CHEMICAL KINETICS

SYNOPSIS

Chemical kinetics is a branch of science which deals with the rate of the reaction and the factors affecting rate of the reaction.

The rate of a reaction is the change in the concentration of the product or reactant per unit time.

$$Rate = \frac{change \text{ in concentration}}{time} \qquad unit \rightarrow mole\ litre^{-1}\ sec^{-1}$$
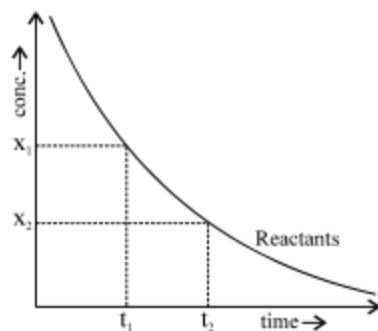
There are two kinds of rate.

1. **Average rate** $\left(\dfrac{\Delta x}{\Delta t}\right)$

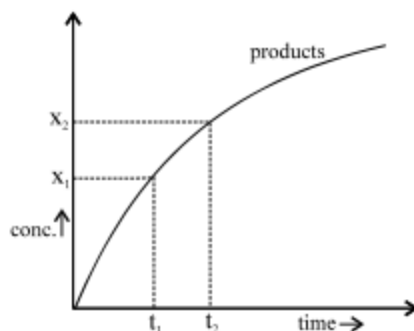   The rate of a reaction in a time interval 'Δt' is known as average rate.

   In the reaction $PCl_5 \rightarrow PCl_3 + Cl_2$, the conc.changes are $\Delta[PCl_5], \Delta[PCl_3], \Delta[Cl_2]$

   Then rate = $\dfrac{-\Delta[PCl_5]}{\Delta t} = \dfrac{\Delta[PCl_3]}{\Delta t} = \dfrac{\Delta[Cl_2]}{\Delta t}$
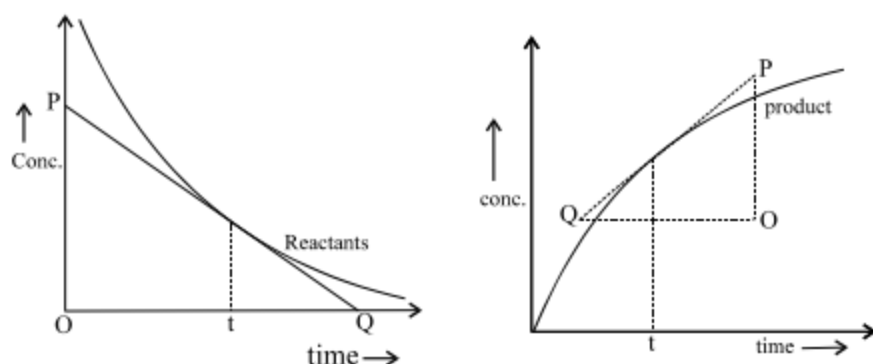

$$Rate = \frac{-(x_2 - x_1)}{(t_2 - t_1)} \qquad\qquad Rate = \frac{(x_2 - x_1)}{t_2 - t_1}$$

2. **Instantaneous rate** $\left(\dfrac{dx}{dt}\right)$

   It is the rate of a reaction at an instant of time $r_{inst} = \dfrac{-d[PCl_5]}{dt} = \dfrac{d[PCl_3]}{dt} = \dfrac{d[Cl_2]}{dt}$

Rate $r_{inst} = \dfrac{OP}{OQ}$ in both cases

Rate of reaction in terms of reactant and product.

In the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, in the small time interval Δt, the conc. changes are $D[N_2]$, $D[H_2]$, $D[NH_3]$.

$$\text{Rate} = \frac{-\Delta[N_2]}{\Delta t} = \frac{-1}{3}\frac{\Delta[H_2]}{\Delta t} = \frac{1}{2}\frac{\Delta NH_3}{\Delta t}.$$

Factors affecting rate of a reaction

1. Nature of reactant:

    In a reaction there is breaking of old bonds and formation of new bonds. Different reactant molecules have different kinds of bonds and so rate depends on nature of reactant molecule.

2. Temperature:

    Rate of reaction increases with increase in temperature.

3. Surface area of reactant:

    Rate of reaction increases with increase in the surface area of reactant.

4. Concentration:

    Rate increases with increase in conc. of reactants.

5. Catalyst:

    It generally increases rate of reaction.

6. Presence of radiation:

    Rate of photochemical reactions increases with increase in the intensity of the light.

Variation of rate of a reaction with concentration

Consider a general reaction, aA + bB —> products. By law of mass action,

Rate a $[A]^a.[B]^b$ but experimentally it is found that the rate of reaction depend upon a, (the conc. of A) and b, (the conc. of B).

Hence $R \propto [A]^\alpha[B]^\beta$, $R = k[A]^\alpha[B]^\beta$ where k is constant called rate constant or velocity constant or specific reaction rate.

Rate = k, when conc. of A and B = 1.

Rate const. is the rate of the reaction when molar concentration of the reactants is unity.

k is a constant at constant temp and increases with increase in temp. Its unit depends upon order of reaction and value of k provides information about the rate of reaction.

The rate of a reaction is directly proportional to conc. of the reactant and hence rate decreases with
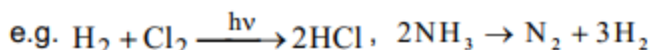
increase in time.
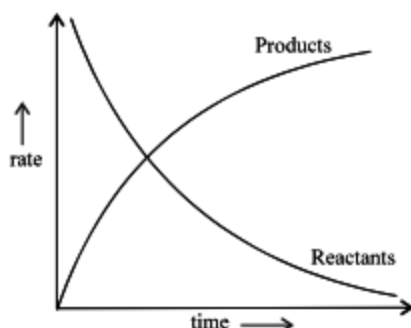
Order of a reaction

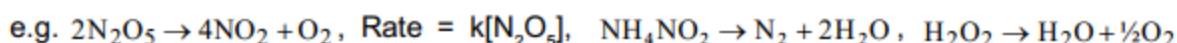It is the sum of the powers to which the conc. terms are raised in the rate equation.

In the eq. Rate = k $[A]^a$ $[B]^b$ a - the order with respect to A. b = the order with respect to B.
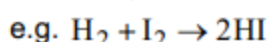
Then a + b is the overall order. When
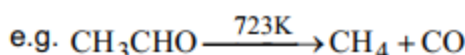
a + b = 0 it is a zero order reaction.

e.g. $H_2 + Cl_2 \xrightarrow{hv} 2HCl$, $2NH_3 \rightarrow N_2 + 3H_2$

a + b = 1; 1st order reaction

e.g. $2N_2O_5 \rightarrow 4NO_2 + O_2$, Rate = $k[N_2O_5]$, $NH_4NO_2 \rightarrow N_2 + 2H_2O$, $H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$

a + b = 2; 2nd order reaction

e.g. $H_2 + I_2 \rightarrow 2HI$

Fractional order reactions

e.g. $CH_3CHO \xrightarrow{723K} CH_4 + CO$

Rate = $k[CH_3CHO]^{3/2}$

Unit of rate constant
for an nth order reaction

$$\frac{dx}{dt} = k[conc]^n \qquad k = \frac{dx}{dt} \times \frac{1}{(conc)^n}$$

$$dx \rightarrow conc, \quad dt \rightarrow time \quad = \frac{[conc]}{time} \times \frac{1}{[conc]^n} \ = [conc]^{1-n} time^{-1}$$

Zero order, n = 0

$$\therefore k = \left[mol\,lit^{-1}\right]^{1-0} sec^{-1} = mol\ lit^{-1}\ sec^{-1}$$

1st order, n = 1

$$k = \left[mol\ lit^{-1}\right]^{1-1} sec^{-1} = sec^{-1}$$

2nd order, n = 2

$$k = \left[mol\,lit^{-1}\right]^{1-2} sec^{-1} = mol^{-1}lit\,sec^{-1}$$

For zero order reactions, unit of rate and rate constant are equal.

**Difference between rate and rate constant**

Rate	Rate Const.
1. Change in conc. of reactant/product in unit time	1. It is the rate of a reaction when molar concentration of the reactant is unity
2. Not a constant, decreases with time	2. It is a constant
3. Unit is const	3. Unit varies with order

Molecularity of a reaction

It is the no. of atoms or molecules of reactants that participate in the rate determining step of the reaction.

In simple reactions, i.e. takes place in one step, molecularity is the sum of the reactant molecules present in balanced equations. For example,

$F_2O_2 \rightarrow F_2 + O_2$ where molecularity 1

$2HI \rightarrow H_2 + I_2$ where molecularity 2
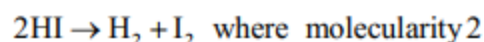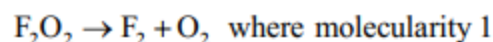
In a complex reaction, molecularity has no meaning. Complex reactions takes place in more than one step. In such cases the rate determining step is the slowest step. The molecularity is determined on the basis of the slowest step.

Difference between order and molecularity

Order

1. Sum of the powers to which each conc terms are raised.
2. Need not be a whole number
3. Can be determined experimentally only
4. For overall reaction
5. For elementary reaction order need not be equal to the sum of reactant molecules

Molecularity

1. No. of molecules, atoms, ions that take part in effective collision
2. It is a whole number
3. Can be calculated
4. For simple reaction, molecularity is the sum of the molecules in the balanced equation.

Integrated rate equations

Since the instantaneous rate is determined from the graphical data, it is not convenient. Hence we use integrated rate equations.

The integrated rate equations are different for different order reactions.

Zero order reaction

Zero order reaction means the rate of a reaction is proportional to the zeroth power of the conc. of the reactant. Consider the reaction $A \rightarrow P$

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

Any quantity raised to the power zero is unity hence, $\dfrac{-d[A]}{dt} = k$

$$d[A] = -k\,dt$$

On integration

$$A = -kt + I \dots\dots\dots (1)$$

I = integration constant

At $t = 0$ $\qquad\qquad [A] = [A_0]$

From equation (1) $\qquad\qquad A_0 = I$

$$[A] = -kt + [A_0] \dots\dots (2)$$

$$kt = [A_0] - [A]$$

when the reacted amount in time 't' $[A_0] - [A] = x$, then

$$k = \frac{x}{t}$$

when $t = t_{½}$ $\qquad x = \dfrac{A_0}{2}$ $\qquad t_{½} = \dfrac{A_0}{2k}$

First order reaction

Consider the reaction A —> Product. We initially start with 'a' moles/lit and in a time 't', x moles/lit will be reacted. so

rate $\dfrac{dx}{dt} \propto (a-x)$, $\quad \dfrac{dx}{dt} = k(a-x)$ $\qquad |$ ln = $\log_e$

$\dfrac{dx}{a-x} = kdt$ $\qquad$ Integrating both sides,

$\displaystyle\int \frac{dx}{(a-x)} = \int kdt$ $\Rightarrow -\ell n(a-x) = kt + 1$, where I is integration const, when t = 0, x = 0
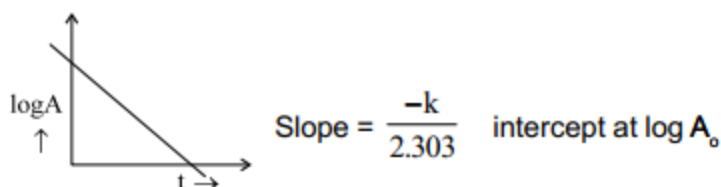
$\Rightarrow I = -\ell n\,a$

i.e., $-\ell n(a-x) = kt + -\ell n\,a$, $\quad \ell n\,a - \ell n(a-x) = kt$, $\quad \ell n\dfrac{a}{(a-x)} = kt$

$2.303\log\dfrac{a}{a-x} = kt$ $\qquad \boxed{\therefore k = \dfrac{2.303}{t}\log\dfrac{a}{a-x}}$

Instead of 'a', 'A$_0$' is used and for (a - x), 'A' is used so the equation becomes, $k = \dfrac{2.303}{t}\log\dfrac{A_0}{A}$

i.e., $\dfrac{kt}{2.303} = \log\dfrac{A_0}{A}$, i.e. $\dfrac{kt}{2.303} = \log A_0 - \log A$ $\qquad \therefore \log A = \dfrac{-kt}{2.303} + \log A_0$

It is in the form y = mx + c. The graph plotted will be as :,

$$\text{Slope} = \frac{-k}{2.303} \quad \text{intercept at } \log A_o$$

Exponentially it can be represented as

$$kt = \ln \frac{A_o}{A}, \quad e^{kt} = \frac{A_o}{A}$$

Half Life Period ($t_{1/2}$)

It is the time required to reduce the concentration of the reactant to half of its initial value.

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} \quad t = \frac{2.303}{k} \log \frac{a}{(a-x)} \quad \text{when } t = t_{1/2}, x = a/2$$

$$t\tfrac{1}{2} = \frac{2.303}{k} \log \frac{a}{a-a/2} = \frac{2.303}{k} \log \frac{a}{a/2}$$

$$t\tfrac{1}{2} = \frac{2.303}{k} \log 2 = \frac{0.693}{k} \quad \text{i.e. } t\tfrac{1}{2} = \frac{0.693}{k} \quad \boxed{A_o = A \times e^{Kt}}$$

For 1st order $t_{1/2}$ is independent of initial conc.

Amount after $nt_{1/2}$ of a 1st order reaction

The amount after $\boxed{nt_{1/2} = \dfrac{A_o}{2^n}}$ where A_o is the initial amount.

The $t_{1/n}$ of a first order reaction

$$t = \frac{2.303}{k} \log \frac{a}{(a-x)} = \frac{2.303}{k} \log \frac{a}{a-a/n} = \frac{2.303}{k} \log \frac{a}{\frac{an-a}{n}} \quad \text{when } t = t^{1/n}, x = a/n$$

$$= \frac{2.303}{k} \log \frac{1}{\frac{n-1}{n}} \quad t = \frac{2.303}{k} \log \frac{n}{(n-1)}$$

Pseudo first order reaction

Consider the reaction $A + B \rightarrow C+D$. rate $= k[A][B]$

When we take sum of the powers, it is second order, but if one of the reactants(B) is present in excess, its conc., practically remains constant during the reaction. Hence rate $= k[A]$

Such reactions are called Pseudo first order reactions.

For example, during the hydrolysis of ethyl acetate into acetic acid and ethyl alcohol, the conc. of H_2O does not affect the rate of the reaction since it is present in large quantity.

Determination of the order of reaction

There are several methods to determine the order of the reaction.

1) **Graphical method**

This method is applicable when the reaction has only one type of reactant. i.e. $A \rightarrow P$. For zero order, Rate = $k[A]^0$ = k. If it is 1st order, Rate = k[A], 2nd order, Rate = $k[A]^2$, 3rd order, Rate = $k[A]^3$

On plotting rate against [A], $[A]^2$, $[A]^3$, the one that gives a straight line is the rate equation. Further the rate law can be verified by substituting the value of rate and conc. of the reactant. The equation which will give a const value of K is the rate equation.

2) **Initial rate method**

Consider a reaction $n_1A + n_2B + n_3C \rightarrow$ product. With known the conc. of A, B and C, the initial rate is determined. By changing conc. of A and keeping the conc. of B and C unchanged, rate is again determined. In a similar way rates are determined by changing the concentrations of B and C

1) When only [A] is changed suppose the rate is $R = k[A]^2$
2) When only [B] is changed, suppose R = k[B]
When only [C] is changed R = $k[C]^0$
Total rate is $k[A]^2 [B] [C]^0$
overall order of the reaction = 2 +1+0 = 3
Thus the order of reaction with respect to A can be determined. In the same manner, the order of the reaction with respect to other reactants can also be determined and the overall order of the reaction is the sum of all the exponents. ie. order of the reaction n = a + b + c

3) **Use of integrated rate equations**
This method is also known as trial and error method. In this method we apply the given rates to different order reactions and thus find the value of rate constant k. Whenever the data fits the equation for the correct order of reaction, it will give constant value of the rate constant for concentrations at different times.
The order can be verified by plotting graph also. For example, for zero order reaction, a plot of concentration vs time gives a straight line with slope equal to -k. Similarly for first order reactions, a graph between in [R] against t gives a straight line with slope equal to -k. For second order reaction plot of $\dfrac{1}{[R]}$ against t gives a straight line with slope equal to k.

4) **Half life method**
The half life period depends differently on the initial concentration of the reactant for different order reactions. Thus we have

For zero order reaction $t_{1/2} \propto [R]_0$

For first order reaction $t_{1/2}$ is independent of $[R]_0$

For second order reaction $t_{1/2} \propto \dfrac{1}{[R]_0}$

For n^{th} order reaction $t_{1/2} \propto \dfrac{1}{[R_0]^{n-1}}$

From the variation of $t_{1/2}$ with $[R]_0$ it becomes easy to find the order of the reaction.

Mechanism of a reaction

A series of steps which are proposed for the overall reaction is called mechanism of the reaction. It is strictly on based expt. evidence (detection of short-lived species). The molecularity of each step must be '3' or lower. The slowest step (called rate determining step) must involve the molecules on which the

rate of reaction depends. Further, the sum of the step reactions must satisfy the overall stoichiometry of the reaction.
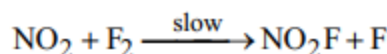
Thermal decomposition of dinitrogen pentoxide

e.g. :1. $N_2O_5 \xrightarrow{\text{slow}} NO_3 + NO_2$

$N_2O_5 + NO_3 \xrightarrow{\text{fast}} 3NO_2 + O_2$ Rate = $K[N_2O_5]$
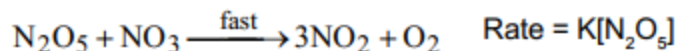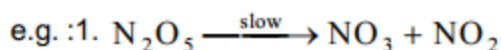
over all reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$

The slow step is unimolecular whereas the fast step is biomolecular. Hence, the reaction is a unimolecular reaction or a reaction of the first order.

2. Combination of NO_2 and F_2 to form NOF

$NO_2 + F_2 \xrightarrow{\text{slow}} NO_2F + F$

$NO_2 + F \xrightarrow{\text{fast}} NO_2F$ }Rate = $K[NO_2][F_2]$

Overall reaction, $2NO_2 + F_2 \rightarrow 2NO_2F$

The slow step in this reaction is bimolecular. Hence the reaction must be a bimolecular reaction or a second order reaction.

Arrhenius equation

This equation gives the quantitative effect of temperature on rate constant of a reaction.

$k = A.e^{\frac{-Ea}{RT}}$, where A is a const called frequency factor.

$Ea \rightarrow$ activation energy $T \rightarrow$ temperature in K. $e^{\frac{-Ea}{RT}}$ is the fraction of molecule having energy greater or equal to activation energy.

$$k = A \times e^{\frac{-Ea}{RT}}, \quad \ell nk = \ell nA - \frac{Ea}{RT}, \quad \ell nk = \ell nA = \frac{-Ea}{RT}, \quad \ell n\frac{k}{A} = \frac{-Ea}{RT}, \quad 2.303\log\frac{k}{A} = \frac{-Ea}{RT}$$

$$\log\frac{k}{A} = \frac{-Ea}{2.303RT} \quad \text{i.e. } \log k - \log A = \frac{-Ea}{2.303RT}, \quad \log k = \frac{-Ea}{2.303RT} + \log A$$

This is in the form y = mx + c. The graph that can be plotted is as

intercept = logA, Slope = $\dfrac{-Ea}{2.303T}$
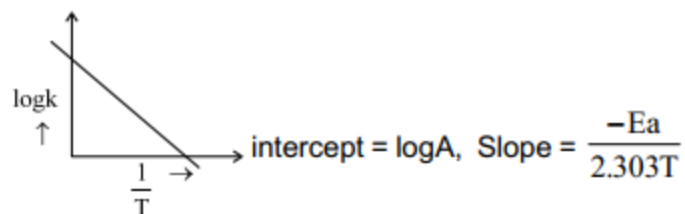
$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] k_1, k_2 \text{ are the rate constants at temp } T_1 \text{ and } T_2$$

Collision Theory

According to this theory a chemical reaction take place by the collision of the reactant molecule. But all the collision won't lead to product formations. The collision which leads to product formation is called **effective collision.**

The minimum energy required for the reactant molecule to take part in effective collision is called Threshold energy. The energy absorbed by the reactant molecule to take part in effective collision is called activation energy. It is energy difference between threshold energy and energy of reactant.
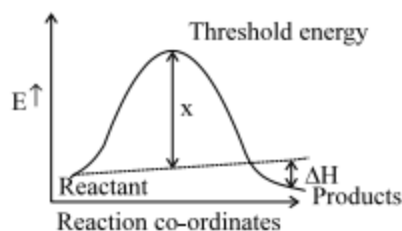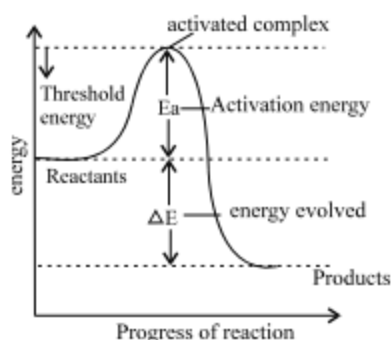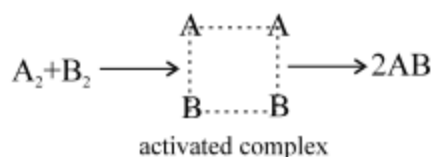

The rate of the reaction increases with increase in temp due to increase in the collisions and also increase in the no. of molecules having energy greater than threshold energy.

Temp coefficient $n = \dfrac{K \text{ at } 308 \text{ K}}{K \text{ at } 298 \text{ K}}$. The value of n lies in between 2 and 3. i.e. $2 < n < 3$

Transition state theory

According to this theory, the reactant molecules come together to form an activated complex, whose energy is higher than the reactant molecules, before forming the products. The extra energy needed for this process is called **activation energy.**

$$A_2 + B_2 \longrightarrow \begin{matrix} A \cdots\cdots A \\ \vdots \quad\quad \vdots \\ B \cdots\cdots B \end{matrix} \longrightarrow 2AB$$

activated complex

Effect of catalyst

A catalyst increases the rate of the reaction by creating a new path with lower activation energy.
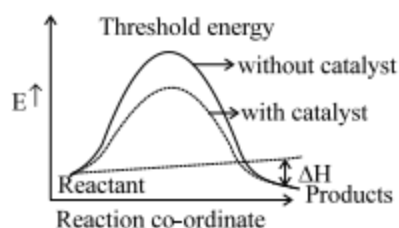
PART-I (JEE MAIN)

SECTION-I- Straight objective type questions

1. Consider the chemical reaction, $N_2(g)+3H_2(g) \rightarrow 2NH_3(g)$. The correct relationship amongst the following for rate of this reaction is

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

   2) Rate $= -\dfrac{d[N_2]}{dt} = -3\dfrac{d[H_2]}{dt} = 2\dfrac{d[NH_3]}{dt}$

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

   4) Rate $= -\dfrac{d[N_2]}{dt} = -\dfrac{d[H_2]}{dt} = \dfrac{d[NH_3]}{dt}$

2. If $\dfrac{d[NH_3]}{dt} = 34$ ghr⁻¹ for the reaction $N_2 + 3H_2 \longrightarrow 2NH_3$

   Then $\dfrac{d[H_2]}{dt}$ is .... g hr¹

   1) 6   2) –51   3) 51   4) –6

3. Identify the incorrect statement from the following

   1) Molecularity of a third order elementary reaction is three

   2) Moelcularity is applicable only for elementary reactions

   3) Order of a reaction cannot be a fraction

   4) Reactions with molecularity greater than three are very rare and slow to proceed

4. For the reaction system $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$, volume is suddenly reduced to half of its value by increasing the pressure on it. If the reaction is first order with respect to O_2 and second order with respect to NO, the rate of reaction will

   1) increase to four times of its initial value

   2) diminish to one-fourth of its initial value

   3) diminish to one-eight of its initial value

   4) increase to eight times of its initial value

5. The rate of reaction $2X + Y \rightarrow Products$ is given by $-\dfrac{d[Y]}{dt} = k[X]^2[Y]$. If X is present in large excess, the order of the reaction is

   1) 0   2) 2   3) 1   4) 3

6. Rate of a first order reaction is 0.04 mol L^{-1} s^{-1} at 10 s and 0.03 mol $L^{-1}s^{-1}$ at 20 s, then the rate constant is [Given : log 2 = 0.3 and log 3 = 0.5]

   1) 2.3×10^{-2} s^{-1} 2) 3.5×10^{-2} s^{-1} 3) 7.1×10^{-2} s^{-1} 4) 3.1×10^{-2} s^{-1}

7. Which of the following graphs are correct for a first order reaction, $R \rightarrow P$?

   a)
   b)
   c)
   d)
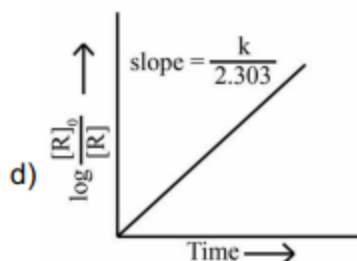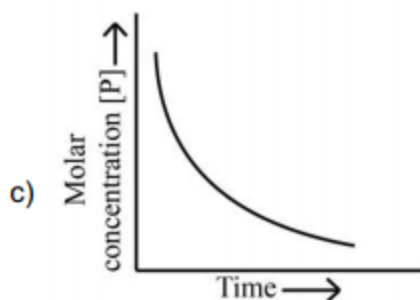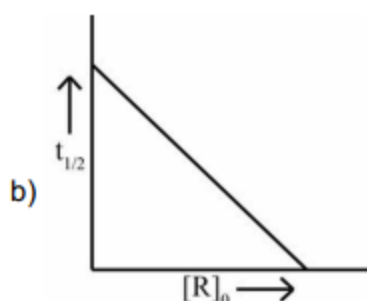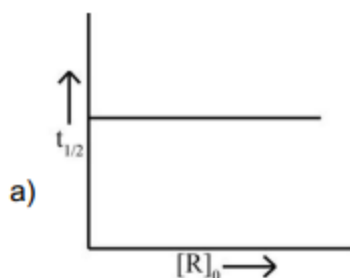
   1) a and c only   2) a and d only   3) a, c and d only   4) b, c and d only

8. Half-life of a first order and a zero order reaction are the same. Then the ratio of the initial rates of first order reaction to that of the zero order reaction is :

   1) $\dfrac{1}{2 \times 0.693}$ 2) 2×0.693 3) 0.693   4) $\dfrac{2}{0.693}$

9. The reaction, $vA \rightarrow$ products, is zero order with respect to A. Its half-life is given as [k_0 is the rate constant]

   1) $[A]_0/v, k_0$
   2) $[A]_0/k_0$
   3) $[A]_0/2vk_0$
   4) $v[A]_0/2k_0$

10. The temperature coefficient of a reaction is :

    1) The square of rate constant

    2) The rate constant at 308 K

    3) The ratio of rate constant at two temperatures differing by 10°C, $\dfrac{k_T}{k_{T+10}}$

    4) The ratio of rate constant at two temperatures differing by 10°C, $\dfrac{k_{T+10}}{k_T}$

11. The activation energy of exothermic reaction $A \rightarrow B$ is 80 kJ. The magnitude of enthalpy of reaction is 200 kJ. The activation energy for the reaction $B \rightarrow A$ will be

    1) 60 kJ
    2) 120 kJ
    3) 280 kJ
    4) 200 kJ

12. **Assertion (A)** : The enthalpy of reaction remains constant in the presence of a catalyst.

    Reason (R) : A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same

    Choose the correct option

    1) Both A and R are correct but R is not correct explanation of A

    2) Both A and R are correct and R is correct explanation of A

    3) A is correct but R is incorrect

    4) A is incorrect but R is correct

13. Identify the wrong statement regarding the collision theory of chemical reactions from the following

    1) It considers atoms/molecules as hard spheres and ignores their structural aspects

    2) All collisions do not lead to the formation of products

    3) Activation energy and proper orientation of molecules together determine the rate of a chemical reaction

    4) For a reacton $A+B \longrightarrow$ Products, $\text{Rate} = PZ_{AB}e^{E_a/RT}$, where P is the steric factor and Z_{AB} is the collision frequency

SECTION-II - Numerical Type Questions

14. A reaction $X_{2(g)} \rightarrow Z_{(g)} + \dfrac{1}{2}Y_{(g)}$ exhibits an increase in pressure from 150 mm Hg to 170 mm Hg in 10 min. The average rate of disappearance of X_2 in this time interval is .... mm Hg min^{-1}

15. Half of a substance is consumed in 40 min. When the quantity of the substance taken is reduced to half, the half-life of the change is 20min. The order of reaction is ....

16. If the activation energy of a reaction is 80.9 kJ mol^{-1}, the fraction of molecules at 700 K, having enough energy to react to form products is e^{-x}. The value of x is .... (Rounded off to the nearest integer) [Use R = 8.31 JK^{-1} mol^{-1}]

PART-II (JEE ADVANCED)

Section-III - Only one option correct type

17. For a homogenous gaseous reaction:

$A \longrightarrow Q + R + S$, the initial pressure was P_0 while pressure after time 't' was P (P is more than P_0). The expression for the rate constant (K) is

A) $K = \dfrac{2.303}{t} \log_{10}\left(\dfrac{P_0}{P_0 - P}\right)$

B) $K = \dfrac{2.303}{t} \log_{10}\left(\dfrac{3P_0}{2P_0 - P}\right)$

C) $K = \dfrac{2.303}{t} \log_{10}\left(\dfrac{2P_0}{3P_0 - P}\right)$

D) $K = \dfrac{2.303}{t} \log_{10}\left(\dfrac{2P_0}{4P_0 - P}\right)$

18. If a reaction follows the Arrhenius equation, the plot lnk Vs $\dfrac{1}{(RT)}$ gives a straight line with a slope of (-y) unit. The activation energy of the reaction is
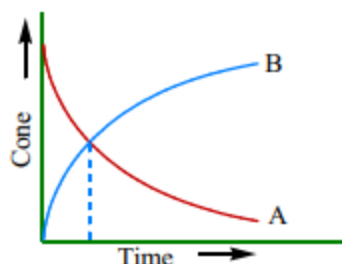
A) y unit   B) R/y unit   C) yR unit   D) y/R unit

19. The following plot presents the variation of the concentration of species A and B against time for the reaction, $A \rightarrow B$

The point of intersection of the two curves represens :

A) $t_{1/2}$ B) $t_{3/4}$ C) $t_{2/3}$ D) $t_{1/3}$

20. Aqueous AB_2 decompose according to the 1st order reaction $AB_2(aq) \rightarrow A(g) + 2B(l)$.

The volume of A(g) collected during this reaction after 20 minutes is 20 mL and that collected after a very long time is 40 mL. The rate constant for the reaction is

A) 1.435 x 10^{-2} min^{-1} B) 3.45 x 10^{-2} min^{-1} C) 1.73 x 10^{-2} min^{-1} D) 6.93 min^{-1}

21. For the chemical reaction $A \to$ products, the rate of disappearance of A is given by

$$r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{(1 + k_2 C_A)}, \text{ where } C_A \text{ is the molar concentration of A.}$$

At very low values of C_A, the order and rate constant of the reaction would be respectively:

A) 1, $\dfrac{k_1}{1+k_2}$ B) 1, k_1 C) 0, $\dfrac{k_1}{1+k_2}$ D) 1, $\dfrac{k_1}{k_2}$

Section IV - One or more option correct type

22. A graph of volume of hydrogen released vs time for the reaction between zinc and dil.HCl is given in figure. On the basis of this mark the correct option(s)
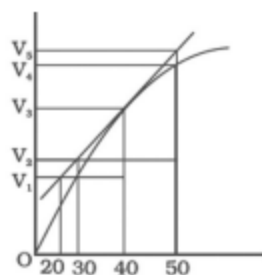

A) Average rate upto 40 s is $\dfrac{V_3 - V_2}{40}$

B) Instantaneous rate at 40 s is $\dfrac{V_3 - V_2}{40 - 30}$

C) Average rate upto 40 s is $\dfrac{V_3}{40}$

D) Average rate upto 30 s is $\dfrac{V_2 - V_1}{30 - 20}$

23. The reaction between A and B is first order with respect to A and zero order with respect to B.

Experiment	[A]/ mol L^{-1}	[B]/ mol L^{-1}	Inital rate / mol L^{-1} min^{-1}
I	0.1	0.1	2.0×10^{-2}
II	X	0.2	4.0×10^{-2}
III	0.4	0.4	Y
IV	Z	0.2	2.0×10^{-2}

Choose the correct option(s)

A) X = 0.1 M   B) Y = 8.0 × 10^{-2} mol L^{-1} min^{-1}

C) Z = 0.1 M   D) Y = 16.0 × 10^{-2} mol L^{-1} min^{-1}

24. A certain reaction $A \rightarrow B$ follows the given concentration-time graph.
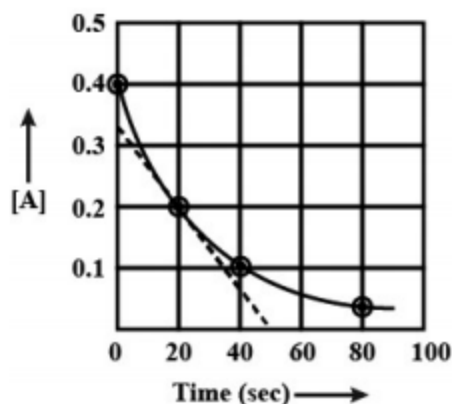
Choose the incorrect option(s)

A) The reaction is second order with respect to A

B) The rate of reaction at 40 second is approximately 3.465×10^{-3} Ms^{-1}

C) The rate of reaction at 80 second is approximately 1.75×10^{-1} Ms^{-1}

D) The concentration of B at 60 second is 0.35 M

25. The reaction $2NO + Br_2 \rightarrow 2NOBr$ follows the mechanism:

Step I: $NO + Br_2 \underset{\longleftarrow}{\overset{Fast}{\longrightarrow}} NOBr_2$

Step II: $NOBr_2 + NO \xrightarrow{Slow} 2NOBr$
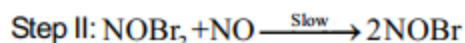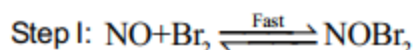
Which of the following statements is/are true regarding the above reaction?

A) The order of the reaction with respect to NO is two

B) The molecularity of the steps (A) and (B) are two each

C) The molecularity of the overall reaction is three

D) The overall order of the reaction is three

Section V - Numerical type questions

26. Consider the following graph for the reaction, $A \rightarrow$ products.
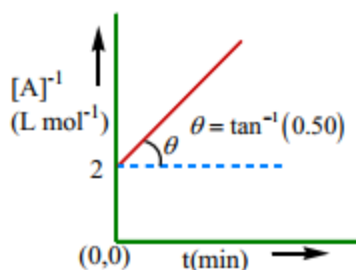
Order of the reaction is ....

27. The following results were obtained during kinetic studies of the reaction: $2A + B \longrightarrow Products$

Experiment	[A] mol L^{-1}	[B] mol L^{-1}	Initial rate of reaction (molL^{-1} min^{-1})
I	0.10	0.20	6.93 × 10^{-3}
II	0.10	0.25	6.93 × 10^{-3}
III	0.20	0.30	1.386 ×10^{-2}

The time (in minutes) required to consume half of A is ....

28. In an elementary reaction $A(g) + 2B(g) \rightarrow C(g)$ the initial pressure of A and B are P_A=0.40 atm and P_B=0.60atm respectively. At time T, if pressure of C is observed 0.1 atm, then find the value of

$$\frac{r_i \left(\text{initial rate of reaction}\right)}{r_T \left(\text{rate of reaction at time T}\right)}$$

29. Consider the following parallel reactions (both conversions follow first order kinetics)
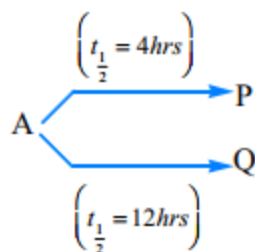
The half-life for the decay of A is .... hours

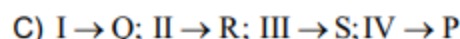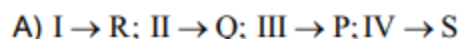## Section-VI - Matrix match type

30. Match the following

Column-I

I) $\frac{3}{2} \times t_{1/2}$

II) $2 \times t_{1/2}$

III) $10 \times t_{1/2}$

IV) $\frac{10}{3} \times t_{1/2}$

Column-II

P) Time for 99.9% completion of first order reactions

Q) Time for 75% completion of zero order reactions

R) Time for 75% completion of first order reactions

S) Time for 90% completion of first order reactions

A) I $\rightarrow$ R; II $\rightarrow$ Q; III $\rightarrow$ P; IV $\rightarrow$ S

B) I $\rightarrow$ Q; II $\rightarrow$ R; III $\rightarrow$ P; IV $\rightarrow$ S

C) I $\rightarrow$ Q; II $\rightarrow$ R; III $\rightarrow$ S; IV $\rightarrow$ P

D) I $\rightarrow$ R; II $\rightarrow$ Q; III $\rightarrow$ S; IV $\rightarrow$ P