Rate of reaction  $X + Y \rightarrow$  products is given below as a fraction of different initial concentrations of X and Y.

[X] mol litre <sup>-1</sup>	[Y] mol litre <sup>-1</sup>	Initial rate mole litre <sup>-1</sup> min <sup>-1</sup>
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

Find out the order of reaction with respect to X and Y. What is the half life of X in the reaction.

7. While studying the decomposition of  $N_2O_5$ , it is observed that a plot of its partial pressure versus time is linear. What kinetic parameters can be obtained from this observation.
8. The rate law for the following reaction

$\text{Ester} + H^+ \rightarrow \text{Acid} + \text{Alcohol}$  is  $\frac{dx}{dt} = K [\text{ester}] [H_3O^+]^0$  what would be the effect on rate if

- (a) Concentration of ester is doubled
  - (b) Concentration of  $H^+$  ion is doubled
9. For the reaction  $X + 2Y \rightarrow 2Z$  following data were obtained

X	Y	litre <sup>-1</sup> min <sup>-1</sup>
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

write down the rate law for the reaction giving explanation.

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10. A first order reaction has  $k = 1.5 \times 10^{-6}$  per second at  $200^\circ\text{C}$ . 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 of the reaction ?
11. A first order reaction is 50% completed in 30 min at  $27^\circ\text{C}$  and in 10 minutes at  $47^\circ\text{C}$ . Calculate the rate constant at  $27^\circ\text{C}$  and the energy of activation of the reaction in kJ per mole.
12. The optical rotation of sucrose in 0.5 M HCl at  $35^\circ\text{C}$  at different time intervals are given below. Show that the reaction follows first order kinetics.
- |                    |       |       |       |       |       |          |
|--------------------|-------|-------|-------|-------|-------|----------|
| Time (min.)        | 0     | 10    | 20    | 30    | 40    | $\infty$ |
| Rotation (degrees) | +32.4 | +28.8 | +25.5 | +22.4 | +19.6 | -11.1    |
13.  $T_{1/2}$  of a reaction is halved as the initial concentration of the reaction is doubled. find out the order of the reaction.
14. The rate constant of a reaction is  $1.5 \times 10^{-7} \text{ sec}^{-1}$  at  $50^\circ\text{C}$  and  $4.5 \times 10^{-7} \text{ sec}^{-1}$  at  $100^\circ\text{C}$ . Evaluate the Arrhenius parameters A and  $E_a$ .
15. A substance reacts according to the law of first order reaction the velocity constant of the reaction is  $1.0 \times 10^{-2} \text{ sec}^{-1}$ . If initial conc. of the substance is 1.0 M.
- Find out the initial rate
  - Find out the rate after 1 min.
16. What will be the initial rate of a reaction if its rate constant is  $10^{-3} \text{ min}^{-1}$  and the concentration of reactant is  $0.2 \text{ mol dm}^{-3}$ . How much of reactant will be converted into products in 200 minutes.
17. A first order reaction is 20% complete in 10 minutes. Calculate
- Specific rate constant of the reaction and
  - Time taken for the reaction to go to 75% completion
-

# ANSWERS

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## Objective Questions

- |             |             |             |             |               |
|-------------|-------------|-------------|-------------|---------------|
| 1. (b)      | 2. (c)      | 3. (b)      | 4. (b)      | 5. (b)        |
| 6. (d)      | 7. (c)      | 8. (c)      | 9. (d)      | 10. (d)       |
| 11. (b)     | 12. (d)     | 13. (a)     | 14. (a)     | 15. (b)       |
| 16. (b)     | 17. (a)     | 18. (a)     | 19. (a)     | 20. (b)       |
| 21. (d)     | 22. (d)     | 23. (b)     | 24. (c)     | 25. (c)       |
| 26. (c)     | 27. (c,d)   | 28. (a,b,d) | 29. (a,b,c) | 30. (a,b,c,d) |
| 31. (b,d)   | 32. (a,b,d) | 33. (a,b,c) | 34. (a,b,c) | 35. (a,b,c)   |
| 36. (a,b,c) |             |             |             |               |

## Miscellaneous Assignment

- |         |         |         |         |         |
|---------|---------|---------|---------|---------|
| 1. (b)  | 2. (a)  | 3. (a)  | 4. (b)  | 5. (d)  |
| 6. (b)  | 7. (c)  | 8. (c)  | 9. (d)  | 10. (d) |
| 11. (d) | 12. (b) | 13. (1) | 14. (0) | 15. (6) |
| 16. (8) | 17. (8) | 18. (5) | 19. (3) | 20. (8) |
| 21. (8) | 22. (0) |         |         |         |

## Previous Year Questions

### IIT-JEE/JEE-ADVANCE QUESTIONS

- |         |         |         |        |         |
|---------|---------|---------|--------|---------|
| 1. (a)  | 2. (b)  | 3. (d)  | 4. (a) | 5. (d)  |
| 6. (d)  | 7. (a)  | 8. (d)  | 9. (a) | 10. [0] |
| 11. (9) | 12. (d) | 13. (b) |        |         |

### DCE QUESTIONS

- |         |         |        |        |         |
|---------|---------|--------|--------|---------|
| 1. (b)  | 2. (a)  | 3. (b) | 4. (b) | 5. (a)  |
| 6. (d)  | 7. (a)  | 8. (c) | 9. (a) | 10. (b) |
| 11. (a) | 12. (b) |        |        |         |

### MAINS QUESTIONS

- |        |        |        |        |         |
|--------|--------|--------|--------|---------|
| 1. (a) | 2. (a) | 3. (b) | 4. (c) | 5. (a)  |
| 6. (a) | 7. (a) | 8. (b) | 9. (b) | 10. (c) |
-

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11. (d)      12. (d)      13. (b)      14. (a)      15. (c)  
16. (b)      17. (a)      18. (b)      19. (c)      20. (b)  
21. (c)      22. (b)      23. (a)

### ***Subjective Problems***

1. 161 minutes
2.  $55.33 \text{ kJ mole}^{-1}$
3. rate =  $K[A] [13]^2$  rate will become 8 times.
4.  $k = 1.05 \times 10^{-2}$
5.  $1.3 \times 10^{-2}$ , 73%
6.  $T_{1/2} = 1.386 \text{ min}$
7. Reaction is of first order
8.  $r_1 = 2r_2, r_1 = r_3$
9. 1 w.r.t. X, 0 w.r.t. Y
10. Percentage conversion = 53%,  $T_{1/2} = 128.33 \text{ hrs}$
11.  $K_{27} = 3.85 \times 10^{-4} \text{ sec}^{-1}$   $K_{47} = 11.55 \times 10^{-4} \text{ sec}^{-1}$ ,  $E = 43.78 \text{ kJ/mol}$
12. It is first order kinetics with  $k = 8.64 \times 10^{-3}$
13. 2
14.  $E_a = 2.2 \times 10^4$   
 $A = 5.42 \times 10^{10}$
15. (a)  $= 1 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$  (b)  $= 5.495 \times 10^{-3} \text{ mol}^{-1} \text{ l}^{-1} \text{ s}^{-1}$
16. Rate =  $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1}$   $x = 18.12\%$
17.  $K = 0.02231 \text{ min}^{-1}$   $t = 62.07 \text{ min}$
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