Chapter

18

Chemical Kinetics

RATE OF A CHEMICAL REACTION

It is defined as the change in the concentration of reactant or product in unit time. It is always a positive quantity. It can be expressed in terms of:

(i) rate of decrease in concentration of any one of the reactant

(ii) rate of increase in concentration of any one of the product.

For ex; For a reaction, $A \rightarrow B$

$$\text{Rate of disappearance of A} = \frac{\text{Decrease in conc. of A}}{\text{Time taken}}$$

$$= \frac{-\Delta[B]}{\Delta t}$$

$$\text{Rate of appearance of B} = \frac{\text{Increase in conc. of B}}{\text{Time taken}} = \frac{+\Delta[B]}{\Delta t}$$

where $\Delta[A] = A_2 - A_1 = A_{\text{final}} - A_{\text{initial}}$

$\Delta[B] = B_2 - B_1 = B_{\text{final}} - B_{\text{initial}}$

$\Delta t = t_2 - t_1$ = change in time

This is **average rate of reaction, r_{av}.** which is rate of reaction over a certain measurable period of time during the course of reaction.

To express the rate at a particular moment of time, we determine the **instantaneous rate, r_{inst}**. It is given by:

$$r_{av} = \frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t} \quad (\because \text{time interval is the smallest})$$

As $t \rightarrow 0$,

$$r_{inst} = \frac{-d[A]}{dt} = \frac{d[B]}{dt}$$

Rate of Reaction in the Form of Stoichiometry of a Chemical Reaction

Let us consider a reaction :

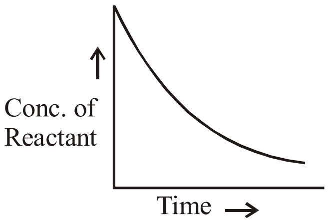
$$m_1A + m_2B + \text{-------} \longrightarrow n_1P + n_2Q + n_3R + \text{---------}$$

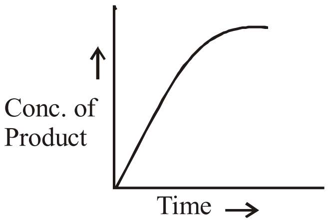
Rate of reaction

$$= -\frac{1}{m_1}\frac{d[A]}{dt} = -\frac{1}{m_2}\frac{d[B]}{dt} = \frac{1}{n_1}\frac{d[P]}{dt} = \frac{1}{n_2}\frac{d[Q]}{dt}$$

Units of rate of reaction are conc/time i.e., mol $L^{-1}s^{-1}$.

Graphically, it is shown as:





FACTORS AFFECTING RATE OF A REACTION

(i) **Nature of reactants :** Reactions involving lesser bond rearrangement proceed much faster than those which involve larger bond rearrangement.

(ii) **Concentration of reactants :** More will be the concentration of reactant greater will be the rate of reaction.

(iii) **Temperature :** When temperature increases, the rate of reaction increase because large number of molecules cross the energy barrier. For all reactions, rate of reaction increases with increase in temperature whether reaction is exothermic or endothermic.

(iv) **Presence of catalyst:** Catalyst increased rate without itself getting consumed in reaction

(v) **Surface area of reactants :** The more the surface area, the more is the rate of reaction.

(vi) **Presence of light :** Some reactions do not occur in dark but occur in presence of light. Such reactions are known as photochemical reactions.

RATE LAW, RATE CONSTANT, ORDER OF REACTION

Rate Law

For a general reaction,

$aA + bB \rightarrow cC + dD$

the rate expression is given by:

Rate $\propto [A]^a[B]^b$ (Law of mass action)

$\boxed{\text{Rate} \propto [A]^x\,[B]^y}$ Rate Law or Rate expression

where x and y may or may not be equal to a and b

Again, Rate $= k\,[A]^x\,[B]^y$

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

This is called **Differential rate equation**. This equation which relates the rate of reaction to concentration of reactants is called rate law or rate expression. Rate law or for any reaction is determined experimentally.

Rate Constant

k is constant of proportionality called **Rate constant/ Velocity constant/ specific reaction rate**.

$$[A] = [B] = 1$$
$$\text{Rate} = k$$

In general rate constant may be defined as the rate of the reaction when the concentration of each of the reactants is unity.

Characteristics of rate constant :

(i) The value of k is different for different reactions.

(ii) At fixed temperature the value of k is constant.

(iii) It is independent of concentration but depends on temperature.

(iv) The larger the value of k the faster is the reaction and vice versa.

'k' for different reaction order are given below:

Order of reaction	Units of rate constant
Zero $(n = 0)$	$(\text{mol L}^{-1})^{1-0}\text{s}^{-1} = \text{mol L}^{-1}\text{s}^{-1}$
First order $(n = 1)$	$(\text{mol L}^{-1})^{1-1}\text{s}^{-1} = \text{s}^{-1}$
Second order $(n = 2)$	$(\text{mol L}^{-1})^{1-2}\text{s}^{-1} = \text{mol L}^{-1}\text{s}^{-1}$

Order of reaction

It is defined as the sum of the exponents to which the concentration terms in the rate law expression are raised to express the observed rate of reaction.

For the reaction

$$\alpha A + \beta B \longrightarrow \text{Products}$$

then, Rate $= k\,[A]^{\alpha}\,[B]^{\beta}$,

then the sum of exponents of concentration terms

$$= \alpha + \beta = \text{Order of reaction}$$

where α = Order with respect to reactant A

β = Order with respect to reactant B

(i) The order of a reaction may be zero, (–)ve, (+)ve or fractional.

(ii) The order of a reaction is determined by the slowest step of mechanism.

(iii) Reactions of higher order (more than 3) are rare.

Note : Order of a reaction is experimentally determined quantity. It can be obtained from rate law equation not from balanced chemical equation.

Molecularity of a Reaction

The reactions taking place in one step are called elementary reactions. The reactions which do not occur in one step are called complex reactions.

The total number of moles of atoms or ions or molecules or reacting species in a balanced chemical equation is called molecularity of the reaction.

For an elementary reaction, molecularity is the sum of the molecules of different reactants as represented by balanced chemical equation whereas complex reaction, molecularity has no meaning.

It can only be defined for an elementary reaction.

The main points of different between order and molecularity of a reaction are:

Difference Between Order and Molecularity of Reaction

Order of reaction		Molecularity of reaction	
1.	It can be fractional as well as zero.	1.	It is always a whole number. It cannot be zero or fractional.
2.	It can be determined experimentally only.	2.	It can be calculated by simply adding the molecules of the slowest step.
3.	It is applicable to elementary as well as complex reactions.	3.	It is applicable only to elementary reactions. For a complex reaction, molecularity of the slowest step is same as the overall order of reaction.
4.	It cannot be obtained from balanced or stoichiometric equation.	4	It can be obtained.
5	It is changed when one reactant is taken in large excess	5	It undergoes no change.

INTEGRATED RATE EQUATIONS

The integrated rate equations are different for reactions of different orders. Some of these are:

Zero Order Reaction

$$X \rightarrow Y$$

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

$$\frac{-d[X]}{dt} = k \Rightarrow d[X] = -kdt$$

On integrating both sides

$$[X] = -kt + C \qquad \text{..........(i)}$$

At $t = 0$ $[X] = [X]_0$

$$[X]_0 = C$$

Substituting in equation (i) we get,

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

$$k = \frac{[X]_0 - [X]}{t} \qquad \text{..........(ii)}$$

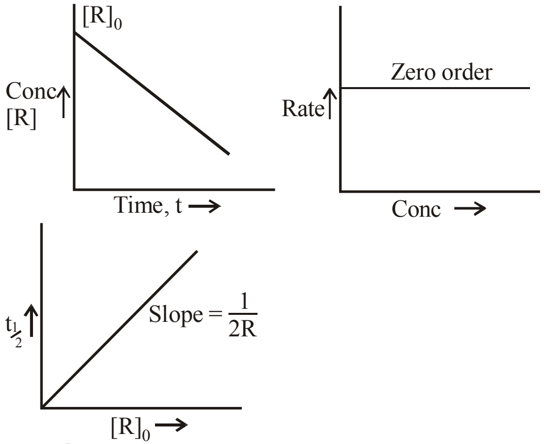
Half-life for zero order reaction :

At $t = t_{1/2}$ $\quad [X] = \frac{1}{2}[X]_0$

By putting these values in equation (ii)

$$k = \frac{[X]_0 - \frac{1}{2}[X]_0}{t_{1/2}} \qquad t_{1/2} = \frac{[X]_0}{2k}$$

Graphical representation for zero order reaction



First Order Reaction

$$X \rightarrow Y$$

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

On integrating both sides

$$\ln [X] = -kt + C \quad \text{.......... (i)}$$

when $t = 0$, $[X] = [X]_0$

$$\ln [X]_0 = C$$

Substituting in equation (i) we get

$$\ln [X] = -kt + \ln [X]_0$$

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

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

$$kt = \ln \frac{[X]_0}{[X]} \Rightarrow k = \frac{1}{t} \ln \frac{[X]_0}{[X]}$$

$$k = \frac{2.303}{t} \log \frac{[X]_0}{[X]} \quad \text{.......... (ii)}$$

Half-life for first order reaction :

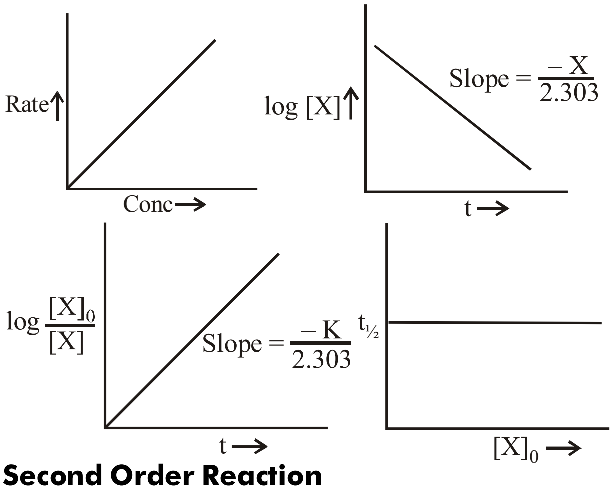
When $t = t_{1/2}$, $[X] = \frac{[X]_0}{2}$

By putting values in equation (ii)

$$k = \frac{2.303}{t_{1/2}} \log \frac{[X]_0}{[X]_{0/2}}$$

$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{0.693}{k}$$

Graphical representation for first order reaction



Second Order Reaction

These are of two types :

(i) $2A \longrightarrow$ Products

Rate $\propto [A]^2$

(ii) $A + B \longrightarrow$ Product

Rate $\propto [A][B]$

For reaction, $2X \longrightarrow$ Product

$$k = \frac{1}{t} \frac{X}{[X]_0([X]_0 - [X])} \quad \text{...... (i)}$$

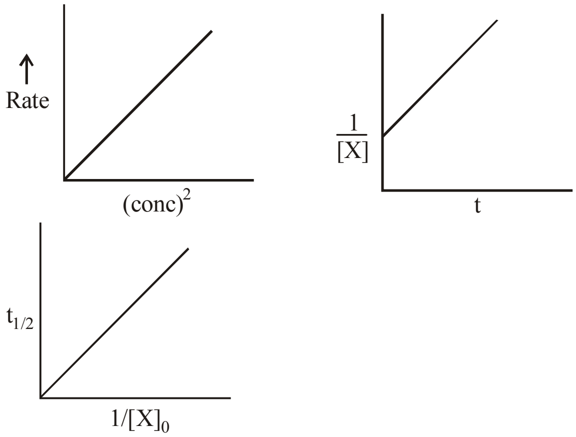
Half life period for second order rection :

When $t = t_{1/2}$, $[X] = \frac{[X]_0}{2}$

By putting values in equation (i)

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

Graphical representation for second order reaction



On summarising we get,

Order	Reaction	Differential Rate Law	Integrated Rate Law	Half – life	Units of R
0	$X \rightarrow Y$	$\frac{d[X]}{dt} = -k$	$kt = [X]_0 - [X]$	$[X]_0 / 2k$	Conc. time^{-1}or mol L^{-1}s^{-1}
1	$X \rightarrow Y$	$\frac{d[X]}{dt} = -k[X]$	$[X] = [X]_0 e^{-kt}$ or $kt = \ln \frac{[X]_0}{[X]}$	$\ln 2 / k$	time^{-1}or s^{-1}
2	$2X \rightarrow$ Product		$k = \frac{[X]}{t[X]_0([X]_0 - [X])}$	$\frac{1}{k[X]_0}$	conc^{-1}time^{-1}or mol s^{-1}

Half-life Period for the nth Order Reaction

When the order of reaction is n, $t_{1/2}$ is given by

$$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1}-1}{a^{n-1}}\right]$$

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

Unit of k = $(\text{conc})^{1-n}$. time^{-1}

For a first order gas phase reaction, $A(g) \rightarrow B(g) + C(g)$

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

where p_i is initial pressure of A, $p_t \rightarrow$ total pressure at time t

$(p_t = p_A + p_B + p_C)$

PSEUDO FIRST ORDER REACTIONS

Reactions are not truly of first order but under certain conditions become reactions of first order are called pseudo-first order reactions.

For ex:

(i) acid-catalysed hydrolysis of ethyl acetate

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Rate of reaction $\propto [CH_3COOC_2H_5]$

(ii) acid-catalysed inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

Rate of reaction $\propto [C_{12}H_{22}O_{11}]$

This is because that water is present in such large excess that its concentration remains almost constant during the reaction.

ACTIVATION ENERGY

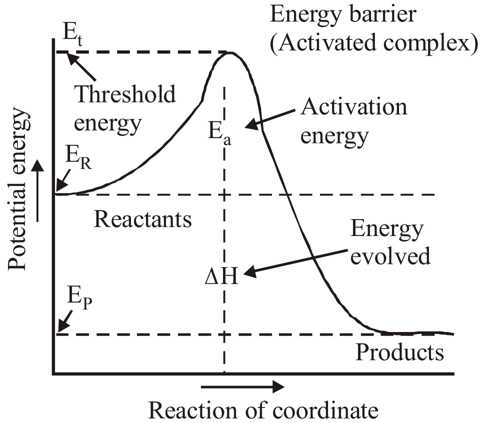
The minimum energy which the colliding molecules must have in order that the collision between them may be effective is called **threshold energy.**

The minimum extra amount of energy absorbed by reactant molecules so that their energy becomes equal to threshold value is called **activation energy.** Thus,

Activation energy = Threshold energy – Avg KE of reactant

For fast reaction activation energy is low while for slow reaction activation energy is high.

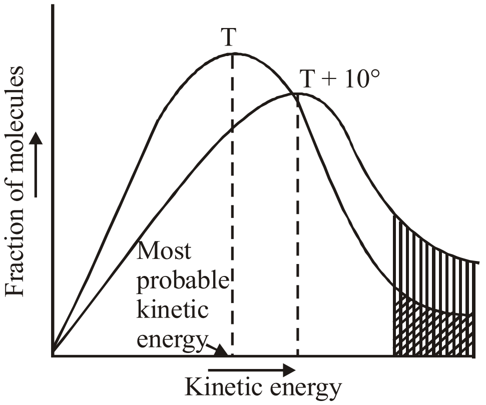
Graphically, it is shown as:



Temperature Dependence of Reaction

For a chemical reaction, with 10°C rise in temperature, the rate constant is nearly doubled. This is because on increasing the temperature, the fraction of molecules colliding with energies greater than E_a increases. At (T + 10)°C, the fraction of molecules having energy equal to or greater than E_a gets doubled leading to doubling the rate of a reaction.

Diagrammatically, it is shown as:



Mathematically, temperature dependence of rate of reaction is given by **Arrhenius equation** given as:

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

Where A → Arrhenius factor or frequency factor or pre-exponential factor

R → gas constant

$E_a \rightarrow$ activation energy

If rate constant of a reaction at a particular temperature is known, its value at another temperature can be calculated, provided E_a is known. It is as follows:

Taking logerithm on both sides of equation (i)

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

If the value of rate constant at temperatures T_1 and T_2 are k_1 and k_2

$$\ln k_1 = \ln A - E_a/RT_1$$
$$\ln k_2 = \ln A - E_a/RT_2$$

On substracting the two equations we get

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

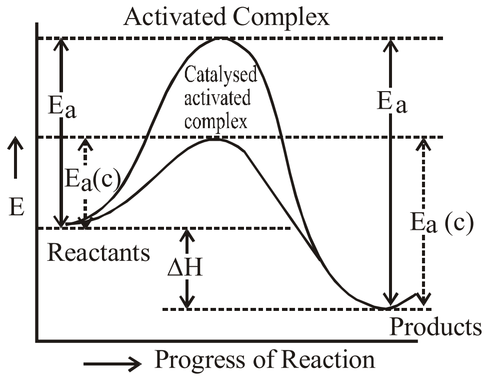
$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

EFFECT OF CATALYST ON RATE OF REACTION

A catalyst alters the rate of a reaction without itself undergoing any permanent chemical change.

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.

The graphical representation is as follows:



Where,

E_a = Activation energy without catalyst

$E_a(c)$ = Activation energy with catalyst.

COLLISION THEORY OF CHEMICAL REACTIONS

Chemical reaction occurs as a result of effective collision between reaction molecules. For this two things are important.

(i) proper orientation of reaction molecules

(ii) possession of energy more than threshold energy.

Collision Frequency

Total number of collisions which occur among the reacting molecules per second per unit volume is called collision frequency. Its value is given by

$$z = \sqrt{2}\,\pi\,\bar{v}\,\sigma^2 n^2$$

$\bar{v}$ = average velocity, σ = molecular diameter in cm.,

n = number of molecules per cc.

Rate of Reaction from Collision Theory

It is given by

Rate of reaction $= f \times z$

z = collision frequency,

f = fraction of effective collisions

$$= \frac{\Delta n}{N} = e^{-E_a/RT}$$

$\therefore$ Rate (k) = $Ze^{-E_a/RT}$

For effective collision another factor P, called **steric factor** has to be taken into consideration.

Then rate of reaction can be expressed as

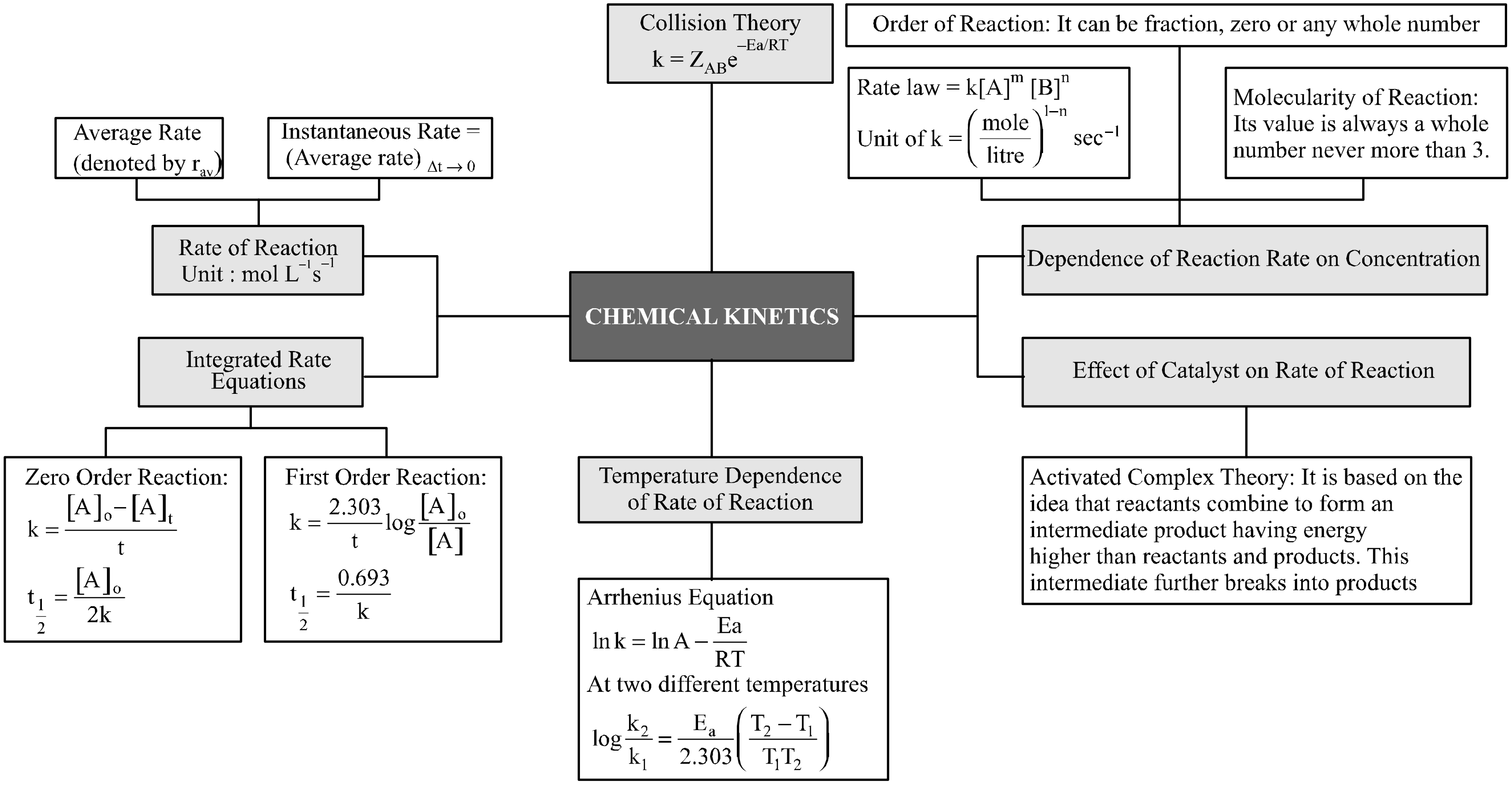
$$\text{Rate} = PZ_{AB}\, e^{-Ea/RT}$$

Where P → Probability or steric factor

Z_{AB} → collision frequency of reactants A and B

$e^{-Ea/RT}$ → fraction of molecules with energies equal to or greater than E_a.

CONCEPT MAP



CHEMICAL KINETICS

Collision Theory
$k = Z_{AB}e^{-Ea/RT}$

Rate of Reaction
Unit : mol $L^{-1}s^{-1}$

Average Rate (denoted by r_{av})

Instantaneous Rate = $(\text{Average rate})_{\Delta t \to 0}$

Integrated Rate Equations

Zero Order Reaction:
$$k = \frac{[A]_o - [A]_t}{t}$$
$$t_{\frac{1}{2}} = \frac{[A]_o}{2k}$$

First Order Reaction:
$$k = \frac{2.303}{t}\log\frac{[A]_o}{[A]}$$
$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Temperature Dependence of Rate of Reaction

Arrhenius Equation
$$\ln k = \ln A - \frac{Ea}{RT}$$
At two different temperatures
$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

Dependence of Reaction Rate on Concentration

Order of Reaction: It can be fraction, zero or any whole number

Rate law = $k[A]^m\,[B]^n$
Unit of k = $\left(\frac{\text{mole}}{\text{litre}}\right)^{1-n}$ sec^{-1}

Molecularity of Reaction: Its value is always a whole number never more than 3.

Effect of Catalyst on Rate of Reaction

Activated Complex Theory: It is based on the idea that reactants combine to form an intermediate product having energy higher than reactants and products. This intermediate further breaks into products

EXERCISE - 1

Conceptual Questions

1. The rate constant of first order reaction is 3×10^{-6} per second. The initial concentration is 0.10 M. The initial rate is:

(a) 3×10^{-7} moles/litre/sec

(b) 3×10^{-8} moles/litre/sec

(c) 3×10^{-5} moles/litre/sec

(d) 3×10^{-8} moles/litre/sec

2. Which of the following statement is true for the reaction, $H_2 + Br_2 \rightarrow 2HBr$. The rate law is $\frac{dx}{dt} = k[H_2][Br_2]^{1/2}$:

(a) order of reaction is 1.5

(b) molecularity of the reaction is 2

(c) by increasing the concentration of Br_2 four times the rate of reaction is doubled

(d) all the above are correct.

3. The rate constant *k*, for the reaction

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

is $1.3 \times 10^{-2} s^{-1}$. Which equation given below describes the change of $[N_2O_5]$ with time ? $[N_2O_5]_0$ and $[N_2O_5]_t$ corrospond to concentration of N_2O_5 initially and at time *t*.

(a) $[N_2O_5]_t = [N_2O_5]_0 + kt$

(b) $[N_2O_5]_0 = [N_2O_5]_t e^{kt}$

(c) $\log [N_2O_5]_t = \log [N_2O_5]_0 + kt$

(d) In $\frac{[N_2P_5]_0}{[N_2P_5]_t} = kt$

4. For the reaction $2A + B \rightarrow 3C + D$

Which of the following does not express the reaction rate ?

(a) $-\frac{d[B]}{dt}$ (b) $\frac{d[D]}{dt}$

(c) $-\frac{1}{2}\frac{d[A]}{dt}$ (d) $-\frac{1}{3}\frac{d[C]}{dt}$

5. Consider the reaction : $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

The equality relationship between $\frac{d[NH_3]}{dt}$ and $-\frac{d[H_2]}{dt}$ is

(a) $+\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$ (b) $+\frac{d[NH_3]}{dt} = -\frac{3}{2}\frac{d[H_2]}{dt}$

(c) $\frac{d[NH_3]}{dt} = -\frac{d[H_2]}{dt}$ (d) $\frac{d[NH_3]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt}$

6. For the reaction system :

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

(a) diminish to one-eighth of its initial value

(b) increase to eight times of its initial value

(c) increase to four times of its initial value

(d) diminish to one-fourth of its initial value

7. For reaction $aA \rightarrow xP$, when [A] = 2.2 mM, the rate was found to be 2.4 mMs^{-}. On reducing concentration of A to half, the rate changes to 0.6 mMs^{-1}. The order of reaction with respect to A is :

(a) 1.5 (b) 2.0

(c) 2.5 (d) 3.0

8. The rate of reaction is doubled for every 10°C rise in temperature. The increase in reaction rate as a result of temperature rise from 10°C to 100°C is :

(a) 614 (b) 400

(c) 512 (d) 112

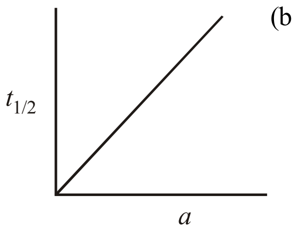
9. In the reaction $2A + B \rightarrow A_2B$, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will:

(a) increase 2 times (b) increase 4 times

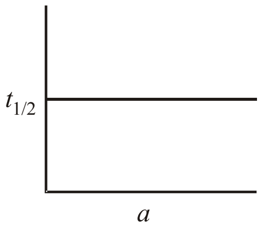
(c) decrease 2 times (d) remain the same

10. Which of the following graphs represent relation between initial concentration of reactants and half-life for third order reaction?

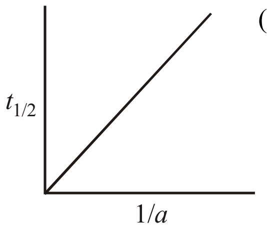
(a)



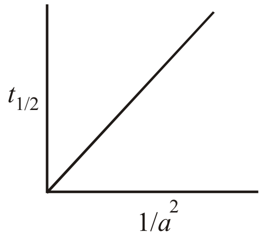
(b)



(c)



(d)



11. The differential rate law for the reaction

$H_2(g) + I_2(g) \rightarrow 2HI(g)$ is

(a) $-\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$

(b) $\frac{d[H_2]}{dt} = \frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$

(c) $\frac{1}{2}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[I_2]}{dt} = -\frac{d[HI]}{dt}$

(d) $-2\frac{d[H_2]}{dt} = -2\frac{d[I_2]}{dt} = \frac{d[HI]}{dt}$

12. Select the rate law that corresponds to data shown for the following reaction

$A + B \longrightarrow$ products.

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

(a) rate = $k\,[B]^3$ (b) rate = $k\,[B]^4$
(c) rate = $k\,[A]\,[B]^3$ (d) rate = $k\,[A]^2\,[B]^2$

13. For the reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, rate and rate constant are 1.02×10^{-4} mol lit^{-1} sec^{-1} and 3.4×10^{-5} sec^{-1} respectively then concentration of N_2O_5 at that time will be
(a) 1.732M (b) 3M
(c) 3.4×10^5M (d) 1.02×10^{-4}M

14. For a first order reaction, to obtain a positive slope, we need to plot {where [A] is the concentration of reactant A}
(a) $-\log_{10}[A]$ *vs* t (b) $-\log_e[A]$ *vs* t
(c) $\log_{10}[A]$ *vs* log t (d) [A] *vs* t

15. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is:
(a) 2×10^4 (b) 3.45×10^{-5}
(c) 1.386×10^{-4} (d) 2×10^{-4}

16. The rate constant for the reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$ is 3.10×10^{-5} sec^{-1}. If the rate is 2.4×10^{-5} mol litre^{-1} sec^{-1} then the concentration of N_2O_5 (in mol litre^{-1}) is :
(a) 0.04 (b) 0.8 (c) 0.07 (d) 1.4

17. T_{50} of first -order reaction is 10 min. Starting with 10 mol L^{-1}, rate after 20 min is
(a) 0.0693 mol L^{-1} min^{-1}
(b) 0.0693 × 2.5 mol L^{-1} min^{-1}
(c) 0.0693 × 5 mol L^{-2} min^{-1}
(d) 0.0693 × 10 mol L^{-1} min^{-1}

18. Velocity constant K of a reaction is affected by
(a) Change in the concentration of the reactant
(b) Change of temperature
(c) Change in the concentration of the product
(d) None of the above

19. The first order rate constant for a certain reaction increases from 1.667×10^{-6} s^{-1} at 727°C to 1.667×10^{-4} s^{-1} at 1571°C. The rate constant at 1150°C, assuming constancy of activation energy over the given temperature range is [Given : log 19.9 = 1.299]
(a) 3.911×10^{-5} s^{-1} (b) 1.139×10^{-5} s^{-1}
(c) 3.318×10^{-5} s^{-1} (d) 1.193×10^{-5} s^{-1}

20. For the following reaction scheme (homogeneous), the rate constant has units : $A + B \xrightarrow{K} C$
(a) sec^{-1} mole (b) sec^{-1}
(c) sec^{-1} litre mole^{-1} (d) sec

21. A substance 'A' decomposes by a first order reaction starting initially with [A] = 2.00 M and after 200 min, [A] becomes 0.15 M. For this reaction $t_{1/2}$ is
(a) 53.72 min (b) 50.49 min (c) 48.45 min (d) 46.45 min

22. After how many seconds will the concentration of the reactants in a first order reaction be halved, if the decay constant is 1.155×10^{-3} sec^{-1}.
(a) 200 (b) 400 (c) 600 (d) 800

23. The plot of concentration of the reactant vs time for a reaction is a straight line with a negative slope. The reaction follows a rate equation
(a) zero order (b) first order
(c) second order (d) third order

24. Half life of a first order reaction is 4s and the initial concentration of the reactant is 0.12 M. The concentration of the reactant left after 16 s is
(a) 0.0075 M (b) 0.06 M (c) 0.03 M (d) 0.015 M

25. $3A \rightarrow B + C$, it would be a zero order reaction when
(a) the rate of reaction is proportional to square of concentration of A
(b) the rate of reaction remains same at any concentration of A
(c) the rate remains unchanged at any concentration of B and C
(d) the rate of reaction doubles if concentration of B is increased to double

26. A first order reaction is 50% completed in 30 minutes at 27°C. Its rate constant is :
(a) 2.31×10^{-2} minute^{-1} (b) 3.21×10^{-5} minute^{-1}
(c) 4.75×10^{-2} minute^{-1} (d) 1.33×10^{-3} minute^{-1}

27. The reaction $A \rightarrow B$ follows first order kinetics. The time taken for 0.8 mole of A to produce 0.6 mole of B is 1 hour. What is the time taken for conversion of 0.9 mole of A to produce 0.675 mole of B?
(a) 2 hours (b) 1 hour (c) 0.5 hour (d) 0.25 hour

28. Out of the following reaction which will proceed in forward direction if volume of container is increased?
(a) $H_2 + Cl_2 \longrightarrow 2HCl$
(b) $CaCO_3 \longrightarrow CaO + CO_2$
(c) $N_2 + 3H_2 \longrightarrow 2NH_3$
(d) $N_2 + 2O_2 \longrightarrow N_2O_4$

29. The rate of a first order reaction is 1.5×10^{-2} mol L^{-1} min^{-1} at 0.5 M concentration of the reactant. The half life of the reaction is
(a) 0.383 min (b) 23.1 min (c) 8.73 min (d) 7.53 min

30. For a first order reaction $A \longrightarrow B$ the reaction rate at reactant concentration of 0.01 M is found to be 2.0×10^{-5} mol L^{-1} s^{-1}. The half life period of the reaction is
(a) 30 s (b) 220 s (c) 300 s (d) 347 s

31. For a chemical reaction which can never be a fraction :
(a) rate constant (b) order
(c) molecularity (d) half life

32. If half-life of a substance is 5 yrs, then the total amount of substance left after 15 years, when initial amount is 64 grams is

(a) 16 grams (b) 2 grams (c) 32 grams (d) 8 grams.

33. In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is

(a) 7.5 minutes (b) 15 minutes

(c) 30 minutes (d) 60 minutes

34. The concentration of a reactant X decreases from 0.1 M to 0.005 M in 40 min. If the reaction follows first order kinetics, the rate of the reaction when the concentration of X is 0.01 M will be

(a) 1.73×10^{-4} M min^{-1} (b) 3.47×10^{-4} M min^{-1}

(c) 3.47×10^{-5} M min^{-1} (d) 7.5×10^{-4} M min^{-1}

35. The order of a reaction with rate equal to $k[A]^{3/2}[B]^{-1/2}$ is :

(a) 1 (b) $-\frac{1}{2}$ (c) $-\frac{3}{2}$ (d) 2

36. The rate constant for a first order reaction whose half-life, is 480 seconds is :

(a) 2.88×10^{-3} sec^{-1} (b) 2.72×10^{-3} sec^{-1}

(c) 1.44×10^{-3} sec^{-1} (d) 1.44 sec^{-1}

37. In a reaction, when the concentration of reactant is increased two times, the increase in rate of reaction was four times. Order of reaction is :

(a) zero (b) 1 (c) 2 (d) 3

38. The rate constant of a first order reaction is $6.9 \times 10^{-3} s^{-1}$. How much time will it take to reduce the initial concentration to its 1/8th value?

(a) 100 s (b) 200 s (c) 300 s (d) 400 s

39. In a 1st order reaction, reactant concentration *C* varies with time *t* as :

(a) $\frac{1}{C}$ increases linearly with *t*

(b) log *C* decreases linearly with *t*

(c) *C* decreases with $\frac{1}{t}$

(d) log *C* decreases with $\frac{1}{t}$

40. A substance 'A' decomposes by a first order reaction starting initially with [A] = 2.00 mol/litre and after 200 sec, [A] = 0.15 mol/litre. For this reaction, what is the value of k ?

(a) 1.29×10^{-2} sec^{-1} (b) 2.03×10^{-3} sec^{-1}

(c) 1.80×10^{-3} sec^{-1} (d) 1.55×10^{-2} sec^{-1}

41. A reaction proceeds by first order, 75% of this reaction was completed in 32 min. The time required for 50% completion is

(a) 8 min (b) 16 min (c) 20 min (d) 24 min

42. For the third order reaction, $3A \longrightarrow$ products, with 0.1 M as the initial concentration of A, $t_{1/2}$ is 8 hr 20 minute. The rate constant of the reaction is

(a) 5×10^{-3} lit^2 mole^{-1} sec^{-1}

(b) 50 lit^2 mole^{-2} sec^{-1}

(c) 5.0×10^{-3} lit^2 mole^{-2} sec^{-1}

(d) 5×10^{-2} lit^2 mole^{-2} sec^{-1}

43. What is order with respect to A, B, C, respectively

[A]	[B]	[C]	rate (M/sec.)
0.2	0.1	0.02	8.08×10^{-3}
0.1	0.2	0.02	2.01×10^{-3}
0.1	1.8	0.18	6.03×10^{-3}
0.2	0.1	0.08	6.464×10^{-2}

(a) –1, 1, 3/2 (b) –1, 1, 1/2

(c) 1, 3/2, –1 (d) 1, –1, 3/2

44. For a chemical reaction $t_{1/2}$ is 2.5 hours at room temperature. How much of the reactant will be left after 7.5 hours if initial weight of reactant was 160 gm?

(a) 10 gm (b) 40 gm (c) 80 gm (d) 20 gm

45. For the reaction,

$$CH_3COCH_3 + I_2 \xrightarrow{H^+} \text{products}$$

The rate is governed by expression

$$\frac{dx}{dt} = k[\text{acetone}][H^+]$$

The order w.r.t. I_2 is:

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

46. In the following first order competing reactions

X + reagent → product

Y + reagent → product

The ratio of $\frac{k_1}{k_2}$ if only 50% of Y will have been reacted when 94% of X has been reacted is

(a) 3.06 (b) 1.06

(c) 4.06 (d) 0.06

47. The rate constant of a reaction is 3.00×10^3 L mol^{-1} sec^{-1}. The order of this reaction will be:

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

48. Point out the wrong statement:

For a first order reaction

(a) time for half-change ($t_{1/2}$) is independent of initial concentration

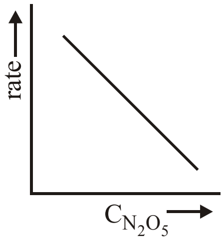
(b) change in the concentration unit does not change the rate constant (k)

(c) time for half-change × rate constant = 0.693

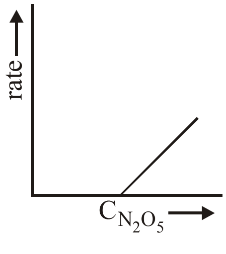
(d) the unit of k is mole^{-1} min^{-1}

49. Which one of the following plots is true for the first order decomposition of N_2O_5 ?

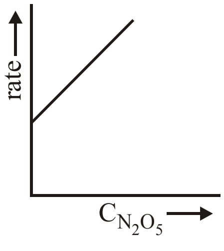
(a)



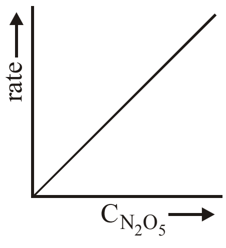
(b)



(c)



(d)



50. The first order rate constant for the decomposition of N_2O_5

is 6.2×10^{-4} sec^{-1}. The half life period for this decomposition in seconds is

(a) 1117.7 (b) 111.7 (c) 223.4 (d) 160.9

51. For a certain reaction, rate = $k \times [H^+]^n$. If pH of reaction changes from two to one, the rate becomes 100 times of its value at pH = 2, the order of reaction is –

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

52. The half-life of a reaction is inversely proportional to the square of the initial concentration of the reactant. Then the order of the reaction is

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

53. Ethylene is produced by $C_4H_8 \xrightarrow{\Delta} 2C_2H_4$

The rate constant is 2.3×10^{-4} sec^{-1}. Approximately in what time will the molar ratio of ethylene to cyclobutane in mixture attain the value equal to one ?

(log 2 = 0.3, log 3 = 0.47)

(a) 1700 sec (b) 1600 sec
(c) 2000 sec (d) 1200 sec

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

(a) 0.75/k (b) 0.69/k (c) 0.29/k (d) 0.10/k

55. What is the half life of a radioactive substance if 87.5% of any given amount of the substance disintegrates in 40 minutes ?

(a) 20 minutes (b) 10 minutes
(c) 13 minutes 32 sec (d) 160 minutes

56. The rate law for the reaction $2X + Y \rightarrow Z$ is Rate = k[X][Y]. The correct statement with regard to this relation is

(a) the unit of k is s^{-1}
(b) the rate of the reaction is independent of [X] and [Y]
(c) for this reaction $t_{1/2}$ is independent of initial concentrations of reactant
(d) the rate of formation of Z is half of the rate of disappearance of X

57. For an exothermic reaction, the energy of activation of the reactants is

(a) equal to the energy of activation of products
(b) less than the energy of activation of products
(c) greater than the energy of activation of products
(d) sometimes greater and sometimes less than that of the products

58. A chemical reaction is catalyzed by a catalyst X. Hence X

(a) reduces enthalpy of the reaction
(b) decreases rate constant of the reaction
(c) increases activation energy of the reaction
(d) does not affect equilibrium constant of the reaction

59. Consider the following statements:

I. Increase in concentration of reactant increases the rate of a zero order reaction.
II. Rate constant k is equal to collision frequency A if $E_a = 0$.
III. Rate constant k is equal to collision frequency A if $E_a = \infty$.
IV. In k vs T is a straight line.
V. In k vs 1/T is a straight line.

Correct statements are

(a) I and IV (b) II and V
(c) III and IV (d) II and III

60. Activation energy of a chemical reaction can be determined by

(a) evaluating rate constant at standard temperature
(b) evaluating velocities of reaction at two different temperatures
(c) evaluating rate constants at two different temperatures
(d) changing concentration of reactants

61. The rate law for the reaction

$xA + yB \longrightarrow mP + nQ$ is Rate = k $[A]^c[B]^d$. What is the total order of the reaction?

(a) (x + y) (b) (m + n)
(c) (c + d) (d) x/y

62. The temperature dependence of rate constant (k) of a chemical reaction is written in terms of Arrhenius equation, $k = Ae^{-E_a^*/RT}$. Activation energy (E_a^*) of the reaction can be calculated by plotting

(a) $\log k \text{ vs} \frac{1}{\log T}$ (b) k vs T

(c) $k \text{ vs} \frac{1}{\log T}$ (d) $\log k \text{ vs} \frac{1}{T}$

63. For a first order reaction, the time taken to reduce the initial concentration by a factor of $\frac{1}{4}$ is 20 minutes. The time required to reduce initial concentration by a factor of $\frac{1}{16}$ is

(a) 20 min (b) 10 min
(c) 80 min (d) 40 min

64. The activation energy for a simple chemical reaction $A \rightarrow B$ is E_a in forward direction. The activation energy for reverse reaction

(a) is always double of E_a
(b) is negative of E_a
(c) is always less than E_a
(d) can be less than or more than E_a

65. Rate of a reaction can be expressed by Arrhenius equation as : $k = Ae^{-E_a/RT}$

In this equation, E_a represents

(a) the total energy of the reacting molecules at a temperature, T
(b) the fraction of molecules with energy greater than the activation energy of the reaction
(c) the energy below which all the colliding molecules will react
(d) the energy below which colliding molecules will not react

66. The minimum energy a molecule should possess in order to enter into a fruitful collision is known as

(a) reaction energy (b) collision energy
(c) activation energy (d) threshold energy

67. Which one of the following reactions is a true first order

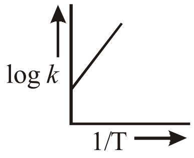
reaction?
(a) Alkaline hydrolysis of ethyl acetate
(b) Acid catalyst hydrolysis of ethyl acetate
(c) Decomposition of N_2O
(d) Decomposition of gaseous ammonia on a hot platinum surface

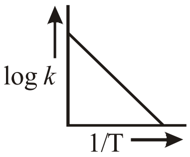
68. The reason for almost doubling the rate of reaction on increasing the temperature of the reaction system by 10°C is
(a) The value of threshold energy increases
(b) Collision frequency increases
(c) The fraction of the molecule having energy equal to threshold energy or more increases
(d) Activation energy decreases

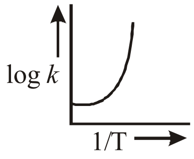
69. For a reaction, activation energy $(E_a) = 0$ and rate constant $(k) = 3.2 \times 10^6 s^{-1}$ at 300 K. What is the value of the rate constant at 310 K
(a) $3.2 \times 10^{-12} s^{-1}$ (b) $3.2 \times 10^6 s^{-1}$
(c) $6.4 \times 10^{12} s^{-1}$ (d) $6.4 \times 10^6 s^{-1}$

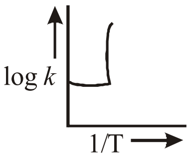
70. In the Arrhenius plot of ln k vs $\frac{1}{T}$, a linear plot is obtained with a slope of -2×10^4 K. The energy of activation of the reaction (in kJ mole^{-1}) is (R value is 8.3 J K^{-1} mol^{-1})
(a) 83 (b) 166 (c) 249 (d) 332

71. A graph plotted between log k vs 1/T for calculating activation energy is shown by

(a) 

(b) 

(c) 

(d) 

72. Consider an endothermic reaction $X \rightarrow Y$ with the activation energies, respectively, in general
(a) $E_b < E_f$
(b) $E_b > E_f$
(c) $E_b = E_f$
(d) There is no definite relation between E_b and E_f

73. When a biochemical reaction is carried out in laboratory in the absence of enzyme then rate of reaction obtained is 10^{-6} times, then activation energy of reaction in the presence of enzyme is
(a) $\frac{6}{RT}$
(b) different from E_a obtained in laboratory
(c) P is required
(d) can't say anything

74. In a first order reaction, the concentration of the reactant is reduced to $\frac{1}{8}$ of the initial concentration in 75 minutes at 298 K. What is the half-life period of the reaction in minutes?
(a) 50 (b) 15 (c) 45 (d) 25

75. The reaction of hydrogen and iodine monochloride is given as:

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

The reaction is of first order with respect to $H_2(g)$ and $ICl(g)$, following mechanisms were proposed.
Mechanism A:

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

Mechanism B:

$$H_2(g) + ICl(g) \longrightarrow HI(g); \text{slow}$$

$$HI(g) + ICl(g) \longrightarrow HCl(g) + I_2(g); \text{fast}$$

Which of the above mechanism(*s*) can be consistent with the given information about the reaction?
(a) A and B both (b) neither A nor B
(c) A only (d) B only

76. In a first-order reaction $A \rightarrow B$, if k is rate constant and inital concentration of the reactant A is 0.5 M, then the half-life is
(a) $\frac{\log 2}{k}$ (b) $\frac{\log 2}{k\sqrt{0.5}}$ (c) $\frac{\ln 2}{k}$ (d) $\frac{0.693}{0.5k}$

77. The bromination of acetone that occurs in acid solution is represented by this equation.

$$CH_3COCH_3\,(aq) + Br_2\,(aq) \rightarrow CH_3COCH_2Br\,(aq) + H^+\,(aq) + Br^-\,(aq)$$

These kinetic data were obtained for given reaction concentrations.

Initial Concentrations, M			**Initial rate, disappearance of Br_2, Ms^{-1}**
[CH_3COCH_3]	**[Br_2]**	**[H^+]**	
0.30	0.05	0.05	5.7×10^{-5}
0.30	0.10	0.05	5.7×10^{-5}
0.30	0.10	0.10	1.2×10^{-4}
0.40	0.05	0.20	3.1×10^{-4}

Based on given data, the rate equations is:
(a) Rate = $k[CH_3COCH_3][H^+]$
(b) Rate = $k[CH_3COCH_3][Br_2]$
(c) Rate = $k[CH_3COCH_3][Br_2][H^+]^2$
(d) Rate = $k[CH_3COCH_3][Br_2][H^+]$

78. For the reaction, $N_2 + 3H_2 \rightarrow 2NH_3$,

$\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$ mol L^{-1} s^{-1}, the value of $\frac{-d[H_2]}{dt}$ would be :
(a) 4×10^{-4} mol L^{-1} s^{-1} (b) 6×10^{-4} mol L^{-1} s^{-1}
(c) 1×10^{-4} mol L^{-1} s^{-1} (d) 3×10^{-4} mol L^{-1} s^{-1}

79. In the reaction

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

The rate of appearance of bromine (Br_2) is related to rate of disappearance of bromide ions as following:

(a) $\frac{d[Br_2]}{dt}=-\frac{5}{3}\frac{d[Br^-]}{dt}$ (b) $\frac{d[Br_2]}{dt}=\frac{5}{3}\frac{d[Br^-]}{dt}$

(c) $\frac{d[Br_2]}{dt}=\frac{3}{5}\frac{d[Br^-]}{dt}$ (d) $\frac{d[Br_2]}{dt}=-\frac{3}{5}\frac{d[Br^-]}{dt}$

80. Half life period of a first-order reaction is 1386 seconds. The specific rate constant of the reaction is :

(a) $0.5\times10^{-2}\ s^{-1}$ (b) $0.5\times10^{-3}\ s^{-1}$

(c) $5.0\times10^{-2}\ s^{-1}$ (d) $5.0\times10^{-3}\ s^{-1}$

81. For the reaction $A+B\longrightarrow$ products, it is observed that:

(1) On doubling the initial concentration of A only, the rate of reaction is also doubled and

(2) On doubling the initial concentrations of both A and B, there is a change by a factor of 8 in the rate of the reaction.

The rate of this reaction is given by:

(a) rate = $k\,[A]\,[B]^2$ (b) rate = $k\,[A]^2\,[B]^2$

(c) rate = $k\,[A]\,[B]$ (d) rate = $k\,[A]^2\,[B]$

82. For the reaction [$N_2O_5(g)\longrightarrow 2NO_2(g)+1/2\ O_2(g)$] the value of rate of disappearance of N_2O_5 is given as $6.25\times10^{-3}\ mol\ L^{-1}s^{-1}$. The rate of formation of NO_2 and O_2 is given respectively as :

(a) $6.25\times10^{-3}\ mol\ L^{-1}s^{-1}$ and $6.25\times10^{-3}\ mol\ L^{-1}s^{-1}$

(b) $1.25\times10^{-2}\ mol\ L^{-1}s^{-1}$ and $3.125\times10^{-3}\ mol\ L^{-1}s^{-1}$

(c) $6.25\times10^{-3}\ mol\ L^{-1}s^{-1}$ and $3.125\times10^{-3}\ mol\ L^{-1}s^{-1}$

(d) $1.25\times10^{-2}\ mol\ L^{-1}s^{-1}$ and $6.25\times10^{-3}\ mol\ L^{-1}s^{-1}$

83. For an endothermic reaction, energy of activation is E_a and enthalpy of reaction of ΔH (both of these in kJ/mol). Minimum value of E_a will be.

(a) less than ΔH (b) equal to ΔH

(c) more than ΔH (d) equal to zero

84. During the kinetic study of the reaction, $2A+B\rightarrow C+D$, following results were obtained:

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

Based on the above data which one of the following is correct?

(a) rate = $k\,[A]^2\,[B]$ (b) rate = $k[A]\,[B]$

(c) rate = $k[A]^2[B]^2$ (d) rate = $k[A]\,[B]^2$

85. The rate of the reaction $2NO+Cl_2\longrightarrow 2NOCl$ is given by the rate equation rate = k $[NO]^2\,[Cl_2]$

The value of the rate constant can be increased by:

(a) increasing the concentration of NO.

(b) increasing the temperature.

(c) increasing the concentration of the Cl_2

(d) doing all of these

86. Which one of the following statements for the order of a reaction is incorrect ?

(a) Order can be determined only experimentally.

(b) Order is not influenced by stoichiometric coefficient of the reactants.

(c) Order of reaction is sum of power to the concentration terms of reactants to express the rate of reaction.

(d) Order of reaction is always whole number.

87. The unit of rate constant for a zero order reaction is

(a) $mol\ L^{-1}\ s^{-1}$ (b) $L\ mol^{-1}\ s^{-1}$

(c) $L^2\ mol^{-2}\ s^{-1}$ (d) s^{-1}

88. In a zero-order reaction for every 10° rise of temperature, the rate is doubled. If the temperature is increased from 10°C to 100°C, the rate of the reaction will become :

(a) 256 times (b) 512 times (c) 64 times (d) 128 times

89. Activation energy (E_a) and rate constants (k_1 and k_2) of a chemical reaction at two different temperatures (T_1 and T_2) are related by :

(a) $\ln\frac{k_2}{k_1}=-\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$ (b) $\ln\frac{k_2}{k_1}=-\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$

(c) $\ln\frac{k_2}{k_1}=-\frac{E_a}{R}\left(\frac{1}{T_2}+\frac{1}{T_1}\right)$ (d) $\ln\frac{k_2}{k_1}=\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

90. The energies of activation for forward and reverse reactions for $A_2+B_2\rightleftharpoons 2AB$ are 180 kJ mol^{-1} and 200 kJ mol^{-1} respectively. The presence of a 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 a catalyst will be (in kJ mol^{-1})

(a) 20 (b) 300 (c) 120 (d) 280

91. Consider the reaction, $2A+B\rightarrow$ products. When concentration of B alone was doubled, the half-life did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is

(a) s^{-1} (b) $L\ mol^{-1}\ s^{-1}$

(c) no unit (d) $mol\ L^{-1}\ s^{-1}$.

92. 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

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

93. The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be (log 2 = 0.301)

(a) 23.03 minutes (b) 46.06 minutes

(c) 460.6 minutes (d) 230.03 minutes

94. For a first order reaction (A) → products the concentration of A changes from 0.1 M to 0.025 M in 40 minutes.

The rate of reaction when the concentration of A is 0.01 M is :

(a) 1.73×10^{-5} M/min (b) 3.47×10^{-4} M/min

(c) 3.47×10^{-5} M/min (d) 1.73×10^{-4} M/min

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

(a) $53.6\ kJ\ mol^{-1}$ (b) $48.6\ kJ\ mol^{-1}$

(c) $58.5\ kJ\ mol^{-1}$ (d) $60.5\ kJ\ mol^{-1}$

96. The rate of reaction depends upon the ***[1995]***

(a) volume (b) force

(c) pressure (d) conc. of reactants

97. Half life of a first order reaction is 4 s and the initial concentration of the reactants is 0.12 M. The concentration of the reactant left after 16 s is ***[1999]***

(a) 0.0075 M (b) 0.06 M

(c) 0.03 M (d) 0.015 M

98. The plot of concentration of the reactant vs. time for a reaction is a straight line with a negative slope. The reaction follows a ***[1996]***

(a) zero order rate equation

(b) first order rate equation

(c) second order rate equation

(d) third order rate equation

99. Select the rate law that corresponds to data shown for the following reaction ***[1994]***

$A + B \longrightarrow$ products.

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

(a) rate = $k[B]^3$

(b) rate = $k[B]^4$

(c) rate = $k[A][B]^3$

(d) rate = $k[A]^2[B]^2$

100. Activation energy of a chemical reaction can be determined by ***[1998]***

(a) evaluating rate constant at standard temperature

(b) evaluating velocities of reaction at two different temperatures

(c) evaluating rate constants at two different temperatures

(d) changing concentration of reactants

EXERCISE - 2

Applied Questions

1. The rate equation for a reaction,

$N_2O \longrightarrow N_2 + 1/2O_2$

is Rate = $k[N_2O]^0 = k$. If the initial concentration of the reactant is a mol Lit^{-1}, the half-life period of the reaction is

(a) $t_{\frac{1}{2}} = \dfrac{a}{2k}$ (b) $-t_{\frac{1}{2}} = ka$

(c) $t_{\frac{1}{2}} = \dfrac{a}{k}$ (d) $t_{\frac{1}{2}} = \dfrac{k}{a}$

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) (m + n) (b) (n – m) (c) $2^{(n-m)}$ (d) $\dfrac{1}{2^{(m+n)}}$

3. 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 that the

(a) rate of formation of C is twice the rate of disappearance of A

(b) $t_{1/2}$ is a constant

(c) unit of k must be s^{-1}

(d) value of k is independent of the initial concentrations of A and B

4. For a first order reaction the rate constant is $6.909\ min^{-1}$.

The time taken for 75% conversion in minutes is

(a) $\frac{3}{2}\log 2$ (b) $\frac{2}{3}\log 3$

(c) $\frac{2}{3}\log 2$ (d) $\frac{3}{2}\log\left(\frac{3}{4}\right)$

5. Rate of a reaction can be expressed by following rate expression

Rate = $k[A]^2$ [B], if concentration of A is increased by 3 times, and concentration of B is increased by 2 times, how many times rate of reaction increases?

(a) 9 times (b) 27 times

(c) 18 times (d) 8 times

6. The decomposition of N_2O_5 occurs as

$2N_2O_5 \longrightarrow 4NO_2 + O_2$ and follows Ist order kinetics, hence:

(a) the reaction is unimolecular

(b) the reaction is bimolecular

(c) $t_{1/2} \propto a^0$

(d) None of these

7. The decomposition of ammonia on tungsten surface at 500 K follows zero order kinetics. The half-life period of this reaction is 45 minutes when the initial pressure is 4 bar. The half-life period (minutes) of the reaction when the initial pressure is 16 bar at the same temperature is

(a) 120 (b) 60 (c) 240 (d) 180

8. Diazonium salt decomposes as

$C_6H_5N_2^+Cl^- \rightarrow C_6H_5Cl + N_2$

At 0°C, the evolution of N_2 becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is

(a) a first order reaction

(b) a second order reaction

(c) independent of the initial concentration of the salt

(d) a zero order reaction

9. If '*I*' is the intensity of absorbed light and '*C*' is the concentration of *AB* for the photochemical process, $AB + h\nu \longrightarrow AB^*$, the rate of formation of AB^* is directly proportional to

(a) C (b) I (c) I^2 (d) C.I

10. The rate constant of a reaction becomes equal to the pre-exponential factor when

(a) the absolute temperature is zero

(b) the activation energy is infinity

(c) the absolute temperature is infinity

(d) the temperature in Celsius is zero.

11. The rate of reaction is doubled for every 10°C rise in temperature. The increase in reaction rate as a result of temperature rise from 10°C to 100°C is

(a) 112 (b) 512 (c) 400 (d) 614

12. For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$

if $\frac{\Delta[NH_3]}{\Delta t} = 2\times10^{-4}$ mol l^{-1} s^{-1}, the value of $\frac{-\Delta[H_2]}{\Delta t}$ would be

(a) 1×10^{-4} mol L^{-1} s^{-1} (b) 3×10^{-4} mol L^{-1} s^{-1}

(c) 4×10^{-4} mol L^{-1} s^{-1} (d) 6×10^{-4} mol L^{-1} s^{-1}

13. Lead is the final product formed by a series of changes in which the rate determining stage is the radioactive decay of uranium-238 with a half-life of 4.5×10^9 years. What would be the age of a rock sample originally lead free in which the molar proportion of uranium to lead is now 1 : 3?

(a) 1.5×10^9 years (b) 2.25×10^9 years

(c) 4.5×10^8 years (d) 9.0×10^9 years

14. For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$, the experimental data suggest, rate = $k[H_2][Br_2]^{1/2}$. The molecularity and order of the reaction are respectively

(a) $2, \frac{3}{2}$ (b) $\frac{3}{2}, \frac{3}{2}$ (c) 1, 1 (d) $1, \frac{1}{2}$

15. 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) remain unchanged (b) triple

(c) increase by a factor of 4 (d) double

16. Which among the following plots are linear $(a - x)$ is the concentration of reactant remaining after time, t

(1) $(a - x)$ vs t, for a first order reaction

(2) $(a - x)$ vs t, for a zero order reaction

(3) $(a - x)$ vs t, for a second order reaction

(4) $1/(a - x)$ vs t, for a second order reaction

(a) 1 and 2 (b) 1 and 3

(c) 2 and 3 (d) 2 and 4

17. A reaction was observed for 15 days and the percentage of the reactant remaining after the days indicated was recorded in the following table :

Time(days	0	2	4	6	8	10	12	14	15
% reactant remaining	100	50	39	25	21	18	15	12.5	10

Which one of the following best describes the order and the half-life of the reaction?

Reaction Order	**Half-life (days)**
(a) First	2
(b) First	6
(c) Second	2
(d) Zero	6

18. A first order reaction is half completed in 45 minutes. How long does it need 99.9% of the reaction to be completed

(a) 5 hours (b) 7.5 hours

(c) 10 hours (d) 20 hours

19. In the first order reaction, the concentration of the reactant is reduced to 25% in one hour. The half life period of the reaction is

(a) 2 hr (b) 4 hr (c) 1/2 hr (d) 1/4 hr

20. The half-life of 2 samples are 0.1 and 0.4 seconds. Their respective concentration are 200 and 50 respectively. What is the order of the reaction

(a) 0 (b) 2 (c) 1 (d) 4

21. The rate constant of a first order reaction is doubled when the temperature is increased from 20°C to 25°C. How many times the rate constant will increase if the temperature is raised from 20°C to 40°C ?

(a) 4 (b) 8 (c) 16 (d) 32

22. Cyclopropane rearranges to form propene

 $\longrightarrow CH_3-CH=CH_2$

This follows first order kinetics. The rate constant is 2.714×10^{-3} sec $^{-1}$. The initial concentration of cyclopropane is 0.29 M. What will be the concentration of cyclopropane after 100 sec

(a) 0.035 M (b) 0.22 M
(c) 0.145 M (d) 0.0018 M

23. The rate constant is doubled when temperature increases from 27°C to 37°C. Activation energy in kJ is

(a) 34 (b) 54 (c) 100 (d) 50

24. The rate constant, the activation energy and the arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} s^{-1}$, 104.4 kJ mol^{-1} and 6.0×10^{14} s^{-1} respectively. The value of the rate constant as $T \to \infty$ is

(a) 2.0×10^{18} s^{-1} (b) 6.0×10^{14} s^{-1}
(c) Infinity (d) 3.6×10^{30} s^{-1}

25. The activation energy for a reaction is 9.0 kcal/mol. The increase in the rate constant when its temperature is increased from 298K to 308K is

(a) 63% (b) 50% (c) 100% (d) 10%

26. For the following reaction: $NO_2(g) + CO(g) \to NO(g) + CO_2(g)$, the rate law is: Rate = k $[NO_2]^2$. If 0.1 mole of gaseous carbon monoxide is added at constant temperature to the reaction mixture which of the following statements is true?

(a) Both k and the reaction rate remain the same
(b) Both k and the reaction rate increase
(c) Both k and the reaction rate decrease
(d) Only k increases, the reaction rate remain the same

27. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in aproximately

(a) 45 minutes (b) 60 minutes
(c) 40 minutes (d) 50 minutes

28. The rate constants k_1 and k_2 for two different reactions are $10^{16} \cdot e^{-2000/T}$ and $10^{15} \cdot e^{-1000/T}$, respectively. The temperature at which $k_1 = k_2$ is :

(a) 1000 K (b) $\frac{2000}{2.303}$ K (c) 2000 K (d) $\frac{1000}{2.303}$ K

29. The rate of the reaction $2N_2O_5 \to 4NO_2 + 2O_2$ can be written in three ways :

$$\frac{-d[N_2O_5]}{dt} = k[N_2O_5], \qquad \frac{d[NO_2]}{dt} = k'\ [N_2O_5]$$

$$\frac{d[O_2]}{dt} = k''[N_2O_5]$$

The relationship between k and k' and between k and k'' are:

(a) $k' = 2k$; $k' = k$ (b) $k' = 2k$; $k'' = k/2$
(c) $k' = 2k$; $k'' = 2k$ (d) $k' = k$; $k'' = k$

30. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial velocity is ten times the permissible value, after how many days will it be safe to enter the room?

(a) 100 days (b) 1000 days
(c) 300 days (d) 10 days.

31. The time for half life period of a certain reaction $A \longrightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction ?

(a) 4 h (b) 0.5 h (c) 0.25 h (d) 1 h

32. Consider the reaction :

$$Cl_2(aq) + H_2S(aq) \to S(s) + 2H^+(aq) + 2Cl^-(aq)$$

The rate equation for this reaction is

rate = $k[Cl_2][H_2S]$

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

A. $Cl_2 + H_2S \to H^+ + Cl^- + Cl^+ + HS^-$ (slow)

$Cl^+ + HS^- \to H^+ + Cl^- + S$ (fast)

B. $H_2S \rightleftharpoons H^+ + HS^-$ (fast equilibrium)

$Cl_2 + HS^- \to 2Cl^- + H^+ + S$ (Slow)

(a) B only (b) Both A and B
(c) Neither A nor B (d) A only

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

(a) 10 times (b) 24 times (c) 32 times (d) 64 times

34. Consider a reaction *aG* + *bH* → Products. When concentration of both the reactants *G* and *H* is doubled, the rate increases by eight times. However, when concentration of *G* is doubled keeping the concentration of *H* fixed, the rate is doubled. The overall order of the reaction is

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

35. Under the same reaction conditions, initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio (k_1/k_0) of the rate constant for first order (k_1) and zero order (k_0) of the reaction is –

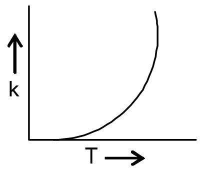
(a) 0.5 mol^{-1} dm^3 (b) 1.0 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) 2.0 mol^{-1} dm^3

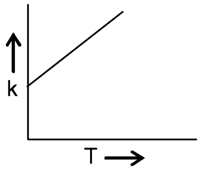
36. For a first order reaction A→P, the temperature (T) dependent rate constant (*k*) was found to follow the equation

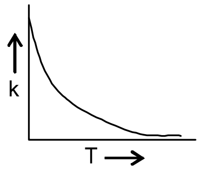
$\log k = -\ (2000)\frac{1}{T} + 6.0$. The pre-exponential factor A and the activation energy E_a, respectively, are

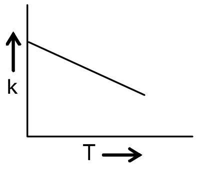
(a) 1.0×10^6 s^{-1} and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(c) $1.0 \times 10^6 s^{-1}$ and 16.6 kJ mol^{-1}
(d) $1.0 \times 10^6 s^{-1}$ and 38.3 kJ mol^{-1}

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

(a) 

(b) 

(c) 

(d) 

38. For a reaction $A + B \longrightarrow C + 2D$, experimental results were collected for three trials and the data obtained are given below:

Trial	[A], M	[B], M	Initial Rate, M s^{-1}
1	0.40	0.20	5.5×10^{-4}
2	0.80	0.20	5.5×10^{-4}
3	0.40	0.40	2.2×10^{-3}

The correct rate law of the reaction is

(a) rate = $k[A]^0 [B]^2$ (b) rate = $k[A] [B]^2$
(c) rate = $k[A] [B]$ (d) rate = $k[A] [B]^0$

39. The decomposition of ammonia on tungsten surface at 500 K follows zero order kinetics. The half-life period of this reaction is 45 minutes when the initial pressure is 4 bar. The half-life period (minutes) of the reaction when the initial pressure is 16 bar at the same temperature is

(a) 120 (b) 60
(c) 240 (d) 180

40. The initial rates of reaction $3A + 2B + C \longrightarrow$ Products, at different initial concentrations are given below:

Initial rate, Ms^{-1}	**$[A]_0$, M**	**$[B]_0$, M**	**$[C]_0$, M**
5.0×10^{-3}	0.010	0.005	0.010
5.0×10^{-3}	0.010	0.005	0.015
1.0×10^{-2}	0.010	0.010	0.010
1.25×10^{-3}	0.005	0.005	0.010

The order with respect to the reactants, A, B and C are respectively

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

41. Which one of the following reactions is a true first order reaction?

(a) Alkaline hydrolysis of ethyl acetate
(b) Acid catalyst hydrolysis of ethyl acetate
(c) Decomposition of N_2O
(d) Decomposition of gaseous ammonia on a hot platinum surface

42. In a first order reaction, the concentration of the reactant is reduced to $\frac{1}{8}$ of the initial concentration in 75 minutes at 298 K. What is the half-life period of the reaction in minutes?

(a) 50 (b) 15
(c) 45 (d) 25

43. In the Arrhenius plot of ln k vs $\frac{1}{T}$, a linear plot is obtained with a slope of -2×10^4 K. The energy of activation of the reaction (in kJ $mole^{-1}$) is (R value is 8.3 J K^{-1} mol^{-1})

(a) 83 (b) 166
(c) 249 (d) 332

44. For a first order reaction, the time taken to reduce the initial concentration by a factor of $\frac{1}{4}$ is 20 minutes. The time required to reduce initial concentration by a factor of $\frac{1}{16}$ is

(a) 20 min (b) 10 min
(c) 80 min (d) 40 min

45. The rate law for the reaction $xA + yB \longrightarrow mP + nQ$ is Rate = $k [A]^c [B]^d$. What is the total order of the reaction?

(a) (x + y) (b) (m + n)
(c) (c + d) (d) x/y

46. Consider the following statements:

I. Increase in concentration of reactant increases the rate of a zero order reaction.
II. Rate constant k is equal to collision frequency A if $E_a = 0$.
III. Rate constant k is equal to collision frequency A if $E_a = \infty$.
IV. In k vs T is a straight line.
V. In k vs 1/T is a straight line.

Correct statements are

(a) I and IV (b) II and V
(c) III and IV (d) II and III

DIRECTIONS for Qs. 47 to 50 : These are Assertion-Reason type questions. Each of these question contains two statements: Statement-1 (Assertion) and Statement-2 (Reason). Answer these questions from the following four options.

(a) Statement- 1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement -1
(b) Statement -1 is True, Statement -2 is True ; Statement-2 is NOT a correct explanation for Statement - 1
(c) Statement - 1 is True, Statement- 2 is False
(d) Statement -1 is False, Statement -2 is True

47. **Statement-1 :** If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
Statement-2 : Lower the activation energy, faster is the reaction.

48. **Statement-1 :** If in a zero order reaction, the concentration of the reactant is doubled. the half-life period is also doubled.
Statement-2 : For a zero order reaction, the rate of reaction is independent of initial concentration.

49. **Statement-1 :** If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
Statement-2 : Lower the activation energy, faster is the reaction.

50. **Statement-1 :** According to steady state hypothesis, in a multistep reaction, the change in concentration with time for reactive intermediates is zero.
Statement-2 : The intermediates are so reactive that after a brief initial period their concentrations rise from zero to a small value and remains constant for most of the duration of the reaction.

EXERCISE - 3

Exemplar & Past Years NEET/AIPMT Questions

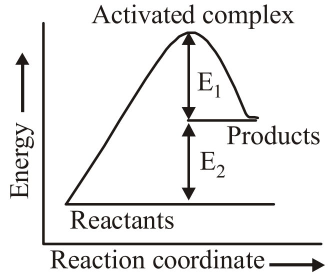
Exemplar Questions

1. The role of a catalyst is to change ....
- (a) Gibbs energy of reaction
- (b) enthalpy of reaction
- (c) activation energy of reaction
- (d) equilibrium constant

2. In the presence of a catalyst, the heat evolved or absorbed during the reaction ....
- (a) increases
- (b) decreases
- (c) remains unchanged
- (d) may increase or decrease

3. Activation energy of a chemical reaction can be determined by ....
- (a) determining the rate constant at standard temperature
- (b) determining the rate constant at two temperatures
- (c) determining probability of collision
- (d) using catalyst

4. Consider figure and mark the correct option.



- (a) Activation energy of forward reaction is $E_1 + E_2$ and product is less stable than reactant
- (b) Activation energy of forward reaction is $E_1 + E_2$ and product is more stable than reactant
- (c) Activation energy of both forward and backward reaction is $E_1 + E_2$ and reactant is more stable than product
- (d) Activation energy of backward reaction is E_1 and product is more stable than reactant

5. Consider a first order gas phase decomposition reaction given below

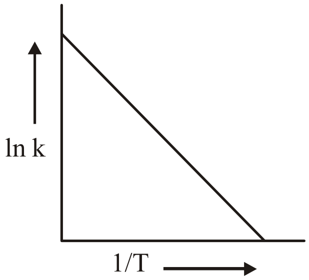
$$A(g) \rightarrow B(g) + C(g)$$

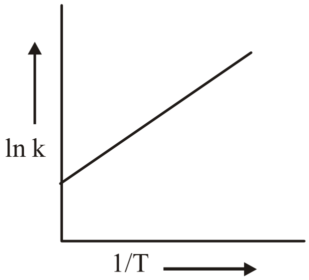
The initial pressure of the system before decomposition of A was p_i. After lapse of time 't' total pressure of the system increased by x units and became 'p_t'. The rate constant k for the reaction is given as ....

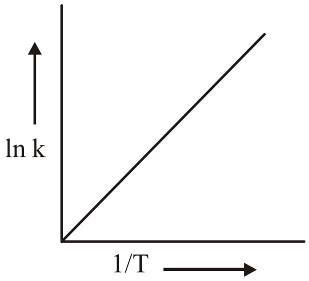
(a) $k = \frac{2.303}{t} \log \frac{p_i}{p_i - x}$ (b) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i - p_t}$

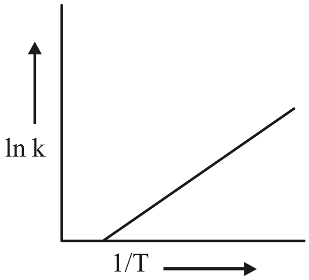
(c) $k = \frac{2.303}{t} \log \frac{p_i}{2p_i + p_t}$ (d) $k = \frac{2.303}{t} \log \frac{p_i}{p_i + x}$

6. According to Arrhenius equation rate constant k is equal to $A\ e^{-E_a/RT}$. Which of the following options represents the graph of ln k vs $\frac{1}{T}$?

(a)


(b)


(c)


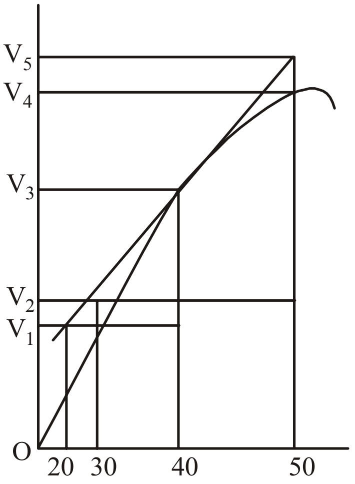
(d)


7. Consider the Arrhenius equation given below and mark the correct option.

$$k = Ae^{-\frac{E_a}{RT}}$$

- (a) Rate constant increases exponentially with increasing activation energy and decreasing temperature
- (b) Rate constant decreases exponentially with increasing activation energy and decreasing temperature
- (c) Rate constant increases exponentially with decreasing activation energy and decreasing temperature
- (d) Rate constant increases exponentially with decreasing activation energy and increasing temperature

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



(a) Average rate upto 40s is $\frac{V_3 - V_2}{40}$

(b) Average rate upto 40s is $\frac{V_3 - V_2}{40 - 30}$

(c) Average rate upto 40s is $\frac{V_3}{40}$

(d) Average rate upto 40s is $\frac{V_3 - V_1}{40 - 20}$

9. Which of the following statements is not correct about order of a reaction?

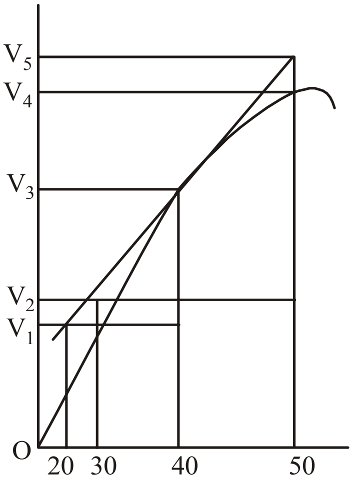
(a) The order of a reaction can be a fractional number

(b) Order of a reaction is experimentally determined quantity

(c) The order of a reaction is always equal to the sum of the stoichiometric coefficients of reactants in the balanced chemical equation for a reaction

(d) The order of a reaction is the sum of the powers of molar concentration of the reactants in the rate law expression

10. Consider the graph given in figure. Which of the following options does not show instantaneous rate of reaction at 40th second?



(a) $\frac{V_5 - V_2}{50 - 30}$ (b) $\frac{V_4 - V_2}{50 - 30}$

(c) $\frac{V_3 - V_2}{40 - 30}$ (d) $\frac{V_3 - V_1}{40 - 20}$

11. Which of the following statements is correct?

(a) The rate of a reaction decreases with passage of time as the concentration of reactants decreases.

(b) The rate of a reaction is same at any time during the reaction.

(c) The rate of a reaction is independent of temperature change.

(d) The rate of a reaction decreases with increase in concentration of reactant(s).

12. Which of the following expressions is correct for the rate of reaction given below?

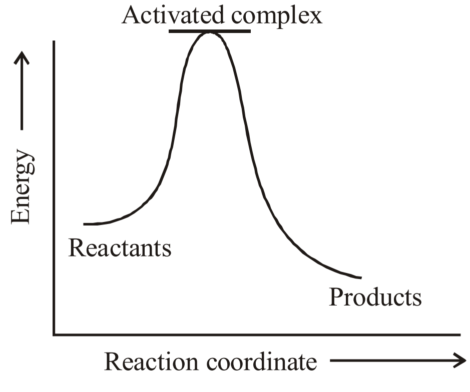
$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

(a) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ (b) $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{\Delta t}$

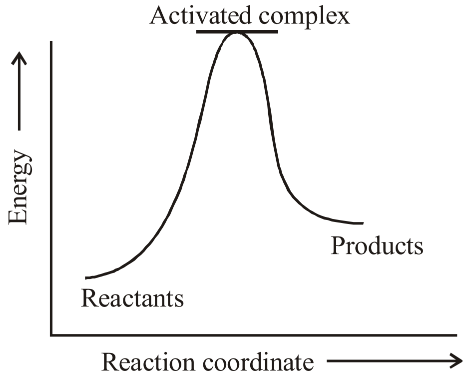
(c) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ (d) $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$

13. Which of the following graphs represents exothermic reaction?

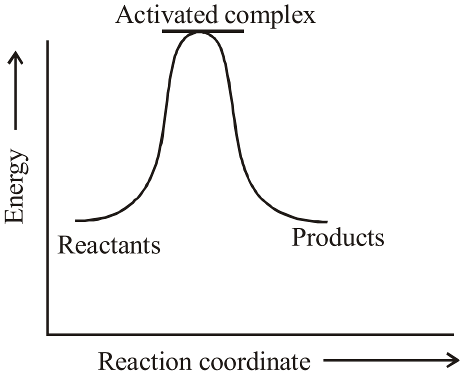
(I)



(II)



(III)



(a) Only (I) (b) Only (II)
(c) Only (III) (d) Both (I) and (II)

14. Rate law for the reaction $A + 2B \longrightarrow C$ is found to be

Rate = k[A] [B]

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be ....

(a) the same (b) doubled
(c) quadrupled (d) halved

15. Which of the following statements is incorrect about the collision theory of chemical reaction?

(a) It considers reacting molecules or atoms to be hard spheres and ignores their structural features
(b) Number of effective collisions determines the rate of reaction
(c) Collision of atoms or molecules possessing sufficient threshold energy results into the product formation
(d) Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective

16. A first order reaction is 50% completed in 1.26×10^{14} s. How much time would it take for 100% completion?

(a) 1.26×10^{15} s (b) 2.52×10^{14} s
(c) 2.52×10^{28} s (d) Infinite

17. Compounds 'A' and 'B' react according to the following chemical equation.

$A(g) + 2B(g) \longrightarrow 2C(g)$

Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.

Experiment	Initial concentration of [A]/mol L^{-1}	Initial concentration of [B]/mol L^{-1}	Initial concentration of [C]/mol $L^{-1}s^{-1}$
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

(a) Rate = k $[A]^2[B]$ (b) Rate = k [A] $[B]^2$
(c) Rate = k [A] [B] (d) Rate = k $[A]^2[B]^0$

18. Which of the following statement is not correct for the catalyst?

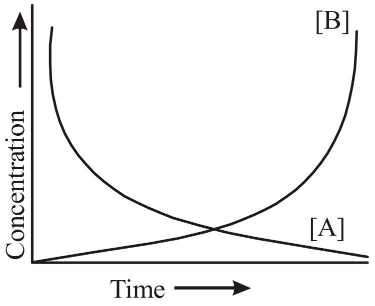
(a) It catalyses the forward and backward reactions to the same extent
(b) It alters ΔG of the reaction
(c) It is a substance that does not changes the equilibrium constant of a reaction
(d) It provides an alternate mechanism by reducing activation energy between reactants and products.

19. The value of rate constant of a pseudo first order reaction.............

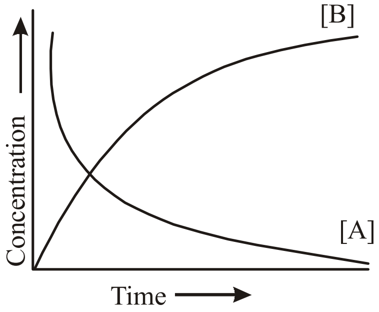
(a) depends on the concentration of reactants present in small amount
(b) depends on the concentration of reactants present in excess
(c) is independent of the concentration of reactants
(d) depends only on temperature

20. Consider the reaction $A \rightarrow B$. The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?

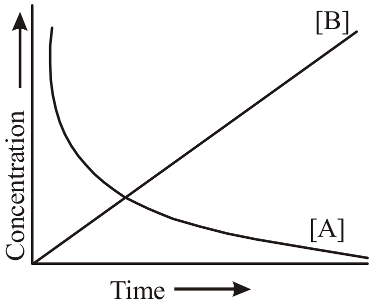
(a)



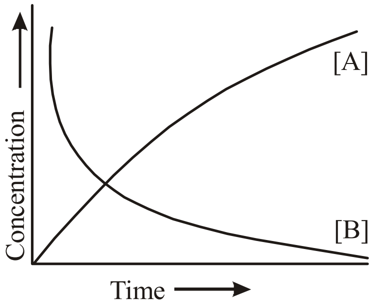
(b)



(c)



(d)



NEET/AIPMT (2013-2017) Questions

21. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 20°C to 35°C? (R = 8.314 J mol^{-1} K^{-1}) ***[2013]***

(a) 269 kJ mol^{-1} (b) 34.7 kJ mol^{-1}

(c) 15.1 kJ mol^{-1} (d) 342 kJ mol^{-1}

22. A reaction having equal energies of activation for forward and reverse reaction has : ***[2013]***

(a) $\Delta G = 0$ (b) $\Delta H = 0$

(c) $\Delta H = \Delta G = \Delta S = 0$ (d) $\Delta S = 0$

23. A reaction is 50% completed in 2 hours and 75% completed in 4 hours. The order of reaction is ***[NEET Kar. 2013]***

(a) 0 (b) 1

(c) 2 (d) 3

24. For a reaction between A and B the order with respect to A is 2 and the order with respect to B is 3. The concentrations of both A and B are doubled, the rate will increase by a factor of: ***[NEET Kar. 2013]***

(a) 10 (b) 12

(c) 16 (d) 32

25. The activation energy of a reaction can be determined from the slope of which of the following graphs ? ***[2015]***

(a) $\frac{\ln K}{T}$ vs.T (b) $\ln K$ vs.$\frac{1}{T}$

(c) $\frac{T}{\ln K}$ vs.$\frac{1}{T}$ (d) $\ln K$ vs . T

26. When initial concentration of a reactant is doubled in a reaction, its half-life period is not affected. The order of the reaction is : ***[2015]***

(a) First

(b) Second

(c) More than zero but less than first

(d) Zero

27. The rate constant of the reaction $A \rightarrow B$ is 0.6×10^{-3} mole per second. If the concentration of A is 5 M then concentration of B after 20 minutes is : ***[2015 RS]***

(a) 1.08 M (b) 3.60 M

(c) 0.36 M (d) 0.72 M

28. The rate of a first -order reaction is 0.04 mol $\ell^{-1}s^{-1}$ at 10 seconds and 0.03 mol $\ell^{-1}s^{-1}$ at 20 seconds after initiation of the reaction. The half-life period of the reaction is ***[2016]***

(a) 24.1 s (b) 34.1 s

(c) 44.1 s (d) 54.1 s

29. The addition of a catalyst during a chemical reaction alters which of the following quantities? ***[2016]***

(a) Entropy (b) Internal energy

(c) Enthalpy (d) Activation energy

30. Mechanism of a hypothetical reaction ***[2017]***

$X_2 + Y_2 \rightarrow 2XY$ is given below :

(i) $X_2 \rightarrow X + X$(fast)

(ii) $X + Y_2 \rightleftharpoons XY + Y$ (slow)

(iii) $X + Y \rightarrow XY$ (fast)

The overall order of the reaction will be :

(a) 2 (b) 0

(c) 1.5 (d) 1

31. A first order reaction has a specific reaction rate of 10^{-2} sec^{-1}. How much time will it take for 20g of the reactant to reduce to 5 g ? ***[2017]***

(a) 138.6 sec (b) 346.5 sec

(c) 693.0 sec (d) 238.6 sec

Hints & Solutions

EXERCISE - 1

1. (a) $\frac{dc}{dt} = k[c] = 3 \times 10^{-6} \times 0.1$

$\frac{dc}{dt} = 3 \times 10^{-7}$ mol litre^{-1} sec^{-1}

2. (d) All the statements are correct.

Order of reaction $= 1 + \frac{1}{2} = 1.5$

Molecularity $= 1 + 1 = 2$

$\frac{dx}{dt} \propto [Br_2]^{1/2}$

So, reaction rate will be doubled if concentration of Br_2 is increased by 4 times.

3. (d) As the unit of rate constant is sec^{-1}, so the reaction is first order reaction. Hence

$$k = \frac{1}{t} = \log\frac{a}{(a-x)} \quad \text{or} \quad kt = \log\frac{[N_2O_5]_0}{[N_2O_5]_t}$$

4. (d) In the given options $-\frac{d[C]}{3.dt}$ will not represent the reaction rate. It should not have –ve sign as it is a product.

$\frac{1}{3}\frac{d[C]}{dt}$ shows the rate of formation of product C.

5. (a) If we write rate of reaction in terms of concentration of NH_3 and H_2, then

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

So, $\frac{d[NH_3]}{dt} = -\frac{2}{3}\frac{d[H_2]}{dt}$

6. (b) $r = k[O_2][NO]^2$. When the volume is reduced to 1/2, the conc. will double

$\therefore$ New rate $= k[2O_2][2\,NO]^2 = 8\,k[O_2][NO]^2$

The new rate increases to eight times of its initial.

7. (b) When the concentration of reactant is reduced to half its initial value, the rate is reduced by $\frac{2.4}{0.6} = 4$ times

It means, rate $\propto$ [reactant]^2

So, order of reaction = 2

8. (c) Increase in temperature = 100°C – 10°C = 90°C

$\therefore \quad n = 9$

Increase in reaction rate $= 2^n = 2^9 = 512$ times

9. (a) $2A + B \longrightarrow A_2B$

$r_1 = k[A]^2[B]$ ...(i)

When, $[A] = [2A]$, $[B] = \left[\frac{B}{2}\right]$

$$r_2 = k[2A]^2\left[\frac{B}{2}\right] = k\,4[A]^2\frac{[B]}{2}$$

$$= k\,2[A]^2[B] = 2r_1 \left(\because\ r_1 = k[A]^2[B]\right)$$

$\therefore$ Rate of reaction is increased two times.

10. (d) Graph (d) represents graph between $t_{1/2}$ and initial concentration for 3rd order reaction :

(a) Zero order reaction

(b) 1st order reaction

(c) 2nd order reaction.

11. (d) rate of appearance of HI $= \frac{1}{2}\frac{d[HI]}{dt}$

rate of formation of $H_2 = \frac{-d[H_2]}{dt}$

rate of formation of $I_2 = \frac{-d[I_2]}{dt}$

hence $\frac{-d[H_2]}{dt} = -\frac{d[I_2]}{dt} = \frac{1}{2}\frac{d[HI]}{dt}$

or $-\frac{2d[H_2]}{dt} = -\frac{2d[I_2]}{dt} = \frac{d[HI]}{dt}$

12. (a) From data 1 and 3, it is clear that keeping (B) const, [A] is doubled, rate remains unaffected. Hence rate is independent of [A]. From 1 and 4, keeping [A] constant, [B] is doubled, rate become 8 times. Hence rate $\propto [B]^3$.

13. (b) $2N_2O_5 \rightarrow 4NO_2 + O_2$

from the unit of rate constant it is clear that the reaction follow first order kinetics. Hence

by rate law equation, $r = k[N_2O_5]$

where $r = 1.02 \times 10^{-4}$, $k = 3.4 \times 10^{-5}$

$1.02 \times 10^{-4} = 3.4 \times 10^{-5}[N_2O_5]$

$[N_2O_5] = 3M$

14. (b) For a first order reaction the positive slope is obtained when we plot $-\log_e[A]$ vs t.

15. (c)

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

$$\therefore \quad k = \frac{2.303}{2 \times 10^4}\log\frac{800}{50} = 1.386 \times 10^{-4}\,s^{-1}$$

16. (b) Given $dx/dt = 2.400 \times 10^{-5}$ mol litre^{-1} sec^{-1}

$k = 3.10 \times 10^{-5}$ sec^{-1}

For first order reaction

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

$\frac{dx}{dt} = k[N_2O_5]$

or $2.4 \times 10^{-5} = 3.0 \times 10^{-5}[N_2O_5]$

or $[N_2O_5] = \frac{2.4 \times 10^{-5}}{3.0 \times 10^{-5}} = 0.8$ mol. litre^{-1}

17. (b) Initial concentration = 10 mol L^{-1}

$\therefore$ Conc. after 20 min (two half lives) = 2.5 mol L^{-1}

Now, $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10\,\text{min}}$

or $\quad 0.0693\ \text{min}^{-1}$

∴ $\quad \text{rate} = k \times [\text{reactant}]$

$= 0.0693 \times 2.5\ \text{mol L}^{-1}\ \text{min}^{-1}$

18. (b) Velocity constant 'K' is characteristic constant of a reaction and depends only on temperature and catalyst.

19. (c) $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

or $2.303\log\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$2.303\log\left[\frac{1.667\times10^{-4}}{1.667\times10^{-6}}\right] = -\frac{E_a}{R}\left[\frac{1}{1844} - \frac{1}{1000}\right]$$

$$2.303\times2 = \frac{E_a}{R}\times\frac{844}{1844\times1000} \qquad \text{........(1)}$$

$$\therefore \frac{E_a}{R} = \frac{4.606\times1844\times1000}{844}$$

$$2.303\log\left[\frac{k_3}{1.667\times10^{-6}}\right] = \frac{E_a}{R}\times\frac{1423-1000}{1423\times1000}$$

$$= \frac{E_a}{R}\times\frac{423}{1423\times1000} \qquad \text{........(2)}$$

Dividing equation (2) by equation (1)

$$\frac{\log\left[\frac{k_3}{1.667\times10^{-6}}\right]}{2} = \frac{423}{1423\times1000}\times\frac{1844\times1000}{844}$$

$$\therefore \log\left[\frac{k_3}{1.667\times10^{-6}}\right] = 2\times\frac{423\times1844}{1423\times844} = 1.299$$

On taking Antilog, $k_3 = 19.9$

∴ $k_3 = 19.9\times1.667\times10^{-6} = 3.318\times10^{-5}\ \text{s}^{-1}$

20. (c)

21. (a) Given initial concentration (a) = 2.00 M; Time taken (t) = 200 min and final concentration ($a - x$) = 0.15 M. For a first order reaction rate constant,

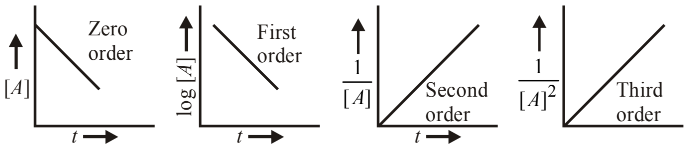
$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{200}\log\frac{2.00}{0.15}$$

$$= \frac{2.303}{200}\times(0.301 + 0.824) = 1.29\times10^{-2}\ \text{min}^{-1}.$$

Further $(t_{1/2}) = \frac{0.693}{k} = \frac{0.693}{1.29\times10^{-2}} = 53.72\,\text{min}.$

22. (c) $T_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.155\times10^{-3}} = \frac{693}{1.155} = 600\ \text{sec}$

23. (a) Plots of conc. [A] Vs time, t



24. (a) $t_{1/2} = 4\text{s} \qquad T = 16\text{s}$

$$n = \frac{T}{t_{1/2}} = \frac{16}{4} = 4 \qquad (\therefore T = n\times t_{½})$$

$$[A] = [A]_0\left(\frac{1}{2}\right)^n = 0.12\times\left(\frac{1}{2}\right)^4 = \frac{0.12}{16} = 0.0075\ \text{M}$$

Where $[A]_o$ = initial concentration and [A] = concentration left after time t

25. (b) For reaction $3A \longrightarrow B + C$

If it is zero order reaction $r = k = [A]^0$, i.e., the rate remains same at any concentration of 'A'. i.e., independent of concentration of A.

26. (a) $k = \frac{0.693}{T_{1/2}} = \frac{0.693}{30} = 2.31\times10^{-2}\,\text{min}^{-1}$

27. (b) $A \rightarrow B$ For a first order reaction

Given $a = 0.8$ mol, $(a - x) = 0.8 - 0.6 = 0.2$

$$k = \frac{2.303}{1}\log\frac{0.8}{0.2} \text{ or } k = 2.303\log 4$$

again $a = 0.9,\ a - x = 0.9 - 0.675 = 0.225$

$$k = \frac{2.303}{t}\log\frac{0.9}{0.225}$$

$$2.303\log4 = \frac{2.303}{t}\log 4$$

Hence t = 1 hour

28. (b) $CaCO_3 \longrightarrow CaO + CO_2$

This reaction will proceed in forward direction if volume of container is increased.

29. (b) For a first order reaction, A → products

$$r = k[A] \text{ or } k = \frac{r}{[A]}$$

$$\Rightarrow k = \frac{1.5\times10^{-2}}{0.5} = 3\times10^{-2}$$

Further, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3\times10^{-2}} = 23.1$

30. (d) Given [A] = 0.01 M

Rate = $2.0\times10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1}$

For a first order reaction

Rate = k[A]

$$k = \frac{2.0\times10^{-5}}{[0.01]} = 2\times10^{-3}$$

$$t_{1/2} = \frac{0.693}{2\times10^{-3}} = 347\ \text{sec}$$

31. (c) Molecularity can never be fraction. It is the number of reacting species undergoing simultaneous collision in the elementary or simple reaction. It is a theoretical concept.

32. (d) $t_{1/2} = 5$ years, $T = 15$ years hence total number of half life periods $= \frac{15}{5} = 3$.

$$\therefore \text{ Amount left } = \frac{64}{(2)^3} = 8\text{g}$$

33. (c) As the concentration of reactant decreases from 0.8 to 0.4 in 15 minutes hence the $t_{1/2}$ is 15 minutes. To fall the concentration from 0.1 to 0.025 we need two half lives as

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

$$\frac{0.1}{0.025} = \left(\frac{1}{2}\right)^n$$

$n = 2$

i.e., 30 minutes

34. (d) For a first order reaction, we have

$$k = \frac{2.303}{t} \log \frac{N_0}{N}$$

$$\therefore \quad k = \frac{2.303}{40 \text{ min}} \log \frac{0.1}{0.005}$$

$$= \frac{2.303}{40 \text{ min}} \times \log 20 = \frac{2.303}{40} \times 1.3010$$

Now rate = k × [reactant]

When [x] = 0.01 M

$$\therefore \quad \text{rate} = \frac{2.303}{40} \times 1.3010 \times 0.01 \text{ M min}^{-1}$$

$$= 7.5 \times 10^{-4} \text{ M min}^{-1}.$$

35. (a) Given $r = k [A]^{3/2} [B]^{-1/2}$

$$\text{Order} = 3/2 - 1/2 = \frac{3-1}{2} = \frac{2}{2} = 1$$

36. (c) For first order reaction, $k = \frac{0.693}{t_{1/2}}$

where k = rate constant

$t_{1/2}$ = half life period = 480 sec.

$$\therefore \qquad k = \frac{0.693}{480} = 1.44 \times 10^{-3} \text{ sec}^{-1}$$

37. (c) Since rate of reaction becomes four times on doubling concentration of reactant, it is second order reaction.

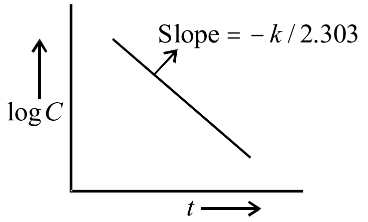
38. (c) $[A] = [A]_0 \left(\frac{1}{2}\right)^n$ where $[A]_0$ = initial concentration

$$\frac{1}{8} = 1\left(\frac{1}{2}\right)^n ; n = 3$$

$$t_{1/2} = \frac{0.693}{6.9 \times 10^{-3}} = 100 \text{ sec}$$

$$\therefore T = n \times t_{1/2} = 3 \times 100 = 300 \text{ sec.}$$

39. (b)



40. (a) For a first order reaction, we have

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

Substituting the given values

$$k = \frac{2.303}{200 \text{ sec}} \log \frac{2.0}{0.15} = \frac{2.303}{200} (\log 2.0 - \log 0.15) \text{ sec}^{-1}$$

$$= \frac{2.303}{200} \times 1.1249 \text{ sec}^{-1} = 1.29 \times 10^{-2} \text{ sec}^{-1}$$

41. (b) Given: 75% reaction gets completed in 32 min

$$\text{Thus, } k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{32} \log \frac{100}{(100-75)}$$

$$= \frac{2.303}{32} \log 4 = 0.0433 \text{ min}^{-1}$$

Now we can use this value of k to get the value of time required for 50% completion of reaction

$$t = \frac{2.303}{k} \log \frac{a}{(a-x)} = \frac{2.303}{0.0433} \log \frac{100}{50}$$

$$= \frac{2.303}{0.0433} \log 2 = 16 \text{ min}$$

42. (a) The half life period of a 3rd order reaction,

$$3[A] \longrightarrow \text{product,}$$

is given by the equation

$$t_{1/2} = \frac{3}{2k[A]_0^2}$$

where $[A]_0$ is initial concentration.

Here $t_{1/2}$ = 8 hr 20 min = 500 min. = 30000 sec and $[A_0]$ = 0.1M

$$\therefore k = \frac{3}{2t_{1/2}[A]_0^2} = \frac{3}{2 \times (30000 \text{ sec})(0.10 \text{ mol L}^{-1})^2}$$

$$= \frac{3}{60000 \times 0.01} = 5 \times 10^{-3} \text{ L}^2 \text{ mol}^{-2} \text{ sec}^{-1}$$

43. (d) If rate = $k[A]^x [B]^y [C]^z$

From first two given data

$8.08 \times 10^{-3} = k [0.2]^x [0.1]^y [0.02]^z$ .... (1)

$2.01 \times 10^{-3} = k [0.1]^x [0.2]^y [0.02]^z$ .... (2)

Divide (1) by (2) we get, $4 = 2^x (1/2)^y$

Similarly, from second and third data

$(9)^y (9)^z = 3$

$2y + 2z = 1$.

From first and fourth data $4^z = 8 = 2^3$

$2z = 3$. So $z = 3/2, y = -1, x = 1$

44. (d) Using the relation

$[A] = [A]_0 (1/2)^n$ [n = number of half-lives]

$T = n \times ty_2$

Here, $n = \frac{7.5}{2.5} = 3$

$$\therefore [A] = 160 \times \left(\frac{1}{2}\right)^3 = 160 \times \frac{1}{8}$$

or 20 gm i.e., (d)

45. (b) The order w.r.t. I_2 is zero because the rate is not dependent on the concentration of I_2.

46. (c) For the reaction,

$$X + \text{reagent} \xrightarrow{k_1} \text{product},$$

the value of k_1 when 94% of X has been reacted is given by

$$k_1 = \frac{2.303}{t}\log\frac{100}{100-94}$$

$$\Rightarrow k_1 = \frac{2.303}{t}\log\left(\frac{100}{6}\right) \quad ......(1)$$

Similarly, for the reaction

$$Y + \text{reagent} \xrightarrow{k_2} \text{product},$$

the value of k_2 when 50% of Y have been reacted is given by,

$$k_2 = \frac{2.303}{t}\log\frac{100}{100-50}$$

$$\Rightarrow k_2 = \frac{2.303}{t}\log(2) \quad ....(2)$$

Dividing equ. (1) by equ. (2), we get

$$\frac{k_1}{k_2} = \frac{\log\left(\frac{100}{6}\right)}{\log 2} = 4.059$$

47. (c) As we know that, units of rate constant.
$= (\text{unit of conc.})^{1-n}\,(\text{unit of time})^{-1}$
$= (\text{mol L}^{-1})^{1-n}\,(\text{sec})^{-1}$
On comparing these units with the given units of rate constant, we get
$(\text{mol L}^{-1})^{1-n}\,(\text{sec})^{-1} = \text{L mol}^{-1}\text{ sec}^{-1}$
$\Rightarrow \text{L}^{n-1}\text{ mol}^{1-n}\text{ sec}^{-1} = \text{L mol}^{-1}\text{ sec}^{-1}$
On comparing the powers, we get
$n - 1 = 1 \Rightarrow n = 2$
So, reaction is of second order.

48. (d) Unit of k for Ist order reaction is $(\text{Time})^{-1}$

49. (d) For first order decomposition of N_2O_5, rate law is given by
rate, $r = k[N_2O_5]$
On plotting rate on y-axis and concn $[N_2O_5]$ on x-axis and then comparing it with $y = mx + c$, we get a line starting from origin with slope 'k'. Its positive slope suggests that line is giong up. Hence graph shown in option (d) is the correct choice.

50. (a) $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2 \times 10^{-4}} = 1117.7\text{ sec}.$

51. (b) pH = 2 ; $r_1 = k \times (10^{-2})^n$ {∵ $[H^+] = 10^{-pH}$}
pH = 1 ; $r_2 = k \times (10^{-1})^n$

Given $r_2 = 100\, r_1 \Rightarrow \left(\frac{10^{-1}}{10^{-2}}\right)^n = 100$

$\Rightarrow 10^n = 100$
$\therefore n = 2$

52. (d) $t_{1/2} \propto \frac{1}{a^2}$

We know that $t_{1/2} \propto \frac{1}{a^{n-1}}$

i.e. n = 3
Thus reaction is of 3rd order.

53. (a)

	$C_4H_8 \longrightarrow$	$2C_2H_4$
Moles at $t = 0$	a	0
Moles at $t = t$	$(a - x)$	$2x$

when $\frac{2x}{a - x} = 1$ then $x = \frac{a}{3}$

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

$$= \frac{2.303}{2.3 \times 10^{-4}}\log\frac{a}{a - \frac{a}{3}} = 1700\text{ sec}$$

54. (c) $t_{1/4} = \frac{2.303}{k}\log\frac{1}{3/4} = \frac{2.303}{k}\log\frac{4}{3}$

$$= \frac{2.303}{k}(\log 4 - \log 3) = \frac{2.303}{k}(2\log 2 - \log 3)$$

$$= \frac{2.303}{k}(2 \times 0.301 - 0.4771) = \frac{0.29}{k}$$

55. (c) Given initial mass = a
Mass left after time $t = x = 0.875\, a$
$t = 40$ minutes.

$$k = \frac{2.303}{t}\log\frac{a}{a - x} = \frac{2.303}{40}\log\frac{a}{a - 0.875\, a}$$

$$= \frac{2.303}{40}\log 8 = 0.052\text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.052} = 13\text{ minutes } 32\text{ sec.}$$

56. (d) None of the given options is correct.
The given reaction is : $2X + Y \longrightarrow Z$

$$-\frac{d[X]}{2dt}=\frac{d[Z]}{dt}$$

∴ Rate of formation of Z is half of the rate of disappearance of X.

$$\frac{-d[X]}{2dt}=\frac{-d[Y]}{dt}$$

Rate of X is not equal to rate of disappearance of Y.

57. (b) Activation energy of reactant is less than the energy of activation of products.

58. (d) A catalyst affects equally both forward and backward reactions, therefore it does not affect equilibrium constant of reaction.

59. (b) According to Arrhenius equation, $k = Ae^{-E_a/RT}$

∴ when $E_a = 0, k = A$

Also ln k υs 1/T is a straight line with slope $= -E_a/R$.

∴ Statements (ii) and (v) are correct.

60. (c) We know that the activation energy of chemical reaction is given by formula $= \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$, where k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2 and E_a is the activation energy. Therefore activation energy of chemical reaction is determined by evaluating rate constant at two different temperatures.

61. (c) Order is the sum of the powers to which the concentration terms are raised in the rate equation.

62. (d) $k = Ae^{-Ea/RT}$

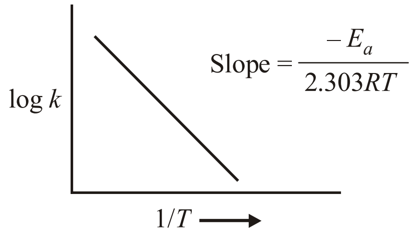
or $\log k = \log A - \frac{E_a}{2.303\ RT}$

Comparing the above equation with

$y = mx + c$

$y = \log k,\ x = \frac{1}{T}$

Thus *a* plot of log k vs 1/T should be a straight line, with slope equal to $-E_a/2.303$ RT and intercept equal to log A



∴ Slope $= \frac{-E_a}{2.303R}$

or $E_a = -2.303R \times$ Slope

63. (d) ∵ $\frac{N}{N_0} = \left(\frac{1}{2}\right)^n$

For first condition

$\frac{1}{4} = \left(\frac{1}{2}\right)^n$ ∴ n = 2

$t_{1/2} = \frac{20}{2} = 10$

For second condition

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

n = 4 ∴ T = 4 × 10 = 40 min

64. (d) The activation energy of reverse reaction will depend upon whether the forward reaction is exothermic or endothermic.

As $\Delta H = E_{a\ (\text{forward reaction})} - E_{a(\text{backward reaction})}$

For exothermic reaction

$\Delta H = -ve$

∴ $-\Delta H = E_{a(f)} - E_{a(b)}$

or $E_{a(f)} = E_{a(b)} - \Delta H$

∴ $E_{a(f)} < E_{a(b)}$

for endothermic reaction

$\Delta H = +$ ve

∴ $\Delta H = E_{a(f)} - E_{a(b)}$ or $E_{a(f)} = \Delta H + E_{a(b)}$

∴ $E_{a(f)} > E_{a(b)}$.

65. (d) In Arrhenius equation $k = Ae^{-E_a/RT}$, E_a is the energy of activation, which is required by the colliding molecules to react resulting in the formation of products.

66. (d) The definition of threshold energy.

67. (c) $N_2O \longrightarrow N_2 + \frac{1}{2}O_2$

$\frac{dx}{dt} \propto [N_2O]^1$

i.e. order of reaction = 1

68. (b) When the temperature is increased, energy in form of heat is supplied which increases the kinetic energy of the reacting molecules. this will increase the number of collisions and ultimately the rate of reaction will be enhanced.

69. (b) When $E_a = 0$ rate constant is independent of temperature.

70. (b) $k = Ae^{-E_a/RT}$

$\ln k = \ln A - E_a/RT$

For ln k vs 1/T

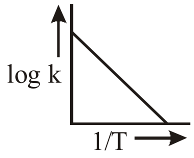
ln A = intercept

$-E_a/R = \text{slope} = -2 \times 10^4$ K

∴ $E_a = 8.3 \times 2 \times 10^4$ J mol^{-1}

$= 16.6 \times 10^4$ J mol^{-1} or 166 kJ mol^{-1}

71. (b) A graph plotted between log *k* vs $\frac{1}{T}$ for calculating activation energy is shown as



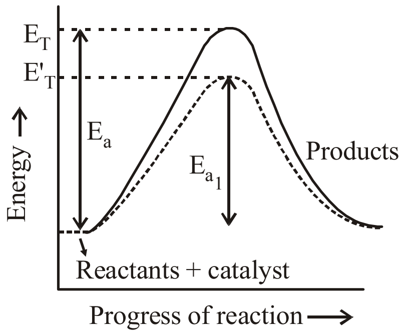
from Arrhenius equation

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

72. (a) For endothermic reaction $\Delta H = +ve$

Then from equation $\Delta H = E_{FR} - E_{BR};\ E_{BR} < E_{FR}$

73. (b) The presence of enzyme (catalyst) increases the speed of reaction by lowering the energy barrier, i.e., a new path is followed with lower activation energy.



Here E_T is the threshold energy.

E_a and E_{a_1} is energy of activation of reaction in absence and presence of catalyst respectively.

74. (d) For a first order reaction,

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

$$k = \frac{2.303}{75}\log\frac{1}{1/8} = \frac{2.303\times 0.903}{75}\text{min}^{-1}$$

First order reaction

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693\times 75}{2.303\times 0.903} = 25\,\text{min}$$

75. (d) As the slowest step is the rate determining step thus the mechanism B will be more consistent with the given information also because it involve one molecule of H_2 and one molecule of ICl it can expressed as

$r = k[H_2][ICl]$

Which shows that the reaction is first order w.r.t. both H_2 & ICl.

76. (c) For a first order reaction

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

when $t = t_{1/2}$

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

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

77. (a) Rewriting the given data for the reaction

$$CH_3COCH_3(aq) + Br_2(aq) \xrightarrow{H^+} CH_3COCH_2Br(aq) + H^+(aq) + Br^-(aq)$$

S. No.	Initial concentration of CH_3COCH_3 in M	Initial concentration of Br_2 in M	Initial concentration of H^+ in M	Rate of disappearance of Br_2 in Ms^{-1} i.e. $-\frac{d}{dt}[Br_2]$ or $\frac{dx}{dt}$
1	0.30	0.05	0.05	5.7×10^{-5}
2	0.30	0.10	0.05	5.7×10^{-5}
3	0.30	0.10	0.10	1.2×10^{-4}
4	0.40	0.05	0.20	3.1×10^{-4}

Actually this reaction is autocatalyzed and involves complex calculation for concentration terms.

We can look at the above results in a simple way to find the dependence of reaction rate (i.e., rate of disappearance of Br_2).

From data (1) and (2) in which concentration of CH_3COCH_3 and H^+ remain unchanged and only the concentration of Br_2 is doubled, there is no change in rate of reaction. It means the rate of reaction is independent of concentration of Br_2.

Again from (2) and (3) in which ($CH_3CO\,CH_3$) and (Br_2) remain constant but H^+ increases from 0.05 M to 0.10 i.e. doubled, the rate of reaction changes from 5.7×10^{-5} to 1.2×10^{-4} (or 12×10^{-5}), thus it also becomes almost doubled. It shows that rate of reaction is directly proportional to $[H^+]$. From (3) and (4), the rate should have doubled due to increase in conc of $[H^+]$ from 0.10 M to 0.20 M but the rate has changed from 1.2×10^{-4} to 3.1×10^{-4}. This is due to change in concentration of CH_3COCH_3 from 0.30 M to 0.40 M. Thus the rate is directly proportional to $[CH_3\,COCH_3]$. We now get

$\text{rate} = k\,[CH_3COCH_3]^1[Br_2]^0[H^+]^1$

$= k\,[CH_3COCH_3][H^+]$.

78. (d) Rate of disappearance of H_2 = rate of formation of NH_3.

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

$$\Rightarrow \frac{-d[H_2]}{dt} = \frac{3}{2}\frac{d[NH_3]}{dt} = \frac{3}{2}\times2\times10^{-4}$$

$$= 3\times10^{-4}\,\text{mol L}^{-1}\text{s}^{-1}$$

79. (d) Rate of disappearance of Br^-

= rate of appearance of Br_2

$$\Rightarrow -\frac{1}{5}\frac{d[Br^-]}{dt} = \frac{1}{3}\frac{d[Br_2]}{dt}$$

$$\Rightarrow \frac{1}{3}\frac{d[Br_2]}{dt} = -\frac{1}{5}\frac{d[Br^-]}{dt}$$

$$\Rightarrow \frac{d[Br_2]}{dt} = -\frac{3}{5}\frac{d[Br^-]}{dt}$$

80. (b) For a first order reaction

$$t_{1/2} = \frac{0.693}{k};\; k = \frac{0.693}{1386} = 0.5\times10^{-3}\text{s}^{-1}$$

81. (a) When concentration A is doubled, rate is doubled. Hence order with respect to A is one.

When concentrations of both A and B are doubled, rate increases by 8 times hence order with respect to B is 2.

$\therefore$ rate = $k\,[A]^1\,[B]^2$

Total order = 1 + 2 = 3

82. (b) $N_2O_5\,(g) \longrightarrow 2NO_2(g) + 1/2\;O_2\,(g)$

$$-\frac{d}{dt}[N_2O_5] = +\frac{1}{2}\frac{d}{dt}[NO_2] = 2\frac{d}{dt}[O_2]$$

$$\frac{d}{dt}[NO_2] = 1.25\times10^{-2}\ \text{mol L}^{-1}\text{s}^{-1}\ \text{and}$$

$$\frac{d}{dt}[O_2] = 3.125\times10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$$

83. (b)

84. (d) In case of (II) and (III), keeping concentration of [A] constant, when the concentration of [B] is doubled, the rate quadruples. Hence it is second order with respect to B. In case of I & IV Keeping the concentration of [B] constant. when the concentration of [A] is increased four times, rate also increases four times. Hence, the order with respect to A is one. hence

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

85. (b) $2\,NO\,(g) + Cl_2(g) \rightleftharpoons 2\,NOCl(g)$

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

The value of rate constant can be increased by increasing the temperature.

∴ Correct choice : (b)

86. (d) order of reaction may be zero, whole number or fractional.

87. (a) $\text{Rate} = k[A]^{\circ}$

Unit of $k = \text{mol L}^{-1}\text{ sec}^{-1}$

88. (b) $\frac{r_{100^\circ C}}{r_{10^\circ C}} = 2^{\left(\frac{T_2-T_1}{10}\right)} = 2^{\left(\frac{100-10}{10}\right)} = 2^9 = 512$ (where 2 is temperature coefficient of reaction)

89. (b, d)

According to Arrhenius equation

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\frac{k_1}{K_2} = -\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

90. (a) Presence of catalyst does not affect enthalpy change of reaction $\Delta H_R = E_f - E_b = 180 - 200 = -20\,\text{kJ/mol}$

91. (b) Since doubling the concentration of *B* does not change half life, the reaction is of 1st order w.r.t. *B*.

Order of reaction with respect to *A* = 1 because rate of reaction doubles when concentration of A is doubled keeping concentration of *B* constant.

∴ Order of reaction = 1 + 1 = 2 and units of second order reaction are $\text{L mol}^{-1}\text{ sec}^{-1}$.

92. (b) The rates of reactions for the reaction

$$\frac{1}{2}A \longrightarrow 2B$$

can be written either as

$-2\frac{d}{dt}[A]$ with respect to 'A'

or $\frac{1}{2}\frac{d}{dt}[B]$ with respect to 'B'

$$-2\frac{d}{dt}[A] = \frac{1}{2}\frac{d}{dt}[B]$$

or $-\frac{d}{dt}[A] = \frac{1}{4}\frac{d}{dt}[B]$

i.e., correct answer is (b)

93. (b) For first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{6.93}$$

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

$$\frac{0.693}{6.93} = \frac{2.303}{t}\log\frac{100}{1}$$

$$\frac{0.693}{6.93} = \frac{2.303\times2}{t}$$

$t = 46.06\,\text{min}$

94. (b) For a first order reaction

$$k = \frac{2.303}{t}\log\frac{a}{a-x} = \frac{2.303}{40}\log\frac{0.1}{0.025}$$

$$= \frac{2.303}{40}\log4 = \frac{2.303\times0.6020}{40}$$

$$= 3.47\times10^{-2}\text{ min}^{-1}$$

$\text{Rate} = k[A] = 3.47\times10^{-2}\times0.01$

$= 3.47\times10^{-4}\,\text{M/min}$

95. (a) Activation energy can be calculated from the equation

$$\frac{\log k_2}{\log k_1} = \frac{-E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Given $\frac{k_2}{k_1} = 2$; $T_2 = 310\,K$; $T_1 = 300\,K$

$$= \log2 = \frac{-E_a}{2.303\times8.314}\left(\frac{1}{310} - \frac{1}{300}\right)$$

$E_a = 53598.6\,\text{J/mol} = 53.6\,\text{kJ/mol}$.

96. (d) The rate of a reaction is the speed at which the reactants are converted into products. It depends upon the concentration of reactants. e.g for the reaction

$A + B \longrightarrow \text{Product}$; $\quad r \propto [A][B]$

97. (a) $t_{1/2} = 4$ s $\quad T = 16$

$n = \frac{T}{t_{1/2}} = \frac{16}{4} = 4 \quad (\because T = n\times t_{1/2})$

$$A = A_0\left(\frac{1}{2}\right)^n = 0.12\times\left(\frac{1}{2}\right)^4 = \frac{0.12}{16} = 0.0075\text{ M}$$

where A_0 = initial concentration &

A = concentration left after time t.

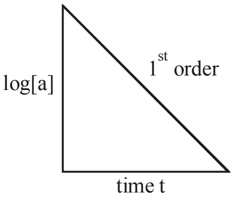
98. (b) For a first reaction $\frac{dx}{dt} = k(a-x)$ on intergration

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

i.e $-\ell n\,(a-x) = kt + c$ or $kt = \ell n\,a - \ell n\,(a-x)$

or $kt = 2.303\,[\log a - \log(a-x)]$

Thus if we plot a graph between log a & t we get



99. (a) From data 1 and 3, it is clear that keeping (B) const, When [A] is doubled, rate remains unaffected. Hence rate is independent of [A]. from 1 and 4, keeping [A] constant, when [B] is doubled, rate become 8 times. Hence

rate $\propto [B]^3$.

100. (c) We know that the activation energy of chemical reaction is given by formula = $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$, where k_1 is the rate constant at temperature T_1 and k_2 is the rate constant at temperature T_2 and E_a is the activation energy. Therefore activation energy of chemical reaction is determined by evaluating rate constant at two different temperatures.

EXERCISE - 2

1. (a) For a zero order reaction

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

2. (c) $Rate_1 = k\,[A]^n\,[B]^m$; $Rate_2 = k\,[2A]^n\,[½B]^m$

$$\therefore \frac{Rate_2}{Rate_1} = \frac{k[2A]^n[½B]^m}{k[A]^n[B]^m} = [2]^n\,[½]^m = 2^n.2^{-m} = 2^{n-m}$$

3. (d) The velocity constant depends on temperature only. It is independent of concentration of reactants.

4. (c) Given, $k = 6.909\ min^{-1}$

For a first order reaction

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

$$6.909 = \frac{2.303}{t}\log\left(\frac{100}{100-75}\right) = \frac{2.303}{t}\log\left(\frac{100}{25}\right)$$

$$\Rightarrow t = \frac{2.303}{6.909}\log 4 \Rightarrow t = \frac{1}{3}\log(2^2) = \frac{2}{3}\log 2.$$

5. (c) Reaction Rate $R_1 = k\,[A]^2\,[B]$

Now increase conc. of A by three times and conc. of B by two times. Then new rate

$R_2 = k\,[3A]^2\,[2B]$

$$\frac{R_1}{R_2} = \frac{k[A]^2[B]}{k[3A]^2[2B]} = \frac{1}{3^2}\times\frac{1}{2} = \frac{1}{18}$$

$R_2 = 18 \times R_1$

Hence rate increases by 18 times.

6. (c) Half life time ($t_{1/2}$) for nth order reaction is given by,

$t_{1/2} \propto [a]^{1-n}$

where n is the order of reaction and a is concentration of reactant.

As decomposition of N_2O_5 follows 1st order kinetic.

So, $\Rightarrow t_{1/2} \propto [a]^{1-1}$ $\Rightarrow t_{1/2} \propto a^0$

7. (d) For a zero order reaction,

$t_{1/2} \propto a_0$ (initial concentration or initial pressure)

$(t_{1/2})_1 \propto P_1$

$(t_{1/2})_2 \propto P_2$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{P_2}{P_1},\quad \frac{(t_{1/2})_2}{45} = \frac{16}{4}$$

$$(t_{1/2})_2 = \frac{16}{4}\times 45 = 180\ min$$

8. (a) As doubling the initial conc. doubles the rate of reaction, order = 1

9. (b) The rate of photochemical process varies with the intensity of absorption.

Since greater the intensity of absorbed light more photons will fall at a point, and further each photon causes one molecule to undergo reaction.

$$H_2O \xrightarrow{\text{Photolysis}} OH^- + H^+$$

10. (c) According to Arrhenius equation, the rate constant of reaction is given by,

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

where A is pre-exponential factor, E_a is activation energy and T is absolute temperature.

when $T \to \infty$, $\frac{E_a}{RT} \to 0$

then $k = Ae^0$

or $k = A$

11. (b) As the rate of reaction get doubled for every 10°C rise in temperature. Hence the increase in reaction rate as a result of temperature rise from 10°C to 100°C is equal to $= 2^9 = 512$

12. (b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

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

$$\therefore \frac{-\Delta[H_2]}{\Delta t} = \frac{3}{2}\times\frac{\Delta[NH_3]}{\Delta t} = \frac{3}{2}\times 2\times 10^{-4}$$

$= 3 \times 10^{-4}\ mol\ litre^{-1}sec^{-1}$

13. (d) Here, $t_{1/2} = 4.5 \times 10^9$ years

Molar ratio of $U^{238} : Pb^{206} = 1 : 3$

Age of the rock can be determined according to the formula

$$t = \frac{2.303\times t_{1/2}}{0.693}\log\left[1+\frac{Pb^{206}}{U^{238}}\right] = \frac{2.303\times 4.5\times 10^9}{0.693}\log\,[1+3]$$

$$= \frac{2.303\times 4.5\times 10^9}{0.693}\times 0.6020$$

$\therefore\ t = 9 \times 10^9$ years.

14. (a) The order of reaction is $\frac{3}{2}$ and molecularity is 2.

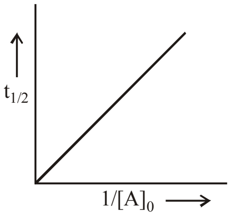
15. (c) Since $-\frac{dx}{dt} \propto [CO]^2$ so on doubling the concentration of CO the rate of reaction will increase by 4 times.

16. (d)

17. (c) $100 \xrightarrow{2\text{ days}} 50 \qquad 50 \xrightarrow{4\text{ days}} 25$

$25 \xrightarrow{8\text{ days}} 12.5$

From the data given above we conclude $t_{1/2} \propto \frac{1}{[A]_0}$. If we plot a graph between half life and $1/[A]_0$ it will look like



Above graph is a characteristic of second order reaction. $t_{1/2}$ of reaction = 2 days.

18. (b) $k = \frac{0.693}{45}\text{min}^{-1} = \frac{2.303}{t_{99.9\%}}\log\frac{a}{a-0.999a}$ or

$$t_{99.9\%} = \frac{2.303 \times 45}{0.693}\log 10^3 = 448 \text{ min} \approx 7.5 \text{ hrs}$$

19. (c) $k = \frac{2.303}{1\text{ hr}}\log\frac{100}{25} = \frac{2.303}{t}\log\frac{100}{50}$

$$\therefore \log 4 = \frac{1}{t}\log 2 \qquad \therefore 2\log 2 = \frac{1}{t}\log 2;\ t = \frac{1}{2}\text{hr.}$$

20. (b) $t_{1/2} \propto a^{1-n} \Rightarrow \frac{0.1}{0.4} = \frac{(200)^{1-n}}{(50)^{1-n}} \Rightarrow \frac{1}{4} = \left[\frac{4}{1}\right]^{1-n} = \left[\frac{1}{4}\right]^{n-1}$

$$\Rightarrow \frac{1}{4'} = \frac{1}{4^{n-1}} \therefore n-1 = 1; n = 2$$

21. (c) Increase in rate $= 2^{(T_2-T_1)/5} = 2^{(40-20)/5} = 2^4 = 16$ times

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

$(a-x)$ is the concentration left after 100 sec.

$$2.7 \times 10^{-3} = \frac{2.303}{100}\log\frac{0.29}{(a-x)}$$

$$\Rightarrow \frac{0.27}{2.303} = \log\frac{0.29}{(a-x)} \Rightarrow 0.117 = \log\frac{0.29}{(a-x)}$$

$\Rightarrow (a-x) = 0.22\,M.$

23. (b) $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

If $\frac{k_2}{k_1} = 2$

$$\log 2 = \frac{Ea}{2.303 \times 8.314}\left[\frac{1}{300} - \frac{1}{310}\right]$$

$$E_a = 0.3010 \times 2.303 \times 8.314\left(\frac{300 \times 310}{10}\right)$$

$= 53598.59 = 54$ kJ.

24. (b) $T_2 = T$(say), $T_1 = 25°C = 298K$,
$E_a = 104.4\text{ kJ mol}^{-1} = 104.4 \times 10^3\text{ J mol}^{-1}$
$k_1 = 3 \times 10^{-4}$, $k_2 = ?$,

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

$$\log\frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3\text{ J mol}^{-1}}{2.303 \times (8.314\text{ J K}^{-1}\text{mol}^{-1})}\left[\frac{1}{298} - \frac{1}{T}\right]$$

As $T \to \infty, \frac{1}{T} \to 0$

$$\therefore \log\frac{k_2}{3 \times 10^{-4}} = \frac{104.4 \times 10^3\text{ J mol}^{-1}}{2.303 \times 8.314 \times 298}$$

$$\log\frac{k_2}{3 \times 10^{-4}} = 18.297, \frac{k_2}{3 \times 10^{-4}} = 1.98 \times 10^{18}$$

$$k_2 = (1.98 \times 10^{18}) \times (3 \times 10^{-4}) = 6 \times 10^{14}\text{s}^{-1}$$

25. (a) $2.303\log\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

$$\log\frac{k_2}{k_1} = \frac{9.0 \times 10^3}{2.303 \times 2}\left[\frac{308 - 298}{308 \times 298}\right]$$

$$\frac{k_2}{k_1} = 1.63;\ k_2 = 1.63k_1;$$

Increase in $k_1 = \frac{k_2 - k_1}{k_1} \times 100$

$$= \frac{1.63k_1 - k_1}{k_1} \times 100 = 63.0\%$$

26. (a) k remains constant at constant temperature and CO does not effect the rate of reaction.

27. (a) For a first order reaction

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

when $t = 60$ and $x = 60\%$

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

Now,

$$t_{\frac{1}{2}} = \frac{2.303}{0.0153}\log\frac{100}{100-50} = \frac{2.303}{0.0153} \times \log 2$$

$$= \frac{2.303}{0.0153} \times 0.3010 = 45.31\text{ min.}$$

28. (d) Given, $k_1 = 10^{16}.e^{-\frac{2000}{T}}$

and $k_2 = 10^{15}.e^{-\frac{1000}{T}}$

when k_1 and k_2 are equal at any temperature T, we have

$$10^{16}.e^{-\frac{2000}{T}} = 10^{15}.e^{-\frac{1000}{T}}$$

or $10 \times 10^{15}.e^{-\frac{2000}{T}} = 10^{15}.e^{-\frac{1000}{T}}$

or $10.e^{-\frac{2000}{T}} = e^{-\frac{1000}{T}}$

or $\ln 10 - \frac{2000}{T} = -\frac{1000}{T}$

or $\ln 10 = \frac{2000}{T} - \frac{1000}{T}$

or $2.303 \log 10 = \frac{1000}{T}$

or $2.303 \times 1 \times T = 1000$ $[\therefore \log 10 = 1]$

or $T = \frac{1000}{2.303} K$

29. (b) Rate of disappearance of reactant = Rate of appearance of products

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\frac{1}{2}k[N_2O_5] = \frac{1}{4}k'[N_2O_5] = k''[N_2O_5]$$

$$\frac{k}{2} = \frac{k'}{4} = k'' \qquad k' = 2k,\ k'' = \frac{k}{2}$$

30. (a) Since initial velocity is ten times the permissible value

$\therefore A_0 = 10A$

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t_{1/2} = \frac{2.303}{\lambda}\log\frac{A_0}{A} = \frac{2.303}{0.693/30}\log\frac{10A}{A}$$

$$= \frac{2.303 \times 30}{0.693} \times \log 10 = 100 \text{ days.}$$

31. (c) For the reaction

$A \rightarrow$ Product

given $t_{1/2} = 1$ hour

for a zero order reaction

$$t_{1/2} = \frac{[A_0]}{2k}$$

or $k = \frac{[A_0]}{2t_{1/2}} = \frac{2}{2 \times 1} = 1 \text{ mol lit}^{-1} \text{hr}^{-1}$

Further for a zero order reaction

$$k = \frac{dx}{dt} = \frac{\text{change in concentration}}{\text{time}}$$

$$1 = \frac{0.50 - 0.25}{\text{time}}$$

$\therefore$ time = 0.25 hr.

32. (d) Since the slow step is the rate determining step hence if we consider option (A) we find

Rate = $k[Cl_2][H_2S]$

Now if we consider option (B) we find

Rate = $k[Cl_2][HS^-]$ ...(i)

For equation,

$H_2S \rightleftharpoons H^+ + HS^-$

$$K = \frac{[H^+][HS^-]}{H_2S} \text{ or } [HS^-] = \frac{K[H_2S]}{H^+}$$

Substituting this value in equation (i) we find

$$\text{Rate} = k[Cl_2]K\frac{[H_2S]}{H^+} = k'\frac{[Cl_2][H_2S]}{[H^+]}$$

Thus slow step should involve 1 molecule of Cl_2 and 1 molecule of H_2S.

hence only, mechanism (A) is consistent with the given rate equation.

33. (c) Since for every 10ºC rise in temperature rate doubles for 50ºC rise in temperature increase in reaction rate $= 2^5 = 32$ times

34. (d) Overall order = sum of orders w.r.t each reactant.

Let the order be x and y for G and H respectively

Exp.No.	[G]mole litre^{-1}	[H]mole litre^{-1}	rate(mole litre^{-}time^{-1})
1	a	b	r
2	$2a$	$2b$	$8r$
3	$2a$	b	$2r$

$\because$ For (1) and (3), the rate is doubled when conc. of G is doubled keeping that of H constant i.e.,

rate $\propto [G]$ $\therefore x = 1$

From (2) and (3), $y = 2$

$\therefore$ Overall order is 3.

35. (a) The values of rate constants k_0, k_1 for zero order and first order reaction, respectively, are given by the following equation:

$$k_0 = \frac{A_0}{2 \times t_{1/2}}$$ [where A_0 = initial concentration, and $t_{1/2}$ = half-life period]

and $k_1 = \frac{0.693}{t_{1/2}}$

Substituting various given values, we get

$$k_0 = \frac{1.386 \text{ mol litre}^{-1}}{2 \times 20 \text{ sec}} \quad \text{...(i)}$$

$$\text{and } k_1 = \frac{0.693}{40 \text{ sec}} \quad \text{...(ii)}$$

Dividing (ii) by (i), we get

$$\frac{k_1}{k_0} = \frac{0.693}{40} \times \frac{2 \times 20}{1.386 \text{ mol dm}^{-3}}$$

$$= \frac{0.693}{1.386} = 0.5$$

$= 0.5 \text{ mol}^{-1} \text{dm}^3$

Thus the correct answer is (a).

36. (d) $\log k = \log A - \dfrac{E_a}{2.303RT}$ …(1)

Also given $\log k = 6.0 - (2000)\dfrac{1}{T}$ …(2)

On comparing equations, (1) and (2)

$\log A = 6.0 \Rightarrow A = 10^6\,\mathrm{s}^{-1}$

and $\dfrac{E_a}{2.303\,R} = 2000$;

$\Rightarrow E_a = 2000 \times 2.303 \times 8.314 = 38.29\ \mathrm{kJ\ mol^{-1}}$

37. (a) As per Arrhenius equation $(k = Ae^{-E_a/RT})$, the rate constant increases exponentially with temperature.

38. (a) From the first set of data (i) and (ii) it is observed that on keeping concentration of [B] constant and on doubling the concentration of [A] rate does not changes hence order of reaction with respect to A is zero.

From the second set of data (i) and (iii) it is observed that rate becomes 4 times on doubling the concentration of [B] keeping [A] constant hence order with respect to [B] will be 2

rate $= k[A]^0\,[B]^2$

39. (d) For a zero order reaction,

$t_{1/2} \propto a_0$ (initial concentration or initial pressure)

$(t_{1/2})_1 \propto P_1$

$(t_{1/2})_2 \propto P_2$

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \frac{P_2}{P_1}, \quad \frac{(t_{1/2})_2}{45} = \frac{16}{4}$$

$$(t_{1/2})_2 = \frac{16}{4} \times 45 = 180\ \text{min}$$

40. (d) From 1st and 2nd sets of data - no change in rate is observed with the change in concentration of 'C'. So the order with respect to 'C' is zero.

From 1st and 4th sets of data

Dividing eq. (4) by eq. (1)

$$\frac{1.25 \times 10^{-3}}{5.0 \times 10^{-3}} = \left[\frac{0.005}{0.010}\right]^x$$

or $0.25 = (0.5)^x$ or $(0.5)^2 = (0.5)^x$

$\therefore x = 2$

The order with respect to 'A' is 2 from the 1st and 3rd sets of data Dividing eq. (1) by eq. (3)

$$\frac{5.0 \times 10^{-3}}{1.0 \times 10^{-2}} = \left[\frac{0.005}{0.010}\right]^y$$

or $(0.5)^1 = (0.5)^y \Rightarrow y = 1$

The order with respect to 'B' is 1

So the order with respective the reactants A, B and C is 2, 1 and 0.

41. (c) $N_2O \longrightarrow N_2 + \frac{1}{2}O_2$

$$\frac{dx}{dt} \propto [N_2O]^1$$

i.e. order of reaction = 1

42. (d) For a first order reaction,

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

$$k = \frac{2.303}{75}\log\frac{1}{1/8} = \frac{2.303 \times 0.903}{75}\,\text{min}^{-1}$$

First order reaction

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 75}{2.303 \times 0.903} = 25\,\text{min}$$

43. (b) $k = Ae^{-E_a/RT}$

$\ln k = \ln A - E_a/RT$

For ln k vs 1/T

ln A = intercept

$-E_a/R = \text{slope} = -2 \times 10^4\ \mathrm{K}$

$\therefore E_a = 8.3 \times 2 \times 10^4\ \mathrm{J\ mol^{-1}}$

$= 16.6 \times 10^4\ \mathrm{J\ mol^{-1}}$ or $166\ \mathrm{kJ\ mol^{-1}}$

44. (d) $\because \dfrac{N}{N_0} = \left(\dfrac{1}{2}\right)^n$

For first condition

$\dfrac{1}{4} = \left(\dfrac{1}{2}\right)^n \quad \therefore\ n = 2$

$t_{1/2} = \dfrac{20}{2} = 10$

For second condition

$\left(\dfrac{1}{16}\right) = \left(\dfrac{1}{2}\right)^n$

$n = 4 \ \therefore\ T = 4 \times 10 = 40\ \text{min}$

45. (c) Order is the sum of the powers to which the concentration terms are raised in the rate equation.

46. (b) According to Arrhenius equation, $k = Ae^{-E_a/RT}$

$\therefore$ when $E_a = 0, k = A$

Also $\ln k$ υs 1/T is a straight line with slope $= -E_a/R$.

$\therefore$ Statements (ii) and (v) are correct.

47. (b) According to Arrhenius equation, $k = Ae^{-E/RT}$

When $E_a = 0, k = A$

48. (b) For a zero order reaction, $t_{1/2}[A_0]/2k$

49. (b) According to Arrhenius equation, $k = Ae^{-E_a/RT}$.

EXERCISE - 3

Exemplar Questions

1. (c) The role of a catalyst is to change the activation energy of reaction.

2. (c) The heat absorbed or evolved during the reaction remains unchanged in presence of catalyst as there is no change in stability of reactant and product.

3. (b) Arrhenius equation relates activation energy of a chemical reaction with rate constant of a reaction at two different temperatures.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

4. (a) The minimum energy required to convert reactant molecules into product molecules.

i.e. Activation energy $= E_1 + E_2$

Energy of product is greater than the reactants so less stable.

5. (b) $A(g) \longrightarrow B(g) + C(g)$

Initially p_i $\quad 0 \quad 0$

At time t $p_i - x$ $\quad x \quad x$

Total pressue at equilibrium, $p_t = p_i - x + x + x = p_i + x$

For first order reaction $x = p_t - p_i$

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

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

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

6. (a) According to Arrhenius equation, $k = A\,e^{-E_a/RT}$

Taking log on both side $\ln k = \ln\left(A\,e^{-\frac{E_a}{RT}}\right)$

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

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \ln A$$

From the graph, it is clear that slope $= \frac{-E_a}{R}$ and intercept $= \ln A$.

7. (d) As per Arrhenius equation $k = A\,e^{-E_a/RT}$

So, $\quad k \propto e^{-E_a}$

$$k \propto e^{-\frac{1}{T}}$$

$$\propto e^{T}$$

These relations show that rate constant increases with decreasing activation energy and increasing temperature.

8. (c) $Zn + \text{dil. } HCl \longrightarrow ZnCl_2 + H_2 \uparrow$

Rate of reaction

$$= \frac{\text{Change in concentration of } H_2}{\text{Change in time}} = \frac{V_3 - 0}{40 - 0} = \frac{V_3}{40}$$

9. (c) Order of reaction may or may not be equal to sum of stoichiometric coefficients of reactants in the balanced chemical equation.

10. (b) Instantaneous rate of reaction

$$= \frac{\text{Change in volume}}{\text{Time interval close to 40s}}$$

$$r_{inst}(20s) = \frac{V_4 - V_2}{50 - 30} \text{ incorrect, correct is } \frac{V_5 - V_2}{50 - 30}$$

11. (a) Concentration of reactant decreases with passage of time, so rate of reaction decreases because rate changes with change in concentration of reactant or product with time.

12. (c)

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

Rate law expression as

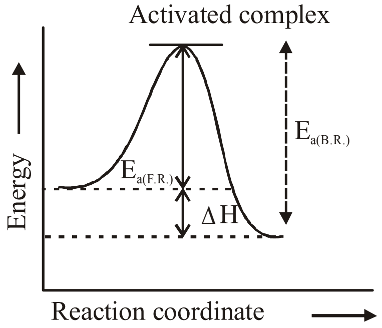
$$-\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = \frac{-1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{+1}{3}\frac{\Delta[Br_2]}{\Delta t}$$

$$\Rightarrow -\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = \frac{-5}{6}\frac{\Delta[H^+]}{\Delta t}$$

$$\Rightarrow \quad \frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$$

13. (a) $E_{a(F.R.)} + \Delta H = E_{a(B.R.)}$

$\Delta H = -\text{ve}$



14. (b) Rate of reaction w.r.t B is of first order

$R_1 = k\,[A]\,[B]$

when concentration of reactant 'B' is doubled then rate (R_2) will be :

$R_2 = k\,[A]\,[2B]$

$R_2 = 2k\,[A]\,[B]$

$R_2 = 2\,R_1$

15. (c) In collision theory of reaction rates the key factors which determine whether a particular collision will result in a reaction is the energy of collision and the orientation of the collision.

16. (d) The time in which the concentration of a reactant is reduced to half of its original value is called half-life period of the reaction.

But it is impossible to perform 100% of the reaction. Because substance never reacts completely as in every half-life, 50% of the substance reacts. So, time taken for 100% completion of a reaction is infinite.

17. (b) $r = k\,[A]^x[B]^y$

$$\frac{\text{Rate of exp. 1}}{\text{Rate of exp. 2}} = \frac{[0.30]^x\,[0.30]^y}{[0.30]^x\,[0.60]^y}$$

$$\frac{0.10}{0.40} = \frac{[0.30]^y}{[0.60]^y}$$

$$\frac{1}{4} = \left[\frac{1}{2}\right]^y$$

$$\left[\frac{1}{2}\right]^2 = \left[\frac{1}{2}\right]^y$$

$y = 2$

$$\frac{\text{Rate of exp. 1}}{\text{Rate of exp. 3}} = \frac{[0.30]^x\,[0.30]^y}{[0.60]^x\,[0.30]^y}$$

$$\frac{0.10}{0.20}=\left[\frac{0.30}{0.60}\right]^x\left[\frac{0.30}{0.30}\right]^y$$

$$\frac{1}{2}=\left[\frac{1}{2}\right]^x[1]^y$$

$$\frac{1}{2}=\left[\frac{1}{2}\right]^x$$

i.e., $x = 1$

∴ Rate = $k\,[A]^x[B]^y$

Rate = $k\,[A]^1[B]^2$

18. (b) Catalyst does not change Gibbs free energy because Gibbs free energy is related to concentration of reactant & product which is not changed by catalyst.

19. (b) Pseudo first order reaction is a chemical reaction in which rate of reaction depends upon concentration of only one reactant while concentration of another reactant has no effect on rate of reaction.

20. (b) $A \rightarrow B$

As time increases concentration of reactant decreases and concentration of product increases exponentially.

NEET/AIPMT (2013-2017) Questions

21. (b) $\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$

$$\log 2=\frac{E_a}{2.303\times 8.314}\left[\frac{1}{293}-\frac{1}{308}\right]$$

$$0.3=\frac{E_a}{2.303\times 8.314}\times\frac{15}{293\times 308}$$

$$E_a=\frac{0.3\times 2.303\times 8.314\times 293\times 308}{15}.$$

$= 34673\ \text{J mol}^{-1} = 34.7\ \text{kJ mol}^{-1}$

22. (b) DH = $E_{a_f} - E_{a_b} = 0$

23. (b) For a first order reaction,

$t_{75\%} = 2 \times t_{50\%}$

24. (d) $\text{Rate}_1 = k[A]^2[B]^3$

when concentrations of both A and B are doubled then

$\text{Rate}_2 = k[2A]^2[2B]^3 = 32\,k[A]^2[B]^3$

∴ rate will increase by a factor of 32.

25. (b) Arrhenius equation

$$K = A.e^{-E_a/RT} \Rightarrow \ln K = \ln A - \frac{E_a}{RT}$$

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

so, activation energy of reaction can be determined from the slope of ln K vs $\frac{1}{T}$

26. (a) $t_{1/2}=\frac{0.693}{k}$

For first order $t_{1/2}$ is independent of initial concentration of reactant.

27. (d) Rate constant $k = 0.6 \times 10^{-3}$ mole per second. (unit mole per second shows zero order reaction)

For a zero order reaction

$$[A] = [A]_0 - kt$$

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

$= 0.6 \times 10^{-3} \times 20 \times 60 = 0.72\ \text{M}$

28. (a) For a first order reaction

$$K=\frac{2.303}{(t_2-t_1)}\log\frac{(a-x_1)}{(a-x_2)}$$

$$K=\frac{2.303}{(20-10)}\log\left(\frac{0.04}{0.03}\right)$$

$$K=\frac{2.303\times 0.1249}{10}$$

$$\frac{0.6932}{t_{1/2}}=\frac{2.303\times 0.1249}{10}$$

$$t_{1/2}=\frac{0.6932\times 10}{2.303\times 0.1249}=24.1\ \text{sec}$$

29. (d) A catalyst provides an alternative route for the reaction with a lower activation energy.

30. (c) The overall reaction rate depends on the rate of the slowest step.

i.e., Overall rate = Rate of slowest step (ii)

$= k[X][Y_2]$ ...(1)

k = rate constant

Assuming step (i) to be reversible, its equilibrium constant,

$$k_{eq}=\frac{[X]^2}{[X_2]} \Rightarrow [X]^2 = k_{eq}[X_2];$$

$[X] = k_{eq}^{\frac{1}{2}}[X_2]^{\frac{1}{2}}$ ...(2)

From eq (1) and (2)

$$\text{Rate} = k k_{eq}^{\frac{1}{2}}[X_2]^{\frac{1}{2}}[Y_2]$$

$$\text{Overall order} = \frac{1}{2}+1=\frac{3}{2}=1.5$$

31. (a) Half life for a first order reaction,

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

So, $t_{1/2}=\frac{0.693}{10^{-2}}\text{sec}$.

Also, for the reduction of 20 g or reactant to 5 g, two half lives will be required.

∴ For 20 g of the reactant to reduce to 5g, time taken,

$$t = 2 \times \frac{0.693}{10^{-2}}\text{sec} = 138.6\ \text{sec.}$$