

18. CHEMICAL KINETICS

1. INTRODUCTION

Chemical kinetics deals with the study of rate of chemical reactions. Rate of reaction is defined as change in concentration of reactants or products per unit time. It is influenced by various factors such as nature of substance, physical state of substance, temperature, concentration, presence of catalyst, etc.

2. RATE OF REACTIONS

The rate of reaction is expressed in $\text{mol L}^{-1} \text{s}^{-1}$.

$$\text{Rate of reaction} = \frac{\text{Change in the concentration of reactants or(Products)}}{\text{Time}}$$

2.1 Average Rate of Reaction

Average rate of reaction is defined as change in the concentration of reactants (or products) during large interval of time. If ΔC is the change in the concentration of reactants and products in Δt time, then

$$\text{Average rate} = \frac{\text{Change in the concentration of reactants or(Products)}}{\text{Time}} = \pm \frac{\Delta C}{\Delta t} = \pm \frac{C_2 - C_1}{t_2 - t_1}$$

The graph shows the progress of reaction with respect to time.

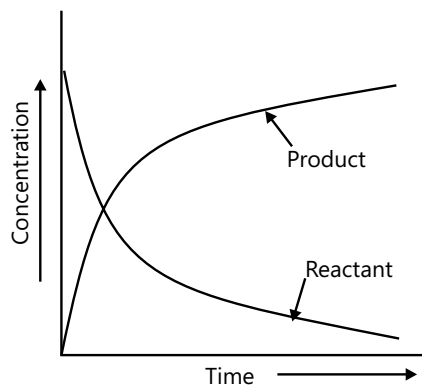


Figure 18.1: Concentration vs Time

$$\text{Unit of average rate of reaction} = \frac{\text{Unit of concentration}}{\text{Unit of time}} = \frac{\text{gram mole / Litre}}{\text{second}} = \text{g mol L}^{-1} \text{sec}^{-1}$$

PLANCESS CONCEPTS

For gases, pressure is replaced by concentration. Thus, unit will be atm sec^{-1}

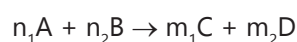
$$PV = nRT \text{ or } P = \left[\frac{n}{V} \right] RT \text{ or } P = CRT$$

$$\frac{\Delta[P]}{\Delta t} = \frac{\Delta[C]}{\Delta t} \cdot RT \text{ or Rate in [atm/sec]} = \text{Rate in [molarity/sec]} \times RT$$

Vaibhav Krishnan (JEE 2009, AIR 22)

2.2 Expression of Rate of Reaction

For the following reaction



$$\text{rate of reaction} = -\frac{1}{n_1} \frac{\Delta[A]}{\Delta t} = -\frac{1}{n_2} \frac{\Delta[B]}{\Delta t} = +\frac{1}{m_1} \frac{\Delta[C]}{\Delta t} = +\frac{1}{m_2} \frac{\Delta[D]}{\Delta t}$$

For the reaction $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

$$\text{The rate of reaction} = \frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{H}_2\text{O}_2]}{\Delta t}$$

2.3 Instantaneous Rate of Reaction

Instantaneous rate of reaction is defined as the average reaction rate during a very short interval of time or rate of reaction at a particular time.

$$\text{Instantaneous rate} = \pm \lim_{\Delta t \rightarrow 0} \frac{\Delta c}{\Delta t} = \frac{dc}{dt}$$

Note: For the reaction $n_1A + n_2B \rightarrow m_1C + m_2D$

$$\text{Instantaneous rate of reaction} = -\frac{1}{n_1} \frac{d[A]}{dt} = -\frac{1}{n_2} \frac{d[B]}{dt} = +\frac{1}{m_1} \frac{d[C]}{dt} = +\frac{1}{m_2} \frac{d[D]}{dt}$$

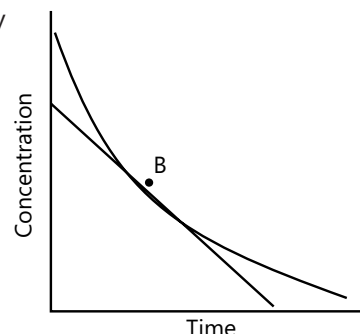


Figure 18.2: Instantaneous Plot

PLANCESS CONCEPTS

Rate of reaction and rate of change of concentration of a reactant (or product) are two different terms, except when stoichiometric coefficient involved is unity. On the other, rate of reaction is equal to the rate of change of concentration of a reactant (or a product) divided by the corresponding stoichiometric coefficient.

Nikhil Khandelwal (JEE 2009, AIR 94)

2.4 Reaction Life Time

It is defined as the time taken to complete 98% of the reaction. The shorter the life time, the faster the reaction. Half-life period is defined as either the time taken to complete half of the reaction or during which the concentration of the reactant is reduced to one half of its initial value. It is denoted by $t_{1/2}$.

Illustration 1: For the reaction $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 min. Calculate the average rate of reaction using units of time both in minutes and seconds. **(JEE MAIN)**

Sol: Average rate = $-\frac{\Delta[R]}{\Delta t} = -\frac{[R]_2 - [R]_1}{t_2 - t_1} = -\frac{0.02M - 0.030M}{25\text{minutes}} = -\frac{-0.01M}{25\text{minutes}}$

$$= 4 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1} = \frac{0.01M}{25 \times 60s} = 6.66 \times 10^{-6} \text{ mol L}^{-1} \text{ sec}^{-1}.$$

Illustration 2: Decomposition of N_2O_5 is expressed by the equation, $N_2O_5 \longrightarrow 2NO_2 + \frac{1}{2}O_2$

If, during a certain time interval, the rate of decomposition of N_2O_5 is $1.8 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$. Calculate the rates of formation of NO_2 and O_2 during the same interval. **(JEE MAIN)**

Sol: Decomposition of N_2O_5 has the following rate expression:

$$-\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \frac{\Delta[NO_2]}{\Delta t} = 2 \frac{\Delta[O_2]}{\Delta t}$$

So, $\frac{\Delta[NO_2]}{\Delta t} = 2 \frac{\Delta[N_2O_5]}{\Delta t} = 2 \times 1.8 \times 10^{-3} = 3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$

and $\frac{\Delta[O_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2} \times 1.8 \times 10^{-3} = 9 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$

(Rate is always positive and hence $-\frac{\Delta[N_2O_5]}{\Delta t}$ is taken positive.)

Illustration 3: During the analysis of the products, even when a portion of the mixture is removed, the rate of reaction in the remaining mixture is not affected. Explain. **(JEE ADVANCED)**

Sol: The rate of reaction depends on concentration, which remains constant even if a portion of the mixture is removed, i.e. amount of substance is independent of the concentration and hence remains unaffected.

Illustration 4: For the reaction $A + B \rightarrow C + D$, the rate law equation = $K_1 [A] + K_2 [A] [B]$, where K_1 and K_2 represent two different constants and the products are formed by two different mechanisms. Explain the relative magnitudes of the rates of two individual mechanisms? **(JEE ADVANCED)**

Sol: The rate of formation of products for both the reaction mechanisms must be of the same order of magnitude. Different magnitude reflects only the rate of reaction of the one which is faster among the two mechanisms. Also, it involves rate of formation of product from A as well as product from A and B.

3. RATE CONSTANT

Consider a simple reaction $A \rightarrow B$

At a particular instant, if C_A is the molar concentration or active mass of A, then $\frac{dx}{dt} \propto C_A$ or $\frac{dx}{dt} = kC_A$

where k is a proportionality constant, called velocity constant or rate constant or specific reaction rate.

At a fixed temperature, if $C_A = 1$, then rate = $\frac{dx}{dt} = k$... (i)

Thus, rate constant can be defined as rate of reaction at unit concentration of the reactants. Let us consider a general reaction $aA + bB \rightarrow \text{Product}$

$$\text{Rate} = \left(\frac{dx}{dt} \right) \propto [A]^a [B]^b = k [A]^a [B]^b \text{ when } [A] = [B] = 1 \text{ mol/L, then rate} = k$$

PLANCESS CONCEPTS

For a particular reaction, rate constant is independent of the concentration of the reactants and dependent only on temperature.

Neeraj Toshniwal (JEE 2009, AIR 21)

3.1 Units of Rate Constant

For reactions of different order, unit for rate constant is as follows:

$$\begin{aligned} \text{Unit of rate constant} &= \left[\frac{1}{\text{unit of concentration}} \right]^{n-1} \times \text{time}^{-1} \\ &= \left[\frac{1}{\text{mol/litre}} \right]^{n-1} \times \text{sec}^{-1} = \left[\frac{\text{litre}}{\text{mol}} \right]^{n-1} \times \text{sec}^{-1} \text{ where, } n = \text{order of reaction.} \end{aligned}$$

PLANCESS CONCEPTS

When order of reaction is not mentioned explicitly, then it can be determined using the unit of rate constant. For example, if the unit of rate constant is $\text{M}^{-1}\text{sec}^{-1}$, then order = $1 - (-1) = 2$.

Aman Gour (JEE 2012, AIR 230)

3.2 Rate of Reaction and Reaction Rate Constant

Table 18.1: Difference between rate of reaction and reaction rate constant

S.No.	Rate of reaction	Reaction rate constant
1.	Speed at which reactants converts into products.	Proportionality constant.
2.	Measured as the rate of decrease in concentration of reactants or the rate of increase in concentration of products with time.	Equal to the rate of reaction when the concentration of each of the reactants is unity.
3.	Depends upon the initial concentration of reactants.	Independent of the initial concentration of the reactants and has a constant value at fixed temperature.

3.3 Factors Affecting Rate of Reaction

- Concentration:** According to the law of mass action the greater the concentration of the reactants, the more rapidly the reaction proceeds.
- Pressure (Gaseous reaction):** Increasing the pressure, decreases the volume and simultaneously increases the concentration. Therefore the rate of reaction increases.
- Temperature:** Increase in temperature increases the reaction rate. It has been observed that rate either doubles or triples for every 10°C rise in temperature. Temperature coefficient of reaction rate, $\frac{k_{T+10}}{k_T} \approx 2$ or 3 , where k_{T+10} and k_T are rate constants at two temperature, differing by 10°C .
- Nature of the reactants:** The rate depends upon specific bonds of the reactants involved in the reaction and hence on the nature of reactants.

- (e) **Surface area of the reactants:** In heterogeneous reactions, if the reactants are in more powdered form, then velocity is greater [as more active centres are available].
- (f) **Catalyst:** It has an immense effect on the rate of reaction. Positive catalyst increases the rate of reaction by decreasing the activation energy, while negative catalyst decreases the rate of reaction by increasing the activation energy. Catalyst mainly affects the activation energy of reaction and hence the rate constant and rate of reaction changes.
- (g) **Intensity of radiation:** The rate of photochemical reactions generally increases with increase in intensity of radiation.

Illustration 5: The rate law of a chemical reaction $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ is $K[\text{NO}]^2 [\text{O}_2]$. If the volume of reaction vessel is reduced to $1/4$ th of its original value, then what will be the change in rate of reaction? **(JEE MAIN)**

Sol: For, $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ $\text{Rate} = K[\text{NO}]^2 [\text{O}_2]$

Let us take a moles of NO and b moles of O_2 to start a reaction at any time in a vessel with a capacity of V L.

$$r_1 = K \left[\frac{a}{V} \right]^2 \left[\frac{b}{V} \right] \quad \dots(i)$$

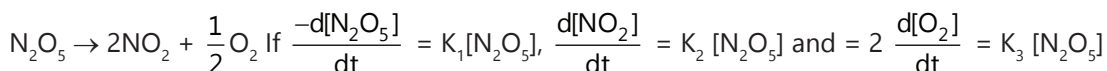
if volume of vessel is reduced to $\frac{V}{4}$, then the rate for same number of NO and O_2 moles.

$$r_2 = K \left[\frac{a}{V/4} \right]^2 \left[\frac{b}{V/4} \right] = 64K \left[\frac{a}{V} \right]^2 \left[\frac{b}{V} \right] \quad \dots(ii)$$

Dividing equation (ii) by (i), $\frac{r_2}{r_1} = 64$ i.e. r_2 is 64 times of r_1

Illustration 6: Dinitrogen pentoxide decomposes as follows:

(JEE ADVANCED)



Derive a relation between K_1 , K_2 and K_3 .

Sol: For the given reaction

$$\frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = 2 \frac{d[\text{O}_2]}{dt} \quad \text{Putting given values}$$

$$\text{or} \quad K_1[\text{N}_2\text{O}_5] = \frac{1}{2} K_2[\text{N}_2\text{O}_5] = 2K_3[\text{N}_2\text{O}_5] \quad \text{or} \quad 2K_1 = K_2 = 4K_3$$

3.4 Rate Law

(a) It may not depend upon the concentration of each reactant or product of the reaction.

Suppose, $m\text{A} + n\text{B} \rightarrow \text{Product}$ $R \propto [\text{A}]^m [\text{B}]^n$.

(b) Rate of chemical reaction is directly proportional to the concentration of reactants.

(c) The rate law represents the experimentally observed rate of reaction, which depends upon the slowest step of the reaction.

(d) Rate law cannot be deduced from the equation for a given reaction. It can be found out by experiments only.

(e) The rate law may not bear a simple relationship for the stoichiometric equation.

(f) It may not depend upon the concentration of species, which do not appear in the equation for the overall reaction.

4. ORDER OF REACTION

The order of any reaction may be defined as the sum of the powers to which the concentration terms are raised in order to determine the rate of reaction.

For the reaction: $m\text{A} + n\text{B} \rightarrow \text{product}$

The experimental data suggests that

Rate $= k[\text{A}]^p[\text{B}]^q$; then the order with respect to A = p and the order with respect to B = q and the total order of the reaction = p + q.

Reactions having order equal to 0 are zero-order reactions.

Reactions having order equal to 1, are 1st order reactions.

Reactions having order equal to 2 are 2nd order reactions.

Reactions having order equal to 3 are 3rd order reactions

PLANCESS CONCEPTS

- Order can be zero, fractional or integer.
- Stoichiometric coefficients m and n of the reactants are always not equal to orders p and q.

B Rajiv Reddy (JEE 2012, AIR 11)

5. MOLECULARITY OF A REACTION

It is defined as the number of molecules, atom or radicals that participate in the reaction. Depending on the number of participating molecules, the reaction can be unimolecular, bimolecular, trimolecular, etc.

Participating molecules	Molecularity
One molecule	unimolecular, 1
Two molecule	bimolecular, 2
Three molecule	trimolecular, 3

PLANCESS CONCEPTS

- Molecularity of a reaction is mostly between 1 to 3, but never zero. It is rare that molecularity exceeds 3.
- Misconception: Order and molecularity are one and the same. But order may or may not be equal to molecularity of the reaction.

Rohit Kumar (JEE 2012, AIR 79)

Table 18.2: Differences between order and molecularity

S. No.	Molecularity	Order of reaction
1.	It is the total number of reacting molecules (atoms or ions) leading to chemical change.	It is the sum of powers of molar concentrations of the reacting molecules in the rate equation of the reaction.
2.	It is always a whole number.	It may be a whole number, zero, fractional, positive or negative.

3.	It is a theoretical concept.	It is experimentally determined.
4.	It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for overall complex reaction.	It is meant for the reaction and not for its individual steps.

Illustration 7: Write the order of the following reactions?

(JEE MAIN)

Reaction	Exp. rate equ.
$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$	$r = k[\text{H}_2]^0[\text{Cl}_2]^0$
$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	$r = k[\text{H}_2][\text{Br}_2]^{1/2}$
$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	$r = k[\text{H}_2][\text{I}_2]$

Sol: Order is the number to which the concentration of the reactants/products are raised corresponding mostly to the coefficients.

Reaction	Exp. rate equ.	Order
$\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$	$r = k[\text{H}_2]^0[\text{Cl}_2]^0$	0
$\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$	$r = k[\text{H}_2][\text{Br}_2]^{1/2}$	3/2
$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$	$r = k[\text{H}_2][\text{I}_2]$	2

Illustration 8: For the reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ At 300 K, following data are obtained:

(JEE ADVANCED)

Expt. No.	Initial Concentration		Initial Rate
	[NO]	[Cl ₂]	
1.	0.010	0.010	1.2×10^{-4}
2.	0.010	0.020	2.4×10^{-4}
3.	0.020	0.020	9.6×10^{-4}

What is the rate law for the reaction and the order of the reaction? Also calculate the specific rate constant.

Sol: Let the rate law for the reaction be

$$\text{Rate} = k [\text{NO}]^x [\text{Cl}_2]^y$$

$$\text{From expt. (1), } 1.2 \times 10^{-4} = k [0.010]^x [0.010]^y \quad \dots(i)$$

$$\text{From expt. (2), } 2.4 \times 10^{-4} = k [0.010]^x [0.020]^y \quad \dots(ii)$$

Dividing Equation (ii) by Equation (i),

$$\frac{2.4 \times 10^{-4}}{1.2 \times 10^{-4}} = \frac{[0.020]^y}{[0.010]^y} \quad \text{or} \quad 2 = (2)^y \quad y = 1$$

$$\text{From expt. (2), } 2.4 \times 10^{-4} = k [0.010]^x [0.020]^y$$

$$\text{From expt. (3), } 9.6 \times 10^{-4} = k [0.020]^x [0.020]^y$$

$$\text{Dividing Equation (iii) by Equation (ii), } \frac{9.6 \times 10^{-4}}{2.4 \times 10^{-4}} = \frac{[0.020]^x}{[0.010]^x} \quad \text{or} \quad 4 = 2^x, \quad x = 2$$

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

Rate law for the reaction is

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

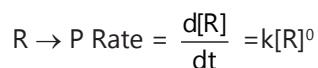
Considering Equation (i) again, $1.2 \times 10^{-4} = k[0.010]^2[0.010]$

$$k = \frac{1.2 \times 10^{-4}}{[0.010]^3} = 1.2 \times 10^2 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

6. REACTION OF VARIOUS ORDERS

6.1 Zero-Order Reactions

Rate of the reaction proportional to zero power of the concentration of reactants is known as zero-order reaction. Consider the reaction



As any quantity raised to power zero is unity

$$\text{Rate} = \frac{d[R]}{dt} = k \times 1 ; d[R] = -k dt$$

Integrating on both sides $[R] = -k t + I$

...(i)

where I is the constant of integration.

At $t = 0$, the concentration of the reactant $R = [R]_0$, where $[R]_0$ is initial concentration of the reactant.

Substituting in equation (i)

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

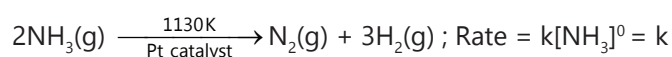
Substituting the value of I in the equation (i)

$$[R] = -kt + [R]_0 \quad \text{...(ii)}$$

Equation of a straight line, $y = mx + c$. We get a straight line with slope $= -k$ and intercept equal to $[R]_0$, when $[R]$ is plotted against t .

$$\text{Simplifying equation (ii), we get the rate constant } k = \frac{[R]_0 - [R]}{t} \quad \text{...(iii)}$$

Zero-order reactions occur only under special conditions and hence they are uncommon. Some enzyme catalyzed reactions and reactions which occur on metal surfaces are a few examples of zero-order reactions. Another example of zero-order reaction is decomposition of gaseous ammonia on a hot platinum surface at high pressure.



Here, platinum acts as a catalyst. The metal surface reacting with gas molecules under high pressure gets saturated. So, a further change in reaction conditions does not alter the amount of ammonia on the surface of the catalyst making rate of the reaction independent of its concentration. The thermal decomposition of HI on gold surface is another example of zero-order reaction.

(A) Unit of rate constant: $k = \frac{[R]_0 - [R]}{t}$ $k \text{ mol L}^{-1} \text{ sec}^{-1}$

Unit of rate of reaction and unit of rate constant are the same.

(B) Half-life period ($t_{1/2}$): It is the time taken to complete half of the reaction.

$$\text{At } t = t_{1/2} ; \quad R = \frac{R_0}{2} \quad \left[t_{1/2} = \frac{R_0}{2K} \right] \quad \text{or} \quad t_{1/2} \propto R_0$$

It is directly proportional to the initial concentration of the reactant.

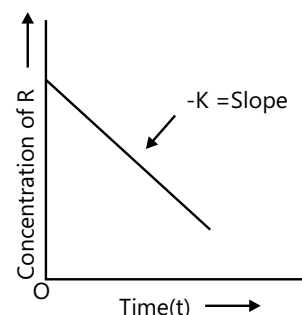


Figure 18.3: Zero order plot

6.2 First-Order Reactions

Rate of the reaction is proportional to the first power of the concentration of the reactant. For example, $R \rightarrow P$

$$\text{Rate} = -\frac{d[R]}{dt} = k[R] \quad \text{or} \quad -\frac{d[R]}{[R]} = -kdt$$

Integrating the above equation, we get $\ln [R] = -kt + I$... (iv)

I is the integration constant ; hence its value can be determined easily.

When $t = 0$, $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant.

Therefore, equation (iv) can be written as $\ln [R]_0 = -k \times 0 + I = I$

Substituting I in equation (iv)

$$\ln [R] = -kt + \ln [R]_0 \quad \dots (v)$$

$$\text{Rearranging this equation } \ln \frac{[R]}{[R]_0} = -kt \text{ or } k = \frac{1}{t} \ln \frac{[R]_0}{[R]} \quad \dots (vi)$$

$$\text{At time } t_1, \text{ from equation (iv) } \ln [R]_1 = -kt_1 + \ln [R]_0 \quad \dots (vii)$$

$$\text{At time } t_2, \ln [R]_2 = -kt_2 + \ln [R]_0 \quad \dots (viii)$$

where $[R]_1$ and $[R]_2$ are the concentrations of the reactants at time t_1 and t_2 respectively. Subtracting (viii) from (vii)

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

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

$$\text{Equation (v) can also be written as } \ln \frac{[R]_1}{[R]_2} = -kt$$

Taking antilog on both sides $[R] = [R]_0 e^{-kt}$

When $\ln [R]$ is plotted against t , we obtain a straight line with slope = $-k$ and intercept equal to $\ln [R]_0$.

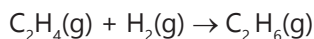
The first-order rate equation (vi) can also be written in the form

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

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

If we plot a graph between $\log [R]_0/[R]$ and t , the slope = $k/2.303$

Hydrogenation of ethene is an example of first-order reaction.



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

All natural and artificial radioactive decay of unstable nuclei takes place by first-order kinetics.

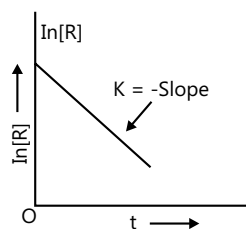


Fig.: A plot between $\ln [R]$ and t for a first-order reaction

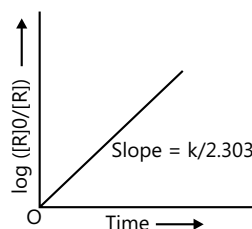
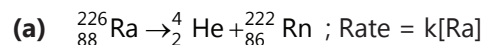


Fig.: Plot of $\log [R]_0/[R]$ vs time for a first-order reaction

Figure 18.4: First order plot

Examples:

(b) Decomposition of N_2O_5 and N_2O are few more examples of first-order reactions.

(i) Unit of rate constant: $K = \frac{2.303}{t} \log \frac{[\text{R}]_0}{[\text{R}]} = \text{sec}^{-1}$

(ii) Half-life period ($t_{1/2}$):

$$\text{At } t = t_{1/2}, R = \frac{R_0}{2}, K = \frac{2.303}{t_{1/2}} \log \frac{R_0}{R_0/2} = \frac{2.303}{t_{1/2}} \times \log 2 = \frac{0.693}{t_{1/2}}$$

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

6.3 Pseudo-Order Reactions

Reactions whose actual order is different from that expected using rate law expression are called pseudo-order reactions, e.g



Expected rate law:

$$\text{Rate} = k [\text{RCl}][\text{H}_2\text{O}]; \text{ expected order} = 1+1 = 2$$

$$\text{Actual rate law: Rate} = k' [\text{RCl}] \quad \text{Actual order} = 1$$

Water is taken in excess; therefore, its concentration may be taken constant. The reaction is, therefore, pseudo first order. Similarly, the acid catalyzed hydrolysis of ester, viz.,

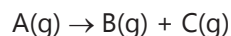


follows first order kinetics: Rate = $k [\text{RCOOR}']$

It is also a pseudo first-order reaction.

6.4 Some Examples of First-Order Reactions and Their Rate Constants**(a) For Gas Phase Reaction**

Let us consider a typical first-order gas phase reaction



Let p_i be the initial pressure of A and p_t the total pressure at time 't'. Integrated rate equation is as follows:

$$\text{Total pressure } p_t = p_A + p_B + p_C \text{ (pressure units)}$$

p_A , p_B and p_C are the partial pressures of A, B and C, respectively

Decreasing x atm pressure of A at time t to form one mole of B and C each.. The increase in pressure of B and C will also be x atm each.

	A(g)	→	B(g)	+	C(g)
At time, $t = 0$	p_i atm		0 atm		0 atm
At time t	$(p_i - x)$ atm		x atm		x atm

Where p_i is the initial pressure at time $t = 0$.

$$P_t = (p_i - x) + x + x = p_i + x$$

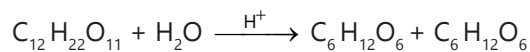
$$x = (p_t - p_i), \text{ where } p_A = p_i - x = p_i - (p_t - p_i) = 2p_i - p_t$$

$$k = \left(\frac{2.303}{t} \right) \left(\log \frac{p_i}{p_A} \right) \quad \dots(\text{xi})$$

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

(b) Pseudo-Unimolecular Reaction:

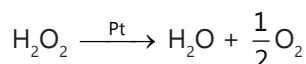
Inversion of cane sugar



Sucrose Glucose Fructose

The progress of the reaction can be studied using a polarimeter. Cane sugar and glucose are dextrorotatory while fructose is laevorotatory. Let θ_0 is polarimetric reading at $t = 0$; θ_t is polarimetric reading after time t and θ_∞ is polarimetric reading after infinite time.

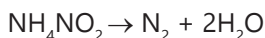
$$k = \frac{2.303}{t} \log \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$$

(c) (i) Decomposition of H_2O_2 

The progress of the reaction can be studied by two methods. (1) Volume of oxygen gas at different intervals of times is measured and or (2) definite amount of reaction mixture is titrated with standard KMnO_4 at different intervals of time. If V_0 represent the initial volume of KMnO_4 and V_t final volume of KMnO_4 at any time t

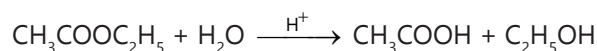
Then, $R_0 \propto V_0, R \propto V_t$

Therefore,
$$K = -\frac{2.303}{t} \log \frac{V_0}{V_t}$$

(ii) Decomposition of Ammonium Nitrite

If V_t is the volume of N_2 evolved at any time t and V_∞ is the volume of N_2 evolved when the decomposition is complete. Then,

$$K = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

(d) Hydrolysis of Ethyl Acetate (Ester)

Kinetics of this reaction is studied by titrating a definite volume of the reaction mixture with standard alkali solution.

If V_0, V_t and V_∞ are volumes of standard alkali needed to neutralize a definite amount of x , will be proportional to $V_t - V_0$ and a , will be proportional to $V_\infty - V_0$

Hence,
$$K = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

(e) Oxide Layer Formation

$$K = \frac{1}{t} \ln \frac{\tau_{\max}}{\tau_{\max} - \tau}$$
 where τ_{\max} is the thickness of oxide layer after ∞ times and τ is the thickness of oxide layer at time ' t '.

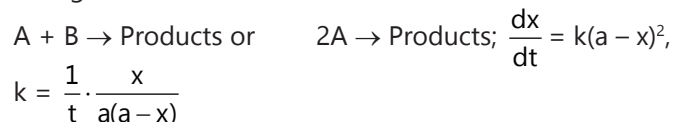
(f) Bacterial Growth:
$$K = \frac{1}{t} \ln \frac{a+x}{a}$$

6.5 Second-Order Reaction

A reaction is said to be of second order if its reaction rate involves two different concentrations.

The kinetics of second-order reactions are given as follows:

- (a) When concentrations of both reactants are same or two molecules of the same reactant are involved in the change, i.e.



Where a is the initial concentration of the reactant or reactants and x is the concentration of the reactant changed in time t .

- (b) When the initial concentrations of the two reactants are different, i.e.,



Initial conc. a b

$$\frac{dx}{dt} = k(a-x)(b-x); \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

$(a-x)$ and $(b-x)$ are the concentrations of A and B, respectively, after time interval, t .

Characteristics of the second-order reactions

- (a) The value of k (velocity constant) depends on the unit of concentration. The unit of k is expressed as $(\text{mol/litre})^{-1} \text{ time}^{-1}$ or $\text{litre mol}^{-1} \text{ time}^{-1}$.

When ' t ' is plotted against $\frac{1}{(a-x)}$ the resultant slope is a straight line.

$$\text{Rearranging equation for } k, t = \frac{1}{k(a-x)} - \frac{1}{ka}.$$

The slope of the line is $\frac{1}{k}$, where ' k ' can be evaluated.

- (b) Half-life period $(t_{1/2}) = \frac{1}{k} \cdot \frac{0.5a}{a \times 0.5a} = \frac{1}{ka}$

Thus, half-life period is inversely proportional to initial concentration.

- (c) Second-order reaction confirms to the first order when one of the reactants is present in large excess.

Consider, $k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$. If $a \gg b$, then $(a-x) \approx a$ and $(a-b) \approx a$

$$\text{Hence, } k = \frac{2.303}{ta} \log_{10} \frac{ba}{a(b-x)} \text{ or } ka = k' = \frac{2.303}{t} \log_{10} \frac{b}{(b-x)}$$

here since ' a ' being very large is a constant after the change. Thus, the reaction follows first-order kinetics with respect to the reactant taken relatively in small amount.

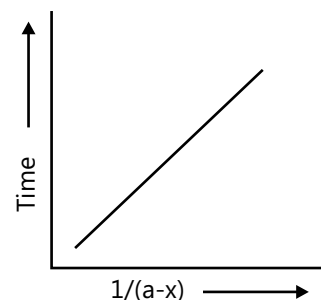
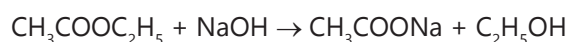


Figure 18.5 Second order plot

Examples of second-order reactions

- (a) Hydrolysis of ester by an alkali (saponification).



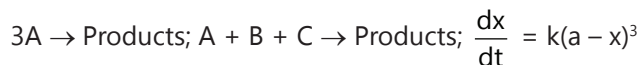
- (b) The decomposition of NO_2 into NO and O_2 . $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$

- (c) Conversion of ozone into oxygen at 100°C . $2\text{O}_3 \rightarrow 3\text{O}_2$

- (d) Thermal decomposition of chlorine monoxide. $2\text{Cl}_2\text{O} \rightarrow 2\text{Cl}_2 + \text{O}_2$

6.6 Third-Order Reaction

Reaction is said to be of third order if its reaction rate involves three different concentrations. When the concentration of all the three reactants is same or three molecules of the same reactant are involved, the rate expression is given as:



Therefore
$$k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

Characteristics of third-order reactions

- Half-life period = $\frac{1}{k} \cdot \frac{0.5a(2a-0.5a)}{2a^2(0.5a)^2} = \frac{1}{k} \cdot \frac{0.5a \times 1.5a}{2a^2 \times 0.5a \times 0.5a} = \frac{3}{2a^2k}$

Thus, half-life is inversely proportional to the square of initial concentration.

- The change in the unit of concentration changes the numerical value of k .
- The unit of k is expressed in $(\text{mol/litre})^{-2} \text{ time}^{-1}$ or $\text{L}^2 \text{ mol}^{-2} \text{ sec}^{-1}$.

Examples of third-order reactions

- Reaction between nitric oxide and oxygen. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
- Reaction between nitric oxide and chlorine. $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$

Examples

For a zero-order reaction, as shown in the following figure, the plot of $[A]$ versus time is a straight line with $k = -\text{ve slope}$. Other graphs are curved for a zero-order reaction.

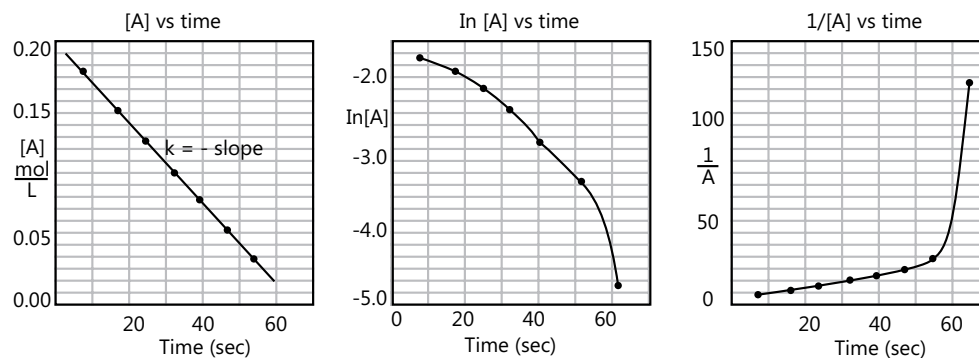


Figure 18.6: Plot of $[A]$ versus time

For a first-order reaction, as shown in the following figure, the plot of the logarithm of $[A]$ versus time is a straight line with $k = -\text{slope}$. Other graphs are curved for a first-order reaction.

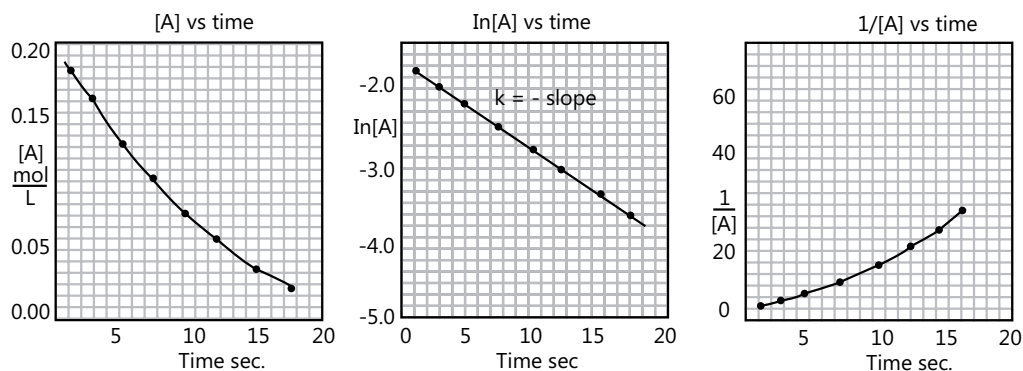


Figure 18.7: Plot of the logarithm of $[A]$ versus time

For a second-order reaction, as shown in the following figure, the plot of $1/[A]$ versus time is a straight line with $k = -\text{slope}$ of the line. Other graphs are curved for a second-order reaction.

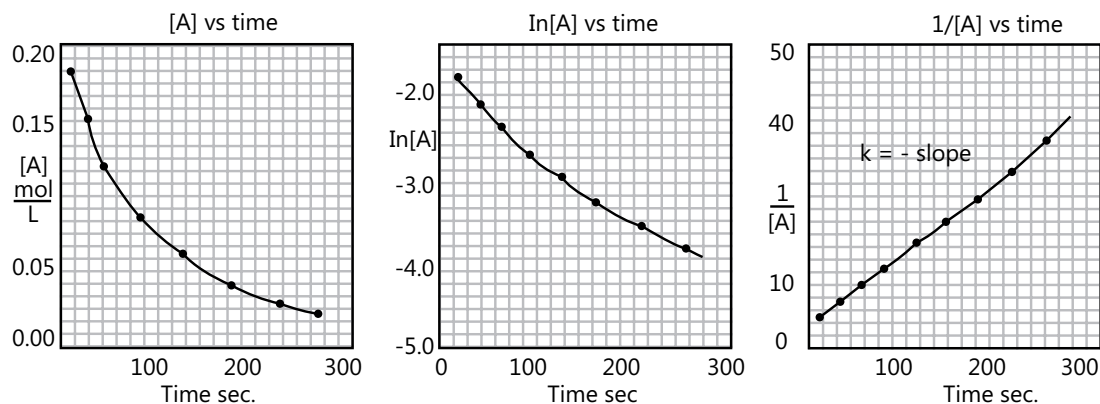
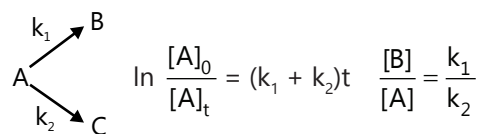


Figure 18.8: Plot of $1/[A]$ versus time

6.7 Parallel Reactions



$$[A] = [A]_0 e^{-kt} \quad [B] = \frac{k_1[A]_0}{k_1 + k_2} (1 - e^{-kt}) \quad [C] = \frac{k_2[A]_0}{k_1 + k_2} (1 - e^{-kt})$$

Variation of concentration A, B and C with time may be graphically represented as,

Examples:

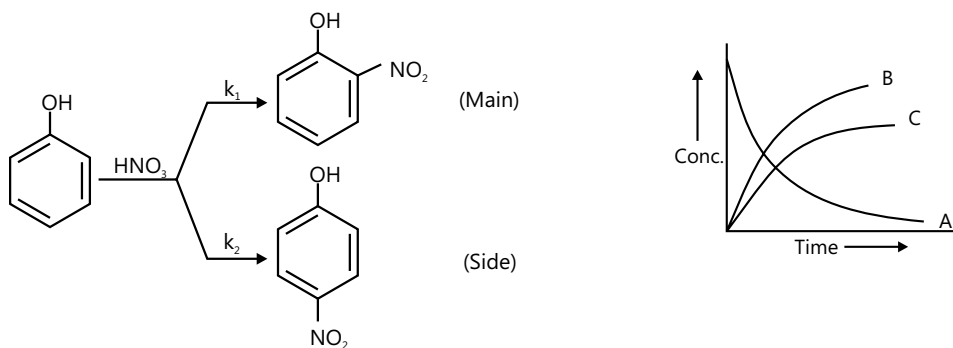
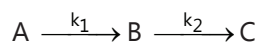


Figure 18.9: Parallel reactions

6.8 Consecutive Reactions



$$[A]_t = [A]_0 e^{-k_1 t} \quad ; \quad [B]_t = \frac{k_1[A]_0}{[k_2 - k_1]} [e^{-k_1 t} - e^{-k_2 t}]$$

$$[C]_t = [A]_0 - ([A]_t + [B]_t) \quad ; \quad [B]_{\max} = [A]_0 \cdot \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}}$$

$$t_{\max} = \frac{1}{K_1 - K_2} \ln \frac{K_1}{K_2}$$

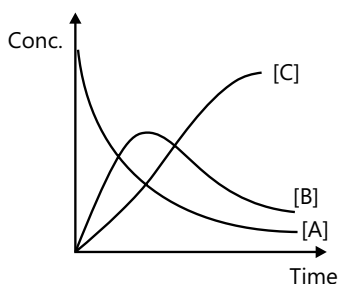
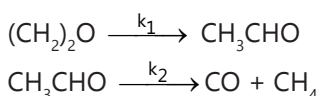
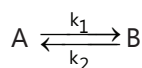


Figure 18.10: Consecutive reactions

Examples: (i) Decomposition of ethylene oxide:



6.9 Reversible Reactions



Initial state ($t = 0$) a 0

Conc. at time (t) $a - x$ x

Equilibrium conc. $(a - x_e)$ x_e ; $k_1 + k_2 = \frac{2.303}{t} \log_{10} \left\{ \frac{x_e}{x_e - x} \right\} \frac{x_{eq}}{a - x_{eq}} = \frac{K_f}{K_b}$

Illustration 9: If the time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes and the decomposition is a first-order reaction, then calculate the rate constant of the reaction. **(JEE MAIN)**

Sol: For a first-order reaction. $k = \frac{0.693}{t_{1/2}}$

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

Illustration 10: Consider a first-order reactions, if it takes 5 minutes for the initial concentration of 0.6 mol L^{-1} to become 0.4 mol L^{-1} . Then how long will it take for the initial concentration to become 0.3 mol L^{-1} ? **(JEE MAIN)**

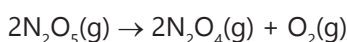
Sol: For a first-order reaction $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$

We have, $[A]_0 = 0.6 \text{ mol L}^{-1}$ $[A]_t = 0.4 \text{ mol L}^{-1}$ $t = 5 \text{ min}$

$$\text{So, } k = \frac{2.303}{5 \text{ min}} \times \log \frac{0.6}{0.4} = \frac{2.303}{5} \log 1.5 \text{ min}^{-1} = \frac{2.303 \times 0.1761}{5} \text{ min}^{-1} = 8.1 \times 10^{-2} \text{ min}^{-1}$$

$$\text{For, } [A]_t = 0.3 \text{ mol L}^{-1}; t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{8.1 \times 10^{-2}} \log \frac{0.6}{0.3} = \frac{2.303}{8.1 \times 10^{-2}} \log 2 = 8.5 \text{ min.}$$

Illustration 11: The following were obtained during the first order thermal decomposition of N_2O_5 (g) at constant volume:



S.No.	Time (sec)	Total Pressure (atm)
1.	0	0.5
2.	100	0.512

Calculate the rate constant.

(JEE ADVANCED)

Sol: Let the pressure of $\text{N}_2\text{O}_5(\text{g})$ decrease by $2x$ atm when two moles of N_2O_5 decompose to give two moles of $\text{N}_2\text{O}_4(\text{g})$ and one mole of $\text{O}_2(\text{g})$. Therefore pressure of $\text{N}_2\text{O}_4(\text{g})$ increases by $2x$ atm and that of $\text{O}_2(\text{g})$ increases by x atm.

	$2\text{N}_2\text{O}_5(\text{g})$	\rightarrow	$2\text{N}_2\text{O}_4(\text{g})$	+	$\text{O}_2(\text{g})$
At $t = 0$	0.5 atm		0 atm		0 atm
At time t	$(0.5 - 2x)$ atm		$2x$ atm		x atm

$$P_t = P_{\text{N}_2\text{O}_5} + P_{\text{N}_2\text{O}_4} + P_{\text{O}_2} = (0.5 - 2x) + 2x + x = 0.5 + x$$

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

$$\text{At } t = 100 \text{ s; } p_t = 0.512 \text{ atm}$$

$$P_{\text{N}_2\text{O}_5} = 0.5 - 2 \times 0.012 = 0.476 \text{ atm}$$

$$\text{Using equation (11) } k = \frac{2.303}{t} \log \frac{P_i}{P_A} = \frac{2.303}{100\text{s}} \log \frac{0.5\text{atm}}{0.476\text{atm}} = \frac{2.303}{100\text{s}} \times 0.0216 = 4.98 \times 10^{-4} \text{ s}^{-1}$$

Illustration 12: In a second-order reaction, in which both the reactants have same concentration, consider 20% of the reaction is completed in 500 sec. What is the time required for 60% completion? (JEE ADVANCED)

Sol: The equation for second order with both the reactants having same concentration is

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)} \quad \text{If } a = 100, x = 20, t = 500 \text{ sec.}$$

$$\text{So, } k = \frac{1}{500} \times \frac{20}{100 \times (100 - 20)} \quad \text{When } a = 100, x = 60, t = ?$$

$$t = \frac{1}{k} \cdot \frac{60}{100 \times 40}$$

Substituting the value of k ,

$$t = \frac{500 \times 100 \times 80}{20} \times \frac{60}{100 \times 40} \quad \text{or } t = 3000 \text{ sec}$$

7. THE REACTION MECHANISM

7.1 Elementary Reactions

Elementary reaction are single step reactions in which order and molecularity are always the same. In another words, rate law and the law of mass action have the same expression.

7.2 Complex Reactions

These are multi-step reactions in which order and molecularity may or may not be same.

- (a) In these types of reactions, intermediates are formed during the reaction which is different from the reactants and the products formed.
- (b) Each step involved in this reaction is an elementary reaction.

- (c) The overall rate of reaction will be equal to the rate of slowest step. Hence the slowest step is called the rate determining step (RDS) of reaction. A reaction can have more than one RDS.
- (d) The overall molecularity of reaction and the molecularity of the RDS are the same. However, it has no significance.
- (e) The order of reaction and the overall order of reaction may not be the same. It depends on the concentrations involved in the rate law expression of RDS. If it is not overall order, it may be determined by equilibrium approach or by steady state approximation.

For a complex reaction, order is not equal to molecularity.

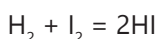
7.3 Reaction Mechanism

The steps involved in a reaction and determining which step is the slowest or rate determining is called mechanism.

A series of steps (known as elementary processes) leading to the formation of products or by which the overall chemical reaction occurs is called the reaction mechanism.

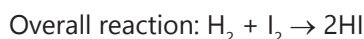
For e.g.

The reaction between H_2 and I_2 to form hydrogen iodide was originally postulated as a simple one-step reaction.



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

But, the formation of HI has been explained on the basis of the following mechanism:

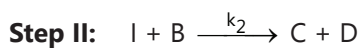
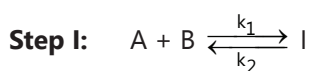


8. DETERMINATION OF RATE LAW FOR A COMPLEX REACTION

8.1 Equilibrium Approach

The concentration of intermediate can be determined from equilibrium constant of the reaction involved.

For example, let the mechanism of reaction $A + 2B \rightarrow C + D$ is



$$\text{Overall rate of reaction, } r = \text{rate of step II} = k_2[I][B] \quad \dots(i)$$

But this cannot be considered as correct because the overall rate of reaction should be in terms of concentrations of A and B (reactants). The concentration of I can be related with the concentrations of A and B with the help of first equilibrium.

$$\text{For step I, equilibrium constant, } K_{eq} = \frac{k_1}{k_{-1}} = \frac{[I]}{[A][B]} \quad \therefore [I] = \frac{k_1}{k_{-1}} [A][B]$$

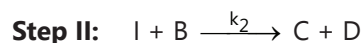
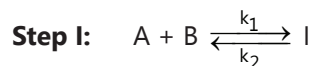
$$\text{Putting this value in equation (i), } r = k_2 \frac{k_1}{k_{-1}} [A][B].[B] = k[A][B]^2, \text{ where, } k = \frac{k_1}{k_{-1}}$$

Hence, the overall rate of reaction is $1 + 2 = 3$

8.2 Steady State Approach

In this method, we assume that the intermediates formed are so reactive that after some time from initiation of reaction (called induction period), the net rate of their formation becomes zero. They react with the same rate of their formation. For example, let the mechanism of reaction

$A + 2B \rightarrow C + D$ is



The rate of reaction may be given as $r = + \frac{d[C]}{dt} = k_2 [I] [B]$... (ii)

Now, from steady state approximation on the intermediate, $I - \frac{d[I]}{dt} = 0$

or $k_1 [A][B] - k_{-1}[I] - k_2[I][B] = 0$ or, $[I] = \frac{k_1[A][B]}{k_{-1} + k_2[B]}$

Substituting this value in equation (ii), $r = k_2 \cdot \frac{k_1[A][B]}{k_{-1} + k_2[B]} \cdot [B] = \frac{k_1 k_2 [A][B]^2}{k_{-1} + k_2[B]}$

PLANCESS CONCEPTS

- When the intermediate is less stable, better results are obtained by steady state approximation, when the intermediate is more stable, better results are obtained by equilibrium approach. More stable intermediate reacts very less and hence, the concentration of intermediate at any time remains nearly equal to its equilibrium concentration.
- When conditions of equilibrium approach are applied on the result obtained from steady state approximation, the same rate law expression is obtained. For the above reaction, step I is faster than step II. As step I is at equilibrium,

$$r_1 = r_{-1} \gg r_2 \text{ or } k_{-1}[I] \gg k_2[I][B] \text{ or } k_{-1} \gg k_2[B]$$

$$\text{therefore, } k_{-1} + k_2[B] \approx k_{-1}$$

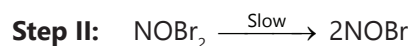
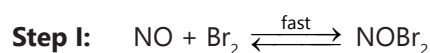
Now, the rate expression obtained from steady state is

$$r = \frac{k_2 k_1 [A][B]^2}{k_{-1} + k_2[B]} \approx [A][B]^2$$

Which is exactly same expression obtained from equilibrium approach.

Aishwarya Karnawat (JEE 2012, AIR 839)

Illustration 13: The reaction $2NO + Br_2 \rightarrow 2NOBr$ obeys the following mechanism:



Suggest the rate expression.

(JEE MAIN)

Sol: The slowest step is the Rate determining step.

Step II is the step that determines the rate of the reaction and hence, $r = k[\text{NOBr}_2][\text{NO}]$... (i)

However, NOBr_2 is an intermediate and thus its concentration is determined step I.

For step I, equilibrium constant $k_{\text{eq}} = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$ $\therefore [\text{NOBr}_2] = k_{\text{eq}}[\text{NO}][\text{Br}_2]$... (ii)

Thus, by equations (i) and (ii), $r = k \cdot k_{\text{eq}}[\text{NO}]^2[\text{Br}_2]$ or, $r = k'[\text{NO}]^2[\text{Br}_2]$

where $k' = k \cdot k_{\text{eq}}$

Illustration 14: The following mechanisms are proposed for the reaction

$\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$ at low temperature:

(a) $2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$ (fast) $\text{N}_2\text{O}_4 + 2\text{CO} \rightarrow 2\text{CO}_2 + 3\text{NO}$ (slow)

(b) $2\text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$ (slow) $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ (fast)

Which of the above mechanism are consistent with the observed rate law: $+\frac{d[\text{CO}_2]}{dt} = k[\text{NO}_2]^2$ (**JEE ADVANCED**)

Sol: For mechanism (a), $r = \text{rate of step II} = k[\text{N}_2\text{O}_4][\text{CO}]^2$... (i)

Now, from step I: $k_{\text{eq}} = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$ or, $[\text{N}_2\text{O}_4] = k_{\text{eq}}[\text{NO}_2]^2$

Hence from (i), $r = k \cdot k_{\text{eq}}[\text{NO}_2]^2[\text{CO}]^2$, but it is not the given rate law

Hence, the mechanism is not consistent with the rate law.

For mechanism (b), $r = \text{rate of step, I} = k[\text{NO}_2]^2$, which is the given rate law.

9. COLLISION THEORY OF REACTION RATE/ARRHENIUS THEORY

Postulates:

- Collision of reactant molecules leads to chemical reaction. The number of collisions taking place per unit time per unit volume of the reaction mixture is known as collision frequency (Z). The value of collision frequency is very high (of the order of 10^{25} to 10^{28}) in case of binary collisions.
- Not every collision brings a chemical change. Only effective collisions bring about a chemical change to form products. The effective collisions are less when compared to the total number of collisions. Collisions that do not form a product are ineffective elastic collisions, i.e. molecules just collide and disperse in different directions with different velocities. For effective collision, the following two barriers are to be cleared.

9.1 Energy Barrier

The minimum energy required by colliding molecules for the chemical reaction to take place is known as threshold energy.

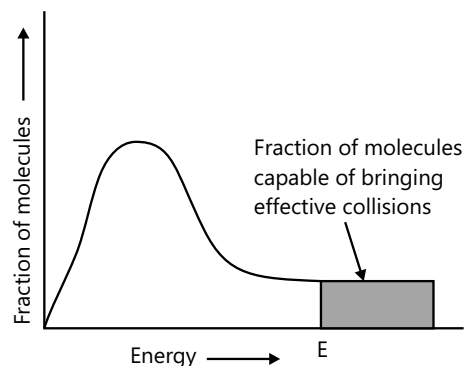


Figure 18.11: Threshold Plot

The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy.

Activation energy = threshold energy – average kinetic energy of reacting molecules.

Threshold energy = initial potential energy of reactant molecules + activation energy.

Collision of high energy molecules that overcomes the forces of repulsion and forms an unstable molecule cluster is called an activated complex. Its life span is very less. Thus, the activated complex breaks to either form reactants again or form new substances, i.e. products. The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reactants and products.

The following graphs show the energy changes during exothermic and endothermic reactions versus the progress of the reaction.

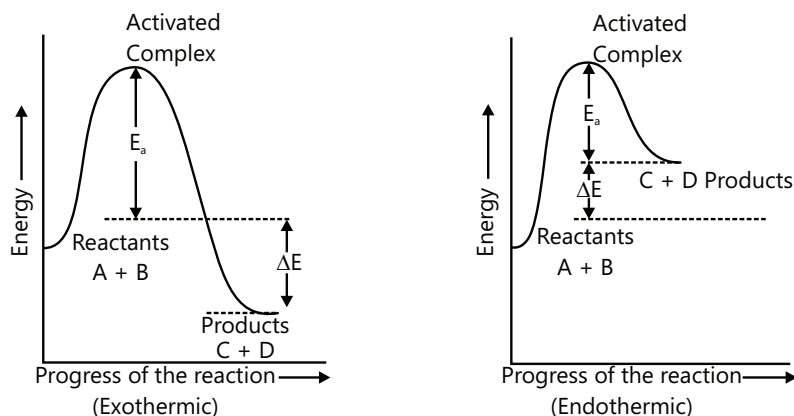


Figure 18.12: Energy profile diagram for exothermic and endothermic reaction

(a) Every reaction, whether exothermic or endothermic, needs to overcome an energy barrier for reactants to get converted to products.

(b) Lower the activation energy, higher will be the fraction of effective collisions leading to faster reaction and vice versa.

(c) Activation energy $E_a = E_{\text{(activated complex)}} - E_{\text{(ground state)}}$

ΔH = activation energy of forward reaction – activation energy of backward reaction.

(i) When $E_{a,f} < E_{a,b}$; $\Delta E = -ve$ and, $\Delta H = -ve$

Thus, when the activation energy for the forward reaction is less than that for the backward reaction, energy is released.

(ii) When $E_{a,f} > E_{a,b}$; $\Delta E = +ve$ and, $\Delta H = +ve$

Thus, when the activation energy for the forward reaction is more than that for the backward reaction, energy is absorbed.

9.2 Orientation Factor

- To form products reactants should have a proper orientation in addition to sufficient energy.
- Rate of reaction is directly proportional to the number of effective collisions.

$$\begin{aligned} \text{Rate} &= -\frac{dx}{dt} = \text{collision frequency} \times \text{fraction of effective collisions} \\ &= Z \times f \end{aligned}$$

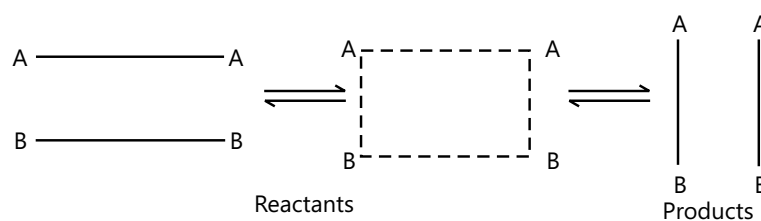


Figure 18.13: Collision theory

9.3 Temperature Dependence of Rate Constant

The temperature dependence of the rate of a chemical reaction can be accurately explained by Arrhenius Equation

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

where, k =Arrhenius factor, E_a =activation energy, R =gas constant, T =temperature

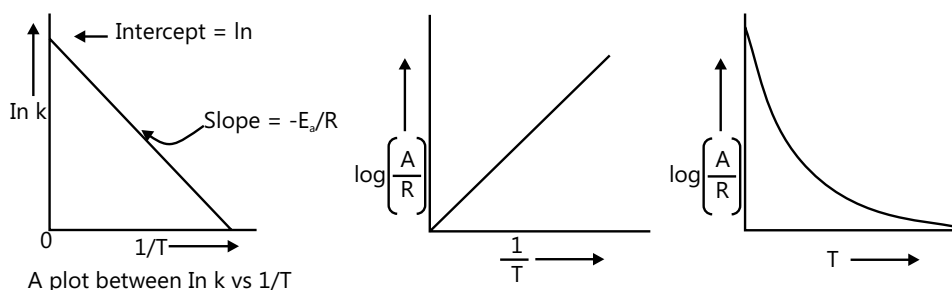
According to the Arrhenius equation, for most reactions, the rate constant increases with increase in temperature. :

The parameters A and E_a for a given reaction are collectively called Arrhenius parameters. Value of E_a is determined from the graph for $\frac{1}{T}$ and $\ln k$ is determined experimentally. Value of A in turn is calculated once E_a is known.

In the Arrhenius equation (i), the factor $e^{-E_a/RT}$ corresponds to the fraction of molecules with kinetic energy greater than E_a .

Taking natural logarithm of both sides of equation (i), we get $\ln k = \ln A - \frac{E_a}{RT}$ (ii)

The plot of $\ln k$ versus $1/T$ gives a straight line according to the equation (ii) as shown in the below figure.

Figure 18.14: Plot of $\ln k$ versus $1/T$

Thus, it has been found from Arrhenius equation (i) that increase in temperature or decrease in activation energy results in an increase in the rate of the reaction and an exponential increase in the rate constant.

In the plot, slope = $-\frac{E_a}{R}$ and intercept = $\ln A$. So we can calculate E_a and A using these values.

At temperature T_1 , equation (ii) becomes $\ln k_1 = -\frac{E_a}{RT_1} + \ln A$ (iii)

At temperature T_2 , equation (ii) becomes $\ln k_2 = -\frac{E_a}{RT_2} + \ln A$ (iv)

(since A is constant for a given reaction)

k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively. Subtracting equation (iii) from (iv), we obtain

$$\ln k_2 - \ln k_1 = \frac{E_a}{RT_1} - \frac{E_a}{RT_2} ; \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] ; \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Maxwell's-Boltzmann Distribution Curve:

The peak of the curve corresponds to the most probable kinetic energy, i.e. kinetic energy of maximum fraction of molecules. Number of molecules decreases with energies higher or lower than this value. When the temperature is raised, the maximum of the molecules moves to the higher energy value (figure) and the curve broadens out, i.e. spreads to the right such that there is a greater proportion of molecules with much higher energies. The area under the curve must be constant since total probability should always be unity at any given time. We can mark the position of E_a on Maxwell Boltzmann distribution curve.

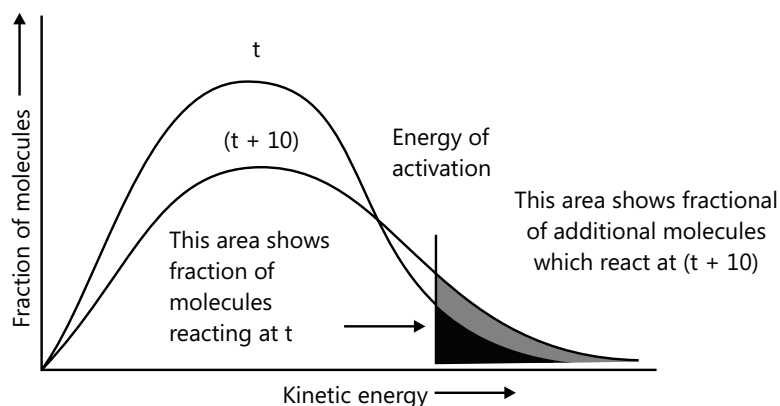


Figure 18.15: Distribution curve showing temperature dependence of rate of a reaction

Increase in the temperature of the substance increases the fraction of molecules, which collide with molecules with energies greater than E_a . It is clear from the diagram that in the curve at $(T + 10)$, the area showing the fraction of molecules having energy equal to or greater than activation energy gets doubled leading to doubling the rate of a reaction.

9.4 Effect of Catalyst

A catalyst is a substance which alters the rate of a reaction without undergoing any permanent chemical change. For example, MnO_2 catalyses the following reaction so as to increase its rate considerably

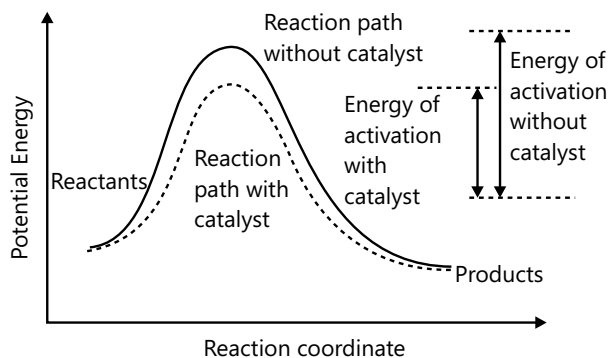
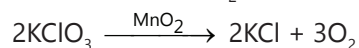


Figure 18.16: Effect of catalyst on activation energy

Catalytic Mechanism: The mechanism of the catalyst can be explained by intermediate complex theory. According to this theory a catalyst reacts with the reactant to form temporary bonds resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier.

According to Arrhenius equation, $k = Ae^{-E_a/RT}$, the lower the value of activation energy, the faster will be the rate of a reaction.

PLANCESS CONCEPTS

For catalysts

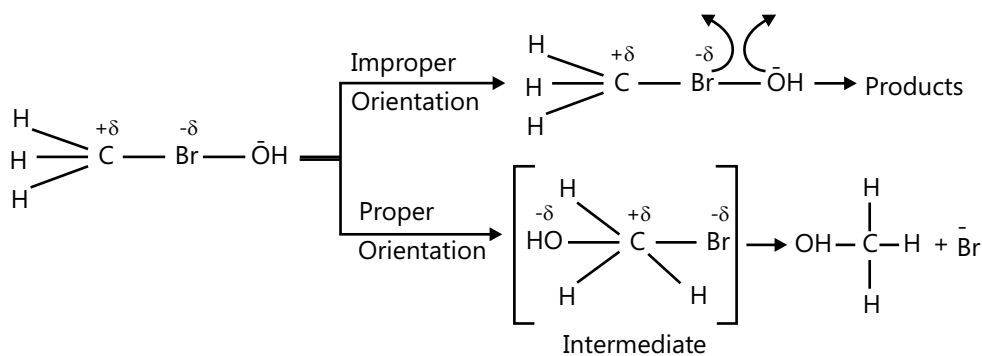
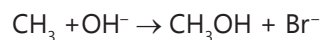
- Even a small amount of the catalyst has the ability to catalyze a large amount of reactants.
- Gibbs energy, ΔG , of a reaction is independent of the catalyst.
- It has an effect on spontaneous reactions but does not catalyse non-spontaneous reactions.
- Catalyst does not change the equilibrium constant of a reaction, rather it helps to attain equilibrium faster, i.e. it catalyses the forward as well as the backward reaction to the same extent so that the equilibrium state remains same and is reached earlier.

For collision theory

- Activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.
- It considers atoms/molecules to be hard spheres and ignores their structural aspect.
- Comparing the equation (vi) with Arrhenius equation, we can say that A is related to collision frequency.

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Note: In the following reaction formation of methanol from bromo-ethane depends upon the orientation of reactant molecules. Only proper orientation of reactant molecules lead to bond formation, else it simply bounce back and no products are formed.



Steric Factor: For effective collisions, the probability or steric factor (P) is introduced. It helps the molecules for a proper oriented i.e., $\text{Rate} = PZ_{AB} e^{-E_a/RT}$

Illustration 15: What will be the effect of temperature on rate constant?

(JEE MAIN)

Sol: Rate constant of a reaction is nearly doubled with rise in temperature by 10°C . The dependence of the rate constant on temperature is given by Arrhenius equation, $k = Ae^{-E_a/RT}$, where A is called frequency factor and E_a is the activation energy of the reaction.

Illustration 16: How is the value of activation energy calculated from the rate constants at two different temperatures. If the value of activation energy is 50 kJ/mol then show that by increasing the temperature from 300 K to 310 K , rate constant becomes nearly double.

(JEE MAIN)

Sol: We know that Arrhenius equation can be written as $\log k = \log A - \frac{E_a}{2.303R} \frac{1}{T}$

If k_1 and k_2 are the rate constants at two different temperature T_1 and T_2 then Arrhenius equation at both the temperatures can be written as

$$\log k_1 = \log A - \frac{E_a}{2.303R} \frac{1}{T_1}; \log k_2 = \log A - \frac{E_a}{2.303R} \frac{1}{T_2}$$

Subtracting equation (i) from (ii), we get $\log k_2 - \log k_1 = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$ or $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

From the values of k_1 and k_2 at temperature T_1 and T_2 , E_a can be calculated.

Given $T_1 = 300\text{K}$, $T_2 = 310\text{K}$, $E_a = 50\text{ kJ or } 50,000\text{ J}$

Put these values in eq. (iii), $\log \frac{k_2}{k_1} = \frac{50000}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{310} \right] = \frac{50000}{2.303 \times 8.314} \left[\frac{310 - 300}{310 \times 300} \right]$

or $\log \frac{k_2}{k_1} = 0.2808 = \text{Antilog } 0.2808 = 1.91 \approx 2$

It is clear that by increasing the temperature from 300 K to 310 K doubles the rate constant.

Illustration 17: Even an exothermic reaction has activation energy. Why?

(JEE ADVANCED)

Sol: A reaction can either be endothermic or exothermic, but it possesses a minimum energy level for the molecules to cross the energy barrier for the reaction to take place. Also

Threshold energy = $\Sigma E_R + E_a$ and $\Delta H = \Sigma E_P - \Sigma E_R$ (ΔH may be +ve or -ve)

For example, burning of carbon is highly exothermic process, yet it does not start of its own. The activation energy of combustion of carbon is quite high and thus, in spite of exothermic nature, the reaction starts only when flame is applied to the heap of carbon contents.

Illustration 18: A first-order reaction is 50% complete in 30 min at 27°C and in 10 min at 47°C. Calculate the rate constants, and the energy of activation of the reaction in kJ/mol.

(JEE ADVANCED)

Sol: Time for the completion of 50% reaction means $t_{1/2}$.

It means $t_{1/2}$ of the reaction at 27°C is 30 min and at 47°C is 10 min.

We know that $k = \frac{0.693}{t_{1/2}}$ or $k = \frac{0.693}{30} = 0.0231\text{ min}^{-1}$ (at 27°C) and $k = \frac{0.693}{10} = 0.0693\text{ min}^{-1}$ (at 47°C)

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

$k_2 = 0.0693\text{ min}^{-1}$, $k_1 = 0.0231\text{ min}^{-1}$, $T_1 = 27 + 273 = 300\text{ K}$, $T_2 = 47 + 273 = 320\text{ K}$,

$R = 8.314\text{ JK}^{-1}\text{ mol}^{-1}$, $E_a = ?$

$$\log \frac{0.0693}{0.0231} = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{320} \right]$$

or $\log 3 = \frac{E_a}{2.303 \times 8.314} \left[\frac{320 - 300}{300 \times 320} \right]$

$$0.4771 = \frac{E_a}{2.303 \times 8.314} \left[\frac{20}{300 \times 320} \right]$$

or $E_a = \left[\frac{0.4771 \times 2.303 \times 8.314 \times 300 \times 320}{20} \right] = 43848.49\text{ J mol}^{-1} = 43.85\text{ kJ mol}^{-1}$

10. METHODS OF DETERMINATION OF ORDER OF REACTION

10.1 Method of Integration (Hit and Trial Method)

The most simple method is the one in which the quantities a , x and t are determined and substituted in the kinetic equations of various orders. The equation which gives the most constant value for the specific rate constant (k) for a series of time intervals is the one corresponding to the order of reaction. If all the reactants are at the same molar concentrations, the kinetic equations are:

$$k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}, \text{ for first-order reactions;}$$

$$k = \frac{1}{t} \left[\frac{1}{(a-x)} - \frac{1}{a} \right], \text{ for second-order reactions;}$$

$$k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right], \text{ for third-order reactions;}$$

10.2 Graphical Method

A graphical method based on the respective rate laws can also be used to determine the order of reaction.

If the plot of $\log(a-x)$ versus ' t ' is a straight line, the reaction follows first order.

If the plot of $\frac{1}{(a-x)}$ versus ' t ' is a straight line, the reaction follows second order.

If the plot of $\frac{1}{(a-x)^2}$ versus ' t ' is a straight line, the reaction follows third order.

In general, for a reaction of n th order, a graph of $\frac{1}{(a-x)^{n-1}}$ versus ' t ' must be a straight line.

10.3 Half-Life Method

A general expression for the half-life, ($t_{1/2}$), is given by $t_{1/2} \propto \frac{1}{a^{n-1}}$

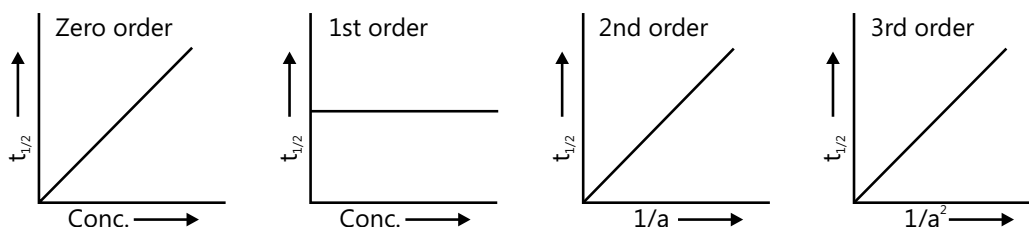


Figure 18.17: Plots of half-lives versus concentration ($t_{1/2} \propto a^{1-n}$)

This relation can be used to determine order of reaction ' n '.

10.4 Van't Hoff Differential Method

Relationship between velocity V of n^{th} order reaction and concentration of reactants C is given by

$$\text{Van't Hoff, } n = \frac{\log(V_1 / V_2)}{\log(C_1 / C_2)}$$

Where, C_1 and C_2 are two different concentrations, while V_1 and V_2 are their velocities.

10.5 Ostwald Isolation Method

This method is used to find out the order of complex reactions. If n_A , n_B and n_C molecules of substance A, B and C, respectively are present in a reaction, then $n_A + n_B + n_C$ will be the order of reaction:

When B and C are in excess, the order of reaction will be n_A .

When A and B are in excess, the order of reaction will be n_C .

When A and C are in excess, the order of reaction will be n_B .

PROBLEM-SOLVING TACTICS

- (a) To determine the average rate for change in concentration over a time period.

Average rate of reaction is the change in concentration of reactants (or products) during large interval of time.

$$\text{Rate} = -\frac{[\text{reactant at } t_2] - [\text{reactant at } t_1]}{t_2 - t_1}$$

Square brackets denote concentration.

Negative sign in the above equation is used to make the rate of reaction positive. Minus sign can be ignored when calculating average rates from products.

$$\text{Rate} = -\frac{\Delta[\text{reactant}]}{\Delta t} \quad \text{or} \quad \text{rate} = \frac{\Delta[\text{product}]}{\Delta t}$$

- (b) To determine instantaneous rate from a plot of concentration versus time: Instantaneous rate at time t is determined as follows:

(i) Calculate the negative slope of the curve between concentration of a reactant and time at t .

(ii) Calculate the slope of the curve between concentration of a product and time at t .

- (c) Problem-solving tactics to determine the initial rate from a plot of concentration versus time: The initial rate of a reaction is the instantaneous rate at the start of the reaction (i.e., when $t = 0$).

Initial rate is equal to the negative slope of the curve between reactant concentration and time at $t = 0$.

- (d) To determining the order of a reaction from its rate law

Rate law of a reaction is used to determine:

- The order of the reaction with respect to one or more reactants.
- The overall order of the reaction.

$$\text{rate} = k[A]^n[B]^m[C]^p$$

For the rate law: Order with respect to A = n ; order with respect to B = m , order with respect to C = p

Reaction or overall order = $n + m + p$

Note: The stoichiometric coefficient in the balanced equation for a chemical reaction is usually different from the order.

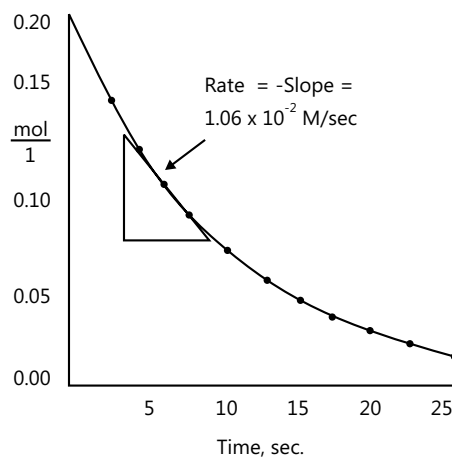


Figure 18.18: Plot of concentration versus time

Reaction	Experimental Rate Law	Order
$\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$	$\text{rate} = k[\text{NO}_2]^2$	2nd order reaction 2nd order in NO_2 0 order in CO
$\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$	$\text{rate} = k[\text{CH}_3\text{CHO}]^2$	2nd order reaction 2nd order in CH_3CHO

(e) To determining rate laws from graphs of concentration versus time (integrated rate laws).

To determine the rate law for a reaction for different concentration (or the values of some function of concentration) versus time, make three graphs.

[A] versus t (linear for a zero-order reaction)

$\ln [A]$ versus t (linear for a 1st order reaction)

$1 / [A]$ versus t (linear for a 2nd order reaction)

The graph that is linear indicates the order of the reaction with respect to A. Then, you can choose the correct rate equation:

For a zero-order reaction,	Rate = k	(k = -ve slope of line)
For a first order reaction,	rate = k[A]	(k = -ve slope of line)
For a second order reaction,	rate = k[A] ²	(k = slope of line)

(f) Regarding questions of half lives:

For a zero-order reaction $A \rightarrow \text{products}$, rate = k, $t_{1/2} = [A_0] / 2k$

For a first-order reaction $A \rightarrow \text{products}$, rate = k[A], $t_{1/2} = 0.693 / k$

For a second-order reaction $2A \rightarrow \text{products}$ or $A + B \rightarrow \text{products}$ (when $[A] = [B]$), rate = k[A]², $t_{1/2} = 1 / k [A_0]$

Graphical Relations and half-lives: Differences in half-lives for reactions of different orders (0, 1st, or 2nd) are determined by plotting graphs between reactant [A] and time (t). Change in time changes the concentration of a reactant to half.

(i) For a zero-order reaction, half-life decreases with decreasing concentration.

(ii) For a 1st order reaction, half-life is constant.

(iii) For a second-order reaction, half-life increases with decreasing concentration.

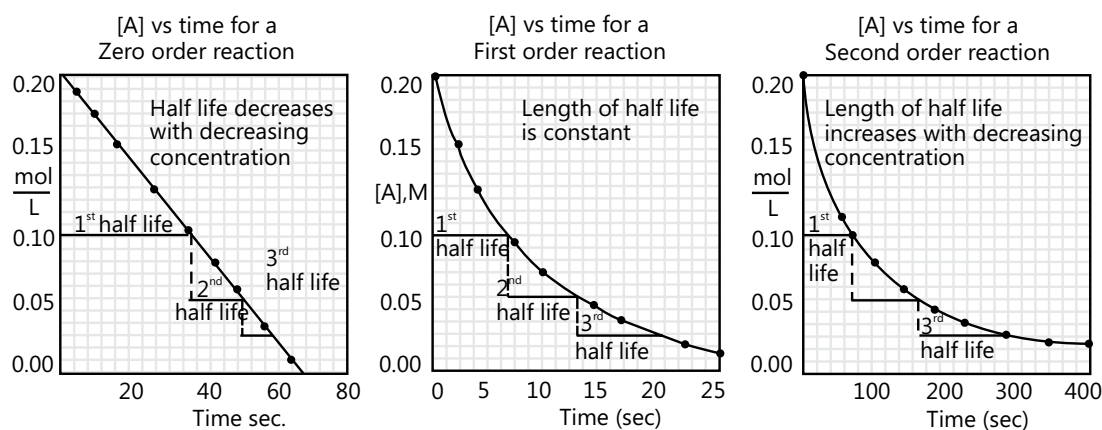


Figure 18.19: Plot of concentration versus change in time

For a first-order reaction:

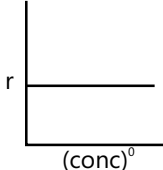
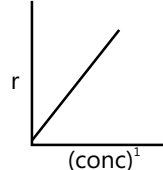
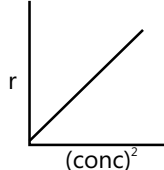
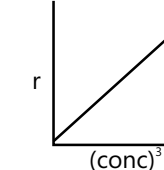
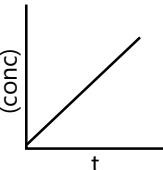
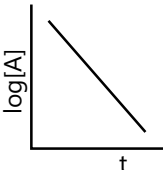
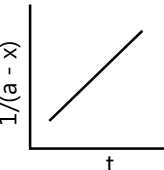
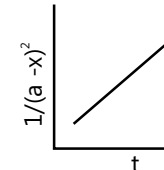
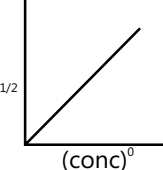
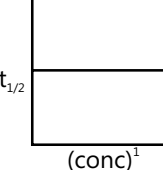
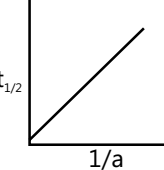
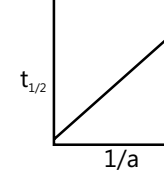
$A \rightarrow \text{products}$, rate = k A $\rightarrow \text{products}$, rate = k[A]

For a second-order reaction:

$2A \rightarrow \text{products}$ / $A + B \rightarrow \text{products}$
(when $[A] = [B]$, rate = k[A]²)

POINTS TO REMEMBER

Topic	Formula				
Average rate of reaction	$\text{Average rate} = \frac{\text{Change in the concentration of reactants or(Products)}}{\text{Time}} = \pm \frac{\Delta C}{\Delta t} = \pm \frac{C_2 - C_1}{t_2 - t_1}$				
Instantaneous rate of reaction	$\text{Instantaneous rate} = \lim_{\Delta t \rightarrow 0} \frac{\Delta C}{\Delta t} = \frac{dC}{dt}$ <p>For the reaction $n_1A + n_2B \rightarrow m_1C + m_2D$</p> $\text{Instantaneous Rate of reaction} = -\frac{1}{n_1} \frac{d[A]}{dT} = -\frac{1}{n_2} \frac{d[B]}{dT} = +\frac{1}{m_1} \frac{d[C]}{dT} = +\frac{1}{m_2} \frac{d[D]}{dT}$				
Factors affecting rate of reaction	<ul style="list-style-type: none"> • Nature of reactants and products • Effect of temperature • Concentration of Reactants • Presence of catalyst • Effect of Sunlight 				
Law of mass action and rate constant	<p>The rate at which a substance is directly proportional to its active mass and the rate at which a reaction proceeds is proportional to the product of the active masses of the reacting substances</p> <p>For a reaction, $aA + bB \rightarrow \text{product}$ rate $= \left(\frac{dx}{dt}\right) \propto [A]^a[B]^b$; $\left(\frac{dx}{dt}\right) = k[A]^a[B]^b$</p> <p>where k is rate constant or velocity constant.</p> <p>When $[A] = [B] = 1 \text{ mol/L}$, then $\frac{dx}{dt} = k$</p>				
Unit of rate constant	$\text{Unit of rate constant} = \left[\frac{\text{litre}}{\text{mol}}\right]^{n-1} \times \text{sec}^{-1}$ <p>When n = order of reaction.</p>				
Various types of reactions	Type of reaction	Integrated rate equation	Unit of rate constant	$t_{1/2}$ Half-life period	$t_{3/4}$ period
	Zero-order reaction	$-\frac{d[A]}{dt} = k_0[A]^0$ $\text{Differential form } \frac{dx}{dt} = k$	Concentration time^{-1}	$\frac{A_0}{2k}$	

	First-order reaction	$k_1 = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$ Differential form $\frac{dx}{dt}$ $= k(a-x)$	Time ⁻¹	$\frac{0.693}{K_1}$	$2 \times \frac{0.693}{K_1} = \frac{1.382}{k_1}$
	Second-order reaction	$k_2 = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$ Differential form $\frac{dx}{dt}$ $= k(a-x)^2$	Mole ⁻¹ litre time ⁻¹	$\frac{1}{K_2 a}$	$\frac{3}{K_2 a}$
	Third-order reaction	$k_3 = \frac{1(2a-x)}{t2a^2(a-x)^2}$ Differential form $\frac{dx}{dt}$ $= k(a-x)^3$	Litre ² mole ⁻² time ⁻¹	$\frac{1}{2} \frac{3}{K_2 a}$	—
Relationship between Rate of reaction and rate constant	<div>Zero Order</div> 	<div>First Order</div> 	<div>Second Order</div> 	<div>Third Order</div> 	
					
					
Half-Life	$t_{1/2} \propto \frac{1}{a^{n-1}}$ where n = order of reaction				
Arrhenius theory	$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$ $k = Ae^{-E_a/RT}$ where k_1 and k_2 are rate constant at temperatures T_1 and T_2 , respectively ($T_2 > T_1$).				

Solved Examples

JEE Main/Boards

Example 1: The half-life period of a first-order reaction is 30 min. Calculate the specific reaction rate of the reaction. What fraction of the reactant remains after 70 min?

$$\text{Sol: } k_1 = \frac{0.6932}{t_{\frac{1}{2}}} = \frac{0.6932}{30} = 0.0231 \text{ min}^{-1}.$$

Let the reaction be $A \rightarrow \text{Product}$

Initial concentration a

Concentration after $(a - x)$ x

70 min

\therefore Fraction of the reaction remained unreacted

$$= \frac{(a - x)}{a} \quad \text{Now, } k_1 = \frac{2.303}{t} \log \frac{a}{a - x} \text{ or } 0.0231$$

$$= \frac{2.303}{70} \log \frac{a}{a - x}$$

$$\log \frac{a}{a - x} = \frac{0.0231 \times 70}{2.303} = 0.7021$$

$$\text{Taking antilog, we get } \frac{a}{a - x} = 5.036$$

$$\therefore \frac{a - x}{a} = \frac{1}{5.036} \approx 0.2$$

Example 2: For the reaction $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$, when the concentration of both reactants is doubled the rate increased by a factor of 8, but when only the concentration of Cl_2 concentration is doubled, the rate doubles. What is the order of the reaction with respect to NO and Cl_2 ?

$$\text{Sol: Rate} = k [\text{NO}]^m [\text{Cl}_2]^n$$

Let the concentrations of NO and Cl_2 be x and y , respectively.

$$R_1 = kx^m y^n \text{ and } R_2 = k(2x)^m (2y)^n$$

$$\therefore \frac{R_2}{R_1} = 2^{m+n} = 8 = 2^3. \text{ (given)}$$

$$\therefore m + n = 3 \text{ Again, } R_3 = k(x)^m (2y)^n$$

$$= kx^m y^n \cdot 2^n. \therefore \frac{R_3}{R_1} = 2^n = 2 \quad \text{(given)}$$

$$\therefore n = 1; m = 3 - 1 = 2.$$

Example 3: In a reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, the rate can be expressed as

$$(i) -\frac{d[\text{N}_2\text{O}_5]}{dt} = k_1[\text{N}_2\text{O}_5]$$

$$(ii) \frac{d[\text{NO}_2]}{dt} = k_2[\text{N}_2\text{O}_5]$$

$$(iii) \frac{d[\text{O}_2]}{dt} = k_3[\text{N}_2\text{O}_5]$$

How are k_1 , k_2 and k_3 related?

Sol: The rate law reaction is rate =

$$-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt} = k[\text{N}_2\text{O}_5]$$

$$\therefore -\frac{d[\text{N}_2\text{O}_5]}{dt} = 2k[\text{N}_2\text{O}_5] = k_1[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{NO}_2]}{dt} = 4k[\text{N}_2\text{O}_5] = k_2[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{O}_2]}{dt} = k[\text{N}_2\text{O}_5] = k_3[\text{N}_2\text{O}_5]$$

$$\therefore \begin{cases} k_1 = 2k \\ k_2 = 4k \\ k_3 = k \end{cases} \text{ or } k = \frac{k_1}{2} = \frac{k_2}{4} = k_3$$

$$\text{or } 2k_1 = k_2 = 4k_3.$$

Example 4: The reaction $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ forms NO_2 at the rate of $0.0072 \text{ mol L}^{-1}\text{s}^{-1}$ after a certain time.

(a) What is the rate of change of $[\text{O}_2]$ at this time?

(b) What is the rate of change of $[\text{N}_2\text{O}_5]$ at this time?

(c) What is the rate of reaction at this time?

Sol: The rate of the reaction is expressed as

$$\text{rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = +\frac{1}{4} \frac{d[\text{NO}_2]}{dt} = +\frac{d[\text{O}_2]}{dt}$$

and given that

$$\frac{d[\text{NO}_2]}{dt} = 0.0072 \text{ mol L}^{-1}\text{s}^{-1}.$$

(a) Rate of appearance of

$$\text{O}_2 = \frac{1}{4} \times \text{rate of appearance of NO}_2$$

$$\frac{d[\text{O}_2]}{dt} = \frac{1}{4} \times \frac{d[\text{NO}_2]}{dt} = \frac{1}{4} \times 0.0072 = 0.0018 \text{ mole/L/s.}$$

(b) Rate of disappearance of $\text{N}_2\text{O}_5 = \frac{1}{2} \times$ rate of appearance of NO_2

$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \times \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \times 0.0072$$

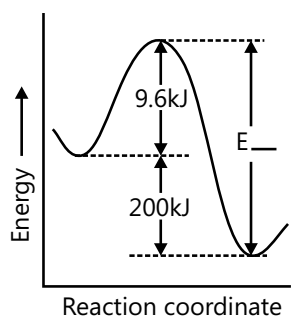
$$= -0.0036 \text{ mole/L/s.}$$

$$\text{(c) Rate of reaction} = \frac{1}{4} \times \frac{d[\text{NO}_2]}{dt}$$

$$= \frac{1}{4} \times 0.0072 = 0.0018 \text{ (mole/L)s}^{-1}.$$

Example 5: The activation energy for the reaction $\text{O}_3(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is 9.6 kJ/mol. Prepare an activation energy plot if ΔH° for this reaction is -200 kJ/mole. What is the energy of activation for the reverse reaction?

Sol: Energy of activation for reverse reaction
 $= 9.6 + 200 \text{ kJ} = 209.6 \text{ kJ.}$

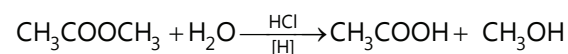


Example 6: 1 mL of methyl acetate was added to 20 mL of 0.5 N HCl and 2 mL of the mixture was withdrawn from time t_c during the progress of hydrolysis of the ester and titrated with a solution of alkali. The amount of alkali needed for titration at various intervals is given below:

Time:	0	20	119	∞	(min)
Alkali used:	19.24	20.73	26.6	42.03	(mL)

Establish that the reaction is of first order.

Sol:



Ini. Conc. a

Conc. after t (a-x) x

HCl acts as a catalyst. The alkali used against HCl is subtracted from the total alkali used (given in the data) to get the volume of alkali used only against CH_3COOH .

At zero time, no CH_3COOH is formed. Hence, alkali used at zero time is only for HCl. Thus we have

Time(min):	0	20	119	∞
Vol. of alkali (mL) used against CH_3COOH	19.24	20.73	26.6	42.03
	-19.24	-19.24	-19.24	-19.24
	= 0	= 1.49	= 7.36	= 22.79
		(x)	(x)	(a)

For $t = 20$;

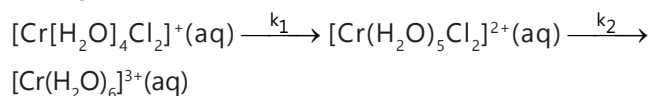
$$k_1 = \frac{2.303}{20} \log \frac{22.79}{22.79 - 1.49} = 0.0033 \text{ min}^{-1}$$

For $t = 119$;

$$k_1 = \frac{2.303}{119} \log \frac{22.79}{22.79 - 7.36} = 0.0032 \text{ min}^{-1}$$

The constancy of k_1 shows that the reaction is of first order.

Example 7: For the reaction

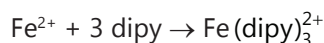


$k_1 = 1.76 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 5.8 \times 10^{-5} \text{ s}^{-1}$ for the initial concentration of $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}_2]^+$ is 0.0174 mol/L at 0°C . Calculate the value of t at which the concentration of $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}_2]^{2+}$ is maximum.

$$\text{Sol: We have, } t = \frac{2.303(\log k_1 - \log k_2)}{k_1 - k_2}$$

$$= \frac{2.303(\log 1.76 \times 10^{-3} - \log 5.8 \times 10^{-5})}{1.76 \times 10^{-3} - 5.8 \times 10^{-5}} = 2005 \text{ seconds.}$$

Example 8: The complexation of Fe^{2+} with the chelating agent dipyridyl has been studied kinetically in both forward and reverse directions.



Rate (forward) = $(1.45 \times 10^{13}) [\text{Fe}^{2+}][\text{dipy}]^3$ and rate (reverse) = $(1.22 \times 10^{-4} [\text{Fe}(\text{dipy})_3^{2+}])$.

Find the stability constant for the complex.

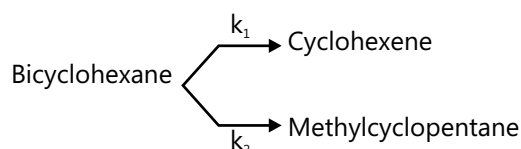
Sol: At dynamic equilibrium, Rate of formation of complex = Rate of its decomposition

$$(1.45 \times 10^{13}) [\text{Fe}^{2+}][\text{dipy}]^3 = (1.22 \times 10^{-4} [\text{Fe}(\text{dipy})_3^{2+}])$$

$$k_a = \frac{[\text{Fe(dipy)}_3^{2+}]}{[\text{Fe}^{2+}][\text{dipy}]^3} = \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.19 \times 10^{17}.$$

Example 9: Bicyclohexane was found to undergo two parallel first order rearrangements. At 730 K, the first order rate constant for the formation of cyclohexene was measured as $1.26 \times 10^{-4} \text{ sec}^{-1}$, and for the formation of methyl cyclopentane the rate constant was $3.8 \times 10^{-5} \text{ sec}^{-1}$. What is the percentage distribution of the rearrangement products?

Sol:



$$\begin{aligned} \text{Percentage of cyclohexene} &= \frac{k_1}{k_1 + k_2} \times 100 \\ &= \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-5}} \times 100 = 77\% \end{aligned}$$

\therefore Percentage of methyl cyclopentane = 23%.

Example 10: A first-order reaction has a specific reaction rate of 10^{-2} sec^{-1} . How much time will it take for 10 g of its reactant to be reduced to 2.5 g?

Sol: Rate constant, $k = 10^{-2} \text{ sec}^{-1}$

Initial reactant conc. $[A]_0 = 10 \text{ g}$

Final reactant conc. $[A]_t = 2.5 \text{ g}$

Time required, $t = ?$

For a first-order reaction.

$$t = 2.303 \times 10^2 \log 4s = 230.3 \times 0.6020s = 138.6s.$$

JEE Advanced/Boards

Example 1: The rate constant of a reaction is given by: $\ln K(\text{sec}^{-1}) = 14.34 - (1.25 \times 10^4)/T$. Calculate (a) the energy of activation and (b) the rate constant at 500 K. (c) At what temperature will its half-life period be 256 min?

Sol: Given:

$$\ln K = 14.34 - [(1.25 \times 10^4)/T] \quad \dots(i)$$

$$\text{Arrhenius equation, } \ln K = \ln A - (E_a/RT) \dots(ii)$$

(a) Comparing equations (i) and (ii),

$$(E_a/R) = 1.25 \times 10^4 \therefore E_a = 1.25 \times 10^4 R$$

$$= 1.25 \times 10^4 \times 1.987 \times 10^{-3} \text{ kcal mol}^{-1} = 24.84 \text{ kcal mol}^{-1}$$

$$(b) \ln K = 14.34 - [(1.25 \times 10^4)/500]$$

$$(\because T = 500 \text{ K})$$

$$\therefore K = 2.35 \times 10^{-5} \text{ sec}^{-1}$$

$$(c) K = \frac{0.693}{256 \times 60} \quad (\text{for first order})$$

$$\therefore \log \frac{0.693}{256 \times 60} = 14.34 - \frac{1.25 \times 10^4}{T}$$

$$\therefore T = 513 \text{ K}$$

Example 2: The specific reaction rate of a first-order reaction is 0.02 sec^{-1} . The initial concentration of the reactant is 2 mol L^{-1} . Calculate (a) initial rate, and (b) rate after 60 sec.

Sol: For a first-order reaction:

Rate of a reaction = $k \times$ molar concentration of the reactant.

$$(a) \therefore \text{Initial rate} = k \times \text{initial concentration}$$

$$= 0.02 \times 2 = 0.04 \text{ mol/L}^{-1} \text{sec}^{-1}.$$

$$(b) \text{Concentration of the reactant after 60 sec } k = \frac{2.303}{60} \log \frac{2}{\text{concentration after 60 s}} = 0.02.$$

$$\therefore \text{Concentration of the reactant after 60 sec} = 0.60 \text{ M.}$$

$$\therefore \text{Rate after 60 sec} = k \times \text{concentration of the reactant after 60 sec.}$$

$$= 0.02 \times 0.60 = 0.012 \text{ mol L}^{-1} \text{sec}^{-1}$$

Example 3: The rate constant is numerically the same for first, second and third order reaction, the unit of concentration being in moles per litre. Which reaction should be the fastest and is this true for all ranges of concentrations?

Sol: Suppose R_1 , R_2 and R_3 are the rates of reactions of first, second and third order, respectively, and k is the rate constant, which is the same for the three reactions,

$$\therefore R_1 = k[A]^1; R_2 = k[A]^2; R_3 = k[A]^3$$

$[A]$ being the concentration of the reactant A in moles per litre.

$$\text{Now if, } [A] = 1, R_1 = R_2 = R_3;$$

$$[A] < 1, R_1 > R_2 > R_3; \text{ and}$$

$$[A] > 1, R_1 < R_2 < R_3.$$

Example 4: For a reaction at 800°C

$2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, the following data were obtained:

$[\text{NO}] \times 10^{-4} \text{ mole/L}$	$[\text{H}_2] \times 10^{-3} \text{ mole/L}$	$d[\text{NO}]/dt \times 10^{-4} \text{ mole/L min}$
(i) 1.5	7.0	4.4
(ii) 1.5	3.5	2.2
(iii) 1.5	2.0	0.24

What is the order of this reaction with respect to NO and H_2 ?

Sol: From the data (i) and (ii), we see that when the concentration of H_2 is halved, the rate is also halved at constant concentration of NO. Hence the reaction is of first order with respect to H_2 . Let us now consider the data (ii) and (iii) to determine the order with respect to NO as $[\text{H}_2]$ is constant.

The rate law of the above reaction is

$$\text{rate} = -\frac{1}{2} \times \frac{d[\text{NO}]}{dt} = k[\text{NO}]^m[\text{H}_2]^1$$

where, m is the order with respect to NO

$$\text{Or } -\frac{d[\text{NO}]}{dt} = 2k[\text{NO}]^m[\text{H}_2]$$

Substituting data (ii) and (iii), we get

$$2.2 \times 10^{-4} = 2k(1.5 \times 10^{-4})^m (2 \times 10^{-3}) \quad \dots(i)$$

$$0.24 \times 10^{-4} = 2k(0.5 \times 10^{-4})^m (2 \times 10^{-3}) \quad \dots(ii)$$

Dividing (i) by (ii),

$$\frac{2.2}{0.24} = \frac{(1.5 \times 10^{-4})^m}{(0.5 \times 10^{-4})^m} = 3^m \text{ or } \frac{220}{24} = 3^m$$

$$\text{Taking log, } \log 220 - \log 24 = m \log 3$$

$$2.4324 - 1.3802 = m \times 0.4771$$

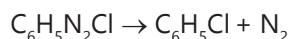
$$\text{Or } 0.9622 = 0.4771 m \text{ or } m = \frac{0.9622}{0.4771} = 2.$$

Hence the reaction is of second and first order with respect to NO and H_2 , respectively.

Example 5: From the following data for the decomposition of diazobenzene chloride, show that the reaction is of first order

Time	20	50	70	∞	(min)
Vol. of N_2	10	25	33	162	(mL)

Sol:



Initial concentration a

After time t $(a-x)$ x

At ∞ time, i.e. when the reaction is complete, the whole of $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ converts into N_2 . Hence volume of N_2 at ∞ time corresponds to the initial concentration 'a' while volumes of N_2 at different time intervals correspond to x as shown above. substituting the given data in equation of first-order reaction, we get the following results.

For $t = 20 \text{ min}$

$$k_1 = \frac{2.303}{20} \log \frac{162}{162-10} = 0.0032 \text{ min}^{-1}$$

For $t = 50 \text{ min}$,

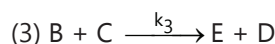
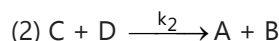
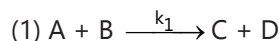
$$k_1 = \frac{2.303}{50} \log \frac{162}{162-25} = 0.0033 \text{ min}^{-1}$$

For $t = 70 \text{ min}$,

$$k_1 = \frac{2.303}{70} \log \frac{162}{162-33} = 0.0032 \text{ min}^{-1}$$

The consistency of k_1 shows that the decomposition of $\text{C}_6\text{H}_5\text{N}_2\text{Cl}$ is a first-order reaction.

Example 6: From the following reaction scheme, write the rate law for the disappearance of A, B and C.



Sol.: The reaction A is removed in step 1 and produced in step 2

$$\therefore -\frac{d[\text{A}]}{dt} = k_1[\text{A}][\text{B}] - k_2[\text{C}][\text{D}] \text{ Similarly}$$

$$-\frac{d[\text{B}]}{dt} = k_1[\text{A}][\text{B}] + k_3[\text{B}][\text{C}] - k_2[\text{C}][\text{D}] \text{ and}$$

$$-\frac{d[\text{C}]}{dt} = k_2[\text{C}][\text{D}] + k_3[\text{B}][\text{C}] - k_1[\text{A}][\text{B}].$$

Example 7: At a certain temperature, the half change period for the catalytic decomposition of ammonia were found as follows:

Pressure (Pascals): 6667 13333 26666

Half life period in hours: 3.52 1.92 1.0

Calculate the order of reaction.

$$\text{Sol: } \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1} \right)^{n-1}$$

where, n is order of reaction

$$\text{From the given data, } \frac{3.52}{1.92} = \left(\frac{13333}{6667} \right)^{n-1}$$

$$(a \propto \text{initial pressure}) = (2)^{n-1}$$

$$\log \frac{3.52}{1.92} = (n-1) \log 2 = 0.3010 \times (n-1)$$

$$0.2632 = 0.3010 \times (n-1); n = 1.87 \approx 2$$

Similar calculations are made between first and third observations, n comes equal to 1.908 (≈ 2).

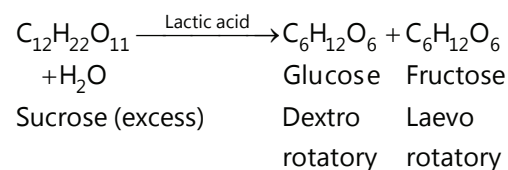
Thus, the reaction is of second order.

Example 8: The optical rotation of can sugar in 0.5 N acid at 25°C at various time intervals are given below:

Time (min):	0	1435	11360	∞
Rotation(°):	34.50°	31.10°	13.98°	-10.77°

Show that the reaction is of first order.

Sol:



Since in this reaction dextro form changes to laevo form, the optical rotation decreases with the progress of the reaction. Thus change in rotation is proportional to the amount of sugar remained after different time intervals. We now have,

Time (min)	0	1435	11360	∞
Change in rotation(°)	34.50 – (-10.77) = 45.27 (a)	31.10 – (-10.77) = 41.87 (a - x)	13.98 – (-10.77) = 24.75 (a - x)	-10.77 – (-10.77) = 0

Substituting the data in equation,

for $t = 1435$ min

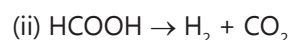
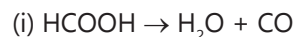
$$k_1 = \frac{2.303}{1435} \log \frac{45.27}{41.87} = 5.442 \times 10^{-5}$$

and for $t = 1136$ min

$$k_1 = \frac{2.303}{1435} \log \frac{45.27}{41.87} = 5.311 \times 10^{-5}$$

The values of k are fairly constant and so the reaction is of first order.

Example 9: The catalytic decomposition of formic acid may take place in two ways:



The rate constant and activation energy for reaction (i) are $2.79 \times 10^{-3} \text{ min}^{-1}$ at 237°C and $12.0 \text{ kcal mol}^{-1}$ respectively. These values for reaction (ii) are $1.52 \times 10^{-4} \text{ min}^{-1}$ at 237°C and $24.5 \text{ kcal mol}^{-1}$ respectively. Find out the temperature at which equimolar quantities of H_2O , CO , CO_2 and H_2 are formed ($R = 2 \text{ cal}$).

Sol: For reaction (a) $K_1 = A_1 e^{-E_a/RT}$

$$\text{or } 2.79 \times 10^{-3} = A_1 e^{-\frac{12 \times 10^3}{RT}} \quad \dots (i)$$

For reaction (b): $K_2 = A_2 e^{-E_a/RT}$

$$1.52 \times 10^{-4} = A_2 e^{-\frac{24.5 \times 10^3}{RT}} \quad \dots (ii)$$

$$\begin{aligned} \text{By equation (i)} \quad A_1 &= \frac{2.79 \times 10^{-3}}{e^{-\frac{12 \times 10^3}{2 \times 510}}} = \frac{2.79 \times 10^{-3}}{7.8 \times 10^{-6}} \\ &= 3.58 \times 10^2 \end{aligned}$$

$$\begin{aligned} \text{By equation (ii)} \quad A_2 &= \frac{1.52 \times 10^{-4}}{e^{-\frac{24.5 \times 10^3}{2 \times 510}}} = \frac{1.52 \times 10^{-4}}{3.7 \times 10^{-11}} \\ &= 4.11 \times 10^6 \end{aligned}$$

If rate constants of two reactions are same, the reactions will give equimolar mixture of products. Let these be same at temperature T , i.e.

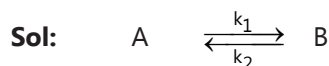
$$\begin{aligned} A_1 e^{-E_{a1}/RT} &= A_2 e^{-E_{a2}/RT} \\ \therefore e^{\frac{E_{a2} - E_{a1}}{RT}} &= \frac{A_2}{A_1} \text{ or } e^{\frac{[24.5 - 12.0] \times 10^3}{RT}} = \frac{A_2}{A_1} \\ &= \frac{4.11 \times 10^6}{3.58 \times 10^2} = 1.15 \times 10^4 \end{aligned}$$

$$\text{Or } \frac{10^3}{RT} \times 12.5 = 9.35 \quad \therefore T = \frac{12.5 \times 10^3}{9.35 \times 2} = 668 \text{ K}$$

$$\therefore T = 668 \text{ K} = 395^\circ\text{C}$$

Example 10: For the reversible reaction in equilibrium:

$\text{A} \xrightleftharpoons[k_2]{k_1} \text{B}$. The values of K_1 and K_2 are $2 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$ and $3 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$ respectively. If we add 0.5 mol of B in the equilibrium mixture, initially containing 2 mol of A. Calculate the time taken for concentration of B to become equal to 3/4 of the concentration of A at initial equilibrium. The volume of mixture is 1 L and remains constant.



$$t = 0 \quad 2 \text{ mol L}^{-1} \quad 0$$

At eq. $(2 - X) \text{ mol L}^{-1}$ X

$K_1 = 2 \times 10^{-3} \text{ mole L}^{-1} \text{ sec}^{-1}$ (zero order)

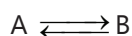
$K_2 = 3 \times 10^{-3} \text{ sec}^{-1}$ (1st order)

$$\frac{dX}{dt} = K_1[A]^0 - K_2[B]^1$$

At equilibrium $\frac{dX}{dt} = 0$

$$\therefore 0 = K_1 - K_2[X]_{\text{eq}}; [X]_{\text{eq}} = \frac{K_1}{K_2} = \frac{2 \times 10^{-3}}{3 \times 10^{-3}}$$

$$= 0.66 \text{ mol L}^{-1} = K_c$$



Initial eq. 1.34 0.66

Moles added 1.34 $0.66 + 0.5 = 1.16$

At eq. at time t $(1.34 - X)$ $(1.16 - X)$

(The reaction will obey back ward direction on addition of B)

$$\therefore [B] = \frac{3}{4} [A]_{\text{eq}} = \frac{3}{4} \times 1.34 = 1.005$$

$$(1.16 - X) = 1.005; \therefore X = 0.155$$

$$\text{Now, } \frac{dX}{dt} = K_1 - K_2[X] = 0.66K_2 - K_2X$$

$$= K_2[0.66 - X]; \therefore \frac{dX}{(0.66 - X)} = K_2 \cdot dt$$

$$\text{or } -2.303 \log (0.66 - X) = K_2 \cdot t + C$$

$$\text{at } t = 0, X = 0 \therefore C = -2.303 \log 0.66$$

$$\therefore K_2 \cdot t = 2.303 \log \frac{0.66}{0.66 - X}$$

$$\therefore t = \frac{2.303}{3 \times 10^{-3}} \log \frac{0.66}{0.66 - 0.155} = 89.24 \text{ sec}$$

(a) Partial pressure becomes half of initial in every 100 min, therefore, order = 1.

$$(b) k \times 100 = \ln \frac{800}{400}$$

$$k \times 100 = \ln 2$$

$$\Rightarrow k = 6.93 \times 10^{-3} \text{ min}^{-1}$$

(c) For 75% reaction; time required

$$= 2 \times \text{half-life} = 200 \text{ min}$$



$$800 - x \quad \frac{3}{2}x$$

$$\text{Total pressure} = 800 + \frac{3}{2}x$$

$$\text{Also } 800 - x = 700 \Rightarrow x = 100$$

$$\Rightarrow \text{Total pressure} = 800 + \frac{3}{2} \times 100 = 950 \text{ mm}$$

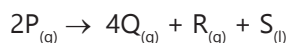
JEE Main/Boards

Exercise 1

Q.1 A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the reaction $A + B \rightarrow C$ occurs. At the end of 1h, A is 75% reacted. How much of A will be left unreacted at the end of 2h if the reaction is (a) first order in A and zero order in B; (b) first order in both A and B; and (c) zero order in both A and B?

Q.2 The reaction $\text{CH}_3\text{CH}_2\text{NO}_2 + \text{OH}^- \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{NO}_2^- + \text{H}_2\text{O}$ obeys the rate law for pseudo first order kinetic in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half minute when the reaction concentration is 0.002 M, What is the pseudo first order rate constant?

Q.3 The decomposition of a compound P at temperature T according to the equation



is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minute, if volume of liquid S is supposed to be negligible, also calculate the tiny fraction $t_{1/8}$.

Given: Vapor pressure of S (l) at temperature T = 32.5 mm Hg.

Q.4 A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a

reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$ the volume of the reagent consumed is 25 ml and at $t = 10$ min, the volume used up is 32 ml. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

Q.5 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.025 M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2 .

Q.6 A metal slowly forms an oxide film which completely protects the metal when the film thickness is 3.956 thousand times of an inch. If the film thickness is 1.281 thou. in 6 weeks, how much longer will it be before it is 2.481 thou.? The rate of film formation follows first order kinetics.

Q.7 An optically active compound A upon acid catalyzed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was -20° . If optical rotation per mole of A, B & C are 60° , 40° & -80° . Calculate half-life of the reaction.

Q.8 A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $CH_3OCH_3(g) \rightarrow CH_4(g) + CO(g) + H_2(g)$. The rate constant of decomposition is $4.78 \times 10^{-3} \text{ min}^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition.

Q.9 At room temperature (20°C) orange juice gets spoilt in about 64 hours. In a refrigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice (b) How long should it take for juice to get spoilt at 40°C ?

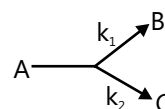
Q.10 A first order reaction, $A \rightarrow B$, requires activation energy of 70 kJ mol^{-1} . When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature.

Q.11 Two reactions

- (i) $A \rightarrow \text{products}$
- (ii) $B \rightarrow \text{products}$,

follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction is half of that of reaction, calculate the rate constant of the reaction (ii) at 300 K

Q.12 A certain organic compound A decomposes by two parallel first order mechanism



If $k_1/k_2 = 1:9$ and $k_1 = 1.3 \times 10^{-5} \text{ s}^{-1}$.

Calculate the concentration ratio of C to A, if an experiment is started with only A and allowed to run for one hour.

Q.13 The reaction $\text{cis} - \text{Cr(en)}_2(\text{OH})_2^+ \xrightleftharpoons[k_2]{k_1} \text{trans} -$

$\text{Cr(en)}_2(\text{OH})_2^+$ is first order in both directions. At 25°C

the equilibrium constant is 0.16 and the rate constant k_1 is $3.3 \times 10^{-4} \text{ s}^{-1}$. In an experiment starting with the pure cis form, how long would it take for half the equilibrium amount of the Trans isomer to be formed?

Q.14 For a reversible first-order reaction $A \xrightleftharpoons[k_2]{k_1} B$ k_1

$= 10^{-2} \text{ s}^{-1}$ and $[B]_{\text{eq}}/[A]_{\text{eq}} = 4$. If $[A]_0 = 0.01 \text{ mole L}^{-1}$ and $[B]_0 = 0$, what will be the concentration of B after 30 s?

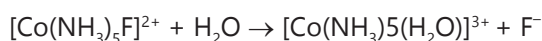
Q.15 For the system $A(g) \rightarrow B(g)$, ΔH for the forward reaction is -33 kJ/mol (Note. $\Delta H = \Delta E$ in this case).

Show that equilibrium constant

$K = \frac{[B]}{[A]} = 5.572 \times 10^5$ at 300 K. If the activation energies

E_f and E_b are in the ratio 20: 31. Calculate E_f and E_b at this temperature. Assume that the pre-exponential factor is the same for the forward and backward reactions

Q.16 The complex $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ reacts with water according to the equation



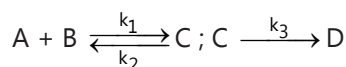
The rate of the reaction = rate const. $\times [\text{complex}]^a \times [\text{H}^+]^b$.
The reaction is acid catalysed i.e. $[\text{H}^+]$ does not change during the reaction.

Thus rate = $k[\text{Complex}]^a$ where $k' = k[\text{H}^+]^b$ calculate 'a' and 'b' given the following data at 25°C.

[Complex]M	$[\text{H}^+]\text{M}$	$T_{1/2}\text{hr}$	$T_{3/4}\text{hr}$
0.1	0.01	1	2
0.2	0.02	0.5	1

Q.17 For the two parallel reactions $\text{A} \xrightarrow{k_1} \text{B}$ and $\text{A} \xrightarrow{k_2} \text{C}$, show that the activation energy E' for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by $E' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$

Q.18 For the mechanism

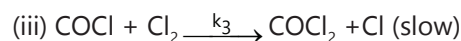
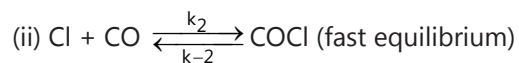
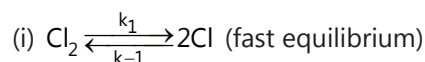


(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.

(b) Assuming that $k_3 \ll k_2$, express the pre-exponential factor A and E_a for the apparent second order rate constant in terms of A_1, A_2 and A_3 and E_{a1}, E_{a2} and E_{a3} for the three steps.

Q.19 The reaction of formation of phosgene from CO and Cl_2 is $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$

The proposed mechanism is

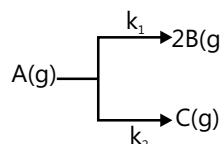


Show that the above mechanism leads to the following

$$\text{rate law } \frac{d[\text{COCl}_2]}{dt} = K[\text{CO}][\text{Cl}_2]^{3/2}.$$

$$\text{Where } K = k_3 \cdot \frac{k_2}{k-2} \left(\frac{k_1}{k-1} \right)^{1/2}.$$

Q.20 For the following first order gaseous reaction



The initial pressure in a container of capacity V litres is 1 atm. Pressure at time $t = 10$ sec is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reaction.

Q.21 A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion?

Q.22 The specific rate constant for a reaction increases by a factor 4 of the temperature is changed from 27°C to 47°C. Find the activation energy for the reaction

Q.23 The reaction $2\text{A} + \text{B} + \text{C} \rightarrow \text{D} + 2\text{E}$ is of first order with respect to A and 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.

Q.24 A first order reaction is 50% completed in 30 min at 27°C and in 10 minutes at 47°C. Calculate the rate constant at 27°C and the energy- of activation of the reaction in kJ per mole

Q.25 The optical rotation of sucrose in 0.5 M HCl at 35°C at different time intervals are given below. Show that the reaction follows first order kinetics

Time (min)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	-11.1

Q.26 $t_{1/2}$ of a reaction is halved as the initial concentration of the reaction is doubled, find out the order of the reaction.

Q.27 The rate constant of a reaction is $1.5 \times 10^{-7} \text{ sec}^{-1}$ at 50°C and $4.5 \times 10^{-7} \text{ sec}^{-1}$ at 100°C. Evaluate the Arrhenius parameters A and E_a .

Q.28 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

(a) Find out the initial rate

(b) Find out the rate after 1 min.

Q.29 What will be initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and concentration of reactant is 0.2 mol dm^{-3} . How much of reactant will be converted into products in 200 minutes.

Q.30 A first order reaction is 20% complete in 10 minutes. Calculate

- (a) Specific rate constant of the reaction and
(b) Time taken for the reaction to go to 75 % completion

Exercise 2

Single Correct Choice Type

Q.1 For the reaction $A + B \rightarrow C$; starting with different initial concentration of A and B, initial rate of reaction were determined graphically in four experiments.

S. No.	[A] ₀ /M (Initial conc.)	[B] ₀ /M (Initial conc.)	rate/ (M sec ⁻¹)
1	1.6×10^{-3}	5×10^{-2}	10^{-3}
2	3.2×10^{-3}	5×10^{-2}	4×10^{-3}
3	1.6×10^{-3}	10^{-1}	2×10^{-3}
4	3.2×10^{-3}	10^{-1}	8×10^{-3}

Rate law for reaction from above data is

- (A) $r = k[A]^2[B]$ (B) $r = k[A]^2[B]$
(C) $r = k[A][B]^2$ (D) $r = k[A][B]$

Q.2 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) $2^{(n-m)}$ (B) $1/2^{m+n}$ (C) $(m+n)$ (D) $(n-m)$

Q.3 In a first order reaction, the concentration of the reactant, decreases from 0.8 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) 30 minutes (B) 15 minutes
(C) 7.5 minutes (D) 60 minutes

Q.4 The rate equation for the reaction

$2A + B \rightarrow C$ is found to be: rate = $k[A][B]$. The correct statement in relation to this reaction is

- (A) Unit of k must be s^{-1}
(B) $t_{1/2}$ is a constant
(C) Rate of formation of C is twice the rate of disappearance of A
(D) Value of k is independent of the initial concentration of A and B

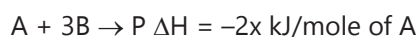
Q.5 $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to 3/4 of its value. If the rate constant for a first order reaction is k, the $t_{3/4}$ can be written as

- (A) $0.69/k$ (B) $0.75/k$ (C) $0.10/k$ (D) $0.29/k$

Q.6 A reaction was found to be second order with respect to the concentration of carbon monoxide. If the 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

Q.7 For a hypothetical reaction,



If these reactions are carried simultaneously in a reactor such that temperature is not changing. If rate of disappearance of B is $y \text{ M sec}^{-1}$ then rate of formation (in M sec^{-1}) of Q is:

- (A) $\frac{2}{3}y$ (B) $\frac{3}{2}y$ (C) $\frac{4}{3}y$ (D) $\frac{3}{4}y$

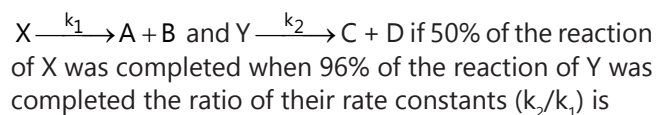
Q.8 Gaseous reaction $A \rightarrow B + C$ follows first order kinetics. Concentration of A changes from 1M to 0.25 M in 138.6 minutes. Find the rate of reaction when concentration of A is 0.1 M.

- (A) $2 \times 10^{-3} \text{ M min}^{-1}$ (B) $10^{-3} \text{ M min}^{-1}$
(C) $10^{-4} \text{ M min}^{-1}$ (D) $5 \times 10^{-4} \text{ M min}^{-1}$

Q.9 The initial rate of zero-order reaction of the gaseous reaction $A(g) \rightarrow 2B(g)$ is $10^{-2} \text{ M min}^{-1}$. If the initial concentration of A is 0.1M. What would be the concentration of B after 60 sec?

- (A) 0.09 M (B) 0.01 M
(C) 0.02 M (D) 0.002 M

Q.10 Consider the following first order competing reactions:



- (A) 4.06 (B) 0.215 (C) 1.1 (D) 4.65

Q.11 At certain temperature, the half-life period for the thermal decomposition of a gaseous substance depends on the initial partial pressure of the substance as follows

P(mm Hg) 500 250

$t_{1/2}$ (in min) 235 950

Find the order of reaction

[Given $\log(23.5) = 1.37$; $\log(95) = 1.97$; $\log 2 = 0.30$]

- (A) 1 (B) 2 (C) 2.5 (D) 3

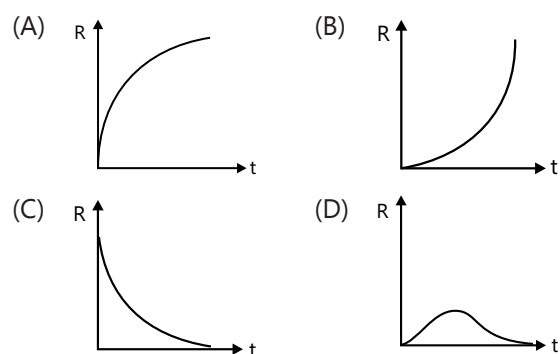
Q.12 Consider the reaction: $A \rightarrow B + C$

Initial concentration of A is 1M. 20 minutes time is required for completion of 20% reaction.

If $\frac{d[B]}{dt} = k[A]$, then half life ($t_{1/2}$) is

- (A) 55.44 min (B) 50 min
(C) 62.13 min (D) None of these

Q.13 If decomposition reaction $A(g) \rightarrow B(g)$ follows first order kinetics then the graph of rate of formation (R) of B against time t will be



Q.14 The rate constant for the forward reaction $A(g) \rightarrow 2B(g)$ is $1.5 \times 10^{-3} \text{ s}^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

- (A) $1.50 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ (B) $1.5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$
(C) $1.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (D) $1.5 \times 10^{-11} \text{ L mol}^{-1} \text{ s}^{-1}$

Q.15 Reaction $A + B \rightarrow C + D$ follows following rate law: $\text{rate} = k[A]^{1/2}[B]^{1/2}$. Starting with initial conc. of 1 M of A and B each, what is the time taken for concentration of A to become 0.25 M.

Given: $k = 2.303 \times 10^{-3} \text{ sec}^{-1}$

- (A) 300sec. (B) 600 sec. (C) 900 sec. (D) 1200 sec.

Q.16 The reaction $A(g) \rightarrow B(g) + 2C(g)$ is a first order reaction with rate constant $3.465 \times 10^{-6} \text{ s}^{-1}$. Starting with 0.1 mole of A in 2 litre vessel, find the concentration of A after 200 sec, when the reaction is allowed to take place at constant pressure and temperature

- (A) 0.05 M (B) 0.025 M
(C) 0.0125 M (D) None of these

Q.17 In respect of the equation $k = A \exp(-E_a / RT)$, which one of the following statements is correct?

- (A) R is Rydberg's constant
(B) k is equilibrium constant
(C) A is adsorption factor
(D) E_a is the energy of activation

Q.18 Rate of a reaction can be expressed by Arrhenius equation 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.

Q.19 The rate constant, the activation energy and the Arrhenius parameter (A) of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^4 \text{ S}^{-1}$ respectively. The value of the rare constant at $T \rightarrow \infty$

- (A) $2.0 \times 10^{-18} \text{ s}^{-1}$ (B) $6.0 \times 10^{14} \text{ s}^{-1}$
(C) Infinity (D) $3.6 \times 10^{30} \text{ s}^{-1}$

Q.20 A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C . The energy of activation of the reaction is

- (A) 43.85kJ/mol (B) 55.14kJ/mol
(C) 11.97kJ/mol (D) 6.65kJ/mol

Q.21 For the first order reaction $A \rightarrow B + C$, carried out at 27°C if $3.8 \times 10^{-16} \%$ of the reaction molecules exists in the activated state, the E_a (activation energy) of the reaction is [$\log 3.8 = 0.58$]

- (A) 12 kJ/mole (B) 831.4kJ/mole
(C) 100 kJ/mole (D) 88.57kJ/mole

Q.22 In a reaction carried out at 400 K, 0.0001% of the total number of collisions are effective. The energy of activation of the reaction is

- (A) Zero (B) 7.37 kJ/mol
(C) 9.212 kJ/mol (D) 11.05 kJ/mol

Previous Years' Questions

Q.1 For a reaction $\frac{1}{2}A \rightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression **(2008)**

- (A) $-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$ (B) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$
(C) $-\frac{d[A]}{dt} = 4 \frac{d[B]}{dt}$ (D) $-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$

Q.2 The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C , the rate of the reaction increases by about **(2011)**

- (A) 10 times (B) 24 times
(C) 32 times (D) 64 times

Q.3 In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^2\text{ sec}$. The rate constant of reaction in sec^{-1} is **(2003)**

- (A) 2×10^4 (B) 3.45×10^{-5}
(C) 1.386×10^{-2} (D) 2×10^{-4}

Q.4 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 **(2007)**

- (A) $\text{L mol}^{-1} \text{s}^{-1}$ (B) No unit
(C) $\text{mol L}^{-1} \text{s}^{-1}$ (D) s^{-1}

Q.5 The rate constant for the reaction, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ is $3 \times 10^{-5} \text{ sec}^{-1}$. If the rate is $2.40 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$.

Then the concentration of N_2O_5 (in mol litre^{-1}) is **(2001)**

- (A) 1.4 (B) 1.2 (C) 0.04 (D) 0

Q.6 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 ($\log 2 = 0.301$)

(2009)

- (A) 230.3 minutes (B) 23.03 minutes
(C) 46.06 minutes (D) 460.6 minutes

Q.7 A reaction involving two different reactants **(2005)**

- (A) Can never be a second order reaction
(B) Can never be a unimolecular reaction
(C) Can never be a bimolecular reaction
(D) Can never be a first order reaction

Q.8 A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled with everything else kept the same, the rate of reaction will **(2006)**

- (A) Remain unchanged (B) Triple
(C) Increase by a factor of 4 (D) Double

Q.9 For the reaction $A + 2B \rightarrow C$, rate is given by $R = [A][B]^2$ then the order of the reaction is **(2002)**

- (A) 3 (B) 6 (C) 5 (D) 7

Q.10 The following mechanism has been proposed for the reaction of NO with Br_2 to form NOBr: $\text{NO(g)} + \text{Br}_2(\text{g}) \rightleftharpoons \text{NOBr}_2(\text{g})$ $\text{NOBr}_2(\text{g}) + \text{NO(g)} \rightarrow 2\text{NOBr}$ (g) If the second step is the rate determining step, the order of the reaction with respect to NO(g) is **(2006)**

- (A) 1 (B) 0 (C) 3 (D) 2

Q.11 Consider the reaction $\text{Cl}_{2(\text{aq})} + \text{H}_2\text{S}_{(\text{aq})} \rightarrow \text{S}_{(\text{s})} + 2\text{H}^+_{(\text{aq})} + 2\text{Cl}^-_{(\text{aq})}$. The rate equation for this reaction is $\text{rate} = k[\text{Cl}_2][\text{H}_2\text{S}]$. Which of these mechanisms is/are consistent with this rate equation

A. $\text{Cl}_2 + \text{H}_2\text{S} \rightarrow \text{H}^+ + \text{Cl}^- + \text{Cl}^- + \text{HS}^-$ (slow)

$\text{Cl}^- + \text{HS}^- \rightarrow \text{H}^+ + \text{Cl}^- + \text{S}$ (fast)

B. $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$ (fast equilibrium)

$\text{Cl}_2 + \text{HS}^- \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{S}$ (slow)

(2010)

- (A) A only (B) B only
(C) Both A and B (D) Neither A nor B

Q.12 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^{-1} , how much time does it take for its concentration to come for 0.50 to 0.25 mol L^{-1} if it is a zero order reaction (2010)

- (A) 1 h (B) 4h (C) 0.5h (D) 0.25 h

Q.13 The energies of activation for forward and reverse reactions for $A_2 + B_2 \longrightarrow 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol^{-1} . The enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1}) (2007)

- (A) 300 (B) -120 (C) 280 (D) -20

Q.14 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 (2005)

- (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

Q.15 If 'I' is the intensity of absorbed light and C is the concentration of AB for the photochemical process $AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to (2001)

- (A) C (B) I (C) I^2 (D) C.I

Q.16 For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of 'A' is related to the rate of appearance of 'B' by the expression (2008)

- (A) $-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$ (B) $-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$
 (C) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$ (D) $-\frac{d[A]}{dt} = 4 \frac{d[B]}{dt}$

Q.17 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 ($\log 2 = 0.301$) (2009)

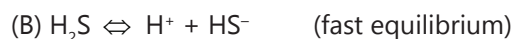
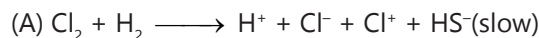
- (A) 230.3 minutes (B) 23.03 minutes
 (C) 46.06 minutes (D) 460.6 minutes

Q.18 The time for half-life period of a certain reaction $A \longrightarrow \text{products}$ is 1 hour. When the initial Concentration of the reactant 'A', is 2.0 mol/L , how much time does it take for its concentration to come from 0.50 to 0.25 mol/L if it is a zero order reaction? (2010)

- (A) 4 h (B) 0.5 h (C) 0.25 h (D) 1 h

Q.19 Consider the reaction: $\text{Cl}_2(\text{aq}) + \text{H}_2\text{S}(\text{aq}) \longrightarrow \text{S}(\text{s}) + 2\text{H}^+(\text{aq}) + 2\text{Cl}^-(\text{aq})$ The rate equation for this reaction is $\text{rate} = k [\text{Cl}_2] [\text{H}_2\text{S}]$

Which of these mechanisms is/are consistent with this rate equation? (2010)



- (A) B only (B) Both A and B
 (C) Neither A nor B (D) A only

Q.20 The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C , the rate of the reaction increases by about: (2011)

- (A) 24 times (B) 32 times
 (C) 64 times (D) 10 times

Q.21 For a first order reaction, (A) $\longrightarrow \text{products}$, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M is: (2012)

- (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) $1.73 \times 10^{-4} \text{ M/min}$

Q.22 The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be : ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.301$) (2013)

- (A) 53.6 kJ mol^{-1} (B) 48.6 kJ mol^{-1}
 (C) 58.5 kJ mol^{-1} (D) 60.5 kJ mol^{-1}

Q.23 . For the non-stoichiometry reaction $2A + B \rightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K. (2014)

Initial Concentration (A)	Initial Concentration (A)	Initial rate of formation (C) (mol L ⁻¹ s ⁻¹)
0.1 M	0.1 M	1.2×10^{-3}
0.1 M	0.2 M	1.2×10^{-3}
0.2 M	0.1 M	2.4×10^{-3}

The rate law for the formation of C is

- (A) $\frac{dC}{dt} = k[A][B]$ (B) $\frac{dC}{dt} = k[A]^2[B]$
 (C) $\frac{dC}{dt} = k[A][B]^2$ (D) $\frac{dC}{dt} = k[A]$

Q.24 Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be:

(2016)

- (A) $6.93 \times 10^{-4} \text{ mol min}^{-1}$ (B) 2.66 L min^{-1} at STP
 (C) $1.34 \times 10^{-2} \text{ mol min}^{-1}$ (D) $6.93 \times 10^{-2} \text{ mol min}^{-1}$

JEE Advanced/Boards

Exercise 1

Q.1 Ammonia and oxygen reacts at higher temperatures as $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

In an experiment, the concentration of NO increases by $1.08 \times 10^{-2} \text{ mol litre}^{-1}$ in 3 seconds. Calculate

- (i) Rate of reaction (ii) Rate of disappearance of ammonia (iii) Rate of formation of water

Q.2 In the following reaction $2H_2O_2 \rightarrow 2H_2O + O$ rate of formation of O_2 is 3.6 M min^{-1}

- (i) What is rate of formation of H_2O ?
 (ii) What is rate of disappearance of H_2O_2 ?

Q.3 In a catalytic experiment involving the Haber process $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of reaction was measured as

$$\text{Rate} = \frac{\Delta[NH_3]}{\Delta t} = 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

If there were no side reactions, what was the rate of reaction expressed in terms of (a) N_2 , (b) H_2 ?

Q.4 The reaction $2A + B + C \rightarrow D + E$ is found to be first order in A second order in B and zero order in C. (1)

Give the rate law for the reaction in the form of differential equation.

- (ii) What is the effect in rate of increasing concentrations of A, B, and C two times?

Q.5 At 27°C it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of reaction (in M sec^{-1}) and rate of reaction in term of pressure.

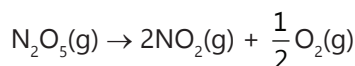
Q.6 For the elementary reaction $2A + B_2 \rightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

Q.7 For the reaction $3BrO^- \rightarrow BrO_3^- + 2Br^-$ in an alkaline aqueous solution the value of the second order (in BrO^-) rate constant at 80°C in the rate law for

$-\frac{\Delta[BrO^-]}{\Delta t}$ was found to be $0.056 \text{ L mol}^{-1} \text{ s}^{-1}$. What is the rate constant when the rate law is written for

- (a) $\frac{\Delta[BrO_3^-]}{\Delta t}$ (b) $\frac{\Delta[Br^-]}{\Delta t}$?

Q.8 Dinitropentoxide decomposes as follows:



Given that $-d[N_2O_5]/dt = k_1[N_2O_5]$

$d[NO_2]/dt = k_2[N_2O_5]$; $d[O_2]/dt = k_3[N_2O_5]$

What is the relation between k_1 , k_2 and k_3 ?

Q.9 Suppose that the Sun consist entirely of hydrogen atom and releases the energy by the nuclear reaction.

$4_1^1\text{H} \longrightarrow {}_2^4\text{He}$ with 26 MeV of energy released. If the total output power of the Sun is assumed to remain constant at 3.9×10^{26} W find the time it will take to burn all the hydrogen. Take the mass of the Sun as 1.7×10^{30} kg.

Q.10 The reaction $\text{A(g)} + 2\text{B(g)} \rightarrow \text{C(g)} + \text{D(g)}$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8$ atm. Calculate the ratio of rate of reaction relative to initial rate when P_C becomes 0.2 atm.

Q.11 In the given reaction, $\text{A} \rightarrow \text{B}$ rate constant is $1.2 \times 10^{-2} \text{ M s}^{-1}$. What is concentration of B after 10 and 20 min, if we start with 10 M of A.

Q.12 For the following data for the zero order reaction $\text{A} \rightarrow \text{products}$. Calculate the value of k.

Time(min)	[A]
0.0	0.10 M
1.0	0.09 M
2.0	0.08 M

Q.13 The rate constant for a zero order reaction is $2 \times 10^{-2} \text{ mol/L sec}^{-1}$, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.

Q.14 A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+ , if the rate constant of disappearance of H^+ is $1 \times 10^7 \text{ mole liter}^{-1} \text{ sec}^{-1}$. How long would it take for H^+ in drop to disappear?

Q.15 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

Q.16 A first order reaction is 75% completed in 72 min. How much time will it take for (i) 50% completion (ii) 87.5% completion.

Q.17 A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant. (ii) the time taken for the reactions to go to 75% completion.

Q.18 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place in ten times that required for half of the reaction.

Q.19 A first order reaction has a rate constant is $1.5 \times 10^{-3} \text{ sec}^{-1}$. How long will 5.0 g of this reactant take to reduce to 1.25 g?

Q.20 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that decomposition is of first order, what will be the expiry time of the drug?

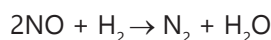
Q.21 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0% of the virus was found to be inactivated per minute. Evaluate k for inactivation process.

Q.22 If a reaction $\text{A} \rightarrow \text{Products}$, the concentrations of reactant A are $C_0, aC_0, a^2C_0, a^3C_0, \dots$ after time interval 0, t, 2t, 3t, where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also calculate the relation between k, a and t.

Q.23 The reaction $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is a first order gas reaction with $k = 2.2 \times 10^{-5} \text{ sec}^{-1}$ at 320°C . What % of SO_2Cl_2 is decomposed on heating this gas for 90 min?

Q.24 Two substances A ($t_{1/2} = 5$ mins) and B ($t_{1/2} = 15$ mins) follow first order kinetics are taken in such a way that initially $[\text{A}] = 4 [\text{B}]$. Calculate the time after which the concentration of both the substance will be equal.

Q.25 At 800°C the rate of reaction



Changes with the concentration of NO and H_2 are

	[NO] in M	[H ₂] in M	$-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ in M sec^{-1}
(i)	1.5×10^{-4}	4×10^{-3}	4.4×10^{-4}
(ii)	1.5×10^{-4}	2×10^{-3}	2.2×10^{-4}
(iii)	3.0×10^{-4}	2×10^{-3}	8.8×10^{-4}

(a) What is the order of this reaction?

(b) What is the rate equation for the reaction?

(c) What is the rate when

$[\text{H}_2] = 1.5 \times 10^{-3} \text{ M}$ and $[\text{NO}] = 1.1 \times 10^{-3} \text{ M}$?

Q.26 The data below are for the reaction if NO and Cl₂ to form NOCl at 295 K

Concentration of Cl ₂ [M]	Concentration of NO	Initial Rate (M s ⁻¹)
0.05	0.05	1 × 10 ⁻³
0.15	0.05	3 × 10 ⁻³
0.05	0.15	9 × 10 ⁻³

- What is the order w. r.t. NO and Cl₂ in the reaction.
- Write the rate expression
- Calculate the rate constant
- Determine the reaction rate when concentration of Cl₂ and NO are 0.2 M & 0.4 M respectively.

Q.27 The catalytic decomposition of N₂O by gold at 900 °C and at an initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes

- What is the order of the reaction?
- Calculate the velocity constant
- How much of H₂O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

Q.28 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below

t (sec)	0	100	200	300
Pa(Pascal)	4 × 10 ³	3.5 × 10 ³	3 × 10 ³	2.5 × 10 ³

Determine the order of reaction, its rate constant.

Q.29 The half -life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Q.30 In this case we have A → B + C

Time	t	∞
Total pressure of A + B + C	P ₂	P ₃

Find k.

Q.31 A → B + C

Time	t	∞
Total pressure of (B + C)	P ₂	P ₃

Find k.

Q.32 A → B + C

Time	0	t
Volume of reagent	V ₁	V ₂

The reagent reacts with A, B and C. Find k.

[Assuming n-factor of A B & C are same]

Q.33 A → 2B + 3C

Time	t	∞
Volume of reagent	V ₂	V ₃

The reagent reacts with A, B and C.

Find k. [Assuming n-factor of A B & C are same]

Q.34 S → G + F

Time	t	∞
Rotation of Glucose & Fructose	r ₁	r _∞

Find k.

Q.35 The reaction $\text{AsH}_3(\text{g}) \rightarrow \text{As}(\text{s}) + \frac{3}{2}\text{H}_2(\text{g})$ was followed at constant volume at 310°C by measuring the gas pressure at intervals. Show from the following figures that reaction is of first order.

Time (in hrs)	0	5	7.5	10
Total pressure (in min)	758	827	856	882

Q.36 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction.

(CH₃)₂O(g) → CH₄(g) + H₂(g) + CO(g) at 500°C is as follow:

Time (sec.)	390	1195	3155	∞
Pressure increase (mm Hg)	96	250	467	619

The initial pressure of ether was 312 mm Hg. Write the rate equation for this reaction and determine the rate constant.

Q.37 From the following data show that decomposition of H₂O₂ in aqueous media is first order.

Time in (minutes)	0	10	20
Volume (in c.c. of KMnO ₄)	22.8	13.3	8.25

Q.38 The following data were obtained in experiment on inversion of cane sugar

Time (minute)	0	60	120	1805	360	∞
Angle of rotation (degree)	+13.1	+11.6	+10.2	+9.0	+5.87	-3.8

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter?

Q.39 At 100°C the gaseous reaction $A \rightarrow 2B + C$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction (d) the half-life period of the reaction?

Q.40 The decomposition of N_2O_5 according to the equation $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ is a first order reaction. After 30 min, from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

Q.41 A definite volume of H_2O_2 undergoing spontaneous decomposition required 22.8 c.c. of standard permanganate solution for titration. After 10 and 20 minutes respectively the volumes of permanganate required were 13.8 and 8.25 c.c.

(a) Find order of reaction. How may the result be explained?

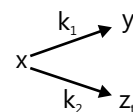
(b) Calculate the time required for the decomposition to be half completed.

(c) Calculate the fraction of H_2O_2 decomposed after 25 minutes.

Q.42 Hydrogen peroxide solution was stored in a mild steel vessel. It was found, however, that the hydrogen peroxide decomposed on the wall of the vessel (a first order reaction). An experiment with 100 ml of a solution gave 10.31 ml oxygen (corrected to 1 atm & 273 K) after 5.1 days. Find how long the peroxide can be stored before the loss of 20.00 ml oxygen occurs (per 100 ml solution) under similar storage conditions if complete decomposition of the H_2O_2 sample gave 46.34 mL oxygen.

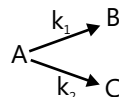
Q.43 The reaction $A(aq) \rightarrow B(aq) + C(aq)$ is monitored by measuring optical rotation of reaction mixture as different time interval. The species A, B and C are optically active with specific rotations 20° , 30° and -40° respectively. Starting with pure A if the value of optical rotation was found to be 2.5° after 6.93 minutes and optical rotation was -5° after infinite time. Find the rate constant for first order conversion of A into B and C.

Q.44 For a reaction



Calculate value of ratio, $\frac{[x]_t}{[y] + [z]}$ at any given instant.

Q.45



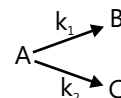
$k_1 = x \text{ hr}^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\frac{[C]}{[A]}$ after one hour

from the start of the reaction. Assuming only A was present in the beginning.

Q.46 How much time would be required for B to reach maximum concentration for the reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$.

Given $k_1 = \frac{\ln 2}{4}$ $k_2 = \frac{\ln 2}{2}$

Q.47 For first order parallel reaction k_1 and k_2 are 8 and 2 min^{-1} respectively at 300 K. If the activation energies for the formation of B and C are respectively 20 and 28.314 kJ/mol respectively find the temperature at which B and C will be obtained in molar ratio of 2:1.



[Given: $\ln 4 = 1.4$]

Q.48 In gaseous reactions important for understanding the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for This reaction is 72 kJ at 500 K and $E_a = 77 \text{ kJ mol}^{-1}$, then calculate E_a for the bimolecular recombination of 2OH radicals to form H_2O and O at 500 K.

Q.49 The energy of activation of a first order reaction is $104.5 \text{ kJ mole}^{-1}$ and pre-exponential factor (A) is $5 \times 10^{11} \text{ sec}^{-1}$. At what temperature, will the reaction have a half-life of 1 minute?

Q.50 The specific rate constant for a reaction increases by a factor of 4. If the temperature is changed from 27°C to 47°C . Find the activation energy for the reaction.

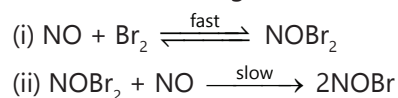
Q.51 The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/mole and $3.46 \times 10^{-3} \text{ sec}^{-1}$ respectively. Determine the temperature at which half life of the reaction is 2 hours.

Q.52 A catalyst lowers the activation energy for a certain reaction from 75 kJ to 25 kJ mol^{-1} . What will be the effect on the rate of reaction at 25°C after things being equal?

Q.53 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate.

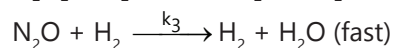
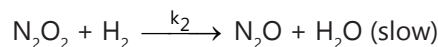
Q.54 At 380°C the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C .

Q.55 The reaction $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$, is supposed to follow the following mechanism



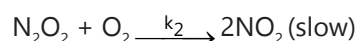
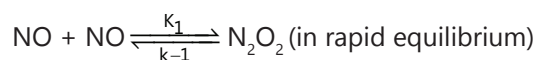
Suggest the rate law expression.

Q.56 For the reaction $2\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, the following mechanism has been suggested $2\text{NO} \rightarrow \text{N}_2\text{O}_2$ equilibrium constant K_1 (fast)



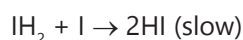
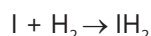
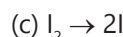
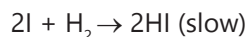
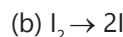
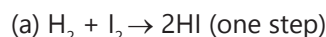
Establish the rate law for given reaction.

Q.57 Reaction between NO and O_2 to form NO_2 is $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ follows the following mechanism



Show that the rate of reaction is given by $\frac{1}{2} \left(\frac{d[\text{NO}_2]}{dt} \right) = K [\text{NO}]^2 [\text{O}_2]$

Q.58 Deduce rate law expressions for the conversion of H_2 and I_2 to HI at 400°C corresponding to each of the following mechanisms:



(d) Can the observed rate law expression

$\text{rate} = k[\text{H}_2][\text{I}_2]$ distinguish among these mechanisms?

(e) If it is known that ultraviolet light causes the reaction of H_2 and I_2 to proceed at 200°C with the same rate law expression, which of these mechanisms becomes most improbable?

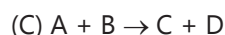
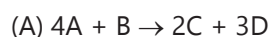
Exercise 2

Single Correct Choice Type

Q.1 The rate of a reaction is expressed in different ways as follows:

$$+\frac{1}{2} \left(\frac{d[\text{C}]}{dt} \right) = -\frac{1}{3} \left(\frac{d[\text{D}]}{dt} \right) = +\frac{1}{4} \left(\frac{d[\text{A}]}{dt} \right) = - \left(\frac{d[\text{B}]}{dt} \right)$$

The reaction is:



Q.2 For the reaction system

$2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$ 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 reaction rate will

(A) Increase to four times of its initial value

(B) Diminish to one-fourth of its initial value

(C) Diminish to one-eighth of its initial value

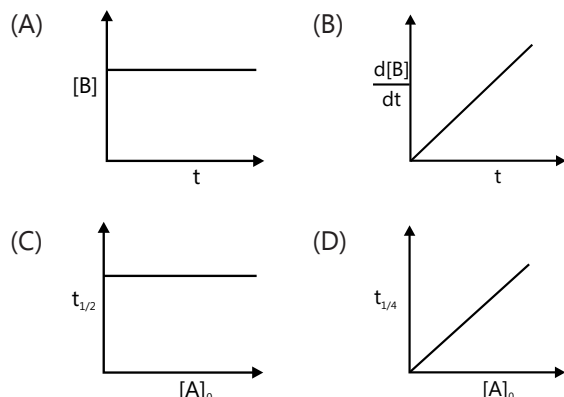
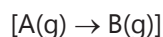
(D) Increase to eight times of its initial value

Q.3 The energies of activation for forward and reverse reactions for $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of catalyst lower the activation energy of both (forward and reverse)

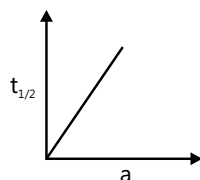
reactions by 100 kJ mol^{-1} . The magnitude of enthalpy change of the reaction ($A_2 + B_2 \rightarrow 2AB$) in the presence of catalyst will be (in kJ mol^{-1}).

- (A) 300 (B) 120 (C) 20 (D) -20

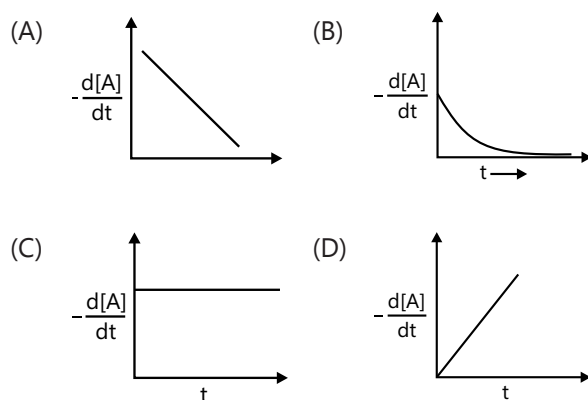
Q.4 Which graph represents zero order reaction



Q.5 Consider the reaction $A \rightarrow B$, graph between half-life ($t_{1/2}$) and initial concentration (a) of the reaction is



Hence graph between $-\frac{d[A]}{dt}$ and time will be

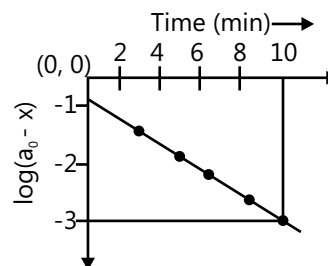


Q.6 The reactions of higher order are rare because

- (A) Many body collisions involve very high activation energy
(B) Many body collisions have a very low probability
(C) Many body collisions are not energetically favoured
(D) Many body collisions can take place only in the gaseous phase.

Q.7 For the first order decomposition of $\text{SO}_2\text{Cl}_2(g)$.

$\text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_2(g) + \text{Cl}_2(g)$ a graph of $\log(a_0 - x)$ vs t is shown in figure. What is the rate constant (sec^{-1})?



- (A) 0.2 (B) 4.6×10^{-1}
(C) 7.7×10^{-3} (D) 1.15×10^{-2}

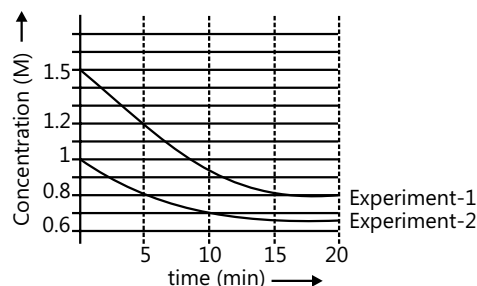
Q.8 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as "16.8 V" was left open due to this, some H_2O_2 decomposed. To determine the new volume strength after 2.303 hours. 20 mL of this solution was diluted to 100 mL. 25 mL of this diluted solution was titrated against 37.5 mL of 0.02 M KMnO_4 solution under acidic conditions [Given: STP is 1 atm and 273 K].

The rate constant (in hr^{-1}) for decomposition of H_2O_2 is:

- (A) 0.15 (B) 0.30 (C) 0.60 (D) 1.3

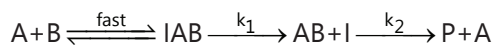
Q.9 The variation of concentration of A with time in two experiments starting with two different initial concentration of A is given in the following graph. The reaction is represented as $A(aq) \rightarrow B(aq)$.

What is the rate of reaction (M/min) when concentration of A in aqueous solution was 1.8 M?

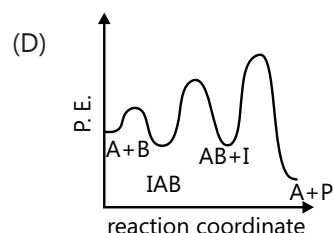
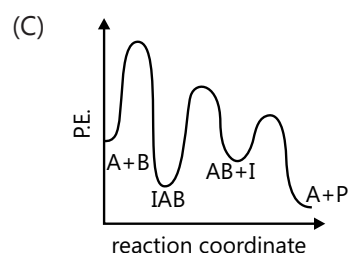
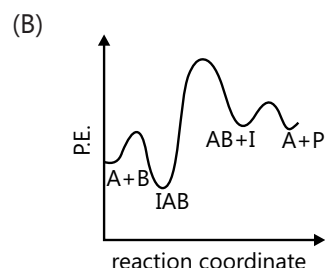
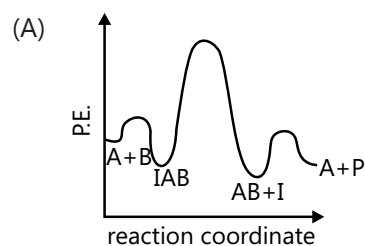


- (A) 0.08 M min^{-1} (B) 0.036 M min^{-1}
(C) 0.13 M min^{-1} (D) 1 M min^{-1}

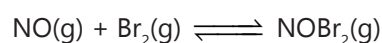
Q.10 The following mechanism has been proposed for the exothermic catalyzed complex reaction.



If k_1 is much smaller than k_2 . The most suitable qualitative plot of potential energy (PE.) versus reaction coordinate for the above reaction.



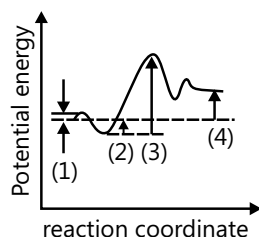
Q.11 The following mechanism has been proposed for the reaction of NO with Br₂ to form NOBr



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

Q.12 Choose the correct set of indentifications.



	(1)	(2)	(3)	(4)
(A)	ΔE for $\text{E} + \text{S} \rightarrow \text{ES}$	E_a for $\text{ES} \rightarrow \text{EP}$	$\Delta E_{\text{overall}}$ for $\text{S} \rightarrow \text{P}$	E_a for $\text{EP} \rightarrow \text{E} + \text{P}$
(B)	E_a for $\text{E} + \text{S} \rightarrow \text{ES}$	ΔE for $\text{E} + \text{S} \rightarrow \text{ES}$	E_a for $\text{ES} \rightarrow \text{EP}$	$\Delta E_{\text{overall}}$ for $\text{S} \rightarrow \text{P}$
(C)	E_a for $\text{ES} \rightarrow \text{EP}$	E_a for $\text{EP} \rightarrow \text{E} + \text{P}$	$\Delta E_{\text{overall}}$ for $\text{S} \rightarrow \text{P}$	ΔE for $\text{EP} \rightarrow \text{E} + \text{P}$
(D)	E_a for $\text{E} + \text{S} \rightarrow \text{ES}$	E_a for $\text{ES} \rightarrow \text{EP}$	E_a for $\text{EP} \rightarrow \text{E} + \text{P}$	$\Delta E_{\text{overall}}$ for $\text{S} \rightarrow \text{P}$
(E)	ΔE for $\text{E} + \text{S} \rightarrow \text{ES}$	$\Delta E_{\text{overall}}$ for $\text{S} \rightarrow \text{P}$	ΔE for $\text{EP} \rightarrow \text{E} + \text{P}$	E_a for $\text{EP} \rightarrow \text{E} + \text{P}$

Multiple Correct Choice Type

Q.13 SO₃ gas is entering the environment at a constant rate of 6.93×10^{-5} gm/L/day due to the emission of polluting gases from thermal power plant but at the same time it is decomposing & following first order kinetics with half-life of 100 days.

Based on above information select the true statement (s).

(A) Concentration of SO₃ in Kota is 1.25×10^{-5} M (Assume SO₃ present in air reaches steady state)

(B) If 10³ L of air is passed through 1L pure water (assuming all SO₃ to be dissolved in it) & resulting solution is titrated against 1 N NaOH solution, 15 ml is required to reach end point

(C) An industry is manufacturing H₂SO₄ at the rate of 980 kg per day with the use of SO₃ in air it should use 8×10^5 litre air/day

(D) If SO₃ emission is stopped then after 1000 days its concentrations will reduce to $\approx 1.2 \times 10^{-3}$ M.

Q.14 For the reaction $\text{A} \rightarrow \text{B}$. The rate law expression is $-\frac{d[\text{A}]}{dt} = k[\text{A}]^{1/2}$. If initial concentration of [A] is [A]₀, then

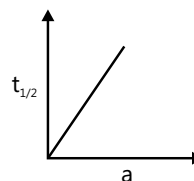
(A) The integrated rate expression is $k = \frac{2}{t}(\text{A}_0^{1/2} - \text{A}^{1/2})$

(B) The graph of $\sqrt{\text{A}}$ vs t will be

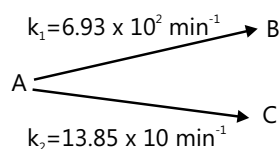
(C) The half-life period $t_{1/2} = \frac{K}{2[\text{A}]_0^{1/2}}$

(D) The time taken for 75% completion of reaction

$$t_{3/4} = \frac{\sqrt{[\text{A}]_0}}{k}$$



Q.15 Consider the reaction,



A, B and C all are optically active compound. If optical rotation per unit concentration of A, B and C are 60° , -72° , 42° and initial concentration of A is 2 M then select write statements(s).

- (A) Solution will be optically active and dextro after very long time
- (B) Solution will be optically active and laevo after very long time
- (C) Half life of reaction is 15 min
- (D) After 75% conversion of A in to B and C angle of rotation of solution will be 36°

Q.16 Which of the following statement is incorrect?

- (A) The order of reaction is the sum of powers of all the concentration terms in the rate equation.
- (B) The order of reaction with respect to one reactant is the ratio of the change of logarithm of the rate of the reaction to the change in the logarithm of the concentration of the particular reactant, keeping the concentrations of all other reactants constant.
- (C) Orders of reactions cannot be fractional.
- (D) The order of a reaction can only be determined from the stoichiometric equation for the reaction.

Q.17 Select incorrect statement(s)

- (A) Unit of pre-exponential factor (A) for second order reaction is $\text{mol L}^{-1} \text{s}^{-1}$
- (B) A zero-order reaction must be a complex reaction
- (C) Molecularity is defined only for RDS in a complex reaction
- (D) Decay constant (λ) of radioactive substance is affected by temperature

Q.18 In a consecutive reaction system $\text{A} \xrightarrow{E_1} \text{B} \xrightarrow{E_2} \text{C}$ when E_1 is much greater than E_2 , the yield of B increase with

- (A) Increase in temperature
- (B) Decreases in temperature
- (C) Increase in initial concentration of A
- (D) Decrease in initial concentration of A

Q.19 Which of the following is/are correct statement?

- (A) Stoichiometry of a reaction tells about the order of the elementary reaction.
- (B) For a zero-order reaction, rate and the rate constant are identical
- (C) A zero-order reaction is controlled by factors other than concentration of reactants.
- (D) A zero-order reaction is always elementary reaction

Assertion Reasoning Type

- (A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I
- (B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I
- (C) Statement-I is true, statement-II is false.
- (D) Statement-I is false, statement-II is true.

Q.20 Statement-I: A fractional order reaction must be a complex reaction.

Statement-II: Fractional order of RDS equals to overall order of a complex reaction.

Q.21 Statement-I: Temperature coefficient of a one step reaction may be negative

Statement-II: The rate of reaction having negative order with respect to a reactant decreases with the increase in concentration of the reactant.

Q.22 Statement-I: The overall rate of a reversible reaction may decrease with the increase in temperature.

Statement-II: When the activation energy of forward reaction is less than that of backward reaction, then the increase in the rate of backward reaction is more than that of forward reaction on increasing the temperature

Q.23 Statement-I: In a reversible endothermic reaction E_a of forward reaction is higher than that of backward reaction.

Statement-II: The threshold energy of forward reaction is more than that of backward reaction.

Q.24 Statement-I: The time of completion of reaction of type $\text{A} \rightarrow \text{product}$ (order < 1) may be determined.

Statement-II: Reactions with order ≥ 1 are either too slow or too fast and hence the time of completion cannot be determined

Q.25 Statement-I: A catalyst provides an alternative path to the reaction in which conversion of reaction into products takes place quickly

Statement-II: The catalyst forms an activated complex of lower potential energy with the reactants by which more number of molecules are able to cross the barrier per unit of time.

Comprehension Type

Paragraph 1

For a hypothetical elementary reaction $A \xrightarrow{k_1} B$
 $A \xrightarrow{k_2} C$

where $\frac{k_1}{k_2} = \frac{1}{2}$. Initially only 2 moles of A is present.

Q.26 The total number of moles of A, B & C at the end of 50% reaction are

- (A) 2 (B) 3 (C) 4 (D) 5

Q.27 Number of moles of B are

- (A) 2 (B) 1 (C) 0.666 (D) 0.33

Paragraph 2

The gaseous reaction: $n_1 A(g) \rightarrow n_2 B(g)$ is first order with respect to A. The true rate constant of reaction is k. The reaction is studied at a constant pressure and temperature. Initially, the moles of A were 'a' and no B were present.

Q.28 How many moles of A are present at time, t?

- (A) $a \cdot e^{-kt}$ (B) $a \cdot e^{-n_1 kt}$
 (C) $a \cdot e^{-n_2 kt}$ (D) $a(1 - e^{-n_2 kt})$

Q.29 If the initial volume of system were v_0 , then the volume of system after time t will be

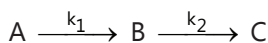
- (A) $\frac{n_1 v_0}{n_2}$
 (B) $\frac{n_2 v_0}{n_1}$
 (C) $v_0 \left[\frac{n_2}{n_1} + \left(1 - \frac{n_2}{n_1} \right) \cdot e^{-n_1 kt} \right]$
 (D) $v_0 \left[\frac{n_2}{n_1} + \left(\frac{n_2}{n_1} - 1 \right) \cdot e^{-n_2 kt} \right]$

Q.30 What will be the concentration of A at time t, if $n_1 = 1$ and $n_2 = 2$?

- (A) $[A_0] \cdot e^{-kt}$ (B) $[A_0] \left(\frac{e^{-kt}}{2 - e^{-kt}} \right)$
 (C) $[A_0] \left(\frac{e^{-kt}}{1 - e^{-kt}} \right)$ (D) $[A_0](1 - 2 \cdot e^{-kt})$

Paragraph 3

For the reaction sequential reaction



the concentration of A, B & C at anytime 't' is given by

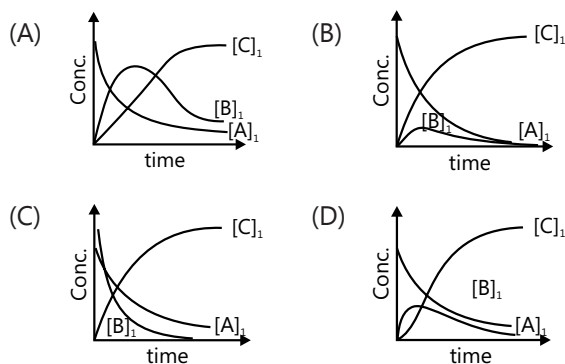
$$[A]_t = [A]_0 e^{-kt}; [B]_t = \frac{k_1 [A]_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]$$

$$[C]_t = [A]_0 - ([A]_t + [B]_t)$$

Q.31 The time at which concentration of B is maximum is

- (A) $\frac{k_1}{k_2 - k_1}$ (B) $\frac{1}{k_2 - k_1} \ln \frac{k_1}{k_2}$
 (C) $\frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$ (D) $\frac{k_2}{k_2 - k_1}$

Q.32 Select the correct option if $k_1 = 1000s^{-1}$ and $k_2 = 20s^{-1}$.



Paragraph 4

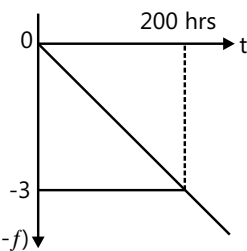
Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidised metal $(1 - f)$ surface thickness relative to maximum thickness (T) of oxidised surface, when metal surface is exposed to air for considerable period of time

Rate law: $= k(1 - f)$, where $f = x/T$,

x = thickness of oxide film at time ' t ' and

T = thickness of oxide film at $t = \infty$

A graph of $\ln(1-f)$ vs t is shown in the adjacent figure.



Q.33 The time taken for thickness to grow 50% of T is

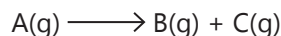
- (A) 23.1 hrs (B) 46.2 hrs
(C) 100 hrs (D) 92.4 hrs

Q.34 The exponential variation of ' f ' with t (hrs) is given by

- (A) $[1 - e^{-3t/200}]$ (B) $e^{-3t/200-1}$
(C) $e^{-3t/200}$ (D) $e^{3t/200}$

Paragraph 5

A reaction is said to be first order if its rate is proportional to the concentration of reactant. Let us consider a reaction



At $t = 0$ a 0 0

At time t $a - x$ x x

The rate of reaction is governed by the expression $\frac{dx}{dt} = k(a - x)$ and integrated rate equation for a given reaction is represented as

$$k = \frac{1}{t} \ln \left(\frac{a}{a-x} \right) \text{ where } a = \text{initial concentration and}$$

$(a - x)$ = concentration of A after time t .

Q.35 Thermal decomposition of compound X is a first order reaction. If 75% of X is decomposed in 100 min. How long will it take for 90% of the compound to decompose? Given: $\log 2 = 0.30$

- (A) 190 min (B) 176.66 min
(C) 166.66 min (D) 156.66 min

Q.36 Consider a reaction $A(g) \longrightarrow 3B(g) + 2C(g)$ with rate constant $1.386 \times 10^{-2} \text{ min}^{-1}$. Starting with 2 moles of A in 12.5 litre vessel initially, if reaction is allowed to take place at constant pressure & at 298 K then find the concentration of B after 100 min.

- (A) 0.04 M (B) 0.36 M
(C) 0.09 M (D) None of these

Match the Columns

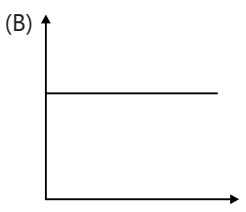
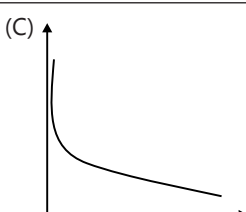
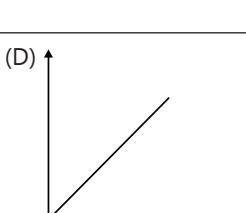
Q.37 For the reaction of type $A(g) \rightarrow 2B(g)$

Column I contains four entries and column II contains four entries. Entry of column I are to be matched with only one entry of column II

Column I	Column II
(A) $\frac{d[B]}{dt}$ vs $\frac{-d[A]}{dt}$ for first order	(p)
(B) $[A]$ vs t for first order	(q)
(C) $[B]$ vs t for first order	(r)
(D) $[A]$ vs t for zero order	(s)

Q.38 Column-I and column-II. Entry of column-I are to be matched with one or more than one entries of column-II and vice versa.

Column-I (Graphs reaction $A \rightarrow \text{Products}$)	Column-II (Co-ordinates)
(A)	(p) $\ln [A]$ (y-axis), t (x-axis) (order = 1)

(B) 	(q) $t_{1/2}$ (y-axis), $[A_0]$ (x-axis) (order = 1)
(C) 	(r) r (y-axis), t (x-axis) (order > 0)
(D) 	(s) r (y-axis), t (x-axis) (order = 0)
	(t) $t_{1/2}$ (y-axis), $[A_0]$ (x-axis) (order > 1)
	(u) $\frac{1}{[A]}$ (y-axis), t (x-axis) (order = 2)
	(v) r (y-axis), $[A]$ (x-axis) (order = 1)

Previous Years' Questions

Q.1 The rate constant of a reaction depends on **(1981)**

- (A) Temperature
- (B) Initial concentration of the reactants
- (C) Time of reaction
- (D) Extent of reaction

Q.2 A catalyst is a substance which **(1983)**

- (A) Increases the equilibrium concentration of the product
- (B) Changes the equilibrium constant of the reaction
- (C) Shortens the time to reach equilibrium
- (D) Supplies energy to the reaction

Q.3 If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process.

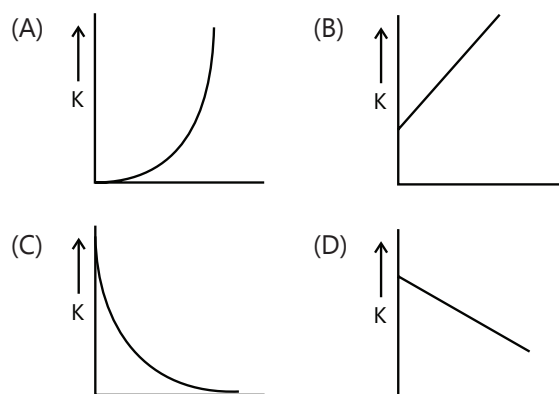
$AB + h\nu \rightarrow AB^*$, the rate of formation of AB^* is directly proportional to **(2001)**

- (A) C
- (B) I
- (C) I^2
- (D) $C.I$

Q.4 Which one of the following statements is incorrect about order of reaction? **(2005)**

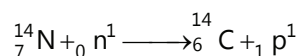
- (A) Order of reaction is determined experimentally
- (B) Order of reaction is equal to sum of the power of concentration terms in differential rate law
- (C) It is not affected with stoichiometric coefficient of the reactants
- (D) Order cannot be fractional

Q.5 Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is **(2010)**



Comprehension (Q.6), (Q.7), (Q.8)

Carbon-14 is used to determine the age of organic material. The procedure is based on the formation of ^{14}C by neutron capture in the upper atmosphere.



^{14}C is absorbed by living organisms during photosynthesis. The ^{14}C content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ^{14}C in the dead being, falls due to the decay which C-14 undergoes $^{14}_6\text{C} \longrightarrow ^{14}_7\text{N} + \beta^-$

The half-life period of ^{14}C is 5770 yr.

The decay constant (λ) can be calculated by using the following formula

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

The comparison of the β^- activity of the dead matter with that of the carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 yr. The proportion of ^{14}C to ^{12}C in living matter is

1: 10^{12} .

(2006)

Q.6 Which of the following option is correct?

- (A) In living organisms, circulation of ^{14}C from atmosphere is high so the carbon content is constant in organism
- (B) Carbon dating can be used to find out the age of earth crust and rocks
- (C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organisms
- (D) Carbon dating cannot be used to determine concentration of ^{14}C in dead beings.

Q.7 What should be the age of fossil for meaningful determination of its age?

- (A) 6 yr
- (B) 6000 yr
- (C) 60,000 yr
- (D) It can be used to calculate any age

Q.8 A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be T_1 and T_2 at the places respectively then

- (A) The age of fossil will increase at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$
- (B) The age of fossil will decrease at the place where explosion has taken place and $T_1 - T_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$
- (C) The age of fossil will be determined to be the same
- (D) $\frac{T_1}{T_2} = \frac{C_1}{C_2}$

Q.9 The concentration of R in the reaction

$\text{R} \rightarrow \text{P}$ was measured as a function of time and the following data 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 **(2010)**

Q.10 Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 yr. What is the rate constant (in yr^{-1}) for the decay? What fraction would remain after 11540 yr? **(1984)**

Q.11 A first order gas reaction has $A' = 1.5 \times 10^{-6}$ per second at 200°C . If the reaction is allowed to run for 10 h, what percentage of the initial concentration would have change in the product? What is the half-life of this reaction? **(1987)**

Q.12 An experiment requires minimum beta activity produced at the rate of 346 beta particles per minute. The half-life period of $^{99}_{42}\text{Mo}$ which is a beta emitter is 66.6 h. Find the minimum amount of $^{99}_{42}\text{Mo}$ required to carry out the experiment in 6.909 h. **(1989)**

Q.13 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 min. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 min? Assume ideal gas behaviour. **(1993)**

Q.14 (a) The rate constant of a reaction is $1.5 \times 10^7 \text{ s}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ s}^{-1}$ at 100°C . Evaluate the Arrhenius parameters A and E_a . **(1998)**

(b) For the reaction, $\text{N}_2\text{O}_5(\text{g}) \rightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

calculate the mole fraction $\text{N}_2\text{O}_5(\text{g})$ decomposed at a constant volume and temperature, if the initial pressure is 600 mm Hg and the pressure at any time is 960 mm Hg. Assume ideal gas behaviour.

Q.15 $2\text{X}(\text{g}) \rightarrow 3\text{Y}(\text{g}) + 2\text{Z}(\text{g})$

Time (in min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate **(2005)**

- (A) Order of reaction
- (B) Rate constant
- (C) Time taken for 75% completion of reaction.
- (D) Total pressure when $p_x = 700$ mm

Q.16 Consider a reaction $a\text{G} + b\text{H} \longrightarrow \text{Products}$. 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 **(2007)**

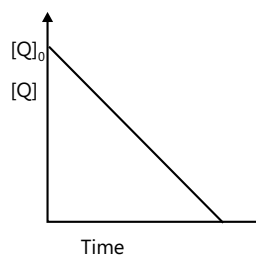
- (A) 0 (B) 1 (C) 2 (D) 3

Q.17 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 **(2008)**

- (A) $0.5 \text{ mol}^{-1} \text{ dm}^3$ (B) 1.0 mol dm^{-3}
(C) 1.5 mol dm^{-3} (D) $2.0 \text{ mol}^{-1} \text{ dm}^3$

Q.18 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 $\log_{10} 2 = 0.3$) **(2013)**

Q.19 In the reaction, $P + Q \longrightarrow R + S$ the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in the figure. The overall order of the reaction is **(2013)**



- (A) 2 (B) 3 (C) 0 (D) 1

Q.20 For the elementary reaction $M \longrightarrow N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is **(2014)**

- (A) 4 (B) 3 (C) 2 (D) 1

Q.21 According to the Arrhenius equation, **(2015)**

- (A) A high activation energy usually implies a fast reaction
(B) Rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy
(C) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant
(D) The pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

PlancEssential Questions

JEE Main/Boards

Exercise 1

- Q.1 Q.4 Q.7 Q.9
Q.12 Q.19 Q.24

Exercise 2

- Q.2 Q.10 Q.16

Previous Years' Questions

- Q.9 Q.14 Q.15

JEE Advanced/Boards

Exercise 1

- Q.7 Q.9 Q.20 Q.36
Q.43 Q.58(e)

Exercise 2

- Q.8 Q.12 Q.28 Q.29
Q.33 Q.34 Q.37

Previous Years' Questions

- Q.12 Q.15

Answer Key

JEE Main/Boards

Exercise 1

- Q.1** (a) 6.25 ; (b) 14.3; (c) 0 %
- Q.2** $2 \times 10^{-2} \text{ min}^{-1}$
- Q.3** $P_1 = 379.55 \text{ mmHg}$, $t^{7/n} = 399.96 \text{ min}$
- Q.4** 0.0207 min^{-1}
- Q.5** $k = 0.022 \text{ hr}^{-1}$
- Q.6** 15.13 week
- Q.7** 20 min
- Q.8** 0.26: 1
- Q.9** (a) $43.46 \text{ kJ mol}^{-1}$ (b) 20.47 hour
- Q.10** % decomposition = 67.21 %
- Q.11** $k = 0.0327 \text{ min}^{-1}$
- Q.12** 0.537
- Q.13** 4.83 mins
- Q.14** 0.0025 m
- Q.15** $E_r = 6 \times 10^4 \text{ J}$; $E_b = 9.3 \times 10^4 \text{ J}$
- Q.16** $a = b = 1$
- Q.17** $E = \frac{E_1 k_1 + E_2 k_2}{k_1 + k_2}$
- Q.18** (a) $\frac{d(D)}{dt} = \frac{k_1 k_3 (A)(B)}{k_2 + k_3}$
 (b) $E_a = E_{a1} + E_{a3} - E_{a2}$ $A = \frac{A_1 A_3}{A_2}$
- Q.20** 0.0805
- Q.21** 161 minutes
- Q.22** $55.33 \text{ kJ mole}^{-1}$
- Q.23** Rate = $K[A][13]^2$ rate will become 8 times
- Q.24** $K_{27} = 3.85 \times 10^{-4} \text{ sec}^{-1}$
 $K_{47} = 11.55 \times 10^{-4} \text{ sec}^{-1}$.
 $E = 43.78 \text{ kJ/mol}$
- Q.25** It is first order kinetics with
 $k = 8.64 \times 10^{-1}$
- Q.26** 2
- Q.27** $E_a = 2.2 \times 10^4$
 $A = 5.42 \times 10^{10}$
- Q.28** (a) $= 1 \times 10^{-2} \text{ mol l}^{-1} \text{ s}^{-1}$
 (b) $= 5.495 \times 10^{-3} \text{ mol l}^{-1} \text{ s}^{-1}$
- Q.29** Rate = $2 \times 10^{-4} \text{ mol dm}^{-3} \text{ min}^{-1} \times 18.12\%$
- Q.30** $k = 0.02231 \text{ min}^{-1}$ $t = 62.07 \text{ min}$

Exercise 2

Single Correct Choice Type

- | | | | | | |
|---------------|---------------|---------------|---------------|---------------|---------------|
| Q.1 B | Q.2 A | Q.3 A | Q.4 D | Q.5 D | Q.6 D |
| Q.7 C | Q.8 B | Q.9 C | Q.10 D | Q.11 D | Q.12 C |
| Q.13 C | Q.14 D | Q.15 B | Q.16 A | Q.17 D | Q.18 C |
| Q.19 B | Q.20 B | Q.21 C | Q.22 D | | |

Previous Years' Questions

- | | | | | | |
|---------------|---------------|---------------|---------------|---------------|---------------|
| Q.1 A | Q.2 C | Q.3 C | Q.4 A | Q.5 D | Q.6 C |
| Q.7 B | Q.8 C | Q.9 A | Q.10 D | Q.11 A | Q.12 D |
| Q.13 D | Q.14 A | Q.15 B | Q.16 B | Q.17 C | Q.18 C |
| Q.19 D | Q.20 B | Q.21 B | Q.22 A | Q.23 D | Q.24 A |

JEE Advanced/Boards

Exercise 1

Q.1 (i) $r = \frac{1}{4} \frac{d[\text{NO}]}{dt} = 9 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$

(ii) $36 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$

(iii) $54 \times 10^{-4} \text{ mol litre}^{-1} \text{ sec}^{-1}$

Q.2 (i) $7.2 \text{ mol litre}^{-1} \text{ min}^{-1}$,

(ii) $7.2 \text{ mol litre}^{-1} \text{ min}^{-1}$

Q.3 (a) $1 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$,

(b) $3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

Q.4 (i) $\frac{dx}{dt} = k [\text{A}][\text{B}]^2$

(ii) Rate increases by 8 times

Q.5 $7.23 \times 10^{-6} \text{ Ms}^{-1}$, $0.012 \text{ atm min}^{-1}$

Q.6 Rate increases by 27 times

Q.7 (a) $0.019 \text{ mol L}^{-1} \text{ s}^{-1}$,

(b) $0.037 \text{ mol L}^{-1} \text{ s}^{-1}$

Q.8 $2k_1 = k_2 = 4k_3$

Q.9 $2.72 \times 10^{18} \text{ sec}$

Q.10 $1/6$

Q.11 (i) 7.2 M , (ii) 10 M

Q.12 $K = 0.01 \text{ M min}^{-1}$

Q.13 0.75 M

Q.14 $6 \times 10^{-9} \text{ sec}$

Q.15 1.2 hr

Q.16 (i) 36 min (ii) 108 min

Q.17 (i) 0.0223 min^{-1} , (ii) 62.17 min

Q.19 924.362 sec

Q.20 Expiry time = 41 months

Q.21 $3.3 \times 10^{-4} \text{ s}^{-1}$

Q.22 $k = \frac{2.303}{t} \log \frac{1}{a}$

Q.23 11.2%

Q.24 15 min

Q.25 (a) Third order, (b) $r = k[\text{NO}]^2[\text{H}_2]$,

(c) $8.85 \times 10^{-3} \text{ M sec}^{-1}$

Q.26 (a) Order w.r.t. $\text{NO} = 2$ and w.r.t. $\text{Cl}_2 = 1$,

(b) $r = K[\text{NO}]^2[\text{Cl}_2]$,

(c) $K = 8 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$,

(d) Rate = $0.256 \text{ mole L}^{-1} \text{ s}^{-1}$

Q.27 (i) First order

(ii) $k = 1.308 \times 10^{-2} \text{ min}^{-1}$

(iii) 73%

Q.28 (i) Zero order, (ii) $K = 5 \text{ Pa/s}$

Q.29 Zero order

Q.30 $k = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$

Q.31 $k = \frac{1}{t} \ln \frac{P_3}{(P_3 - P_2)}$

Q.32 $k = \frac{1}{t} \ln \frac{V_1}{(2V_1 - V_2)}$

Q.33 $k = \frac{1}{t} \ln \frac{4V_3}{5(V_3 - V_2)}$

Q.34 $k = \frac{1}{t} \ln \frac{r_\infty}{(r_\infty - r_1)}$

Q.35 First order

Q.36 (i) $r = K[(\text{CH}_3)_2\text{O}]_2$ $0.000428 \text{ sec}^{-1}$

Q.37 First order

Q.38 966 min

Q.39 (a) 90 mm ,

(b) 47 mm ,

(c) $6.49 \times 10^{-2} \text{ per minutes}$,

(d) 10.677 min .

Q.40 $k_1 = 2.605 \times 10^{-3} \text{ min}^{-1}$

Q.41 (a) first order,

(b) 13.75 minutes ,

(c) $0.716 \text{ } 0.180 \text{ atm}$, 47.69 sec

Q.42 11.45 days

Q.43 0.1 min^{-1}

Q.44 $\frac{1}{e^{(K_1+K_2)t} - 1}$

Q.45 $\frac{[C]}{[A]} = \frac{10}{11} (e^{11x} - 1)$

Q.46 $t = 4 \text{ min}$

Q.47 0379.75 K

Q.48 5 kJ mol^{-1}

Q.49 349.1 K

Q.50 $55.33 \text{ kJ mole}^{-1}$

Q.51 306 K

Q.52 Rate of reaction increases 5.81×10^8 times

Q.53 $10.757 \text{ k cal mol}^{-1}$

Q.54 $t=20.4 \text{ minutes}$ 56. 2000 K

Q.55 $r = K' [\text{NO}]^2 [\text{Br}_2]$

Q.56 $k = k'_2$

Q.57 $r = K[\text{NO}]^2 [\text{H}_2]$, where $K = k_2 \times K_1/k^{-1}$

Q.58 (d) No, (e) mechanism (a) is incorrect

Exercise 2

Single Correct Choice Type

Q.1 B

Q.2 D

Q.3 C

Q.4 D

Q.5 C

Q.6 B

Q.7 C

Q.8 C

Q.9 A

Q.10 A

Q.11 A

Q.12 B

Multiple Correct Choice Type

Q.13 A, D

Q.14 A, B, D

Q.15 A, D

Q.16 C, D

Q.17 A, C, D

Q.18 A, C

Q.19 A, B, C

Comprehension Type

Q.20 C

Q.21 D

Q.22 A

Q.23 C

Q.24 C

Q.25 A

Q.26 B

Q.27 C

Q.28 B

Q.29 D

Q.30 B

Q.31 C

Q.32 C

Q.33 B

Q.34 A

Q.35 C

Q.36 B

Match the Columns

Q.37 $A \rightarrow s; B \rightarrow r; C \rightarrow p; D \rightarrow q$

Q.38 $A \rightarrow p; B \rightarrow q, s; C \rightarrow r, t; D \rightarrow v$

Previous Years' Questions

Q.1 A

Q.2 C

Q.3 D

Q.4 D

Q.5 A

Q.6 A

Q.7 B

Q.8 A

Q.9 0

Q.10 0.25

Q.11 128.33h

Q.12 3.56×10^{-16}

Q.13 0.75 atm

Q.14 $4.15 \times 10^3 \text{ s}^{-1}$, 0.375

Q.15 (a) 1 (b) $693 \times 10^{-3} \text{ min}^{-1}$ (c) 200 min (d) 950 mm

Q.16 D

Q.17 A

Q.18 9

Q.19 D

Q.20 C

Q.21 B, C, D

Solutions

JEE Main/Boards

Exercise 1

Sol 1: (a) $A + B \rightarrow C$

We have, first order in A and 0 order in B.

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^1[B]^0 = \frac{-d[A]}{dt} = -k[A]$$

For first order reaction, we know

$$[A] = [A_0] e^{-kt}$$

We have, at $t = 1$ hour

75% of A reacted

$$[A] = A_0 - 0.75A_0 = \frac{1}{4}A_0$$

$$\frac{1}{4}[A_0] = [A_0] e^{-kt} \Rightarrow k = \ln 4$$

Now $t = 2$ hour,

$$\frac{[A]}{[A_0]} = e^{-2 \times \ln 4} = \frac{1}{16}$$

$$[A] = 6.25\% \text{ of } A_0$$

\therefore 6.25% of A will be left unreacted.

(b) Here, reaction is first order in both A and B

$$\therefore \text{Rate} = \frac{d[A]}{dt} = k[A][B]$$

Since the initial concentration of A and B is the same and they have the same coefficient, their concentration will remain same at any time.

$$\frac{-d[A]}{dt} = k[A]^2$$

$$\Rightarrow \int_{[A_0]}^{[A]} \frac{d[A]}{[A]^2} = \int_0^t -k dt$$

$$\Rightarrow -\frac{1}{[A]} + \frac{1}{[A_0]} = -k(t - 0) = -kt$$

$$\text{At time } t = 1 \text{ hour, } [A] = \frac{[A_0]}{4}$$

$$\therefore -\frac{4}{[A_0]} + \frac{1}{[A_0]} = -k$$

$$\Rightarrow k = \frac{3}{[A_0]}$$

Now, at time $t = 2$ hours,

$$\frac{-1}{[A]} + \frac{1}{[A_0]} = -2 \times \frac{3}{[A_0]} = \frac{-6}{[A_0]}$$

$$\Rightarrow \frac{1}{[A]} = \frac{7}{[A_0]} \Rightarrow \frac{[A]}{[A_0]} = \frac{1}{7}$$

A left is $\frac{100}{7}\%$ or 14.3 %

(c) If the reaction is 0 order

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

$$\Rightarrow \int_{[A_0]}^{[A]} d[A] = \int_0^t k dt$$

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

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

Now, at time $t = 1$ hour

$$[A] = \frac{[A_0]}{4}$$

$$\frac{[A_0]}{4} - [A_0] = -k$$

$$\Rightarrow k = \frac{3}{4}[A_0]$$

We see that, if t or $[A] = 0$

$$t = \frac{[A_0]}{k} = \frac{4}{3} \text{ hours} < 2 \text{ hours}$$

The reactions will be finished before 2 hours and 6 % of A will be left after 2 hours.

Sol 2: $\text{CH}_3\text{CH}_2\text{NO}_2 + \text{OH}^- \rightarrow \text{CH}_3\text{CH}(\text{NO}_2)^- + \text{H}_2\text{O}$

Since this is a first order reaction

$$[A] = [A_0] e^{-kt}$$

Now, we have at time $t = \frac{1}{2}$ minute,

$$[A] = 0.99[A_0]$$

(1 % of nitroethane reacted)

$$\therefore 0.99[A_0] = [A_0] e^{-k \cdot 1/2}$$

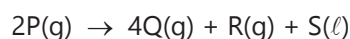
$$\Rightarrow \frac{-k}{2} = \log_e(0.99)$$

$$\Rightarrow \frac{-k}{2} = 0.01 \text{ min.}$$

$$\Rightarrow k = 0.02 \text{ min}^{-1}$$

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

Sol 3: Here, since the volume of liquid is negligible and as the liquid begins to form, pressure due to liquid will always be equal to 32.5 mm Hg. Now, let initial pressure of P(g) be P_0 mm Hg, then according to stoichiometry



at time

t = 0 min	P_0	0	0	0
t = 30 min	$P_0 - 2x$	4x	x	32.5
t = ∞	0	$2P_0$	$\frac{P_0}{2}$	32.5

Now, we are given, $P_t = 317$ mm Hg at $t=30$ min.

$$\therefore P_0 - 2x + 4x + x + 32.5 = 317$$

$$\Rightarrow P_0 + 3x = 284.5 \quad \text{.....(i)}$$

At time, $t = \infty$ (very long time), $P_t = 617$ mm Hg

$$\therefore 2P_0 + \frac{P_0}{2} + 32.5 = 617$$

$$\Rightarrow \frac{5P_0}{2} = 584.5$$

$$\Rightarrow P_0 = 233.8 \text{ mm Hg}$$

Putting this in (i), we get,

$$3x = 284.5 - 233.8$$

$$\Rightarrow x = 16.9$$

Now, since this is first order reaction, we have

$$\text{at } t = 30 \text{ min} \quad a = 233.8 \quad x = 16.9$$

$$k = \frac{2.303}{t} \log \frac{P_0}{P_p} = \frac{2.303}{30} \log \frac{233.8}{233.8 - (2 \times 16.9)}$$

$$\Rightarrow k = 5.2 \times 10^{-3} \text{ min}^{-1}$$

Now, at $t = 75$ min, we have

$$k = \frac{2.303}{t} \log \frac{P_0}{P_p}$$

$$\Rightarrow P_t = P_0 \times 10^{-kt/2.303}$$

$$= 233.8 \times 10^{\frac{-5.2 \times 10^{-3} \times 75}{2.303}}$$

$$P_t = 158.22 \text{ mm Hg}$$

$$\Rightarrow P_0 - 2x = 158.22$$

$$\Rightarrow x = \frac{233.8 - 158.22}{2} = 37.78$$

Now, total pressure at $t = 75$ min

$$P_t = P_0 + 3x + 32.5$$

$$= 233.8 + (3 \times 37.78) + 32.5$$

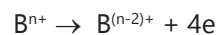
$$P_t = 379.55 \text{ mm Hg}$$

Time fraction, $t_{7/8}$ is time at which $\frac{7}{8}$ th of reaction gets completed, i.e. $P_\Delta = \frac{P_0}{8}$

$$\text{Using rate law, } \frac{P_0}{8} = P_0 e^{-kt} \Rightarrow t = \frac{2.303}{R} \log 8$$

$$t = 399.96 \text{ min.}$$

Sol 4: We have, the reaction as,

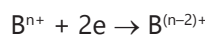


$$\text{At time } t = 0 \quad V_0 \quad 0$$

total time

$$t = 10 \text{ min} \quad V_0 - x \quad x$$

Now, for titration we have



From this, we see that for volume V_0 of B^{n+} , $2V$ volume of titrant is used.

at time $t = 0$, volume of titrant used = 25 mL

$$\Rightarrow 2V_0 = 25 \text{ mL}$$

$$\Rightarrow V_0 = 12.5 \text{ mL}$$

For titration of $B^{(n-1)+}$, we have



i.e. for volume V of $B^{n+} + B^{(n+4)+}$, $5V$ volume of titrant is used.

\therefore At time $t = 10$ min,

Volume of titrant used = 32 mL

$$\Rightarrow 2(V_0 - x) + 5x = 32$$

$$\Rightarrow 2V_0 + 3x = 32$$

$$\Rightarrow 3x = 32 - 25$$

$$\Rightarrow x = \frac{7}{3}$$

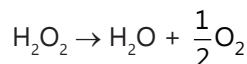
Now, since this is a first order reaction, rate law is

$$k = \frac{2.303}{t} \log \frac{V_0}{V_{B^{n+}}} = \frac{2.303}{10} \log \frac{12.5}{12.5 - x}$$

$$= \frac{2.303}{10} \log \frac{12.5}{12.5 - \frac{7}{3}}; k = 0.0207 \text{ min}^{-1}$$

Sol 5: We have initially, volume strength = 20

According to reaction



1 mole (34g) of H_2O_2 gives $\frac{1}{2}$ moles of O_2 i. e. 11.21 at STP

Now, volume strength is the volume of O_2 given by unit volume of H_2O_2

Let normality of $\text{H}_2\text{O}_2 = N$

$$\text{Then, } N = \frac{\text{weight}}{\text{Eq. weight}}$$

\Rightarrow Weight = 17 N (equivalent weight = 17)

Now, 34 g of H_2O_2 gives 11.21 of O_2

$$\therefore 17 \text{ N g of } \text{H}_2\text{O}_2 \text{ gives } \frac{11.2 \times 17 \text{ N}}{34} \text{ of } \text{O}_2$$

$$\text{Volume strength} = \frac{11.2 \times 17 \text{ N}}{34} = 5.6 \text{ N}$$

Now, initially volume strength = 20

$$\Rightarrow N_0 = \frac{20}{5.6} = 3.75 \text{ N}$$

At time, $t = 6$ hours, let normality be N .

Since, 10 mL of solution be diluted to 100 mL,

$$\text{Now normality} = \frac{N \cdot 10}{100} = 0.1 \text{ N}$$

Now, since this is first order reaction, according to rate law, as N is proportional to number of moles of H_2O_2

$$k = \frac{2.303}{t} \log \frac{N_0}{N} = \frac{2.303}{6} \log \frac{3.75}{3.125}; k = 0.022 \text{ hr}^{-1}$$

Sol 6: We have for oxide film formation.

$$k = \frac{2.303}{6} \log \frac{\tau_{\max}}{\tau_{\max} - \tau}$$

Where, τ_{\max} = maximum thickness of oxide film (at $t \rightarrow \infty$)

τ = thickness at time t

We are given

$$\tau_{\max} = \frac{3.956}{1000} \text{ inch}$$

$$\tau = \frac{1.281}{1000} \text{ inch, at } t = 6 \text{ weeks}$$

$$k = \frac{2.303}{6} \log \frac{3.956}{3.956 - 1.281}$$

$$k = 0.065$$

Now, when, $\tau = \frac{2.481}{1000}$ inch, we have

$$0.065 = \frac{2.303}{t} \log \frac{3.956}{3.956 - 2.481}$$

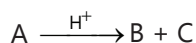
$$\Rightarrow t = \frac{2.303}{0.065} \times 0.49$$

$$t = 15.13 \text{ weeks}$$

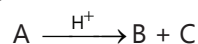
$$t = 15.13 \text{ weeks}$$

$$\text{longer} = 9.13 \text{ weeks}$$

Sol 7: We have,



Let initially x moles of A be present



$$\text{At } t = 0 \quad x \quad 0 \quad 0$$

$$\text{At } t = \infty \quad 0 \quad x \quad x$$

We know optical rotation of B and C are 40° and -80° respectively at completion,

total optical rotation

$$\Rightarrow 40x - 80x = -10$$

$$\Rightarrow x = 0.5$$

Now, optical rotation at $t = 0$

$$\Rightarrow 60 \times 0.5 = 30^\circ$$

Using first order rate law,

$$k = \frac{2.303}{t} \log \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$$

θ_0 = initial optical rotation

$$\text{or } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2.303} + \frac{1}{\log \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}}$$

Putting values

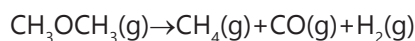
$$t_{1/2} = \frac{0.693}{2.303} + \frac{20}{\log \frac{(30 - 1 - 20)}{(5 - 1 - 20)}}$$

since $\theta = 5^\circ$

$$\text{at } t = 20 \text{ min} = \frac{0.3 \times 20}{\log 2}$$

$$t_{1/2} = 20 \text{ min}$$

Sol 8: Since, volume and temperature is constant, we take $P \propto n$



at

$$\begin{array}{ccccccc} t = 0 & & 0.4 & & 0 & & 0 & & 0 \\ t = 4.5\text{hr.} & & 0.4-x & & x & & x & & x \end{array}$$

We are given $k = 4.78 \times 10^{-3}$, since unit is min^{-1} . It is a first order reaction and

$$\begin{aligned} P_A &= P_0 e^{-kt} \\ &= 0.4 \times e^{-(4.78 \times 10^{-3} \times 4.5 \times 60)} \end{aligned}$$

$$\Rightarrow P_A = 0.11$$

$$0.4 - x = 0.11$$

$$\Rightarrow x = 0.29$$

Now, at $t = 4.5\text{hr}$, mean molecular mass, M_2

$$\begin{aligned} &= \frac{(P_0 - x)M_{\text{CH}_3\text{OCH}_3} + xM_{\text{CH}_4} + M_{\text{CO}} + x + M_0 + xM_{\text{H}_2}}{P + x + x + x + x} \\ &= \frac{0.11 \times 46 + 0.29 \times 16 + 0.29 \times 28 + 0.29 \times 2}{0.11 + 0.29 + 0.29 + 0.29} = 18.77 \end{aligned}$$

at $t = 0$, molecular mass

$$M_1 = M_{\text{CH}_3\text{OCH}_3} = 46$$

$$P_t = 0.4 - x + 3x = 0.4 + 2x = 0.98$$

According to Graham's law

$$\text{Rate of diffusion} \propto \frac{P}{\sqrt{M}}$$

$$\frac{D_0}{D_t} = \frac{P_0}{P_t} \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{18.77}{46}} \times \frac{0.4}{0.98}$$

$$\frac{D_0}{D_t} = 0.26$$

Sol 9: (a) According to Arrhenius equation, we have

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

Here, we have

$$T_1 = (273 + 20)\text{K} = 293\text{K}$$

$$T_2 = (273 + 3)\text{K} = 276\text{K}$$

$$k_2 = \frac{k_1}{3}$$

Putting values

$$\log \frac{1}{3} = \frac{E_A}{2.303 \times 8.314} \left(\frac{1}{293} - \frac{1}{276} \right)$$

$$\therefore E_A = \frac{+(\log 3 \times 2.303 \times 8.314 \times 293 \times 276)}{17}$$

$$E_A = 43.46 \text{ kJ/mol}$$

(b) When $T_2 = (273 + 40)\text{K} = 313\text{K}$,

$$\text{We have, } \log \frac{k_2}{k_1} = \frac{43.460}{303 \times 8.314} \left(\frac{1}{293} - \frac{1}{313} \right)$$

$$\Rightarrow k_2 = 3312 k_1$$

$$\text{Further, as } k \propto \frac{1}{t}$$

$$\therefore \frac{t_2}{t_1} = \frac{k_1}{k_2} \Rightarrow t_2 = \frac{6.4}{3.12}$$

$$t_2 = 20.47 \text{ hours}$$

Sol 10: We have, according to Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E_A}{2.303R} \left(\frac{1}{t_1} - \frac{1}{t_2} \right)$$

Here,

$$E_A = 70 \text{ kJ mol}^{-1}$$

$$t_1 = (273 + 25)\text{K} = 298\text{K}$$

$$t_2 = (273 + 40)\text{K} = 313\text{K}$$

Putting values

$$\log \frac{k_2}{k_1} = \frac{70000}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{313} \right)$$

$$\Rightarrow k_2 = 3.87 k_1$$

Now, equation



According to rate law

$$[A] = [A_0] e^{-kt}$$

At $T = 298\text{K}$, $k = k_1$, ... $t = 20\text{min}$,

$$[A] = \frac{3[A_0]}{4}$$

$$\therefore \frac{3}{4} = e^{-k_1 \cdot 20}$$

$$\Rightarrow k_1 = 0.014 \text{ min}^{-1}$$

$$\therefore k_2 = 3.87 k_1 = 0.055 \text{ min}^{-1}$$

Now, at $T = 313\text{K}$, $t = 20\text{min}$,

$$k = 0.055 \text{ min}^{-1}$$

$$[A] = [A_0] e^{-0.055 \times 20}$$

$$[A] = 0.3279 [A_0]$$

$\therefore 67.21\%$ of A got decomposed.

Sol 11: We have, according to Arrhenius equation

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

For, $A \rightarrow \text{products}$

If k at 310 K is taken to be k

Then, k at 300 K is $\frac{k}{2}$

Putting this in equation, we get

$$\log 2 = \frac{E_A}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{310} \right]$$

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

$$E_A = 53.67 \text{ kJ/mol}$$

Now we are also given at $T = 310 \text{ K}$,

$$t_{1/2} = 30 \text{ min}$$

$$\therefore k \text{ at } 310 \text{ K} = \frac{0.693}{t_{1/2}} = 0.0231 \text{ min}^{-1}$$

At 310 K, for (ii) $B \rightarrow \text{products}$

$$k = 211 \text{ for (i)}$$

$$= 0.0462 \text{ min}^{-1}$$

Further, for (ii)

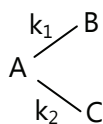
$$E_A = \frac{(E_A)}{2} = 26.802 \text{ kJ/mol}$$

Therefore, using Arrhenius equation, we get

$$\log \frac{k}{0.0769} = \frac{268.02}{2.303 \times 8.314} \left(\frac{1}{310} - \frac{1}{300} \right)$$

$$k = 0.0327 \text{ min}^{-1}$$

Sol 12: We are given,



Here,

$$\frac{k_1}{k_2} = \frac{1}{9}, k = 1.3 \times 10^{-5} \text{ s}^{-1}$$

Now, both are first order reactions

$$\therefore \frac{d[A]}{dt} = -(k_1 + k_2)[A]$$

$$\Rightarrow [A] = [A_0] e^{-(k_1 + k_2)t}$$

Now, for $A \rightarrow C$,

$$\text{We have, } \frac{d[C]}{dt} = k_2[A]$$

$$\Rightarrow \frac{d[C]}{dt} = k_2[A_0] e^{-(k_1 + k_2)t}$$

$$\Rightarrow \int_0^t d[C] = k_2[A_0] \int_0^t e^{-(k_1 + k_2)t} dt$$

$$[C] = \frac{k_2[A_0]}{k_1 + k_2} (1 - e^{-(k_1 + k_2)t})$$

$$\frac{[C]}{[A]} = \frac{k_2[A_0](1 - e^{-(k_1 + k_2)t})}{(k_1 + k_2) \cdot [A_0] e^{-(k_1 + k_2)t}}$$

$$= \frac{k_2}{k_1 + k_2} (e^{(k_1 + k_2)t} - 1)$$

$$\text{Now, we have } k_1 = 1.3 \times 10^{-5} \text{ s}^{-1},$$

$$k_2 = 9k_1 = 1.17 \times 10^{-7} \text{ s}^{-1}$$

$$\text{Time, } t = 1 \text{ hour} = 3600 \text{ s}$$

Putting values,

$$\frac{[C]}{[A]} = \frac{9}{10} (e^{1.3 \times 10^{-4} \times 3600} - 1)$$

$$\frac{[C]}{[A]} = 0.537$$

Sol 13: As $\text{Cis-(en)}_2(\text{OH})_2^+ \xrightleftharpoons[k_b]{k_f} \text{trans-Cr(en)}_2(\text{OH})_2^+$

We have,

$$\text{Eq. constant} = \frac{k_f}{k_b} = 0.16$$

$$\text{and } k_f = k_1 = 3.3 \times 10^{-1} \text{ s}^{-1}$$

$$\Rightarrow k_b = \frac{k_f}{0.16} = 2.0625 \times 10^{-4} \text{ s}^{-1}$$

Now using formula for eq. reactions.

$$\ln \left(\frac{x_{\text{eq}}}{x_{\text{eq}} - x} \right) = (k_f + k_b) t$$

$$\text{We have to find } t \text{ for which } x = \frac{x_{\text{eq}}}{q}$$

$$\ln \left(\frac{x_{\text{eq}}}{x_{\text{eq}} - \frac{x_{\text{eq}}}{2}} \right) = (3.3 \times 10^{-4} + 2.0625 \times 10^{-3}) t$$

$$\Rightarrow t = \frac{\ln 2}{2.3925 \times 10^{-3}} \text{ s}$$

$$t = 289.71 \text{ s} \Rightarrow t = 4.83 \text{ min}$$

Sol 14: We have, $A \xrightleftharpoons[k_2]{k_1} B$

Also, we know, $k_{eq} = \frac{k_1}{k_2} = \frac{[B]_{eq}}{[A]_{eq}}$

$$\Rightarrow \frac{k_1}{k_2} = 4, k_1 = 10^{-2} \text{ s}^{-1}$$

$$\Rightarrow k_2 = \frac{10^{-2}}{4} = 2.5 \times 10^{-3} \text{ s}^{-1}$$

Now at eq., $[A] = [A_0] - x_{eq}$

$$[B] = x_{eq}$$

$$\text{Then, } \frac{x_{eq}}{[A]e^{-x_{eq}}} = 4$$

We are given $[A]_0 = 0.01 \text{ mole L}^{-1}$

$$\frac{x_{eq}}{0.01x_{eq}} = 1$$

$$5x_{eq} = 0 + 60.07$$

$$x_{eq} = 0.008 \text{ mole L}^{-1}$$

Now, using equilibrium first order formula,

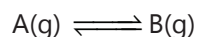
$$\ln\left(\frac{x_{eq}}{x_{eq} - x}\right) = (k_1 + k_2)t$$

At $t = 30 \text{ s}$,

$$\ln\left(\frac{0.008}{0.008 - x}\right) = (12.5 \times 10^{-3}) \times 30 = -0.375$$

$$x = 0.0025 \text{ mole L}^{-1}$$

Sol 15: We have,



For forward reaction, we have

$$\Delta H = \Delta E = -33 \text{ kJ/mol}$$

We know,

$$\ln k = \frac{-\Delta H^\circ}{RT} \text{ (since } \Delta S \approx 0)$$

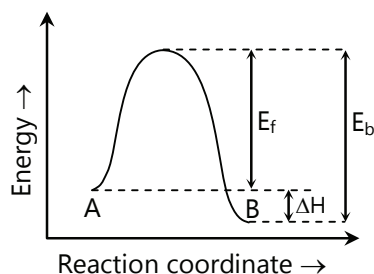
with $T = 300 \text{ K}$, $\Delta H = 33 \text{ kJ/mol}$

we get, $k = 5.57 \times 10^5$

Now, we are given

$$\frac{E_f}{E_b} = \frac{20}{31}$$

Now, we have for this transformation



We see that

$$E_b = E_f + |\Delta H|$$

$$\Rightarrow \text{But } E_f = \frac{20E_b}{31}$$

$$\therefore E_b = \frac{20E_b}{31} + 33 \Rightarrow \frac{11E_b}{31} = 33$$

$$\Rightarrow E_b = 63 \text{ kJ/mol}$$

$$E_f = E_b - 33$$

$$E_f = 30 \text{ kJ/mol}$$

Sol 16: We have rate $k'[\text{complex}]^a$, $k' = k[H^+]^b$

Let's assume that this is Pseudo first order reaction, that is

$$a = 1$$

$$\text{Then, we have } t_{1/2} = \frac{0.693}{k'},$$

$$t_{3/4} = \frac{1.386}{k'}$$

We note that, here $t_{3/4} = 2 \cdot t_{1/2}$

which is true for given data also

Now, when, $[H^+] = 0.01$

$$t_{1/2} = 1 = \frac{0.693}{k'} = \frac{0.693}{k[H^+]^b} \Rightarrow (0.01)^b = \frac{0.693}{k}$$

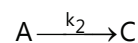
When $[H^+] = 0.02$

$$(0.02)^b = \frac{0.693}{k \cdot t_{1/2}} = \frac{1.386}{k}$$

These both will be satisfied for $b = 1$.

\therefore Taking $a = b = 1$, all the given data can be verified and there are no contradictions

$$\therefore a = b = 1$$



We have, k for disappearance of A, $-\frac{d[A]}{dt} = (k_1 + k_2)t$

$$\therefore k = k_1 + k_2$$

Using Arrhenius equation,

$$Ae^{\frac{-E}{RT}} = A_1 e^{\frac{-E_1}{RT}} + A_2 e^{\frac{-E_2}{RT}}$$

A = Pre exponential constant

Differentiating with respect to $\frac{1}{T}$, we get

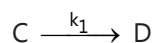
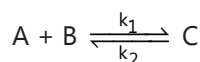
$$\frac{-AE}{R} e^{\frac{-E}{RT}} = \frac{-A_1 E_1}{R} e^{\frac{-E_1}{RT}} + \frac{-A_2 E_2}{R} e^{\frac{-E_2}{RT}}$$

$$\Rightarrow Ek = E_1 k_1 + E_2 k_2$$

$$\Rightarrow E = \frac{E_1 k_1 + E_2 k_2}{k}$$

$$\Rightarrow E = \frac{E_1 k_1 + E_2 k_2}{k_1 + k_2}$$

Sol 18: (a) We have,



Since second step is RDS,

$$\text{Rate} = k_3 [C]$$

$$\text{Also, } \frac{d[C]}{dt} = -k_3 [C] + k_2 [A][B] - k_2 [C]$$

$$\text{Now, at steady state, } \frac{d[C]}{dt} = 0 \Rightarrow [C] = \frac{k_1 [A][B]}{k_3 + k_2}$$

$$\therefore \text{Rate} = \frac{k_1 k_3 [A][B]}{k_3 + k_2}$$

(b) If $k_2 \gg k_3$, then $k_2 + k_3 \approx k_2$

$$\text{Then, Rate} = \frac{k_1 k_3}{k_2} [A][B]$$

Using Arrhenius equation,

$$k = A e^{\frac{-E_a}{RT}}$$

$$k = \frac{A_1 e^{\frac{E_{a1}}{RT}} A_3 e^{\frac{E_{a3}}{RT}}}{A_2 e^{\frac{E_{a2}}{RT}}} = \frac{A_1 A_3}{A_2} e^{\frac{-(E_{a1} + E_{a3} - E_{a2})}{RT}}$$

$$\text{Comparing with } k = A e^{\frac{-E_a}{RT}}$$

$$A = \frac{A_1 A_3}{A_2}$$

$$E_a = E_{a1} + E_{a3} - E_{a2}$$

Sol 19 We have,

$$\text{Rate, } R = k_3 [\text{COCl}] [\text{Cl}_2]$$

(\because (iii) is slowest step (RDS))

Also, from equilibrium of (ii),

$$\frac{k_2}{k_{-2}} = \frac{[\text{COCl}]}{[\text{CO}][\text{Cl}]}$$

And from equilibrium of (i),

$$\frac{k_1}{k_{-1}} = \frac{[\text{Cl}]^2}{[\text{Cl}_2]}$$

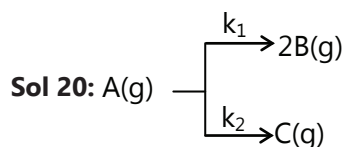
$$[\text{Cl}] = \left(\frac{k_1}{k_{-1}} \right)^{1/2} ([\text{Cl}_2])^{1/2}$$

Putting these values back in rate formula, we get

$$\text{Rate} = k_3 \frac{k_2}{k_{-2}} [\text{CO}] \left(\frac{k_1}{k_{-1}} \right)^{1/2} ([\text{Cl}_2])^{1/2} [\text{Cl}]$$

$$\frac{d[\text{COCl}_2]}{dt} = k_3 \frac{k_2}{k_{-2}} \frac{k_1}{k_{-1}} [\text{CO}][\text{Cl}_2]^{3/2} = k [\text{CO}][\text{Cl}_2]^{3/2}$$

$$k = k_3 \cdot \frac{k_2}{k_{-2}} \left(\frac{k_1}{k_{-1}} \right)^{1/2}$$



We have,

$$\text{Rate} = \frac{-d[A]}{dt} = -(k_1 + k_2)[A]$$

$$[A] = [A]_0 e^{-kt}; k = k_1 + k_2$$

$$\text{Further, Rate} = \frac{1}{2} \frac{d[B]}{dt} = k_1 [A]$$

Putting value of [A] and integrating

$$[B] = \frac{2k_1 [A]_0}{k_1 + k_2} (1 - e^{-kt})$$

$$\text{Similarly, } [C] = \frac{k_2 [A]_0}{k_1 + k_2} (1 - e^{-kt})$$

Now, we are given $[A]_0 = 1 \text{ atm}$

At $t \rightarrow \infty$, $P_t = 1.5 \text{ atm}$

Putting values and taking $t = \infty$, we get

$$\frac{2k_1}{k_1 + k_2} + \frac{k_2}{k_1 + k_2} = 1.5$$

$$\Rightarrow 2k_1 + k_2 = 1.5k_1 + 1.5k_2$$

$$\Rightarrow k_1 = k_2 = \frac{k}{2}$$

Now, taken at $t = 10s$, $P_t = 1.4 \text{ atm}$

$$\therefore [A]_0 e^{-k \cdot 10} = \frac{k[A]_0}{k} (1 - e^{-k \cdot 10})$$

$$\frac{k[A]_0}{2k} (1 - e^{-k \cdot 10}) = 1.7$$

$$[A]_0 = 1,$$

$$\therefore e^{-10R} + 1 - e^{-10R} + \frac{1}{2} - \frac{e^{-10k}}{2} = 1.4$$

$$\Rightarrow e^{-10R} = 0.2$$

$$\Rightarrow k = 0.16$$

$$\Rightarrow k_1 = k_2 = \frac{k}{2} = 0.08$$

Sol 21: For 50% completion, time taken

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

$$\Rightarrow k = \frac{0.693}{69.3} = 0.01 \text{ min}^{-1}$$

Now, for 80%, $[A] = 0.2[A]_0$

$$\text{Using } [A] = [A]_0 e^{-RT} \Rightarrow 0.2 = e^{-RT}$$

$$\Rightarrow t = \frac{\ln 5}{0.01}$$

$$t = 161 \text{ min}$$

Sol 22: We have, from Arrhenius equation,

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

$$\text{Now, } \frac{k_2}{k_1} = 4, T_1 = 27^\circ\text{C} = 300 \text{ K}$$

$$T_2 = 47^\circ\text{C} = 320 \text{ K}$$

Putting values, we find

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{320} \right]$$

$$\Rightarrow E_a = \frac{2 \log 2 \times 320 \times 300 \times 2.303 \times 8.314}{20}$$

$$E_a = 55.33 \text{ kJ mol}^{-1}$$

Sol 23: $2A + B + C \rightarrow D + 2E$

(i) Since, this is first order w. r. t. A, second order w. r. t. B, and 0 order w. r. t. C.

$$\text{Rate law} = k[A][B]^2[C]^0$$

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

$$(ii) \text{ Now rate, } R' = k[2A][2B]^2 = 8k[A][B]^2 = 8k$$

\therefore Rate becomes 8 times

Sol 24: We know, for first order reaction

$$k = \frac{2.303}{30} \log \frac{[A]_0}{[A]_t}$$

At $T = 27^\circ\text{C} = 300 \text{ K}$, at $t = 30 \text{ min}$, 50% of reaction gets completed, i. e. $[A]_t = 0.5[A]_0$

$$k = \frac{2.303}{30} \log 2$$

$$k = 0.0231 \text{ min}^{-1} = 3.85 \times 10^{-4} \text{ s}^{-1}$$

At $T = 47^\circ\text{C} = 320 \text{ K}$, time taken for 50% completion is 10 min.

$$\therefore k = \frac{2.303}{10} \log 2$$

$$k = 0.0693 \text{ min}^{-1} = 11.55 \times 10^{-4} \text{ s}^{-1}$$

Now, by Arrhenius equation

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

$$\text{At } T = 300 \text{ K}, k = 0.0231 \text{ min}^{-1}$$

$$T = 320 \text{ K}, k = 0.0693 \text{ min}^{-1}$$

Putting values

$$\log \frac{0.0693}{0.0231} = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{300} - \frac{1}{320} \right)$$

$$E_a = 43.78 \text{ kJ/mol}$$

Sol 25: Firstly, we assume that reaction is first order and see if the data is consistent.

For first order reaction, we have

$$k = \frac{2.303}{t} \log \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty}$$

At time, $t = 10 \text{ min}$,

$$k = \frac{2.303}{t} \log \frac{32.4 - (-11.1)}{28.8 - (-11.1)}$$

$$k = 8.14 \times 10^{-3} \text{ min}^{-1}$$

At time, $t = 20 \text{ min}$

$$k = \frac{2.303}{t} \log \frac{(32.4 + 11.1)}{25.5 - (-11)}$$

$$k = 8.64 \times 10^{-3} \text{ min}^{-1}$$

At time, $t = 30 \text{ min}$

$$k = \frac{2.303}{t} \log \frac{32.4 - (11.1)}{22.4 - (-11)} = 8.70 \times 10^{-3} \text{ min}^{-1}$$

At $t = 40 \text{ min}$,

$$k = \frac{2.303}{40} \log \frac{32.4 - (11.1)}{19.6 - (-11.1)} = 8.71 \times 10^{-3} \text{ min}^{-1}$$

We see that all values of k are pretty close to each other,

\therefore The reaction is first order.

Sol 26: We know, for n th order reaction $t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$

Here as $[A]_0$ is doubled, $t_{1/2}$ gets halved,

$$\therefore t_{1/2} \propto \frac{1}{[A]_0}$$

$$\text{Or } n - 1 = 1$$

$$\Rightarrow n = 2$$

Hence, second order reaction.

Sol 27: We have, by Arrhenius equation

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

Now, given data,

$$\text{at } t = 50^\circ\text{C} = 323 \text{ K},$$

$$k = 1.5 \times 10^{+7} \text{ sec}^{-1}.$$

$$\text{at } T = 100^\circ\text{C} = 373 \text{ K},$$

$$k = 4.5 \times 10^7 \text{ sec}^{-1}$$

Filling the data,

$$\log 3 = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{323} - \frac{1}{373} \right)$$

$$E_a = A e^{\frac{-E_a}{RT}}$$

$$E_a = 2.2 \times 10^7 \text{ J mol}^{-1}$$

$$\text{Now, } k = A e^{\frac{-E_a}{RT}}$$

$$\Rightarrow A = k e^{\frac{+E_a}{RT}} = 1.5 \times 10^7 e^{\frac{2.2 \times 10^7}{8.214 \times 323}}$$

$$A = 5.42 \times 10^{10} \text{ s}^{-1}$$

Sol 28: Rate = $k[A]$

(i) Initial rate = $k[A]_0$

$$= 1.8 \times 10^{-2} \times 0.1$$

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

(ii) After 60 sec (1 min),

$$\text{Rate} = k[A]_1$$

$$= k[A]_0 e^{-k \times 60}$$

$$= 5.495 \times 10^{-3} \text{ mol sec}^{-1} \text{ L}^{-1}$$

Sol 29: Since, unit of rate constant is min^{-1} , it is first order reaction.

$$\text{Initial rate} = k[A]_0 = 10^{-3} \times 0.2 = 2 \times 10^{-4} \text{ mol min}^{-1} \text{ dm}^{-3}$$

After 200 minutes,

$$[A] = [A]_0 e^{-10^{-3} \times 200} = 0.8187[A]_0$$

\therefore 18.12 % of reactant converted into product.

Sol 30: (i) At time, $t = 10 \text{ min}$, $[A] = 0.8 [A]_0$

$$\therefore 0.8[A]_0 = [A]_0 e^{-10k}$$

$$\Rightarrow k = 0.022 \text{ min}^{-1}$$

(ii) When 75% reaction is completed,

$$[A] = \frac{1}{4} [A]_0,$$

$$\therefore \frac{1}{4} [A]_0 = [A]_0 e^{-0.022t}$$

$$\Rightarrow t = 63.01 \text{ min}.$$

Exercise 2

Sol 1: (B) From the table, we see that when (A) is doubled, rate get becomes 4 times, keeping (B) constant

$$\therefore \text{Rate} \propto (A)^2$$

Also, when (B) is doubled, keeping (A) doubled.

Rate becomes 2 times

$$\therefore \text{Rate} \propto (B)$$

$$\therefore \text{Rate} = k(A)^2(B)$$

Sol 2: (A) Rate, $r_i = k(A)^n(B)^m$

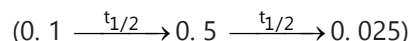
$$r_f = k[2A]^n \left[\frac{B}{2} \right]^m = \frac{k 2^n}{2^m} [A]^n [B]^m$$

$$\frac{r_f}{r_i} = 2^{(n-m)}$$

Sol 3: (A) We have $t_{1/2} = 15 \text{ min}$ ($0.8 \text{ M} \rightarrow 0.4 \text{ M}$)

Now, for 0.1 M to 0.025 M ,

$$t = 2 \times t_{1/2} = 30 \text{ min}$$



Sol 4: (D) Only statement (D) is correct as k is constant at a given temperature.

(A) and (B) are correct for first order reaction. (C) is wrong as

$$\frac{d[C]}{dt} = -\frac{1}{2} \frac{d[A]}{dt} \left(\text{not } 2 \frac{d[A]}{dt} \right)$$

Sol 5: (D) For a first order reaction,

$$[A] = [A]_0 e^{-kt}$$

$$\text{When, } [A] = \frac{3}{4} [A]_0, t = t_{3/4}$$

$$\Rightarrow \frac{3}{4} = e^{-k \cdot t_{3/4}}$$

$$\Rightarrow t_{3/4} = \frac{0.29}{k}$$

Sol 6: (D) rate $\propto [O]^2$

\therefore When $[(O)]$ is doubled, rate becomes 4 times.

Sol 7: (C) $A + 3B \rightarrow P$

$$\Delta H = -2x \text{ kJ/mole of A} \quad \dots(i)$$



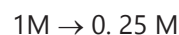
$$\Delta H = -x \text{ kJ/mole of M} \quad \dots(ii)$$

We see that, if these reactions are carried simultaneously energy released from (i) and energy absorbed is (ii) counter each other further, $\Delta H = 2OH$, rate of second reaction will be double of that of (i)

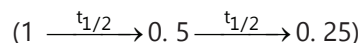
$$\text{Now, rate of first reaction} = \frac{-1}{3} \frac{d[B]}{dt} = \frac{y}{3}$$

$$\text{Rate of second reaction} = \frac{2y}{3} = \frac{1}{2} \frac{d[Q]}{dt} \Rightarrow \frac{d[Q]}{dt} = \frac{4}{3} y$$

Sol 8: (B) We have $t = 138.6 \text{ min}$ for



$$\text{i.e., } 2t_{1/2} = 138.6 = \frac{2 \times 0.693}{k}$$



$$\Rightarrow k = 0.01$$

When $[A] = 0.1$,

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

$$= 0.01 \times 0.1 \text{ M min}^{-1}$$

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

Sol 9: (C) For zero order reaction, rate is always constant.

$$\text{i. e. rate} = 10^{-2} \text{ M min}^{-1}$$



$$t = 0 \quad 0.1$$

$$t = 1 \quad 0.1-x \quad 2x$$

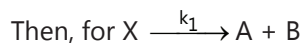
$$\frac{1}{2} \frac{d[B]}{dt} = 10^{-2}$$

$$[B] = 0.02 t$$

$$\text{At } t = 60 \text{ sec} = 1 \text{ minute}$$

$$[B] = 0.02 \text{ M}$$

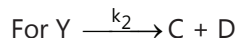
Sol 10: (D) Let time be t



50% reaction gets completed at time t

$$\Rightarrow \frac{1}{2} [X]_0 = [X]_0 e^{-k_1 t}$$

$$k_1 = \frac{\ln 2}{t}$$



96 % of reaction gets completed at time t .

$$\therefore 0.04[Y]_0 = [Y]_0 e^{-k_2 t}$$

$$k_2 = \frac{\ln 25}{t}$$

$$\frac{k_2}{k_1} = \frac{\ln 25}{\ln 2} = 4.65$$

Sol 11: (D) We know, for n th order reaction

$$\propto \frac{1}{P_0^{n-1}} \\ \Rightarrow \frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{P_{01}}{P_{02}} \right)^{n-1}$$

Putting values,

$$\frac{950}{235} = \left(\frac{500}{250} \right)^{n-1}$$

$$\Rightarrow n - 1 = \frac{\log 4.04}{\log 2} = 2; \Rightarrow n = 3$$

Sol 12: (C) We have first order reaction

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

$$\text{at } t = 20 \text{ min, } (A)_t = 0.8(A)_0$$

(Since 20% reaction completed)

$$\Rightarrow k = \frac{2.303}{20} \log \frac{5}{4}$$

$$k = 1.11 \times 10^{-2} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = 62.13 \text{ minutes}$$

Sol 13: (C) Rate = $k(A) = k(A)_0 e^{-kt}$

It follows an exponential decay.

Sol 14: (D) $A(g) \rightarrow 2B(g)$

$$\text{We have, } k_{eq} = \frac{[B]^2}{[A]} = \frac{\left(\frac{100}{V}\right)^2}{\frac{10^{-5}}{V}} = \frac{10^4}{10^{-5}} \cdot \frac{1}{10} = 10^8$$

$$10^8 = \frac{k_f}{k_b} = \frac{1.5 \times 10^{-3}}{k_b}$$

$$\Rightarrow k_b = 1.5 \times 10^{-11} \text{ L mol}^{-1} \text{ s}^{-1}$$

Sol 15: (B) $A + B \rightarrow C + D$

$$t = 0 \quad 1 \quad 1 \quad 0 \quad 0$$

$$t = 1 \quad 1-x \quad 1-x \quad x \quad x$$

We have,

$$\text{Rate} = \frac{-d[A]}{dt} = k(A)^{1/2}(B)^{1/2}$$

$$\Rightarrow \frac{-d[A]}{dt} = k(1-x)^{1/2}(1-x)^{1/2}$$

$$\Rightarrow \frac{-d[A]}{dt} = k(1-x)$$

This can be written as,

$$\frac{-d[A]}{dt} = k(A)$$

$$\Rightarrow (A) = (A)_0 e^{-kt}$$

$$\text{when } (A) = 0.25(A)_0$$

$$t = \frac{2 \ln 2}{k} = \frac{2 \times 2.303 \log 2}{2.303 \times 10^{-3}}$$

$$t = 600 \text{ s}$$

Sol 16: (A) We have for first order,

$$(A) = (A)_0 e^{-kt}$$

$$(A)_0 = \frac{0.1}{2} \text{ mol L}^{-1} = 0.05 \text{ mol L}^{-1}$$

$$k = 3.465 \times 10^{-6} \text{ s}^{-1}, t = 200 \text{ s}$$

$$(A) = 0.05 e^{-3.465 \times 10^{-6} \times 200}$$

$$\approx 0.05 \text{ M}$$

Sol 17: (D) R is universal gas constant

k is rate constant

A is pre exponential factor

E_a is activation energy

Sol 18: (C) This is the correct definition.

Sol 19 (B) $k = A e^{-E_0/RT}$; As $T \rightarrow \infty$,

$$k = A = 6 \times 10^{14} \text{ s}^{-1} (\because e^{-E_0/RT} \rightarrow 1)$$

Sol 20: (B) We have, from Arrhenius equation

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

$$\text{Here, at } T_1 = 27^\circ\text{C} = 300 \text{ K}$$

$$k_1 = \frac{0.693}{20} \text{ min}^{-1}$$

$$\text{At } T_2 = 47^\circ\text{C} = 320 \text{ K}$$

$$k_2 = \frac{0.693}{5} \text{ min}^{-1}$$

Putting these values,

$$\log 4 = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{300} - \frac{1}{320} \right)$$

$$\Rightarrow E_a = 55.14 \text{ kJ/mol}$$

Sol 21: (C) We have, $27^\circ\text{C} = 300 \text{ K}$, 3.8×10^{-16} of reactant molecules exist in the activated region.

$$\text{i. e, } N = 3.8 \times 10^{-16} N_0$$

$$\text{Now, } N = N_0 e^{-E_a/RT}$$

$$E_a = RT \log_e \frac{N_0}{N} = 8.314 \times 300 \log_e$$

$$\frac{N_0}{3.8 \times 10^{-16} N_0}$$

$$E_a = 100 \text{ kJ/mol}$$

Sol 22: (D) Since, at 400 K, 0.0001% ($10^{-4}\%$) of collisions are effective only $10^{-4}\%$ of molecules have their energy above activation energy.

$$E_a = 2.303 RT \log \frac{N_0}{N}$$

$$= 2.303 \times 8.314 \times 400 \log \frac{N_0}{10^{-6}N_0}$$

$$= 45.944 \text{ kJ/mol} = 11.05 \text{ k cal/mol}$$

Previous Years' Questions

Sol 1: (A) $\frac{1}{2}A \rightarrow 2B$; $-2 \frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$; $-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$

Sol 2: (C) $\frac{\text{Rate at } 50^\circ\text{C}}{\text{Rate at } T_1^\circ\text{C}} = (2)^{\frac{\Delta T}{T_1}} = (2)^{\frac{50}{10}} = 2^5 = 32 \text{ times}$

Sol 3: (C) $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$;

$t = 2 \times 10^2$, $a = 800$, $a - x = 50$

$$k = \frac{2.303}{2 \times 10^2} \log_{10} \frac{800}{50} = \frac{2.303}{2 \times 10^2} \log_{10} 16$$

$$= \frac{2.303}{2 \times 10^2} \log_{10} 2^4 = \frac{2.303}{2 \times 10^2} \times 4 \times 0.301 = 1.38 \times 10^{-2} \text{ s}^{-1}$$

Sol 4: (A) $2A + B \rightarrow \text{Product}$

When conc. of B is doubled, the half-life did not change, hence reaction is of first order w.r.t. B. When concentration of A is doubled, reaction rate is doubled, hence reaction is of first order w.r.t. A,

Hence, over all order of reaction is $1 + 1 = 2$

So, unit of rate constant $\text{mol}^{-1} \text{ lit s}^{-1}$.

Sol 5: (D) Rate = $k(\text{N}_2\text{O}_5)$

hence 2.4×10^{-5}

$= 3.0 \times 10^{-5}(\text{N}_2\text{O}_5) \text{ or } (\text{N}_2\text{O}_5)$

$= 0.8 \text{ mol l}^{-1}$

Sol 6 (C) In first order reaction for x% completion

$$k = \frac{2.303}{t} \log \left(\frac{100}{100 - x\%} \right)$$

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \left(\frac{100}{100 - 99} \right)$$

$$\frac{0.693}{6.93} = \frac{2.303 \times 2}{t}$$

So, $t = 46.06 \text{ min.}$

Sol 7: (B) Because two molecules are taking part in elementary reaction.

Sol 8: (C) Since $-\frac{dx}{dt} \propto [\text{CO}]^2$ so on doubling the concentration of CO, the rate of reaction will increase by 4 times.

Sol 9: (A) $R = k(A)(B)^2$ order of reaction $= 2 + 1 = 3$

Sol 10: (D) The differential rate law for,



$$-\frac{dc}{dt} = k[\text{NOBr}_2][\text{NO}]$$

We have, $K_c = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$

Provided the first reaction attains equilibrium rapidly.

$$\therefore -\frac{dc}{dt} = k \times K_c \times [\text{NO}]^2[\text{Br}_2] = k[\text{NO}]^2[\text{Br}_2]$$

\therefore The order of the reaction with respect to NO(g) is 2.

Sol 11: (A) For A

Rate = $k[\text{Cl}_2][\text{H}_2\text{S}]$ (By slow step)

For B

Rate = $k[\text{Cl}_2][\text{HS}^-]$

$$k_{\text{eq}} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]}$$

(According to equilibrium)

$$\text{Rate} = k[\text{Cl}_2] \frac{k_{\text{eq}}[\text{H}_2\text{S}]}{[\text{H}^+]}$$

$$\text{Rate} = k.k_{\text{eq}}[\text{Cl}_2] \frac{[\text{H}_2\text{S}]}{[\text{H}^+]}$$

Sol 12: (D) $t_{1/2} = \frac{a}{2k_0}$ (for zero order reaction)

$$k_0 = \frac{a}{2 \times t_{1/2}} = \frac{2}{2 \times 1} = 1$$

$$k_0 = \frac{A_0 - [A]_t}{t} \Rightarrow k_0 = \frac{0.50 - 0.25}{t} = 1$$

$$t = 0.25 \text{ hr.}$$

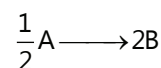
Sol 13: (D) So, $\Delta H_{\text{Reaction}} = E_f - E_b = 80 - 100 = -20$.

Sol 14: (A) For endothermic reaction $\Delta H = +ve$

Then from equation $\Delta H = E_{aF,R} - E_{aB,R}$; $E_{B,R} < E_{F,R}$.

Sol 15: (B) In photochemical reaction, the rate of formation of product is directly proportional to the intensity of absorbed light.

Sol 16: (B)



$$-\frac{d[A]}{dt} = +\frac{d[B]}{2dt}$$

$$-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$$

Sol 17: (C)

$$\therefore \lambda = \frac{0.6932}{t_{1/2}} = \frac{0.6932}{6.93} \text{ min}^{-1}$$

$$\text{Also } t = \frac{2.303}{\lambda} \log \frac{[A_0]}{[A]}$$

$[A_0]$ = initial concentration (amount)

$[A]$ = final concentration (amount)

$$\therefore t = \frac{2.303 \times 6.93}{0.6932} \log \frac{100}{1} = 46.06 \text{ minutes}$$

Sol 18: (C)

For a zero order reaction $k = \frac{x}{t}$ (i)

Where x = amount decomposed

k = zero order rate constant

for a zero order reaction

$$k = \frac{[A]_0}{2t_{1/2}} \text{ (ii)}$$

Since $[A_0] = 2M$, $t_{1/2} = 1\text{hr}$; $k = 1$

\therefore from equation (i)

$$t = \frac{0.25}{1} = 0.25 \text{ hr}$$

Sol 19: (D) Rate equation is to be derived w.r.t slow

Step \therefore from mechanism (A)

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

Sol 20: (B)

Temperature coefficient $\mu = 2$;

$$\mu_{10}^{\frac{\Delta T}{T}} = \frac{k_2}{k_1};$$

$$\mu_{10}^{\frac{50}{10}} = 2^5 = 32 = \frac{k_2}{k_1}$$

$$\text{Therefore } 32k_1 = k_2$$

Sol 21: (B) $k = \frac{2.303}{40} \log \frac{0.1}{0.025};$

$$k = \frac{0.693}{20}$$

For a F.O.R., rate = $\frac{0.693}{20} \times 10^{-2} = 3.47 \times 10^{-4} \text{ M/min.}$

Sol 22: (A) $\log \frac{K_2}{K_1} = \frac{-E_a}{2.030R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$$\frac{K_2}{K_1} = 2; T_2 = 310K \quad T_1 = 300K$$

$$\Rightarrow \log 2 = \frac{-E}{2.303 \times 8.134} \left(\frac{1}{310} - \frac{1}{300} \right)$$

$$\Rightarrow E_a = 53598.6 \text{ J/mol} = 53.6 \text{ KJ/mol}$$

Sol 23: (D)

$$\text{Rate of Reaction} = -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

$$\text{Let rate of Reaction} = k(A)^x(B)^y$$

$$\text{Or, } \frac{d[C]}{dt} = k[A]^x[B]^y$$

Now from table,

$$1.2 \times 10^{-3} = k [0.1]^x [0.1]^y \text{(i)}$$

$$1.2 \times 10^{-3} = k [0.1]^x [0.2]^y \text{(ii)}$$

$$2.4 \times 10^{-3} = k [0.2]^x [0.1]^y \text{(iii)}$$

Dividing equation (i) by (ii)

$$\Rightarrow \frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k[0.1]^x [0.1]^y}{k[0.1]^x [0.2]^y}$$

$$\Rightarrow 1 = \left[\frac{1}{2} \right]^y$$

$$\Rightarrow y = 0$$

Now dividing equation (i) by (iii)

$$\Rightarrow \frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k[0.1]^x [0.1]^y}{k[0.2]^x [0.1]^y}$$

$$\Rightarrow \left[\frac{1}{2} \right]^1 = \left[\frac{1}{2} \right]^y$$

$$\Rightarrow x = 1$$

$$\text{Hence } \frac{d[C]}{dt} = k[A]^1[B]^0$$

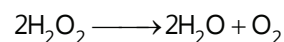
Sol 24: (A) In 50 minutes, concentration of H_2O_2 becomes $\frac{1}{4}$ of initial.

$$\Rightarrow 2 \times t_{1/2} = 50 \text{ minutes}$$

$$\Rightarrow t_{1/2} = 25 \text{ minutes}$$

$$\Rightarrow K = \frac{0.693}{25} \text{ per minutes}$$

$$r_{H_2O_2} = \frac{0.693}{25} \times 0.05 = 1.386 \times 10^{-3}$$



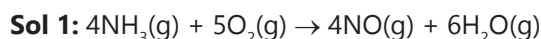
$$r_{O_2} = \frac{1}{2} \times r_{H_2O_2}$$

$$r_{O_2} = 0.693 \times 10^{-3}$$

$$r_{O_2} = 6.93 \times 10^{-4} \text{ mol / minute} \times \text{litre}$$

JEE Advanced/Boards

Exercise 1



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

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

$$(i) \text{ Rate of reaction} = \frac{1}{4} \frac{d[NO]}{dt} = \frac{1}{4} \frac{1.08 \times 10^{-2}}{3}$$

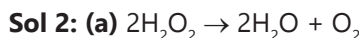
$$= 9 \times 10^{-4} \text{ mol L}^{-1}$$

$$(ii) \frac{-d[NH_3]}{dt} = \left| \frac{+4}{4} \frac{d[NO]}{dt} \right|$$

$$= \frac{+1.08}{3} \times 10^{-2} = 3.6 \times 10^{-3} \text{ mol L}^{-1}$$

$$(iii) \frac{d[H_2O]}{dt} = \frac{6}{4} \frac{d[NO]}{dt}$$

$$= \frac{3}{2} \times \frac{1.08 \times 10^{-2}}{3} = 5.4 \times 10^{-3} \text{ mol L}^{-1}$$

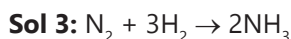


$$\text{We know, } \frac{-1}{2} \frac{d[H_2O_2]}{dt} = \frac{-1}{2} \frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{d[H_2O]}{dt} = 2 \frac{d[O_2]}{dt} = 2 \times 3.6 \text{ M min}^{-1}$$

$$\frac{d[H_2O]}{dt} = 7.2 \text{ M min}^{-1}$$

$$(b) \frac{-d[H_2O_2]}{dt} = \frac{2}{2} \frac{d[H_2O]}{dt} = \frac{-d[H_2O_2]}{dt} = 7.2 \text{ M min}^{-1}$$



$$(a) \frac{d[N_2]}{dt} = \frac{-1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

$$\frac{-d[N_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$

$$= \frac{1}{2} \times 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$(b) \frac{-d[H_2]}{dt} = \frac{3}{2} \times \frac{d[NH_3]}{dt}$$

$$= \frac{3}{2} \times 2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = 3 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

Sol 4: (i) Reaction of first order in A, second order in B and 0 order w. r. t. C.

$$\frac{dx}{dt} = k [A]^1 [B]^2 [C]^0, k = [D]_t$$

$$\Rightarrow \frac{dx}{dt} = k[A] [B]^2$$

(ii) If [A], [B], [C] are all doubled.

$$r_f = k[2A] [2B]^2 = 8k[A] [B]^2 = 8r$$

Rate becomes 8 times

Sol 5: We have, by ideal gas equation

$$PV = nRT \Rightarrow P = \frac{n}{V} RT$$

$$P = CRT$$

$$C = \frac{P}{RT}$$

$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t} = \frac{1}{RT} \frac{\Delta P}{\Delta t}$$

We have, $R = 0.0921 \text{ L atm/mol. K}$

$$T = 27^\circ\text{C} = 300 \text{ K}$$

$$\Delta P = (2 - 1.1) \text{ atm} = 0.9 \text{ atm}$$

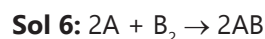
$$\Delta T = 75 \times 605 = 4500 \text{ s}$$

$$\text{Rate of reaction} = \frac{1}{0.0921 \times 300} \times \frac{0.9}{75 \times 60} \text{ Ms}^{-1}$$

$$= 7.23 \times 10^{-6} \text{ Ms}^{-1}$$

Rate of reaction in terms of pressure

$$= \frac{\Delta P}{\Delta t} = \frac{0.9}{75} \text{ atm min}^{-1} = 0.012 \text{ atm min}^{-1}$$



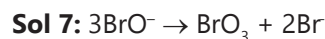
Since, this is an elementary reaction,

$$\text{rate, } r_i = k[A]^2[B_2]$$

If volume of vessel reduced to one-third, $[A]$ and $[B_2]$ becomes 3 times each.

$$\therefore r_f = k[3A]^2[3B_2] = 27k[A]^2[B_2] = 27r_i$$

Hence, rate becomes 27 times.



We have,

$$\begin{aligned} \text{Rate} &= \frac{-1}{3} \frac{\Delta[\text{BrO}^-]}{\Delta t} = \frac{\Delta[\text{BrO}_3]}{\Delta t} \\ &= \frac{1}{2} \frac{\Delta[\text{Br}^-]}{\Delta t} = k[\text{BrO}^-]^2 = \frac{-\Delta[\text{BrO}^-]}{\Delta t} = 3k[\text{BrO}^-]^2 \end{aligned}$$

$$\text{We have, } 3k = 0.056$$

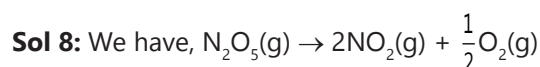
$$k = 0.0186 \text{ mol}^{-1} \text{ s}^{-1}$$

$$(a) \frac{\Delta[\text{BrO}_3]}{\Delta t} = k[\text{BrO}^-]^2 = 0.0186[\text{BrO}^-]^2$$

$$\text{Hence rate constant} = 0.0186 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$(b) \frac{\Delta[\text{Br}^-]}{\Delta t} = 2k[\text{BrO}^-]^2 = 0.037[\text{BrO}^-]^2$$

$$\text{Rate constant} = 0.037 \text{ L mol}^{-1} \text{ s}^{-1}$$

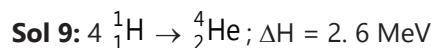


$$\Rightarrow \frac{-d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

$$= \frac{1}{\frac{1}{2}} \frac{d[\text{O}_2]}{dt} = +k[\text{N}_2\text{O}_5]$$

$$\text{Hence, } k_1 = k, k_2 = 2k, k_3 = \frac{k}{2}$$

$$\Rightarrow k_1 = \frac{k_2}{2} = 2k_3 \Rightarrow 2k_1 = k_2 = 4k_3$$



It means 4 atoms of H, eject 26 MeV energy.

Energy released by 1 mole of

$$H = \frac{N_A}{4} = 26 \times 10^6 \times 1.6 \times 10^{-14} \text{ J} = 6.26 \times 10^{11} \text{ J}$$

$$\text{Power output of sun} = 3.9 \times 10^{26} \text{ W} = 3.9 \times 10^{26} \text{ J/s}$$

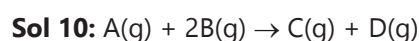
i.e. it radiates $3.9 \times 10^{26} \text{ J}$ in one second.

Number of moles of H required per second

$$= \frac{3.9 \times 10^{26}}{6.26 \times 10^{11}} = 6.23 \times 10^{14}$$

$$\text{Total moles of H on sun} = \frac{1.7 \times 10^{30}}{10^{-3}} = 1.7 \times 10^{33}$$

$$\text{Time taken} = \frac{1.7 \times 10^{33}}{6.23 \times 10^{14}} = 2.72 \times 10^{18} \text{ s}$$



$$t = 0 \quad 0.6 \quad 0.8 \quad 0 \quad 0$$

$$t \quad 0.6-x \quad 0.8-2x \quad x \quad x$$

Since this is elementary reaction

$$\text{Rate, } r = k(B)^2(A)$$

$$\text{Now, } r_i = k(0.6)(0.8)^2 = 0.381 k$$

$$\text{When } P_i = x - 0.2 \text{ atm}$$

$$P_A = 0.6 - x = 0.4 \text{ atm}$$

$$P_B = 0.8 - 2x = 0.8 - 0.4 = 0.4 \text{ atm}$$

$$r_f = k(0.4)(0.4)^2 = 0.064 k$$

$$\frac{r_f}{r_i} = \frac{0.064}{0.384} = \frac{1}{6}$$



$$k = 1.2 \times 10^{-2} \text{ Ms}^{-1}$$

Since unit of rate constant is Ms^{-1} , it is zero order reaction

$$\text{Rate law } [B] = kt$$

$$\text{At } t = 10 \text{ min}$$

$$[B] = 1.2 \times 10^{-2} \times 10 \times 60 \text{ M}$$

$$[B] = 7.2 \text{ M}$$

$$\text{At } t = 20 \text{ min}$$

$$[B] = 1.2 \times 10^{-2} \times 20 \times 60 \text{ M} = 14.4 \text{ M}$$

But, $[A]_0 = 10 \text{ M}$ and $[B]$ cannot be greater than $[A]_0$.
 $\therefore [B] = 14.4 \text{ M}$ implies that reaction has reached completion, i. e.

$$[B]_{\max} = 10 \text{ M}$$

$$[B] = 10 \text{ M}$$

Sol 12: For zero order reaction,

$$[A] = [A]_0 - kt$$

$$\text{At } t = 0, [A] = [A]_0 = 0.1 \text{ M}$$

$$\text{At } t = 1 \text{ min, } [A] = 0.09 \text{ M}$$

$$0.09 = 0.1 - k$$

$$\Rightarrow k = 0.01 \text{ M min}^{-1}$$

$$\begin{aligned} \text{At } t = 2 \text{ min, } [A] &= 0.1 - 0.01 \times 2 \\ &= 0.08 \text{ M, which is the value given.} \end{aligned}$$

$$\therefore k = 0.01 \text{ M min}^{-1}$$

Sol 13: For zero order reaction

$$[A] = [A]_0 - kt$$

We are given,

$$k = 2 \times 10^{-2} \text{ mol L}^{-1} \text{sec}^{-1}$$

$$\text{and at } t = 25 \text{ sec, } (A) = 0.25 \text{ M}$$

$$[A]_0 = [A] + kt$$

$$= 0.25 + 2 \times 10^{-2} \times 25 = 0.75 \text{ M}$$

Sol 14: It is a zero order reaction (\because unit of rate constant is M sec^{-1})

$$[H^+]_0 = \frac{6 \times 10^{-6}}{0.1 \times 10^{-3}} = 6 \times 10^{-2} \text{ M}$$

$$k = 10^7 \text{ mol L}^{-1} \text{sec}^{-1}$$

$$\text{Time taken to disappear} = \frac{[H^+]}{k}$$

$$= \frac{6 \times 10^{-2}}{10^7} \text{ sec} = 6 \times 10^{-9} \text{ sec}$$

Sol 15: Since it is a zero order reaction

$$[A] = [A]_0 - kt$$

$$\text{When } t = 1 \text{ hour, } [A] = \frac{1}{4} [A]_0$$

(\because 75% reacted)

$$\therefore \frac{1}{4} [A]_0 = [A]_0 - k$$

$$\Rightarrow k = \frac{3}{4} [A]_0 \text{ M hr}^{-1}$$

When A is 10% unreacted,

$$[A] = \frac{1}{10} [A]_0$$

$$\therefore \frac{1}{10} [A]_0 = [A]_0 - kt$$

$$\Rightarrow \frac{9}{10} [A]_0 = \frac{3}{4} [A]_0 t$$

$$\Rightarrow t = 1.2 \text{ hr}$$

Sol 16: (i) We know, for first order reaction

$$[A] = [A]_0 e^{-kt}$$

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]}$$

$$\text{At } t = 72 \text{ min, 75\% reaction completed, i. e. } [A] = \frac{1}{4} [A]_0$$

$$\therefore k = \frac{1}{72} \ln 4 = 0.019 \text{ min}^{-1}$$

When reaction is 50% complete,

$$t = t_{1/2} = \frac{\ln 2}{k} = 36 \text{ min}$$

(ii) When reaction is 87.5% complete, $[A] = 0.125 [A]_0$,

$$\therefore t = \frac{1}{k} \ln \frac{1}{0.125}$$

$$t = 108 \text{ min}$$

Sol 17: We have, for first order reaction

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t}$$

(i) At $t = 10 \text{ min}$, reaction is 20% complete, i. e. $[A] = 0.8 [A]_0$

$$k = \frac{1}{10} \ln \frac{[A]_0}{0.8 [A]_0}$$

$$k = 0.0223 \text{ min}^{-1}$$

(ii) When reaction is 75% complete,

$$[A] = \frac{1}{4} [A]_0$$

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t} = \frac{1}{0.0223} \ln \frac{[A]_0}{\frac{1}{4} [A]_0}$$

$$t = 62.17 \text{ min.}$$

Sol 18: Order will be equal to 1.

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t}$$

When reaction is 99.9 % complete,

$$[A]_t = 10^{-3} [A]_0$$

$$t_1 = \frac{1}{k} \ln \frac{[A]_0}{10^{-3} [A]_0} = \frac{3}{k} \ln 10 = \frac{6.909}{k}$$

When reaction is 50% completed, $[A]_t = \frac{[A]_0}{2}$

$$\therefore t_2 = \frac{1}{k} \ln \frac{[A]_0}{0.5[A]_0} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

We see that $t_2 \approx 10t_1$

Sol 19: We have, first order reaction

$$N = N_0 e^{-kt}$$

here, $k = 1.5 \times 10^{-3} \text{ sec}^{-1}$

$$N \propto 1.25 \text{ (wt. } \propto \text{ molar)}$$

$$N \propto 5$$

$$\therefore 1.25 = 5e^{-1.5 \times 10^{-3} t}$$

$$\Rightarrow t = \frac{1}{1.5 \times 10^{-3}} \ln \frac{5}{1.25}$$

$$t = 924.3625$$

Sol 20: We have,

$$[N]_0 = 500$$

At $t = 20$ months, $[N]_t = 420$,

Using first order to rate law,

$$k = \frac{1}{t} \ln \frac{[N]_0}{[N]_t}$$

$$k = 8.717 \times 10^{-3} \text{ month}^{-1}$$

The drug will be ineffective (will expire) when it has decomposed 30%, i. e. $[N] = 0.7 [N]_0$.

$$\therefore t = \frac{1}{k} \log \frac{[N]_0}{[N]_t} = \frac{1}{8.717 \times 10^{-3}} \log \frac{[N]_0}{0.7[N]_0}$$

$$t \approx 41 \text{ months}$$

Sol 21: For first order reaction

$$k = \frac{1}{t} \log \frac{[A]_0}{[A]_t}$$

We are given, 2% of virus gets inactivated every minute at the beginning, i. e., at $t = 1$ min, $[A]_t = 0.98[A]_0$

$$k = \frac{1}{1} \log \frac{[A]_0}{0.98[A]_0}$$

$$k = 0.02 \text{ min}^{-1}$$

$$k = 3.3 \times 10^{-4} \text{ sec}^{-1}.$$

Sol 22: If we assume the reaction to be of first order, then, let $[A]_t = \alpha$ and $[A]_0 = C_0$.

$$a = C_0 e^{-kt}$$

At time

$$t = 0, \alpha = C_0$$

$$t = t, \alpha = C_0 e^{-k} = aC_0, a = e^{-k}$$

$$t = 2t, \alpha = C_0 e^{-2k} = a^2 C_0, a = e^{-k}$$

$$t = 3t, \alpha = C_0 e^{-3k} = a^3 C_0, a = e^{-k}$$

Therefore, taking the reaction to be of first order, we found the concentration of A to be of the form given in question. Therefore, the reaction is of first order.

Sol 23: For first order reaction,

$$[\text{SO}_2\text{Cl}_2] = [\text{SO}_2\text{Cl}_2]_0 e^{-kt}$$

$$k = 2.2 \times 10^{-5} \text{ sec}^{-1},$$

$$t = 90 \text{ min} = 5400 \text{ sec}$$

$$\therefore \frac{[\text{SO}_2\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]_0} = e^{-5400 \times 2.2 \times 10^{-5}} = 0.888$$

11.2 % of $[\text{SO}_2\text{Cl}_2]$ decomposed.

$$\text{Sol 24: For A, } k_1 = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{5}$$

Initial concentration = a_0

$$\text{Let } [A]_t = a$$

$$\text{Then, } a = e_0 e^{-k_1 t}$$

$$\text{For B, } k_2 = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{1.5}$$

Initial concentration

$$[B]_0 = \frac{[A]_0}{4} = \frac{a_0}{4}$$

$$[B]_4 = b$$

$$\text{Then, } b = \frac{a_0}{4} e^{-k_2 t}$$

When $a = b$,

$$a_0 e^{-k_1 t} = \frac{a_0}{4} e^{-k_2 t}$$

$$4 = e^{(k_1 - k_2)t}$$

$$\Rightarrow t = \frac{\ln 4}{k_1 - k_2}$$

$$= \frac{\ln 4}{\frac{\ln 2}{5} - \frac{\ln 2}{15}} = \frac{2 \ln 2}{\ln 2 \left(\frac{1}{5} - \frac{1}{15} \right)} = \frac{2 \times 5 \times 15}{10}$$

$t = 15$ min.

Sol 25: From the data, we observe that, when $[H_2]$ is halved, keeping $[NO]$ constant, reaction rate gets halved. So, order w. r. t H_2 is 1.

When $[NO]$ is doubled, keeping $[H_2]$ constant, reaction rate becomes 4 times so, order w. r. t. NO is 2.

$$\text{Rate} = k[NO]^2 [H_2]$$

$$(a) \text{ Order} = 2 + 1 = 3$$

$$(b) \text{ When, } [NO] = 1.5 \times 10^{-4} \text{ M,}$$

$$[H_2] = 4 \times 10^{-3} \text{ M,}$$

$$\text{Rate} = 4.4 \times 10^{-4} \text{ M sec}^{-1}$$

$$\therefore k = \frac{4.4 \times 10^{-4}}{(1.5 \times 10^{-4})^2 \times (4 \times 10^{-3})^2}$$

$$\text{When } [NO] = 1.1 \times 10^{-3} \text{ M,}$$

$$[H_2] = 1.5 \times 10^{-3} \text{ M}$$

$$(c) \text{ Rate} = 4.88 \times 10^6 \times (1.1 \times 10^{-3})^2 \times (1.5 \times 10^{-3})$$

$$\text{Rate} = 8.85 \times 10^{-3} \text{ M sec}^{-1}$$

Sol 26: From given data, we observe that, when $[Cl_2]$ is tripled, rate becomes 3 times, so, order w. r. t. Cl_2 is 1.

When $[NO]$ is tripled, rate becomes 9 times, so, order w. r. t $[NO]$ is 2.

$$(a) \text{ Order w. r. t. } NO = 2$$

$$Cl = 1$$

$$(b) \text{ Rate} = k[NO]^2 [Cl_2]$$

$$(c) \text{ When } [Cl_2] = 0.05 \text{ M, } [NO] = 0.05 \text{ M,}$$

$$\text{Rate} = 10^{-3}$$

$$k = \frac{\text{rate}}{[NO]^2 [Cl_2]} = \frac{10^{-3}}{(0.05)^2 (0.05)} = 8 \text{ M}^{-2} \text{ sec}^{-1}$$

$$(d) \text{ If } [Cl_2] = 0.2 \text{ M, } [NO] = 0.4 \text{ M,}$$

$$\text{Rate} = k[NO]^2 [Cl_2] = 8 \times (0.4)^2 (0.2)$$

$$\text{Rate} = 0.256 \text{ mol sec}^{-1} \text{ L}^{-1}$$

Sol 27: Let us assume that this is first order reaction.
i. e. $[A] = [A]_0 e^{-kt}$. Using this, we will calculate k at both times. If they are same, then our assumption is correct.
At $t = 53$ min, 50% reaction completed, i. e. $[A] = 0.5[A]_0$

$$\therefore k = \frac{\ln 2}{t} = \frac{0.693}{53} = 0.013 \text{ min}^{-1}$$

(i) We see that both values of k are same, this is first order reaction.

$$(ii) \frac{[N_2O]}{[N_2O]_0} = e^{-kt} = e^{-1.3 \times 10^{-2} \times 100} = 0.27$$

Thus 73% of N_2O will decompose.

Sol 28: As in previous question, we assume order = 0 and calculate k at different time.

$$\text{At } t = 0 \text{ sec, } P = P_0 = 4 \times 10^3 \text{ Pa}$$

$$\text{At } t = 100 \text{ sec, } P = 3.5 \times 10^3 \text{ Pa}$$

$$\text{We have, } k_1 = \frac{P_0 - P}{t} = \frac{(4 - 3.5) \times 10^3}{100} \text{ Pa/s}$$

$$k_1 = 5 \text{ Pa/s}$$

$$\text{At } t = 200 \text{ sec, } P = 2 \times 10^3 \text{ Pa}$$

$$k = k_2 = \frac{(4 - 2) \times 10^3}{200} = 5 \text{ Pa/s}$$

$$\text{At } t = 300 \text{ sec, } P = 2.5 \times 10^3 \text{ Pa}$$

$$k_3 = \frac{(4.25) \times 10^3}{300} = 5 \text{ Pa}$$

We see that $k_1 = k_2 = k_3 = 5 \text{ Pa/s}$ is same for all. Hence this is zero order reaction, rate constant = 5 Pa/s

Sol 29: We know, for n th order reaction

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

$$\text{We have, at } [A]_0, (t_{1/2})_1 = t = 50 \text{ min}$$

$$\text{at } \frac{[A]_0}{2}, (t_{1/2})_2 = 25 \text{ min}$$

$$\therefore \frac{50}{25} = \left[\frac{\left(\frac{[A]_0}{2} \right)}{[A]_0} \right]^{n-1} = \frac{1}{2^{n-1}}$$

$$2 = \frac{1}{2^{n-1}} \Rightarrow 2^{n-1} = 2^{-1}$$

$$n - 1 = -1$$

$$\Rightarrow n = 0$$

Sol 30:

	A	→	B + C
t = 0	P ₀		0 0
t	P ₀ - x		x x
t → ∞	0		P ₀ P ₀

We have, at time t = t₁

$$P_1 = P_t = P_0 - x + x + x$$

$$P_2 = P_0 + x \Rightarrow x = P_2 - P_0$$

At time, t → ∞,

$$P_t = P_3 = 2P_0$$

$$\Rightarrow P_0 = \frac{P_3}{2}$$

Taking first order reaction,

$$k = \frac{1}{t} \ln \frac{(P_A)_0}{(P_A)_t} = \frac{1}{t} \ln \frac{P_0}{P_0 - x} = \frac{1}{t} \ln \frac{P_0}{P_0 - P_2 + P_0}$$

$$k = \frac{1}{t} \ln \frac{P_0}{2P_0 - P_2} = \frac{1}{3} \ln \frac{P_3}{2(P_3 - P_2)}$$

Sol 31: Here, we have, at time t

$$P_B + P_C = P_2 = 2x \Rightarrow x = \frac{P_2}{2}$$

at time t → ∞, P_B + P_C = P₃ = 2P₀

$$\Rightarrow P_0 = \frac{P_3}{2}$$

$$k = \frac{1}{t} \ln \frac{(P_A)_0}{(P_A)_t} = \frac{1}{t} \ln \frac{P_3}{\left(\frac{P_3}{2} - \frac{P_2}{2}\right)} = \frac{1}{t} \ln \frac{P_3}{P_3 - P_2}$$

Sol 32: A → B + C

time

t = 0	n ₀	0	0
t	n ₀ - x	x	x
t → ∞	0	n ₀	n ₀

$$\text{At time, } t = 0, V_r = V_1 = \frac{n_0 - a}{N}$$

$$\Rightarrow n_0 = \frac{NV_1}{a}$$

(n-factor of A, B, C = a)

(using NV₁ = n₀a)

Normality of reagent = N

At time, t = t,

$$V_n = V_2 = \frac{(n_0 - x)a + xa + xa}{N} = \frac{(n_0 + x)a}{N}$$

$$\Rightarrow n_0 + x = \frac{NV_2}{a}$$

$$x = \frac{NV_0}{a} - n_0 = \frac{N}{a}(V_2 - V_1)$$

$$k = \frac{1}{t} \ln \frac{n_0}{n_t} = \frac{1}{t} \ln \frac{n_0}{n_0 - x}$$

$$= \frac{1}{t} \ln \frac{NV_1}{a \left(\frac{NV_1}{a} - \frac{N}{a} \right) (V_2 - V_1)}$$

$$k = \frac{1}{t} \ln \frac{V_1}{2V_1 - V_2}$$

Sol 33: A → 2B + 3C

Time, t = 0 a

Time, t a - x 2x 3x

Time, t → ∞ 0 2a 3a

Let n-factor of A, B and C be n and normality of reagent = N then at time, t

$$N \cdot V_2 = (a - x)n + 2xn + 3xn$$

$$NV_2 = n(a + 4x)$$

$$a + 4x = \frac{NV_2}{n}$$

at time, t → ∞

$$NV_3 = 2a \cdot n + 3a \cdot n$$

$$\Rightarrow a = NV_3 = 5an$$

$$a = \frac{NV_3}{5n}$$

$$\text{Then } 4x = \frac{NV_2}{n} - \frac{NV_3}{5n}$$

$$x = \frac{N}{4n} \left(V_2 - \frac{V_3}{5} \right)$$

$$k = \frac{1}{t} \ln \frac{a}{a - x} = \frac{1}{t} \ln \frac{NV_3}{5n \left(\frac{NV_3}{5n} - \frac{NV_2}{4n} + \frac{NV_3}{20n} \right)}$$

$$= \frac{1}{t} \ln \frac{V_3}{V_3 - \frac{5}{4}V_2 + 4V_3} = \frac{1}{t} \ln \frac{4V_3}{5(V_3 - V_2)}$$

$$k = \frac{1}{t} \ln \frac{4}{5} \frac{V_3}{(V_3 - V_2)}$$

Sol 34: $S \rightarrow G + F$ Time $t = 0$ a 0 0 Time, t $a-x$ x x Time $t \rightarrow \infty$ 0 a a

Let specific rotation of Glucose and Fructose be θ_1 and θ_2 respectively

Then, at time t

$$x\theta_1 + x\theta_2 = r_t$$

$$x = \frac{r_t}{\theta_1 + \theta_2}$$

At time, $t \rightarrow \infty$

$$a\theta_1 + a\theta_2 = r_\infty$$

$$a = \frac{r_\infty}{\theta_1 + \theta_2}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{1}{t} \log \frac{a}{a-x}$$

$$k = \frac{1}{t} \log \frac{r_\infty}{(\theta_1 + \theta_2) \left(\frac{r_\infty}{\theta_1 + \theta_2} - \frac{r_t}{\theta_1 + \theta_2} \right)}$$

$$k = \frac{1}{t} \log \frac{r_\infty}{r_\infty - r_t}$$

Sol 35: $AsH_3(g) \rightarrow As(s) + \frac{3}{2}H_2(g)$

$$t = 0 P_0$$

$$t = 1 P_0 - x + \frac{3}{2}x$$

Since, as a solid, it won't contribute to pressure.

$$\therefore \text{At time } t, P_t = P_0 - x + \frac{3}{2}x = P_0 + \frac{x}{2}$$

Let's assume reaction is first order and calculate k at

$$\text{different times, using } k = \frac{1}{4} \ln \frac{P_0}{P_0 - x}$$

$$t = 0 P_0 = 758 = P_t$$

$$t = 5 \text{ hrs}, P_t = 827 = P_0 + \frac{x}{2}$$

$$827 = 758 + \frac{x}{2}$$

$$\Rightarrow x = 138 \text{ mm}$$

$$k = \frac{1}{5} \ln \frac{758}{758 - 138}$$

$$k = 0.04 \text{ hr}^{-1}$$

$$t = 7.5 \text{ hr}, P_t = 856 = P_0 + \frac{x}{2}$$

$$\Rightarrow \frac{x}{2} = 856 - 758$$

$$x = 196 \text{ mm}$$

$$k = \frac{1}{7.5} \ln \frac{758}{758 - 196}$$

$$k = 0.039 \text{ hr}^{-1}$$

$$t = 10 \text{ hr}, P_t = 889 = P_0 + \frac{x}{2}$$

$$x = 2(889 - 758)$$

$$x = 248 \text{ mm}$$

$$k = \frac{1}{10} \ln \frac{758}{758 - 248}$$

$$k = 0.039 \text{ hr}^{-1}$$

Thus, all 3 values of k are approximately the same, hence first order reaction.

Sol 36: $(CH_3)_2O(g) \rightarrow CH_4(g) + H_2(g) + CO(g)$ Time $t = 0$ P_0 0 0 0 Time, t $P_0 - x$ x x x $t \rightarrow \infty$ 0 P_0 P_0 P_0

Total pressure, at time t ,

$$P_t = P_0 - x + x + x + x = P_0 + 2x$$

$$\text{Increase in pressure} = (P_0 + 2x) - P_0 = 2x$$

We will assume that this is a first order reaction and check the consistency of given data.

$$\text{At } t = 0, P_0 = 312 \text{ mm Hg}$$

$$\text{At } t = 390 \text{ s, pressure increases;}$$

$$\Delta P = 96 \text{ mm Hg} = 2x$$

$$x = 48 \text{ mm Hg}$$

$$\therefore k = \frac{1}{t} \ln \frac{P_0}{P_0 - x} = \frac{1}{390} \ln \frac{312}{312 - 48}$$

$$k = 4.28 \times 10^{-4} \text{ s}^{-1}$$

$$\text{At } t = 1195 \text{ s, } \Delta P = 250 = 2x$$

$$x = 125 \text{ mm Hg}$$

$$k = \frac{1}{1195} \ln \frac{312}{312 - 125} = 4.28 \times 10^{-4} \text{ s}^{-1}$$

$$\text{At } t = 3155 \text{ s, } \Delta P = 467 = 2x$$

$$x = 233.5 \text{ mm Hg}$$

$$k = \frac{1}{3155} \ln \frac{312}{312 - 233.5} = 4.30 \times 10^{-4} \text{ sec}^{-1}$$

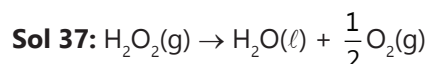
At $t \rightarrow \infty, \Delta P = 2P_0 = 624 \text{ mm Hg}$

$$\approx 619 \text{ mm Hg}$$

Thus, we see that all 3 values of k are approximately the same. Therefore, this is a first order reaction.

So, rate = $k[(\text{CH}_3)_2\text{O}]$, k

$$= 4.28 \times 10^{-4} \text{ sec}^{-1}$$



Here, $V_r \propto [\text{H}_2\text{O}_2]$

Assuming this is a first order reaction

$$k = \frac{2.303}{t} \log \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_t} = \frac{1}{t} \log \frac{V_0}{V_t}$$

At time, $t = 0$, $V_r 22.8 \text{ cc} = V_0$

$t = 10$, $V_r = 13.3 \text{ cc} = V_t$

$$k_1 = \frac{2.303}{10} \log \frac{22.8}{13.3} = 5.4 \times 10^{-2} \text{ min}^{-1}$$

$t = 20$, $V_r = 8.25 \text{ cc} = V_t$

$$k_2 = \frac{2.303}{20} \log \frac{22.8}{8.25} = 5.1 \times 10^{-2} \text{ min}^{-1}$$

k_1 and k_2 are equal within experimental error.

Therefore, first order reaction.

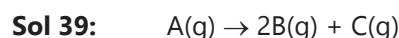
Sol 38: For inversion of cane sugar, assuming first order,

$$k = \frac{1}{t} \log \frac{\theta_0 - \theta_\infty}{\theta_f - \theta_\infty}$$

At time, $t = 0$, $\theta = \theta_0 = +13.1$

At time, $t \rightarrow \infty$, $\theta = \theta_\infty = -3.8$

At time, $t = 60$, $\theta_+ = 11.6^\circ$



Time, $t = 0$ P_0 0 0

Time, t $P_0 - x$ $2x$ x

Time, $t \rightarrow \infty$ 0 $2P_0$ P_0

At, $t \rightarrow \infty$, $P_t = 3P_0 = 270 \text{ mm Hg}$

$P_0 = 90 \text{ mm Hg} = (P_A)$

At, $t = 10 \text{ min}$, $P_t = P_0 - x + 2x + x = P_0 + 2x = 176$

$$2x = 176 - 90$$

$$x = 43 \text{ mm Hg}$$

$$(P_A)_+ = P_0 - x = 90 - 43 = 47 \text{ mm Hg}$$

Now, since, this is first order reaction.

$$k = \frac{2.303}{t} \log \frac{(P_A)_0}{(P_A)_+} = \frac{2.303}{10} \log \frac{90}{47}$$

$$k = 6.49 \times 10^{-2} \text{ min}^{-1}$$

$$k_1 = \frac{1}{60} 2.303 \log \frac{13.1 - (-3.8)}{11.6 - (-3.8)}$$

$$= 1.55 \times 10^{-3} \text{ min}^{-1}$$

At time, $t = 120 \text{ min}$, $\theta_t = +10.2^\circ$

$$k_2 = \frac{2.303}{120} \log \frac{(13.1) - (-3.8)}{(10.2) - (-3.8)} = 1.57 \times 10^{-3} \text{ min}^{-1}$$

At time, $t = 180 \text{ min}$, $\theta_t = +9.0^\circ$

$$k_3 = \frac{2.303}{180} \log \frac{(13.1) - (-3.8)}{(9.0) - (-3.8)} = 1.54 \times 10^{-3} \text{ min}^{-1}$$

At time, $t = 360 \text{ min}$, $\theta_t = +5.87^\circ$

$$k_4 = \frac{2.303}{360} \log \frac{(13.1) - (-3.8)}{(5.87) - (-3.8)} = 1.55 \times 10^{-3} \text{ min}^{-1}$$

We see that, k_1 , k_2 , k_3 and k_4 are all same within experiment value.

Therefore, this is a first order reaction

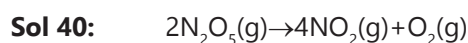
$$\text{Half-life} = \frac{0.693}{k} = \frac{0.693}{6.49 \times 10^{-2}} = 10.677 \text{ min}$$

(i) $(P_A)_i = 90 \text{ mm Hg}$

(ii) $(P_A)_f = 47 \text{ mm Hg}$

(iii) $k = 6.49 \times 10^{-2} \text{ min}^{-1}$

(iv) $t_{1/2} = 10.67 \text{ min}$



time, $t = 0$ P_0 0 0

time, $t = t$ $P_0 - 2x$ $4x$ x

$t \rightarrow \infty$ 0 2 P_0 $\frac{P_0}{2}$

At $t \rightarrow \infty$, $P_t = 584.5 = 2P_0 + \frac{P_0}{2}$

$$\Rightarrow \frac{5P_0}{2} = 584.5$$

$$\Rightarrow P_0 = 233.8 \text{ mm Hg}$$

At $t = 30 \text{ min}$,

$$P_t = 284.5 = P_0 - 2x + 4x + x$$

$$\Rightarrow P_0 + 3x = 284.5$$

$$3x = 284.5 - 233.8$$

$$x = 16.9 \text{ mm Hg}$$

$$P_{\text{N}_2\text{O}_5} = P_0 - 2x$$

$$= 233.8 - 2 \times 16.9 = 200 \text{ mm Hg}$$

We have,

$$\frac{-1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

$$\int_{[\text{N}_2\text{O}_5]_0}^{[\text{N}_2\text{O}_5]_t} \frac{d[\text{N}_2\text{O}_5]}{[\text{N}_2\text{O}_5]} = -2k \int_0^t dt$$

$$\ln \frac{[\text{N}_2\text{O}_5]_t}{[\text{N}_2\text{O}_5]_0} = -2kt$$

$$k = \frac{2.303}{2t} \log \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

$$k = \frac{2.303}{2t} \log \frac{(P_{\text{N}_2\text{O}_5})_0}{(P_{\text{N}_2\text{O}_5})_t} \quad (\because P_{\text{N}_2\text{O}_5} \propto [\text{N}_2\text{O}_5])$$

$$= \frac{2.303}{2 \times 30} \log \frac{233.8}{200}$$

$$k = 2.605 \times 10^{-3} \text{ min}^{-1}$$

Sol 41: (a) Assuming first order reaction

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

$$\text{We have, } V_0 = 22.8 \text{ cc}$$

$$\text{At } t = 10 \text{ min, } V_t = 13.8 \text{ cc}$$

$$k_1 = \frac{2.303}{10} \log \frac{22.8}{13.8} = 5.02 \times 10^{-2} \text{ min}^{-1}$$

$$\text{At } t = 20 \text{ min, } V_t = 8.25 \text{ cc}$$

$$k_2 = \frac{2.303}{20} \log \frac{22.8}{8.25} = 2 \times 10^{-2} \text{ min}^{-1}$$

Since, $k_1 \approx k_2$. This is first order reaction.

$$(b) t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.05 \times 10^{-2}} = 13.75 \text{ min}$$

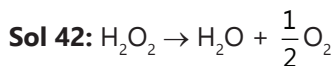
$$(c) \text{ At } t = 25 \text{ min,}$$

$$k = \frac{2.303}{25} \log \frac{V_0}{V_t}$$

Fraction decomposed

$$\frac{V_t}{V_0} = 1.10 \frac{-25 \times 5.05 \times 10^{-2}}{2.303} = 1 - 0.284$$

$$\text{Fraction decomposed} = 0.716$$



We are given complete dissociation gives 46.34 mL O_2 .

$$\text{Also } V_{\text{O}_2} \propto [\text{H}_2\text{O}_2]$$

(V_{O_2} is volume of O_2 a given sample of H_2O_2 can give)

$$\therefore [\text{H}_2\text{O}_2]_0 \propto 46.34$$

$$\text{Also, at } t = 5.1 \text{ days, } V_{\text{O}_2} = 10.31 \text{ mL}$$

$$\text{Then } [\text{H}_2\text{O}_2]_t \propto (46.34 - 10.31)$$

$$\text{So, } k = \frac{2.303}{t} \log \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_t}$$

$$k = \frac{2.303}{5.1} \log \frac{46.34}{46.34 - 10.31}$$

$$k = 4.93 \times 10^{-2} \text{ days}^{-1}$$

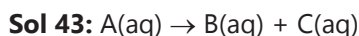
When 20 mL O_2 lost,

$$[\text{H}_2\text{O}_2]_t \propto (46.34 - 20.00)$$

$$t = \frac{2.303}{k} \log \frac{[\text{H}_2\text{O}_2]_0}{[\text{H}_2\text{O}_2]_0 - [\text{H}_2\text{O}_2]_t}$$

$$= \frac{2.303}{4.93 \times 10^{-2}} \log \frac{46.34}{46.34 - 20}$$

$$t = 11.45 \text{ days}$$



$$t = 0 \quad n_0$$

$$t = t \quad n_0 - x \quad x \quad x$$

$$t \rightarrow \infty \quad 0 \quad n_0 \quad n_0$$

$$\text{At } t \rightarrow \infty, \theta_\infty = -5^\circ = n_0 \theta_B + n_0 \theta_C$$

$$\text{We have, } \theta_A = 20^\circ, \theta_B = 30^\circ,$$

$$\theta_C = -40^\circ$$

$$\therefore 30n_0 - 40n_0 = -5$$

$$n_0 = 0.5$$

$$\text{At time, } t = 6.43 \text{ min.}$$

$$\theta_t = (n_0 - x)\theta_A + x(\theta_B + \theta_C) = 2.5$$

$$20n_0 + x(30.40 - 20) = 2.5$$

$$30x = 20 \times 0.5 - 2.5$$

$$30x = 7.5$$

$$x = 0.25$$

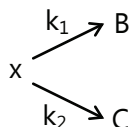
For first order conversion,

$$k = \frac{2.303}{t} \log \frac{n_0}{n_0 - x}$$

$$= \frac{2.303}{6.93} \log \frac{0.5}{0.5 - 0.25}$$

$$k = 0.1 \text{ min}^{-1}$$

Sol 44:



$$(B = y, C = z)$$

We have,

$$\frac{d[x]}{dt} = -(k_1 + k_2)[x]$$

$$\int_{[x]_0}^{[x]_t} \frac{d[x]}{[x]} = -(k_1 + k_2) \int_0^t dt$$

$$\Rightarrow [x]_t = [x]_0 e^{-kt}, k = k_1 + k_2$$

$$\text{Now, } \frac{d[B]}{dt} = k_1[x]_t$$

$$\frac{d[B]}{dt} = k_1[x]_0 e^{-kt}$$

$$\int_0^{[B]_t} d[B] = k_1[x]_0 \int_0^t e^{-kt} dt$$

$$[B]_t = \frac{-k_1[x]_0}{k} e^{-kt} \Big|_0^t$$

$$[B]_t = \frac{-k_1[x]_0}{k_1 + k_2} (1 - e^{-kt})$$

$$\text{Similarly } [C]_t = \frac{k_2[x]_0}{k_1 + k_2} (1 - e^{-kt})$$

$$[B]_t + [C]_t = [y] + [x]$$

$$= \frac{k_1[x]_0}{k} (1 - e^{-kt}) + \frac{k_2[x]_0}{k} (1 - e^{-kt})$$

$$= \left(\frac{k_1 + k_2}{k} \right) [x]_0 (1 - e^{-kt}) = [x]_0 e^{(1 - e^{-kt})}$$

$$\therefore \frac{[x]_t}{[y] + [z]} = \frac{e^{-kt}}{1 - e^{-kt}} = \frac{1}{e^{+(k_1 + k_2)t} - 1}$$

Sol 45: Using results of previous question

$$[C]_t = \frac{k_2[A]_0}{k} (1 - e^{-kt}), k = k_1 + k_2$$

$$[A]_t = [A]_0 e^{-kt}$$

$$\frac{[C]_t}{[A]_t} = \frac{k_2}{k_1 + k_2} \frac{(1 - e^{-kt})}{e^{-kt}} = \frac{1}{1 + \frac{k_1}{k_2}} (e^{-kt} - 1)$$

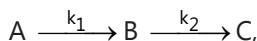
$$\text{We have, } k_1 = x \text{ hr}^{-1}, k_2 = 10 k_1$$

$$= 10 \times \text{hr}^{-1}, t = 1 \text{ hr}$$

$$\therefore \frac{[C]_t}{[A]_t} = \frac{1}{1 + \frac{1}{10}} (e^{(x+10x)} - 1)$$

$$\frac{[C]_t}{[A]_t} = \frac{10}{11} (e^{11x} - 1)$$

Sol 46: We have,



$$k_1 = \frac{\ln 2}{\ln 1}, k_2 = \frac{\ln 2}{2}$$

For [A]

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\Rightarrow [A] = [A]_0 e^{-k_1 t}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$

$$\frac{d[B]}{dt} + k_2[B] - k_1[A]_0 e^{-k_1 t} = 0 \dots (i)$$

This is a linear differential equation.

Solving this, we get

$$[B]_t = \frac{k_1[A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

Now, at $[B]_{\max}$ $\frac{d[B]_t}{dt} = 0$

In (i), putting $\frac{d[B]_t}{dt} = 0$, we get

$$k_1[A]_0 e^{-k_1 t} = k_2[B]$$

$$k_1[A]_0 e^{-k_1 t} = \frac{k_2 k_1 [A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

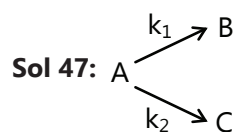
$$k_2 e^{-k_1 t} \cdot k_1 e^{-k_1 t} = k_2 e^{-k_1 t} \cdot k_2 e^{-k_2 t}$$

$$\frac{k_1}{k_2} = e^{(k_1 - k_2)t}$$

$$t = \left(\frac{\log k_1 - \log k_2}{k_1 - k_2} \right) \cdot 2.303$$

$$t = \frac{1}{k_1 - k_2} \ln \frac{\ln 2}{4 \cdot \ln 2} = \frac{-4}{\ln 2} \ln \frac{1}{2} = 4$$

$\therefore t = 4 \text{ min.}$



$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

We need, $\frac{[B]}{[C]} = 2 = \frac{k_1}{k_2}$

Let temperature be T .

By Arrhenius equation.

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

For $A \xrightarrow{k_1} B$, $k_2 = k_1$, $k_1 = 8$,

$E_a = 20 \text{ kJ/mol}$ (E_1), $T_1 = 300$, $T_2 = T$

$$\log \frac{k_1}{8} = \frac{(E_a)_1}{2.303R} \left(\frac{1}{300} - \frac{1}{T} \right)$$

$$k_1 = 8 \text{ antilog} \left[\frac{(E_a)_1}{2.303R} \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

For $A \xrightarrow{k_2} C$, similarly,

$$k_2 = 2 \text{ antilog} \left[\frac{(E_a)_2}{2.303R} \left(\frac{1}{300} - \frac{1}{T} \right) \right]$$

$$\frac{k_1}{k_2} = 2$$

$$4 \text{ antilog} \left[\frac{((E_a)_1 - (E_a)_2)}{2.303R} \right] \left(\frac{1}{300} - \frac{1}{T} \right) = 2$$

$$\frac{(E_a)_1 \cdot (E_a)_2}{2.303R} \left(\frac{1}{300} - \frac{1}{T} \right) = \log \frac{1}{2}$$

$(E_a)_1 = 20 \text{ kJ/mol}$,

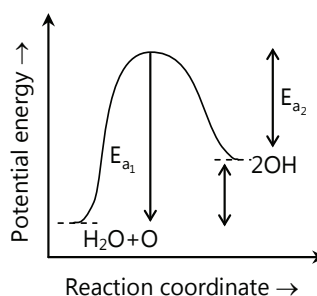
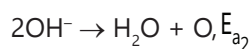
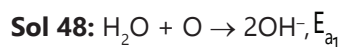
$(E_a)_2 = 2.8314 \text{ kJ/mol}$

$$\Rightarrow \frac{(28.314 - 20) \times 10^3}{8.314} \left(\frac{1}{300} - \frac{1}{T} \right) = 0.7$$

$$\frac{1}{300} - \frac{1}{T} = 7 \times 10^{-4}$$

$$\frac{1}{T} = 2.63 \times 10^{-3}$$

$T = 379.75 \text{ K}$



$$E_{a2} = E_{a1} - \Delta H = (77.72) \text{ kJ mol}^{-1}$$

$$E_{a2} = 5 \text{ kJ mol}^{-1}$$

Sol 49: For $t_{1/2} = 1 \text{ min}$, $k = \frac{0.693}{t_{1/2}}$

$$= 0.693 \text{ min}^{-1} = 1.155 \times 10^{-2} \text{ s}^{-1}$$

Now, $k = A e^{\frac{-E_a}{RT}} \Rightarrow T = \frac{E_a}{R} \left(\ln \frac{A}{k} \right)^{-1}$

$A = 5 \times 10^{13} \text{ sec}^{-1}$

$E_a = 104.5 \text{ kJ mol}^{-1}$

$$T = \frac{104.5 \times 10^3}{8.134} \left(\ln \frac{5 \times 10^{13}}{1.155 \times 10^{-2}} \right)^{-1}$$

$T = 349.1 \text{ K}$

Sol 50: From Arrhenius equation

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

For $T_1 = 27^\circ\text{C} = 300\text{ K}$ and

$$T_2 = 47^\circ\text{C} = 320\text{ K}, \quad \frac{k_2}{k_1} = 4$$

$$\therefore \log 4 = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{300} - \frac{1}{320} \right)$$

$$E_a = \frac{\log 4 \times 2.303 \times 8.314 \times 300 \times 320}{20}$$

$$E_a = 55.33\text{ kJ/mol}$$

$$\textbf{Sol 51:}$$
 For $t_{1/2} = 2\text{ hr}$, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2}\text{ hr}^{-1}$
 $= 9.625 \times 10^{-5}\text{ sec}^{-1}$

So, we have, $k_1 = 3.46 \times 10^{-5}\text{ sec}^{-1}$

$$k_2 = 9.625 \times 10^{-5}\text{ sec}^{-1}$$

$$E_a = 100\text{ kJ mol}^{-1}$$

$$T_1 = 25^\circ\text{C} = 298\text{ K}$$

$$T_2 = T$$

By Arrhenius equation.

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

$$\log \frac{9.625 \times 10^{-5}}{3.46 \times 10^{-5}} = \frac{100 \times 10^3}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{T} \right)$$

$$\Rightarrow \frac{1}{298} - \frac{1}{T} = 8.5 \times 10^{-5}$$

$$T = 306\text{ K}$$

Sol 52: By Arrhenius equation

$$k = A e^{-E_a/RT}$$

$$\frac{k_2}{k_1} = e^{(E_{a1} - E_{a2})/RT}$$

We have,

$$E_{a1} = 75\text{ kJ mol}^{-1}$$

$$E_{a2} = 25\text{ kJ mol}^{-1}$$

$$T = 25^\circ\text{C} = 298\text{ K}$$

$$\therefore \frac{k_2}{k_1} = 5.8 \times 10^8$$

Therefore, rate of reaction increases by 5.8×10^8 times.

$$\textbf{Sol 53:}$$
 Temperature coefficient $= \frac{k_{308\text{K}}}{k_{298\text{K}}} = 1.75$

By Arrhenius equation

$$\log \frac{k_{308\text{K}}}{k_{298\text{K}}} = \frac{E_a}{2.303R} \left(\frac{1}{298} - \frac{1}{308} \right)$$

$$E_a = \frac{\log 1.75 \times 2.303 \times 8.314 \times 298 \times 308}{10}$$

$$= 42.711\text{ kJ mol}^{-1}$$

$$E_a = 10.757\text{ kJ mol}^{-1}$$

Sol 54: At $T_1 = 380^\circ\text{C} = 653\text{ K}$,

$$k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{360} = 1.925 \times 10^{-3}\text{ min}^{-1}$$

$$T_2 = 450^\circ\text{C} = 723\text{ K}, \quad k_2 = k$$

$$E_a = 200\text{ kJ mol}^{-1}$$

By Arrhenius equation

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

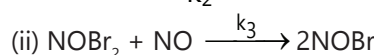
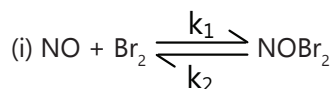
$$\log \frac{k}{1.925 \times 10^{-3}} = \frac{200 \times 10^3}{2.303 \times 8.314} \left(\frac{1}{653} - \frac{1}{723} \right)$$

$$\log \frac{k}{1.925 \times 10^{-3}} = 1.548$$

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

$$\text{Time required for 75 \% reaction} = 2t_{1/2} = \frac{2 \times 0.693}{6.8 \times 10^{-2}}$$

$$\text{Time} = 20.4\text{ minutes}$$

Sol 55: We have,

This is RDS

Here, we use equilibrium approach, as equilibrium is achieved fast

$$\text{Rate} = k_3[\text{NOBr}_2][\text{NO}]$$

For equilibrium of (i),

$$\frac{k_1}{k_2} = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$$

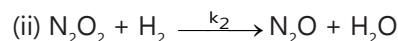
$$[\text{NOBr}_2] = \frac{k_1}{k_2} [\text{NO}] [\text{Br}]$$

$$\text{Hence, rate} = \frac{k_1 k_3}{k_2} [\text{NO}]^2 [\text{Br}] = k [\text{NO}]^2 [\text{Br}_2]$$

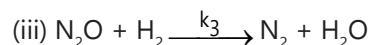
$$k = \frac{k_1 k_3}{k_2}$$

Sol 56: (i) $2\text{NO} \rightarrow \text{N}_2\text{O}_2$

equilibrium constant = k_1 (fast)



RDS



As equilibrium step is fast, we use equilibrium approach

$$\text{from (i), } k_1 = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}$$

$$[\text{N}_2\text{O}_2] = k_1 [\text{NO}]^2$$

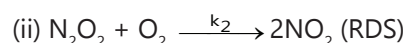
$$\text{Also, from (ii), Rate} = k_2 [\text{N}_2\text{O}_2] [\text{H}_2]$$

$$= k_1 k_2 [\text{NO}]^2 [\text{H}_2]$$

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

$$k = k_2 k_3$$

Sol 57 (i) $\text{NO} + \text{NO} \xrightleftharpoons[k_{-1}]{k_1} \text{N}_2\text{O}_2$ [fast]



from equilibrium of (i),

$$\frac{k_1}{k_{-1}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}$$

$$[\text{N}_2\text{O}_2] = \frac{k_1}{k_{-1}} [\text{NO}]^2$$

from (ii)

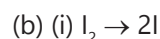
$$\text{Rate} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k_2 [\text{O}_2] [\text{N}_2\text{O}_2] = \frac{k_2 k_1}{k_{-1}} [\text{NO}]^2 [\text{O}_2]$$

$$\text{Rate} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = k [\text{NO}]^2 [\text{O}_2],$$

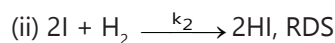
$$k = \frac{k_2 k_1}{k_{-1}}$$

Sol 58: (a) $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$

since, this is one step, rate = $k[\text{H}_2] [\text{I}_2]$



equilibrium constant = k_1 , fast



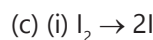
$$\text{from (i) equilibrium, } k_1 = \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$[\text{I}]^2 = k_1 [\text{I}_2]$$

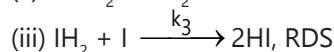
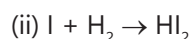
$$\text{from (ii) Rate} = k_2 [\text{I}]^2 [\text{H}_2]$$

$$= k_2 k_1 [\text{I}_2] [\text{H}_2]$$

$$= k [\text{H}_2] [\text{I}_2], \quad k = k_2 k_1$$



equilibrium constant = k_1 , fast



equilibrium constant = k_2 , fast

$$\text{from equilibrium (i), } k_1 = \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$[\text{I}]^2 = k_1 [\text{I}_2]$$

from equilibrium (ii),

$$k_2 = \frac{[\text{HI}_2]^2}{[\text{I}][\text{H}_2]}$$

$$[\text{IH}_2] = k_2 [\text{I}] [\text{H}_2]$$

since (iii) is RDS,

$$\text{Rate} = k_3 [\text{IH}_2] [\text{I}]$$

$$= k_3 k_2 [\text{I}]^2 [\text{H}_2]$$

$$= k_1 k_2 k_3 [\text{I}_2] [\text{H}_2]$$

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

(d) No, it cannot distinguish between the three mechanisms as all the 3 molecules gives the same rate law.

(e) Mechanism (a) becomes most improbable as it just involves one step and it is highly unlikely that I_2 and H_2 will combine directly at 200°C without breaking into radicals.

Exercise 2

Single Correct Choice Type

Sol 1: (B) We know,

$$\text{Coefficient in rate law} = \frac{1}{\text{stoichiometric coefficient}}$$

Given rate law

$$+\frac{1}{2} \frac{d[\text{C}]}{dt} = \frac{-1}{3} \frac{d[\text{D}]}{dt} = \frac{+1}{3} \frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt}$$

Reaction is $3\text{D} + \text{B} \rightarrow 2\text{C} + 4\text{A}$

Sol 2: (D) If volume is reduced to half, pressure will get doubled.

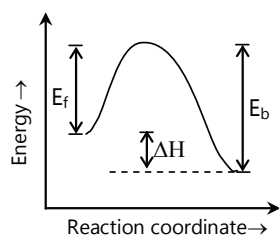
Now, reaction is first order w. r. t O_2 and second order w. r. t N_2

$$\therefore \text{Rate} = k[O_2][N_2]^2$$

$$r_f = k[2O_2][2N_2]^2$$

$$r_f = k[2O_2][2N_2]^2 = 8r_i$$

Sol 3: (C) We have



$$\therefore |\Delta H| = E_b - E_f = (200 - 180) \text{ kJ mol}^{-1}$$

$$|\Delta H| = 20 \text{ kJ/mol}$$

Sol 4: (D) For zero order reaction

$$\text{rate, } \frac{d[B]}{dt} = k$$

$$[B] = kt$$

$$[A] = [A]_0 - kt$$

$$\text{At time } t = t_{3/4}, [A] = \frac{1}{4} [A]_0$$

$$\Rightarrow t = \frac{3[A]_0}{4k}$$

$$\Rightarrow t_{3/4} \propto [A]_0$$

$$\text{Similarly, } t_{1/2} \propto [A]_0$$

Sol 5: (C) Here, $t_{1/2} \propto (A)_0$, therefore, it is a zero order reaction.

So, rate of reaction $\left(\frac{d[A]}{dt}\right)$ will be independent of time.

Sol 6: (B) The given option is correct as there is very little probability for more than 3 atoms to collide simultaneously.

$$\text{Sol 7: (C)} \text{ We have } k = \frac{2.303}{t} \log \frac{a_0}{a_0 - x}$$

$$kt = 2.303 \log a_0 - 2.303 \log(a_0 - x)$$

$$\log(a_0 - x) = \frac{-kt}{2.303} + \log a_0$$

$$\text{Slope of } \log(a_0 - x) \text{ vs. } t \text{ graph is } \frac{-kt}{2.303}$$

$$\text{Slope of given graph} = -3.3 \times 10^{-3} = \frac{-k}{2.303}$$

$$\Rightarrow k = 7.7 \times 10^{-3}$$

Sol 8: (C) Volume strength = 5.6 N_0 = 16.8°

Now, after 2.303 hours, let normality be N .

When 20 mL of this solution is diluted, Normality becomes

$$\frac{N \cdot 20}{100} = \frac{N}{5}$$

It is diluted against 0.02 M $KMnO_4$.

Under acidic conditions, normality of $KMnO_4$ = $M \times 5$

$$= 0.02 \times 5 = 0.1 \text{ N}$$

Now, using $N_1 V_1 = N_2 V_2$

$$\frac{N}{5} \cdot 25 = 0.1 \times 37.5$$

$$N = 0.75 \text{ N}$$

Now volume strength

$$V = N \times 5.6 = 0.75 \times 5.6 = 4.2 \text{ V}$$

Now,

$$k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

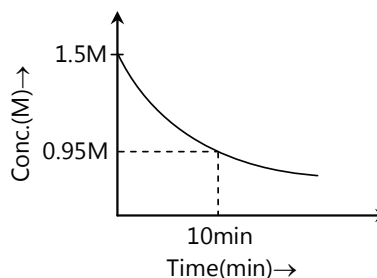
$$t = 2.303 \text{ hours, } V_0 = 16.8 \text{ V,}$$

$$V_f = 4.2 \text{ V}$$

$$k = \frac{2.303}{2.303} \log \frac{16.8}{4.2}$$

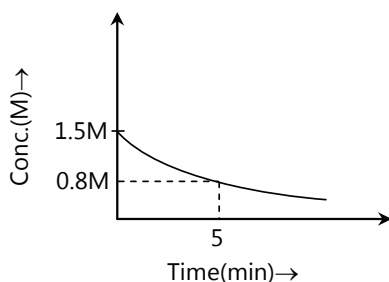
$$k = 0.60 \text{ hr}^{-1}$$

Sol 9: (A) For experiment 1,



$$\text{Average rate} = \frac{-\Delta[A]}{\Delta t} = \frac{0.55}{10} = 0.055 \text{ min}^{-1}$$

For experiment 2,



$$\text{Average rate, } r_2 = \frac{\Delta A}{\Delta t}$$

$$= \frac{0.2}{5} \text{ M min}^{-1} = \frac{1}{25} \text{ M min}^{-1}$$

$$\Rightarrow \frac{r_1}{r_2} = \frac{0.55}{1/25} = 1.375 \approx 1.5 = \frac{[A]_{01}}{[A]_{02}}$$

Hence the reaction is first order

When (A) = 1.8 M

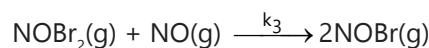
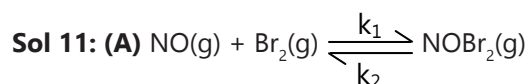
$$\text{Rate, } r = 1.8 \times [x]_2$$

$$= \frac{1.8}{25} \text{ M min}^{-1} = 0.072 \text{ M min}^{-1}$$

$$\approx 0.08 \text{ M min}^{-1}$$

Sol 10: (A) Since $k_1 \ll k_2$ second reaction will have the most activation energy

Further, since the overall reaction is exothermic, therefore the final energy of products should be less than the reactants plot which satisfies above 2 is (A).



We use equilibrium approach

Since second step is RDS,

$$\text{Rate, } R = -k_3[\text{NOBr}_2][\text{NO}]$$

From equilibrium of (i),

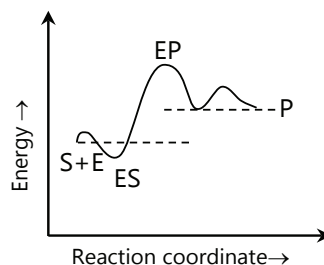
$$\frac{k_1}{k_2} = \frac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$$

$$\Rightarrow [\text{NOBr}_2] = \frac{k_1}{k_2} [\text{NO}][\text{Br}_2]$$

$$\text{Therefore, rate} = \frac{k_3 k_1}{k_2} [\text{NO}]^2 [\text{Br}_2]$$

Order w. r. t. NO = 2

Sol 12: (B)



This is the plot for enzyme catalysed reaction.

Correct option is (B).

Multiple correct choice type

Sol 13: (A, D) We have, emission rate of SO_3

$$= 6.93 \times 10^{-6} \text{ gm/L/day}$$

$$= \frac{6.93 \times 10^{-6}}{80} \text{ mol/L/day}$$

$$= 8.6625 \times 10^{-8} \text{ mol/L/day}$$

For decomposition of SO_3 ,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = 6.93 \times 10^{-3} \text{ day}^{-1}$$

$$\frac{d[\text{SO}_3]}{dt} = 8.6625 \times 10^{-8} - 6.93 \times 10^{-3} [\text{SO}_3]$$

$$\text{At steady state, } \frac{d[\text{SO}_3]}{dt} = 0$$

$$\Rightarrow [\text{SO}_3] = \frac{8.6625 \times 10^{-8}}{6.93 \times 10^{-3}}$$

$$[\text{SO}_3] = 1.25 \times 10^{-5} \text{ M}$$

$$\text{In } 10^{-3} \text{ of air, moles of } \text{SO}_3 = 1.25 \times 10^{-5} \times 10^3$$

$$= 1.25 \times 10^{-2} \text{ mol}$$

When dissolved in water (1 L),

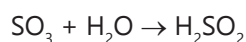
$$[\text{SO}_3] = 1.25 \times 10^{-2} \text{ M}$$

$$\text{Normality of } \text{SO}_3 = 2\text{M} = 2.5 \times 10^{-2} \text{ N}$$

$$N_1 V_1 = N_2 V_2$$

$$2.5 \times 10^{-2} \times 1000 = 1 \times V_2$$

$$V_2 = 25 \text{ mL}$$



Rate of H_2SO_4 production

$$= 980 \text{ kg/day} = \frac{980 \times 10^3}{98} \text{ mol/day} = 10^4 \text{ mol/day}$$

$$\text{SO}_3 \text{ required} = \text{H}_2\text{SO}_4 \text{ manufactured} = 10^4 \text{ mol/day}$$

$$\text{Now } V = \frac{\text{number of moles}}{M}$$

$$= \frac{10^4}{1.25 \times 10^{-5}} = 8 \times 10^8 \text{ L/day}$$

If SO_3 emission stopped,

$$\frac{d[\text{SO}_3]}{dt} = -6.93 \times 10^{-3} [\text{SO}_3]$$

$$\Rightarrow [\text{SO}_3] = [\text{SO}_3]_0 e^{-6.93 \times 10^{-3} t}$$

$$[\text{SO}_3]_0 = [\text{SO}_3]_0 e^{-6.93 \times 10^{-3} t}$$

$$[\text{SO}_3]_0 = 1.25 \times 10^{-5} \text{ M}$$

$$t = 1000 \text{ days}$$

$$\therefore [\text{SO}_3]_0 \approx 1.2 \times 10^{-8} \text{ M}$$

Sol 14: (A, B, D) $\frac{-d[A]}{dt} = k(A)^{1/2}$

$$\int_{[A]_0}^{[A]} \frac{-d[A]}{[A]^{1/2}} = \int_0^t k dt$$

$$2[A]^{1/2} \Big|_{[A]_0}^{[A]} = kt \Big|_0^t$$

$$(A)^{1/2} = [A]_0^{1/2} = \frac{kt}{2}$$

$$k = \frac{-1}{2} (A_0^{1/2} \cdot A^{1/2})$$

$$\sqrt{A} = \frac{kt}{2} + \sqrt{A_0}$$

Straight line

$$\text{At } t = t_{1/2}, (A) = \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{2\sqrt{2}k}{[A_0]^{1/2} - \frac{[A_0]^{1/2}}{\sqrt{2}}}$$

$$\frac{2 \left([A_0]^{1/2} 2 \left([2A]_0^{1/2} - \frac{[A]}{\sqrt{2}} \right)^{1/2} \right)}{k}$$

$$= \frac{2\sqrt{2}k}{(\sqrt{2}-1)[A]_0} = \frac{2[A]_0^{1/2}}{k} (\sqrt{2}-1)$$

$$\text{At } t = t_{3/4}, (A) = \frac{[A]_0}{4}$$

$$\therefore t_{3/4} = \frac{2k}{[A]_0^{1/2} - \frac{[A]_0^{1/2}}{2}}$$

$$\frac{2 \left([A]_0^{1/2} - \frac{[A]_0^{1/2}}{2} \right)}{k}$$

$$t_{3/4} = \frac{\sqrt{[A]_0}}{k}$$

Sol 15: (A, D) Solution will be optically active and dextro after very long time

After 75% conversion of A in to B and C angle of rotation of solution will be 36°

Sol 16: (C, D)

(A) is correct

$$\text{Rate, } R = k[A]^m[B]^n[C]^0$$

$$\log R = \log k + m \log[A] + n \log[B]$$

If all concentration other than (A) are constant,

$$\text{Then } \frac{d(\log k)}{d(\log[A])} = m$$

(C) Order of reaction can be fractional

(D) Order of a reaction can only be determined experimentally

Sol 17: (A, C, D)

(A) Unit of A = Unit of $k \neq \text{mol L}^{-1}\text{s}^{-1}$

(B) Order of an elementary must atleast be 1 (atleast 1 molecule should be present)

(C) Molecularity can be defined for any elementary reaction.

(D) Decay constant (λ) of radioactive substance is independent of temperature.

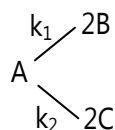
Sol 18: (A, C) With increase in $[A]_0$, rate will increase, leading to increase in yield of B. $A \rightarrow B$ has higher E_a , which means it has lower k and thus with increase in temperature k_1 will increase more than k_2 , resulting in increase in yield of B.

Sol 19: (A, B, C)

(D) A zero order reaction is always complex, rest all are correct.

Assertion Reasoning Type

Sol 20: (C) Order of an elementary reaction cannot be fractional, through the overall order of a reaction can be fractional.



We have, $\frac{[B]}{[C]} = \frac{k_1}{k_2} = \frac{1}{2}$

For every mole of A consumed, $\frac{1}{3}$ mole used for forming B and rest for forming C.

$$[A]_0 = 2 \text{ moles}$$

At end of 50% reaction, $A_0 = 1 \text{ mole}$

$$B_n = \frac{1}{3} \times 2 \times 1 = \frac{2}{3} \text{ moles}$$

$$C_n = \frac{2}{3} \times 2 \times 1 = \frac{4}{3} \text{ moles}$$

[Since, for every mole A, 2 moles of B (or C) is produced]

Sol 21: (D) $A(aq) \rightarrow B(aq) + C(aq)$

$t = 0$	n_0		
$t = t$	$n_0 - x$	x	x
$t \rightarrow \infty$	0	n_0	n_0

$$\text{At } t \rightarrow \infty, \theta_\infty = -5^\circ = n_0 \theta_B + n_0 \theta_C$$

$$\text{We have, } \theta_A = 20^\circ, \theta_B = 30^\circ,$$

$$\theta_C = -40^\circ$$

$$\therefore 30n_0 - 40n_0 = -5$$

$$n_0 = 0.5$$

At time, $t = 6.43 \text{ min.}$

$$\theta_t = (n_0 - x)\theta_A + x(\theta_B + \theta_C) = 2.5$$

$$20n_0 + x(30.40 - 20) = 2.5$$

$$30x = 20 \times 0.5 - 2.5$$

$$30x = 7.5$$

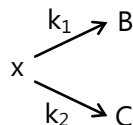
$$x = 0.25$$

For first order conversion,

$$k = \frac{2.303}{t} \log \frac{n_0}{n_0 - x} = \frac{2.303}{6.93} \log \frac{0.5}{0.5 - 0.25}$$

$$k = 0.1 \text{ min}^{-1}$$

Sol 22: (A)



$$(B = y, C = z)$$

We have,

$$\frac{d[x]}{dt} = -(k_1 + k_2)[x]$$

$$\int_{[x]_0}^{[x]_t} \frac{d[x]}{[x]} = -(k_1 + k_2) \int_0^t dt$$

$$\Rightarrow [x]_t = [x]_0 e^{-kt}, k = k_1 + k_2$$

$$\text{Now, } \frac{d[B]}{dt} = k_1 [x]_t$$

$$\frac{d[B]}{dt} = k_1 [x]_0 e^{-kt}$$

$$\int_0^{[B]_t} d[B] = k_1 [x]_0 \int_0^t e^{-kt} dt$$

$$[B]_t = \frac{-k_1 [x]_0}{k} e^{-kt} \Big|_0^t$$

$$[B]_t = \frac{-k_1 [x]_0}{k_1 + k_2} (1 - e^{-kt})$$

$$\text{Similarly } [C]_t = \frac{k_2 [x]_0}{k_1 + k_2} (1 - e^{-kt})$$

$$[B]_t + [C]_t = [y] + [x]$$

$$= \frac{k_1 [x]_0}{k} (1 - e^{-kt}) + \frac{k_2 [x]_0}{k} (1 - e^{-kt})$$

$$= \left(\frac{k_1 + k_2}{k} \right) [x]_0 (1 - e^{-kt}) = [x]_0 e^{(1 - e^{-kt})}$$

$$\therefore \frac{[x]_t}{[y] + [z]} = \frac{e^{-kt}}{1 - e^{-kt}} = \frac{1}{e^{+(k_1 + k_2)t} - 1}$$

Sol 23: (C) Using results of previous question

$$[C]_t = \frac{k_2 [A]_0}{k} (1 - e^{-kt}), k = k_1 + k_2$$

$$[A]_t = [A]_0 e^{-kt}$$

$$\frac{[C]_t}{[A]_t} = \frac{k_2}{k_1 + k_2} \frac{(1 - e^{-kt})}{e^{-kt}} = \frac{1}{1 + \frac{k_1}{k_2}} (e^{-kt} - 1)$$

We have, $k_1 = x \text{ hr}^{-1}$, $k_2 = 10 k_1$

$$= 10 \times \text{hr}^{-1}, t = 1 \text{ hr}$$

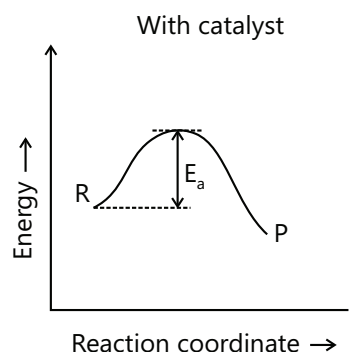
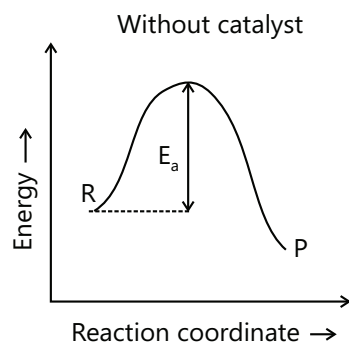
$$\therefore \frac{[C]_t}{[A]_t} = \frac{1}{1 + \frac{1}{10}} (e^{(x+10x)} - 1)$$

$$\frac{[C]_t}{[A]_t} = \frac{10}{11} (e^{11x} - 1)$$

Sol 24: (C) For reactions with order ≤ 1 , time of completion can be determined as those reactions gets fully completed in specific amount of time.

For reactions with order > 1 , reaction never goes to 100 % completion and hence time of completion cannot be determined.

Sol 25: (A)



Comprehension Type

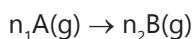
Paragraph 1

Sol 26: (B) Total number of moles $= 1 + \frac{2}{3} + \frac{4}{3} = 3$ moles

Sol 27: (C) Moles of B $= \frac{2}{3} = 0.666$ moles.

Paragraph 2

Sol 28: (B) We have,



time 0 a 0

time t a - $n_1 x$ $n_2 x$

$$\therefore \text{Rate} = k[A] = \frac{-1}{n_1} \frac{d[A]}{dt} = k[A]$$

$$\Rightarrow \int_a^{a_t} \frac{d[A]}{dt} = -n_1 k \int_0^t dt$$

$$\ln \frac{a_t}{a} = -n_1 kt$$

$$a_t = a e^{-n_1 kt}$$

Sol 29: (D) $n_1 A(g) \rightarrow n_2 B(g)$

t = 0 a 0

t = 1 $a e^{-n_1 kt}$ $\frac{n_2}{n_1} a (1 - e^{-n_1 kt})$

Total moles present

$$= a \left[e^{-n_1 kt} + \frac{n_2}{n_1} - \frac{n_2}{n_1} e^{-n_1 kt} \right]$$

$$= a \left[\frac{n_2}{n_1} - \left(\frac{n_2}{n_1} - 1 \right) e^{-n_1 kt} \right]$$

Concentration is to remain same at time t,

$$\therefore \frac{\text{total moles present}(n)}{V} = \frac{a_0}{V_0}$$

$$\Rightarrow V = \frac{V_0 n}{a_0} = V_0 \left[\frac{n_2}{n_1} - \left(\frac{n_2}{n_1} - 1 \right) e^{-n_1 kt} \right]$$

Sol 30: (B) If $n_1 = 1$, $n_2 = 2$

at time t,

$$n_A = a e^{-kt}$$

$$V = V_0 (2 - (2 - 1)e^{-kt})$$

$$= V_0 (2 - e^{-kt})$$

$$(A) = \frac{n_A}{V} = \frac{a e^{-kt}}{V_0 (2 - e^{-kt})} = (A)_0 \left(\frac{e^{-kt}}{2 - e^{-kt}} \right)$$

Paragraph 3

$$\text{Sol 31: (C) } (B) = \frac{k_1[A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

$$\frac{d[B]}{dt} = \frac{k_1[A]_0}{k_2 - k_1} (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t})$$

$$\text{When } (B) \text{ is maximum, } \frac{d[B]}{dt} = 0$$

$$\frac{d[B]}{dt} = 0$$

$$\Rightarrow -k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$$

$$k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$$

$$= \frac{k_1}{k_2}$$

$$(k_1 - k_2)t = \ln \frac{k_1}{k_2} ; \Rightarrow t = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$$

$$\text{Sol 32: (C) For } k_1 = 1000 \text{ s}^{-1}, k_2 = 20 \text{ s}^{-1},$$

$$[A]_t = [A]_0 e^{-1000t}$$

$$[B]_t = \frac{1000}{20 - 1000} [A]_0 [e^{-1000t} - e^{-20t}]$$

$$\approx [A]_0 e^{-20t}, t_{\max} = \frac{1}{1000 - 20} \ln \frac{1000}{20}$$

$[B]_t$ will increase till t_{\max} and then decay exponentially

$$[C]_t = [A]_0 - ([A]_t + [B]_t)$$

$$= [A]_0 - [A]_0 e^{-1000t} - [A]_0 e^{-20t}$$

$$= [A]_0 (1 - e^{-1000t} - e^{-20t})$$

$$\approx [A]_0 (1 - e^{-20t})$$

$[C]_t$ will approach $[A]_0$ asymptotically.

Paragraph 4

$$\text{We have } \frac{df}{dt} = k(1 - f)$$

$$\int_0^f \frac{df}{1 - f} = \int_0^t k dt$$

$$-\ln(1 - f)_0^f = k f \Big|_0^f$$

$$-\ln(1 - f) = kt$$

$$f = 1 - e^{-kt}$$

Sol 33: (B) Slope of $\ln(1 - f)$ vs f graph

$$= -k = \frac{-3}{200} \text{ hr}^{-1}$$

$$\Rightarrow k = \frac{3}{200} \text{ hr}^{-1}$$

$$\text{When } f = \frac{1}{2}$$

$$\frac{1}{2} = 1 - e^{-kt}$$

$$t = \frac{\ln 2}{k} = \frac{0.693 \times 200}{3} = 46.2 \text{ hrs.}$$

Sol 34: (A) $f = 1 - e^{-kt}$

$$f = [1 - e^{-3t/200}]$$

Paragraph 5

Sol 35: (C) For $t = 100 \text{ min}$, $x = \frac{3}{4} a$

$$\therefore k = \frac{1}{100} \ln \frac{a}{a - \frac{3}{4}a} = \frac{\ln 2}{50} \text{ min}^{-1}$$

When $x = 0.9 a$,

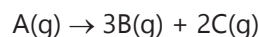
$$k = \frac{1}{t} \ln \frac{a}{a - 0.9a}$$

$$t = \frac{1}{k} \ln 10 = \frac{50 \ln 10}{\ln 2} = \frac{50}{\ln 2} = \frac{50}{0.3} ; = 166.66 \text{ min}$$

$$\text{Sol 36: (B) } [A]_0 = \frac{2}{12.5} = 0.16$$

We have,

$$\frac{1}{3} \frac{d[B]}{dt} = k[A]$$



At time 0 0.16

At time t 0.16 - x $3x$ $2x$

$$\text{Also, } \frac{d[A]}{dt} = -k[A]$$

$$[A] = [A]_0 e^{-kt}$$

$$= 0.16 e^{1.386 \times 10^{-2} \times 100}$$

$$= 0.04$$

$$\text{i.e., } 0.16 - x = 0.04$$

$$x = 0.12$$

$$(B) = 3x = 0.36.$$

Match the Columns

Sol 37: (A) \rightarrow s

We have,

$$\frac{1}{2} \frac{d[B]}{dt} = \frac{-d[A]}{dt}$$

Straight line with slope equal to 2.

(B) \rightarrow r

$$[A] = [A]_0 e^{-kt}$$

exponential decay

(C) \rightarrow p

$$(B) = 2([A]_0 - [A]); = 2[A]_0 (1 - e^{-kt})$$

Exponential graph will approach $2(A)_0$ asymptotically.(D) \rightarrow q

For zero order,

$$[A] = [A]_0 - kt$$

Straight line with slope $-k$.**Sol 38:** We will draw all graphs given in Column-II and then match them with Column-I.(p) $\ln(A)$ vs t (order 1)

$$\text{We have, } [A] = [A]_0 e^{-kt}$$

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

Straight line with negative slope matches (A).

(q) $t_{1/2}$ vs $(A)_0$ (order = 1)

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

It is independent of $[A]_0$, straight line parallel to x-axis.

Matches (B)

(r) r vs t (order > 0)

$$r = k[A]^n, n > 0$$

for order > 0 , rate decreases with increasing t as (A) decreases with t \therefore decreasing graph (not straight line) matches (C).(s) r vs t (order = 0)For order, r is constant of time, graph is straight line parallel to x-axis.(t) $t_{1/2}$ vs $[A]_0$ (order > 1)

We know,

$$t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

decreasing graph

Matches (C).

$$(U) \frac{1}{[A]} \text{ vs } t (\text{order} = 2)$$

we have,

$$\frac{-d[A]}{dt} = \frac{-k}{[A]^2}$$

$$\Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

$$\Rightarrow \frac{-1}{[A]} \Big|_{[A]_0}^{[A]} = -kt \Big|_0^t$$

$$\Rightarrow \frac{1}{[A]_0} - \frac{1}{[A]} = -kt$$

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

Straight line with positive slope and positive intercept.

Matches no option in Column-I.

(V) r vs $[A]$ (order = 1)

$$r = k[A]$$

Straight line with positive slope.

Matches (D)

(A) \rightarrow p(B) \rightarrow q, s(C) \rightarrow r, t(D) \rightarrow v

Previous Years' Questions

Sol 1: (A) The rate constant (k) of all chemical reactions depends on temperature.

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

where, A = Pre-exponential factor, E_a = Activation energy.**Sol 2: (C)** A catalyst increases the rate of reaction but by the same factor to both forward and backward

directions. Hence, a catalyst shorten the time required to reach the equilibrium.

Sol 3: (D) Rate will be directly proportional to both concentration and intensity, i.e, rate of formation of $AB^* \propto C \cdot I$.

Sol 4: (D) Order of a reaction can take any real value, i.e, negative, integer, fraction, etc.

Sol 5: (A) According to Arrhenius equation, rate constant increases exponentially with temperature : $k = Ae^{-E_a/RT}$

Sol 6: (A) Living plants maintain an equilibrium between the absorption of C^{14} (produced due to cosmic radiation) and the rate of decay of C^{14} present inside the plant. This gives a constant amount of C^{14} per gram of carbon in a living plant.

Sol 7: (B) Fossil whose age is closest to half-life of C-14 (5770 yr) will yield the most accurate age by C-14 dating.

Sol 8: (A) $\lambda T = \ln \frac{N_0}{N}$

where N_0 = Number of C^{14} in the living matter and N = Number of C^{14} in fossil. Due to nuclear explosion, amount of C^{14} in the near by area increases. This will increase N_0 because living plants are still taking C-14 from atmosphere, during photosynthesis, but N will not change because fossil will not be doing photosynthesis.

$\Rightarrow T$ (age) determined in the area where nuclear explosion has occurred will be greater than the same determined in normal area.

$$\text{Also, } \lambda T_1 = \ln \frac{C_1}{C}$$

$$\lambda T_2 = \ln \frac{C_2}{C}$$

$$\Rightarrow T_1 - T_2 = \ln \frac{C_1}{C_2}$$

C = Concentration of C-14 in fossil.

Sol 9: Rate of reaction is constant with time.

Sol 10: $k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5770} \text{ yr}^{-1} = 1.2 \times 10^{-4} \text{ yr}^{-1}$

$$\text{Also } kt = \ln \frac{1}{f} = \frac{\ln 2}{5770} \times 11540 = \ln 4$$

$$\Rightarrow f = \frac{1}{4} = 0.25$$

Sol 11: $k = 1.5 \times 10^{-6} \text{ s}^{-1}$

$$kt = \ln \frac{100}{100-x}$$

$$\Rightarrow \ln \frac{100}{100-x}$$

$$= 1.5 \times 10^{-6} \text{ s}^{-1} \times 10 \times 60 \times 60 \text{ s}; = 0.0054$$

$$\Rightarrow \frac{100}{100-x} = 1.055$$

$\Rightarrow x = 5.25\%$ reactant is converted into product

$$\text{Half-life} = \frac{\ln 2}{k} = \frac{0.693}{1.5 \times 10^{-6}} = 462000 \text{ s}; = 128.33 \text{ h}$$

Sol 12: The minimum rate of decay required after 6.909 h is 346 particles min^{-1} .

$$\Rightarrow \text{Rate} = kN$$

$$\Rightarrow N = \frac{\text{Rate}}{k} = \frac{346 \times 66.6 \times 60}{0.693}$$

$$= 1.995 \times 10^6 \text{ atoms}$$

$$\Rightarrow kt = \ln \frac{N_0}{N}$$

$$\Rightarrow \frac{\ln 2}{66.6} \times 6.909 = \ln \frac{N_0}{N} = 0.0715$$

$$\Rightarrow \frac{N_0}{N} = 1.074$$

$$\Rightarrow N_0 = 1.074 \times N = 1.074 \times 1.995 \times 10^6$$

$$= 2.14 \times 10^6 \text{ atoms of Mo}$$

\Rightarrow Mass of Mo required

$$= \frac{2.14 \times 10^6}{6.023 \times 10^{23}} \times 99 = 3.56 \times 10^{-16} \text{ g}$$

Sol 13: $\text{CH}_3\text{--O--CH}_3(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2(\text{g}) + \text{CO}(\text{g})$

At 12 min : 0.40 - p p p p

Total pressure = 0.4 + 2p

$$\text{Also } k \times 12 = \ln \frac{0.40}{0.40-p}$$

$$= \frac{\ln 2}{14.5} \times 12 = \ln \frac{0.40}{0.40-p}$$

$$\Rightarrow p = 0.175$$

$$\Rightarrow \text{Total pressure} = 0.4 + 2p$$

$$= 0.4 + 2 \times 0.175$$

$$= 0.75 \text{ atm.}$$

Sol 14: (A) $\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

$$\Rightarrow \ln \left(\frac{4.5 \times 10^7}{1.5 \times 10^7} \right) = \frac{E_a}{8.314} \left(\frac{50}{323 \times 373} \right)$$

$$\Rightarrow E_a = 22 \text{ kJ}$$

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

At 50°C :

$$\ln A = \ln (1.5 \times 10^7) - \frac{22 \times 1000}{8.314 \times 323} = 8.33$$

$$\Rightarrow A = 4.15 \times 10^3 \text{ s}^{-1}$$



$$\begin{array}{ccc} 600-p & 2p & \frac{p}{2} \end{array}$$

$$\text{Total pressure} = 690 = 600 + \frac{3}{2}p$$

$$\Rightarrow p = 240 \text{ mm}$$

$$\Rightarrow \text{Partial pressure of } \text{N}_2\text{O}_5 (\text{g})$$

remaining

$$= 600 - 240$$

$$= 360 \text{ mm}$$

$$\Rightarrow \text{Mole-fraction} = \frac{360}{960} = 0.375$$

Sol 15: (A) Partial pressure becomes half of initial in every 100 min, therefore, order = 1.

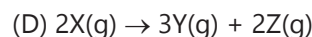
(B) $k \times 100 = \ln \frac{800}{400} = \ln 2$

$$\Rightarrow k = 6.93 \times 10^{-3} \text{ min}^{-1}$$

(C) For 75% reaction; time required

$$= 2 \times \text{half-life}$$

$$= 200 \text{ min}$$



$$\begin{array}{ccc} 800-x & \frac{3}{2}x & x \end{array}$$

$$\text{Total pressure} = 800 + \frac{3}{2}x$$

$$\text{Also } 800 - x = 700$$

$$\Rightarrow x = 100$$

$$\Rightarrow \text{Total pressure}$$

$$= 800 + \frac{3}{2} \times 100 = 950 \text{ mm}$$



$$\text{rate} \propto [\text{G}]^a [\text{H}]^b$$

$$a = 1, b = 2$$

Sol 17: (A) $k_1 = \frac{0.693}{t_{1/2}} = \frac{0.693}{40}$

$$k_0 = \frac{A_0}{2t_{1/2}} = \frac{1.386}{2 \times 20}$$

$$\frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{40}{1.386} = \frac{0.693}{1.386} = 0.5 \text{ mol}^{-1} \text{ litre}$$

Sol 18: $t_{1/8} = \frac{2.303 \log 8}{k} = \frac{2.303 \times 3 \log 2}{k}$

$$t_{1/10} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}$$

$$\left[\frac{t_{1/8}}{t_{1/10}} \right] \times 10 = \frac{\left(\frac{2.303 \times 3 \log 2}{k} \right)}{\left(\frac{2.303}{k} \right)} \times 10 = 9$$

Sol 19: (D) Overall order of reaction can be decided by the data given $t_{75\%} = 2t_{50\%}$

\therefore It is a first order reaction with respect to P.

From graph [Q] is linearly decreasing with time, i.e. order of reaction with respect to Q is zero and the rate expression is $r = k [\text{P}]^1 [\text{Q}]^0$.

Hence (D) is correct.

Sol 20: (C) $\frac{r_1}{r_2} = \frac{1}{8} = \frac{[\text{M}]^n}{[2\text{M}]^n} \Rightarrow n = 3$

Sol 21: (B, C, D) A high activation energy usually implies a slow reaction.