

SAMPLE CHAPTER

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2024 EDITION

OBJECTIVE

KARNATAKA CET

Karnataka Common Entrance Test

MCQs Extracted from Each Line of Latest I & II PUC Textbooks

6000+ MCQs

3 MOCK TEST PAPERS
AS PER LATEST PATTERN

KEY FEATURES...

- Topicwise 10 Years' Trend Analysis
- Comprehensive Theory with Illustrations, Self Tests and Concept Map
- Three Types of Exercises with Detailed Solutions
 - Topicwise KCET Connect
 - KCET Ready
 - KCET Exam Archive : Previous 10 Years' (2014-2023) Questions



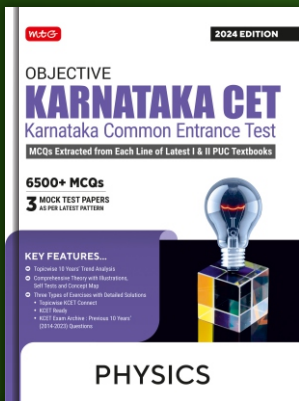
CHEMISTRY

mtg Introducing

OBJECTIVE KARNATAKA CET

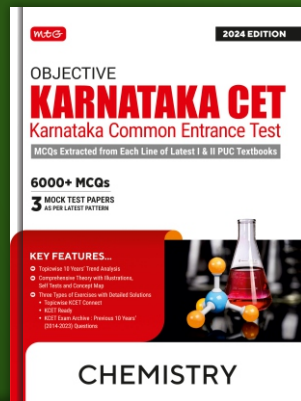
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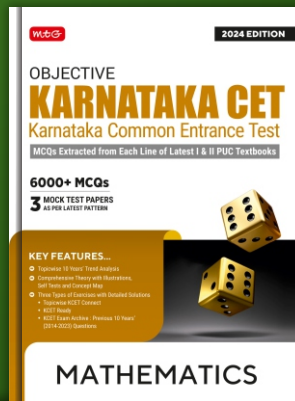
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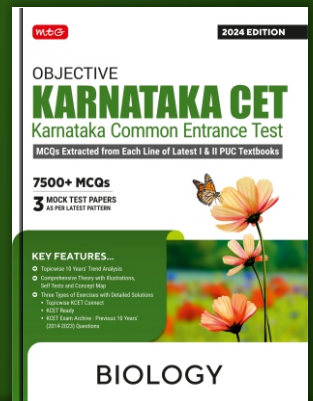
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KEY FEATURES

- ⇒ Topicwise 10 Years' Trend Analysis
- ⇒ Comprehensive theory with illustrations and concepts maps.
- ⇒ Multiple self-tests after each topic.
- ⇒ 3 Mock test papers as per latest syllabus & pattern.
- ⇒ Detailed solutions for all exercises and questions.
- ⇒ Three types of exercises
 - KCET Connect – Level 1 – Topic-wise MCQs
 - KCET Ready – Level 2 – Chapter-wise MCQs
 - KCET Exam Archive – Level 3 – Previous 10 Years' (2014-2023) Questions

3

Chemical Kinetics

10 Years' KCET Topicwise Trend at a Glance

NCERT Topic	No. of Questions									
	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023
3.1 Rate of a Chemical Reaction	-	-	1	1	1	-	1	-	-	-
3.2 Factors Influencing Rate of a Reaction	-	1	1	1	-	2	-	2	1	-
3.3 Integrated Rate Equations	1	2	1	-	1	-	1	1	3	1
3.4 Temperature Dependence of the Rate of a Reaction	-	-	1	1	1	1	-	-	-	2
3.5 Collision Theory of Chemical Reactions	-	-	-	-	-	-	1	1	-	-

Introduction

Chemical kinetics is a branch of chemistry which deals with the study of rate of reaction, mechanism and the factors which affects the rate of reactions.

Study of rate of reaction helps to predict how quickly a reaction approaches the equilibrium. The rate of reaction also provides information of mechanism of reaction.

By studying the reaction rate we can find out that in how many steps the reaction is taking place and which step is rate determining step. By knowing this we can control the rate of a reaction as well. Factor affecting the rate of reaction helps us to increase the rate of our desired reaction.

3.1 Rate of a Chemical Reaction

- The rate of reaction is the change in the concentration of any one of the reactants or products per unit time.

$$\text{Rate} = \frac{\text{Decrease in conc. of reactant}}{\text{Time taken}} = \frac{\text{Increase in conc. of product}}{\text{Time taken}}$$

Consider the hypothetical reaction :



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

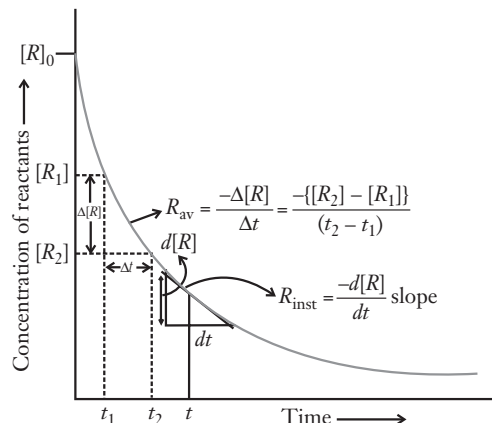
Negative sign shows decrease in concentration with time and positive sign shows increase in concentration with time.

Average and Instantaneous Rate of Reaction

The rate of change in concentration of any reactant or product for a given interval of time is known as average rate of reaction. Consider the reaction :

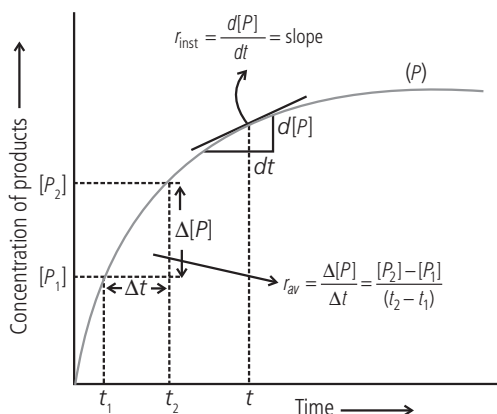


$$r_{av} = -\frac{R_2 - R_1}{t_2 - t_1} = -\frac{\Delta[R]}{\Delta t}$$



where, R_2 and R_1 are the concentrations of R at time t_2 and t_1 respectively. The rate of change in concentration of any reactant or product at a particular instant of time is known as instantaneous rate of reaction.

$$r_{inst} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

**Units of rate of reaction :**

$$\text{Rate} = \frac{\text{Concentration}}{\text{Time}} = \frac{\text{mol/litre}}{\text{sec}} = \text{mol litre}^{-1}\text{sec}^{-1}$$

$$\text{In gaseous reaction} = \frac{\text{Partial pressure}}{\text{Time}} = \text{atm s}^{-1}$$

Illustration : In a chemical reaction $2P \rightarrow 4Q + R$, the concentration of Q is found to be increased by $2.0 \times 10^{-2} \text{ mol L}^{-1}$ in five seconds. Calculate

(i) rate of appearance of Q

(ii) rate of reaction.

Soln.: (i) Rate of appearance of Q

$$\frac{d[Q]}{dt} = \frac{2 \times 10^{-2}}{5} = 0.4 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

(ii) Rate of reaction

$$\frac{1}{4} \frac{d[Q]}{dt} = \frac{1}{4} \times 0.4 \times 10^{-2} = 0.1 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

The reciprocals of coefficients are written for the expression of rate of reaction.

Illustration : How are the rates of formation of NO and H_2O related to the rate of consumption of NH_3 ?

$$\text{Soln.} \quad \frac{1}{4} \frac{d[\text{NO}]}{dt} = \frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt} = -\frac{1}{4} \frac{d[\text{NH}_3]}{dt}$$

$$\therefore \frac{d[\text{NO}]}{dt} = -\frac{d[\text{NH}_3]}{dt}$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = -\frac{6}{4} \frac{d[\text{NH}_3]}{dt} = -1.5 \frac{d[\text{NH}_3]}{dt}$$

Self Test - 1

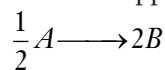
1. For a reaction $P + Q \rightarrow 2R + S$. Which of the following statements is incorrect?

- (a) Rate of disappearance of P
= Rate of appearance of S
- (b) Rate of disappearance of Q =
 $2 \times$ Rate of appearance of R
- (c) Rate of disappearance of P =
Rate of disappearance of Q
- (d) Rate of disappearance of Q =
 $\frac{1}{2} \times$ Rate of appearance of R

2. In the reaction, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, the rate of formation of NO_2 is $0.0072 \text{ mol L}^{-1} \text{ s}^{-1}$. What is the rate of change of $[\text{N}_2\text{O}_5]$ at the same time?

- (a) 0.0018 (b) 0.0144
(c) 0.0036 (d) 0.0072

3. For a reaction rate of disappearance of A is related to the rate of appearance of B by the expression



- (a) $-\frac{d[A]}{dt} = 4 \frac{d[B]}{dt}$ (b) $-\frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$
(c) $-\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$ (d) $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$

4. The rate of disappearance of SO_2 in the reaction, $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ is $1.28 \times 10^{-5} \text{ M s}^{-1}$. The rate of appearance of SO_3 is

- (a) $0.64 \times 10^{-5} \text{ M s}^{-1}$ (b) $0.32 \times 10^{-5} \text{ M s}^{-1}$
(c) $2.56 \times 10^{-5} \text{ M s}^{-1}$ (d) $1.28 \times 10^{-5} \text{ M s}^{-1}$

5. The rate of formation of ammonia by the reaction : $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

$$\text{expressed as } \frac{d[\text{NH}_3]}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

The rate of consumption expressed in terms of H_2 as $-\frac{d[\text{H}_2]}{dt}$ will be

- (a) double (b) three times
(c) same
(d) one and a half time of that expressed in terms of NH_3 .

3.2 Factors Influencing Rate of a Reaction

Rate of reaction depends upon number of factors :

1. Concentration

Rate of reaction is directly proportional to the

concentration of reactants, as the concentration of reactants decreases (or that of products increases) with due course of time, rate of reaction also decreases.

2. Temperature

Rate of reaction increases with increase of temperature and usually becomes double for 10°C rise of temperature.

3. Catalyst

Catalyst generally increases the speed of reaction by lowering the energy barrier *i.e.*, activation energy.

4. Surface Area of Reactant

Greater the surface area (*i.e.*, smaller particle size), faster will be the reaction.

5. Nature of Reactant

Different reactants undergo similar kind of reaction with different rates because the energy factor involved with different bonds are different.

6. Presence of Light

Light provides the necessary activation energy for photochemical reactions.

Rate Expression and Rate constant

- For the reaction, $aA + bB \longrightarrow cC + dD$

Rate $\propto [A]^x [B]^y$ where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants.

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

where k is a proportionality constant called rate constant and this equation is called rate law or rate expression.

- Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Order of Reaction

Order of reaction is the sum of the exponents (powers) to which molar concentrations are raised in the rate law.

$$r = K[A]^x [B]^y$$

Order of reaction (n) = $(x + y)$

Order of a reaction can be 0, 1, 2, 3

It can be zero, whole number, fractional or even negative.

Units of rate constant :

$$k = \frac{\text{Rate}}{[A]^x [B]^y} = \frac{\text{concentration}}{\text{time}} \times \frac{1}{(\text{concentration})^n};$$

(where $[A] = [B]$) ($\therefore n = x + y$)

Taking SI units of concentration, mol L⁻¹ and time, s, the units of k for different reaction order are listed below :

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

Molecularity of a Reaction

- The minimum number of reacting particles (molecules, atoms, or ions) that come together or collide in a rate determining step to form product or products is called molecularity of reaction. It may be unimolecular, bimolecular and trimolecular, etc.
 $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ (unimolecular)
 $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (bimolecular)
 $2\text{FeCl}_3 + \text{SnCl}_2 \rightarrow 2\text{FeCl}_2 + \text{SnCl}_4$ (trimolecular)
- The molecularity is equal to the sum of number of molecules of the reactants involved in a balanced equation. The molecularity of such reactions is determined by the slowest step. Molecularity depends upon the mechanism of the reaction.

Difference between molecularity and order of reaction

S. No.	Molecularity of reaction	Order of reaction
1.	It is the number of molecules of reactants taking part in elementary step of a reaction.	It is the sum of powers raised on concentration terms in the rate expression.
2.	It is a theoretical concept.	The values are derived from rate expression.
3.	Its value cannot be zero or fractional.	Its values can be zero or fractional.
4.	In a multistep reaction, each step reaction has its individual molecularity.	In a multistep reaction the order is determined by slowest step.

Illustration : For a reaction $A + B \rightarrow P$, the rate law is given by, $r = k[A]^{1/2} [B]^2$
What is the order of this reaction?

Soln.: $A + B \rightarrow \text{Product}$

Rate law, $r = k[A]^{1/2} [B]^2$

Order of reaction is sum of the powers of concentration terms,

$$\therefore \text{Order of reaction} = \frac{1}{2} + 2 = \frac{5}{2} = 2.5$$

Illustration : A reaction is of second order with respect to its reactant. How will its reaction rate be affected if the concentration of the reactant is (i) doubled (ii) reduced to half?

Soln.: Let the concentration of the reactant $[A] = a$
 Order of reaction = 2 so that,
 Rate of reaction = $k[A]^2$... (1)
 $= ka^2$

(i) Given that concentration of the reactant is doubled so, that $[A] = 2a$,

Putting the value in equation (1) we get
 New rate of reaction, $R_1 = k(2a)^2 = 4ka^2$

Hence, rate of reaction will increase to 4 times.

(ii) Given that concentration of the reactant is reduced to half

So that, $[A] = (1/2)a$

Putting the value in equation (1), we get

$$\text{New rate of reaction } R_2 = k((1/2)a)^2 \\ = (1/4)ka^2$$

Hence, rate of reaction will reduce to 1/4.

Illustration : How can the rate of simple reaction, $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$, be affected, if volume of the reaction vessel is doubled?

Soln.: Rate (r_1) = $k[\text{NO}]^2[\text{O}_2]$

If volume of reaction vessel is doubled, the concentration of reactants becomes half, then,

$$\text{Rate } (r_2) = k \left[\frac{1}{2} \text{NO} \right]^2 \left[\frac{1}{2} \text{O}_2 \right] \\ = \frac{1}{4} \times \frac{1}{2} k [\text{NO}]^2 [\text{O}_2] = \frac{1}{8} r_1$$

i.e., rate becomes $\left(\frac{1}{8}\right)^{\text{th}}$ of the initial rate.

Illustration : For the reaction, $2A + B_2 \rightarrow 2AB$, following observations were obtained :

Rate of disappearance of B_2 ($\text{mol L}^{-1}\text{s}^{-1}$)	$[A]$ (mol L^{-1})	$[B_2]$ (mol L^{-1})
1.8×10^{-3}	0.015	0.15
1.085×10^{-2}	0.090	0.15
5.4×10^{-3}	0.015	0.45

Find out the following :

- order of reaction
- rate constant
- rate of formation of AB , when $[A] = 0.02$ and $[B_2] = 0.04 \text{ mol L}^{-1}$

Soln.: (a) The rate of disappearance of $B_2 = -\frac{d[B_2]}{dt}$

$$\text{or } r = k[A]^m[B_2]^n \\ \text{then } 1.8 \times 10^{-3} = k[0.015]^m [0.15]^n \quad \dots(i)$$

$$1.085 \times 10^{-2} = k[0.090]^m [0.15]^n \quad \dots(ii)$$

$$5.4 \times 10^{-3} = k[0.015]^m [0.45]^n \quad \dots(iii)$$

From eqns. (i) and (ii),

$$\frac{1.8 \times 10^{-3}}{1.085 \times 10^{-2}} = \left[\frac{0.015}{0.090} \right]^m \Rightarrow m = 1$$

From eqns. (i) and (iii),

$$\frac{1.8 \times 10^{-3}}{5.4 \times 10^{-3}} = \left[\frac{0.15}{0.45} \right]^n \Rightarrow n = 1$$

Order of reaction = $1 + 1 = 2$

(b) Rate of disappearance of $B_2 = k[A]^1[B_2]^1$

$$\therefore 1.8 \times 10^{-3} = k[0.015]^1 [0.15]^1$$

$$k = 0.8 \text{ L mol}^{-1} \text{ sec}^{-1}$$

(c) Now, $\frac{1}{2} \frac{d[AB]}{dt} = -\frac{d[B_2]}{dt}$

$$\frac{d[AB]}{dt} = 2 \times k[A]^1 [B_2]^1$$

$$\text{or } \frac{d[AB]}{dt} = 2 \times 0.8 \times (0.02)^1 (0.04)^1 \\ = 1.28 \times 10^{-3} \text{ mol L}^{-1}\text{s}^{-1}$$

Self Test - 2

- The order of reaction is decided by
 - temperature
 - mechanism of reaction as well as relative concentration of reactants
 - molecularity
 - pressure.
- If initial concentration is reduced to $1/4^{\text{th}}$ in a zero order reaction, the time taken for half the reaction to complete
 - remains same
 - becomes 4 times
 - becomes one-fourth
 - doubles.
- In which of the following cases, does the reaction go farthest to completion?

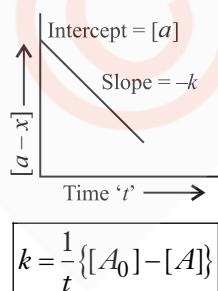
(a) $k = 10^2$	(b) $k = 10^{-2}$
(c) $k = 10$	(d) $k = 1$

4. The rate of formation of a dimer in a second order dimerisation reaction is $9.1 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ at 0.01 mol L^{-1} monomer concentration. What will be the rate constant for the reaction?
- (a) $9.1 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$
 (b) $9.1 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$
 (c) $3 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$
 (d) $27.3 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$
5. Rate constant of two reactions are given below. Identifying their order of reaction.
- (i) $k = 5.3 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$
 (ii) $k = 3.8 \times 10^{-4} \text{ s}^{-1}$
- (a) (i) second order, (ii) first order
 (b) (i) first order, (ii) second order
 (c) (i) zero order, (ii) first order
 (d) (i) second order, (ii) zero order
6. The rate constant for a first order reaction is equal to the initial rate of reaction when the initial concentration of the reactant is
- (a) 100 M (b) $1 \times 10^{-2} \text{ M}$
 (c) 1.0 M (d) 0.1 M
7. On increasing the pressure three fold, the rate of the given reaction
- $$2\text{H}_2\text{S} + \text{O}_2 \longrightarrow \text{products}$$
- would increase
- (a) 3 times (b) 9 times
 (c) 12 times (d) 27 times.
8. For a reaction $X + Y \rightarrow Z$, rate $\propto [X]$. What is (i) molecularity and (ii) order of reaction?
- (a) (i) 2, (ii) 1 (b) (i) 2, (ii) 2
 (c) (i) 1, (ii) 1 (d) (i) 1, (ii) 2
9. The rate of the reaction :
- $$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \rightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$$
- is given by the equation,
 rate = $k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{NaOH}]$
 If concentration is expressed in mol/L, the units of k are
- (a) $\text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ (b) $\text{mol L}^{-1} \text{ s}^{-1}$
 (c) $\text{L mol}^{-1} \text{ s}^{-1}$ (d) s^{-1}
10. Order of a reaction can not be obtained
- (a) experimentally
 (b) from stoichiometry of the reaction
 (c) if the reactants are gases
 (d) if the reactants are in different physical states.

3.3 Integrated rate Equations

The equations which are obtained by integrating the differential rate laws and which give a direct relationship between the concentrations of the reactants and time are called integrated rate laws.

Zero Order Reaction



where, k is rate constant

t is reaction time

$[A_0]$ is initial reactant concentration

$[A]$ is final reactant concentration.

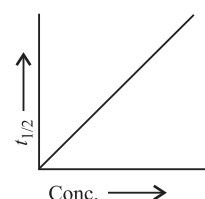
Half-life period

Half-life period ($t_{1/2}$) is the time in which half of the reaction has been completed *i.e.*, half of the reactant concentration undergoes the reaction.

It means final concentration of reactant, $[A] = \frac{[A_0]}{2}$ and, t becomes $t_{1/2}$,

$$\text{then, } k = \frac{1}{t_{1/2}} \left\{ [A_0] - \frac{[A_0]}{2} \right\}$$

$$t_{1/2} = \frac{[A_0]}{2k}$$



Thus, half-life period of a zero order reaction is directly proportional to initial concentration of reactant.

$$\text{i.e., } t_{1/2} \propto [A_0]$$

First order reaction : The reaction in which the rate of reaction is directly proportional to the concentration of reacting substance.

- In first order reaction, the rate is determined by the change of one concentration term only.

For a reaction, $A \longrightarrow \text{product}$

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

$$\text{On integration, } \int \frac{dx}{(a-x)} = \int kdt$$

i.e. $-\ln(a-x) = kt + c$ where, c is integration constant, when $t = 0$, $x = 0$ then $-\ln a = c$

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

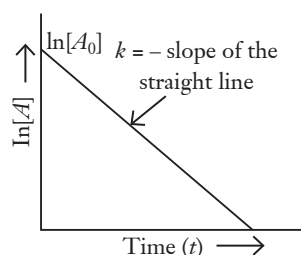
$$\text{or } kt = \ln a - \ln(a-x) \quad \text{or } kt = \ln \frac{a}{a-x}$$

$$k = \frac{1}{t} \ln \frac{a}{(a-x)}$$

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

$$\text{or } k = \frac{2.303}{t} \log \frac{[A_0]}{[A]}$$

Unit of k is sec^{-1} or min^{-1} .



- For first order reaction, $t_{1/2} = \frac{0.693}{k}$
- In general, $t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$, where n = order of reaction
- It is independent of initial concentration for first order reaction.

Info Shots

- General expression for the time taken for n^{th} fraction of reaction of first order.

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

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

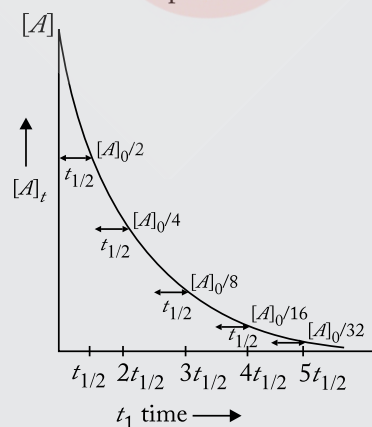
$$t_{1/n} = \frac{2.303}{k} \log \frac{n}{n-1}$$

- Amount of substance left after n half-lives

$$\frac{A}{A_0} = \left(\frac{1}{2}\right)^n \quad \text{where } n = \frac{T}{t_{1/2}}$$

Graphical representation of half life

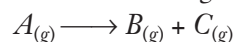
- The graph of concentration, $[A]_t$ of the reactant versus time t can be represented as



- Each successive half life in which reactant concentration decreases to its half value is the same.

Integrated Rate Equation for First Order Gas Phase Reactions

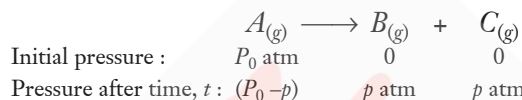
Let us consider the general first order gas phase reaction :



Suppose the initial pressure of $A = P_0$ atm.

After time t , suppose the pressure of A decrease by p atm.

Now, as 1 mole of A decomposes to give 1 mole of B and 1 mole of C , pressure of B and C will increase by p each. Hence, we have



Total pressure of the reaction mixture after time t ,

$$P_t = (P_0 - p) + p + p = P_0 + p \text{ atm} \therefore p = P_t - P_0$$

$$\therefore \text{Pressure of } A \text{ after time } t (P_A) = P_0 - (P_t - P_0) = 2P_0 - P_t$$

But initial pressure of $A (P_0) \propto$ initial conc. of A , i.e., $[A]$ and Pressure of A after time $t (P_A) \propto$ conc. of A at time t , i.e., $[A]$

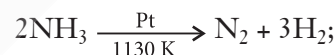
Substituting these values in the first order rate equation,

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}, \text{ we get}$$

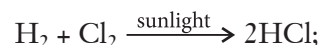
$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

Examples :

• Zero order

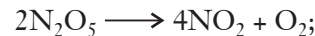


$$\text{Rate} = k[\text{NH}_3]^0 = k$$

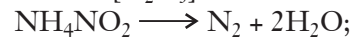


$$\text{Rate} = k[\text{H}_2]^0[\text{Cl}_2]^0 = k$$

• Ist order

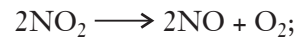


$$\text{Rate} = k[\text{N}_2\text{O}_5]$$



$$\text{Rate} = k[\text{NH}_4\text{NO}_2]$$

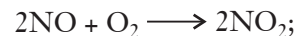
• IInd order



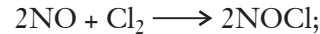
$$\text{Rate} = k[\text{NO}_2]^2$$



• IIIrd order

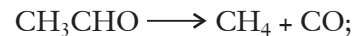


$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$



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

• Fractional order



$$\text{Rate} = k[\text{CH}_3\text{CHO}]^{3/2}$$

- Integrated rate equations for reactions of different orders :

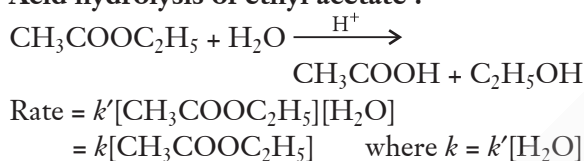
Reaction	Order	Rate law	Rate constant
$R \rightarrow \text{Products}$	0	Rate = $k[R]^0$	$k = \frac{[R]_0 - [R]}{t}$
$R \rightarrow \text{Products}$	1	Rate = $k[R]$	$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

Pseudo first order reactions

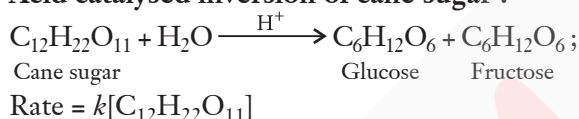
- Reactions which have higher order true rate law but are found to behave as first order are called pseudo first order reactions.

Examples :

- Acid hydrolysis of ethyl acetate :



- Acid catalysed inversion of cane sugar :



Info Shots

Reaction	Order	Rate law	Rate constant
$2R \rightarrow \text{Products}$	2	Rate = $k[R]^2$	$k = \frac{1}{t} \left(\frac{1}{[R]} - \frac{1}{[R]_0} \right)$
$A + B \rightarrow \text{Products}$	2	Rate = $k[A][B]$	$k = \frac{1}{t} \frac{2.303}{\log \frac{[B]_0[A]}{[A]_0[B]}}$
$3R \rightarrow \text{Products}$	3	Rate = $k[R]^3$	$k = \frac{1}{2t} \left[\frac{1}{[R]^2} - \frac{1}{[R]_0^2} \right]$

Illustration : From the following data, show that the decomposition of hydrogen peroxide is a reaction of first order :

t	0	10	20
x	46.1	29.8	19.3

where, t is the time in minute and x is the volume of the standard KMnO_4 solution in cm^3 required for titrating the same volume of the reaction mixture.

Soln.: Volume of KMnO_4 solution used \propto amount of H_2O_2 present. Hence, if the given reaction is of the first order, it must obey the equation :

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

In the present case, $V_0 = 46.1 \text{ cm}^3$

The value of k at each instant can be calculated as follows:

$$t(\text{min}) \quad V_t \quad k = \frac{2.303}{t} \log \frac{V_0}{V_t}$$

$$10 \quad 29.8 \quad k = \frac{2.303}{10 \text{ min}} \log \frac{46.1}{29.8} = 0.0436 \text{ min}^{-1}$$

$$20 \quad 19.3 \quad k = \frac{2.303}{20 \text{ min}} \log \frac{46.1}{19.3} = 0.0435 \text{ min}^{-1}$$

Thus, the value of k comes out to be nearly constant. Hence, it is a reaction of the first order.

Illustration : The rate constant for an isomerisation reaction, $A \rightarrow B$ is $4.5 \times 10^{-3} \text{ min}^{-1}$. If the initial concentration of A is 1 M, calculate the rate of reaction after 1 h.

Soln.: Rate constant in min^{-1} shows that it is a reaction of 1st order.

$$\therefore k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} = \frac{2.303}{60 \text{ min}} \log \frac{1}{[A]_t}$$

$$= 4.5 \times 10^{-3} \text{ min}^{-1} \quad \text{or } \log [A]_t = -0.1172$$

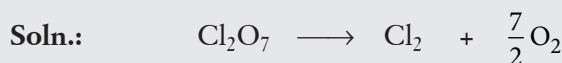
$$\therefore [A]_t = 0.7635 \text{ mol L}^{-1}$$

This is the concentration after 1 hr.

$$\begin{aligned} \text{Rate of reaction after 1h} &= k[A]_t \\ &= 4.5 \times 10^{-3} \times 0.7635 \text{ mol L}^{-1} \text{ min}^{-1} \\ &= 3.44 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

Illustration : The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is of 1st order. After 55 sec at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm, calculate

- the rate constant
- pressure of Cl_2O_7 after 100 sec.



Mole at $t = 0$	a	0	0
Mole at $t = 55 \text{ sec}$	$(a-x)$	x	$7x/2$

(a) Since, pressure of Cl_2O_7 is given so, $a \propto 0.062$

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} = \frac{2.303}{55} \log_{10} \frac{0.062}{0.044}$$

$$k = 6.24 \times 10^{-3} \text{ sec}^{-1}$$

(b) At $t = 100 \text{ sec}$, $(a-x) \propto p_t$

$$\therefore 6.24 \times 10^{-3} = \frac{2.303}{100} \log_{10} \frac{0.062}{p_t}$$

$$\log_{10} \frac{0.062}{p_t} = \frac{6.24 \times 10^{-1}}{2.303} = 0.270 \Rightarrow \frac{0.062}{p_t} = 1.86$$

$$\therefore p_t = 0.033 \text{ atm}$$

Self Test - 3

- The reaction, $X \longrightarrow$ product, follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M will be
 - $1.73 \times 10^{-4} \text{ M min}^{-1}$
 - $3.47 \times 10^{-5} \text{ M min}^{-1}$
 - $3.47 \times 10^{-4} \text{ M min}^{-1}$
 - $1.73 \times 10^{-5} \text{ M min}^{-1}$
- The expression to calculate time required for completion of zero order reaction is
 - $t = \frac{[R_0]}{k}$
 - $t = [R] - [R_0]$
 - $t = \frac{k}{[R_0]}$
 - $t = \frac{[R_0] - [R]}{[R_0]}$
- Half-life period of 2nd order reaction is
 - proportional to initial concentration of reactants
 - independent of initial concentration of reactants
 - inversely proportional to initial concentration of reactants
 - inversely proportional to square of initial concentration of reactants.
- The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one is true for rate of three reactions, if concentration of reactant is greater than 1 M?
 - $r_1 = r_2 = r_3$
 - $r_1 > r_2 > r_3$
 - $r_1 < r_2 < r_3$
 - All of these
- The rate constant of a first order reaction whose half-life is 480 s is
 - $1.44 \times 10^{-3} \text{ s}^{-1}$
 - 1.44 s^{-1}
 - $0.72 \times 10^{-3} \text{ s}^{-1}$
 - $2.88 \times 10^{-3} \text{ s}^{-1}$
- If 'a' is the initial concentration of the reactant, the time taken for completion of the reaction, if it is of zero order, will be
 - $\frac{a}{k}$
 - $\frac{a}{2k}$
 - $\frac{2a}{k}$
 - $\frac{k}{a}$
- A first order reaction has a rate constant $1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?
 - 444 s
 - 400 s
 - 528 s
 - 669 s
- The half-life of a first order reaction is 10 minutes. If initial amount is 0.08 mol/litre and concentration at some instant is 0.01 mol/litre, then $t =$
 - 10 minutes
 - 30 minutes
 - 20 minutes
 - 40 minutes.
- The decomposition of N_2O_5 is a first order reaction represented by $\text{N}_2\text{O}_5 \rightleftharpoons \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2$. After 15 minutes the volume of O_2 produced is 9 mL and at the end of the reaction 35 mL. The rate constant is equal to
 - $\frac{1}{15} \ln \frac{35}{26}$
 - $\frac{1}{15} \ln \frac{44}{35}$
 - $\frac{1}{15} \ln \frac{35}{44}$
 - $\frac{1}{15} \ln \frac{44}{26}$
- In a bimolecular reaction, if one of the reactants is in large excess, then order of reaction is said to be
 - zero
 - pseudo first
 - second
 - third.

3.4 Temperature Dependence of a Rate of Reaction

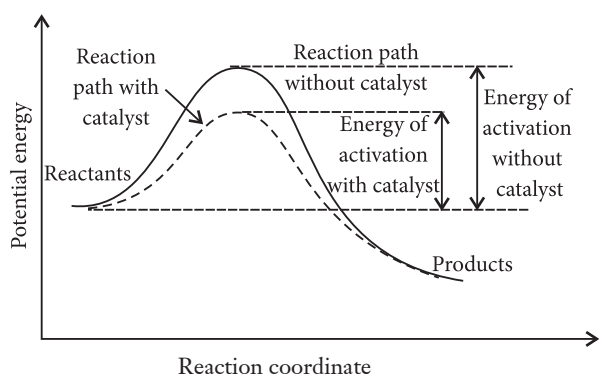
- For a chemical reaction with rise in temperature by 10° , the rate constant is nearly doubled.
- The ratio of the rate constant at 308 K to that at 298 K is called temperature coefficient of the reaction.

Arrhenius equation

- $k = Ae^{-E_a/RT}$
 - Effect of catalyst on the rate of reaction :**
A catalyst is a substance which increases the

rate of a reaction without itself undergoing any permanent chemical change.

- Catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in figure.
- A catalyst does not alter Gibbs energy, ΔG and ΔH of a reaction. It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.



Effect of catalyst on activation energy

- ▶ A catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster.

Calculation of Activation Energy

- The minimum energy that the reacting molecule must possess before undergoing a reaction is called activation energy.

$$k = Ae^{-E_a/RT} \text{ (Arrhenius equation)}$$

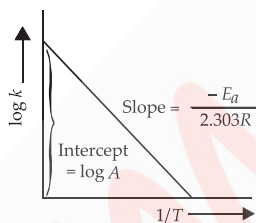
$$2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$$

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

When $\log k$ is plotted against

$$1/T, \text{ slope} = -\frac{E_a}{2.303R}$$

$$E_a = -2.303R \times \text{slope}$$



- Alternatively, let k_1 and k_2 are the rate constants for the reaction at two different temperatures T_1 and T_2 respectively.

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1}$$

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

By solving this, one can calculate activation energy.

Illustration : Temperature coefficient for the saponification of an ester by NaOH is 1.75. Calculate the activation energy.

Soln.: Temperature coefficient *i.e.*, $\frac{k_2}{k_1} = 1.75$

In general practice, T_1 is taken as 25°C *i.e.*, 298 K and T_2 as 35°C *i.e.*, 308 K

$$\text{Thus, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log 1.75 = \frac{E_a}{2.303 \times 1.987} \times \left[\frac{10}{308 \times 298} \right]$$

$$E_a = 10.207 \text{ kcal mol}^{-1}$$

Illustration : In general, it is observed that the rate of a chemical reaction doubles with every 10° rise in temperature. If this generalization holds for a reaction in the temperature range 295 K to 305 K. What would be the value of activation energy for this reaction?

Soln.: $T_1 = 295 \text{ K}$, $k_1 = k$ (say)

$T_2 = 305 \text{ K}$, $k_2 = 2k$, $E_a = ?$

Using Arrhenius equation

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

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \times \frac{305 - 295}{295 \times 305}$$

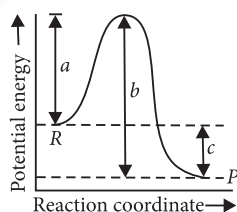
$$E_a = \frac{2.303 \times 8.314 \times 295 \times 305 \times \log 2}{10}$$

$$= \frac{2.303 \times 8.314 \times 295 \times 305 \times 0.3010}{10}$$

$$= 51855.2 \text{ J mol}^{-1} = 51.855 \text{ kJ mol}^{-1}$$

Self Test - 4

- The potential energy diagram for the reaction $R \rightarrow P$ is given below : ΔH° of the reaction corresponds to the energy
 - a
 - b
 - c
 - $a + b$



- By increasing the temperature by 10°C , the rate of forward reaction at equilibrium is increased by a factor of 2. The rate of backward reaction by this increase in temperature
 - remains unaffected

- increases by a factor greater than two
- decreases by a factor lesser than two
- is also increased by a factor of two.

- Which of the following statements is incorrect?
 - Activation energy for the forward reaction equals activation energy for the reverse reaction.
 - For a reversible reaction, an increase in temperature increases the reaction rate for both the forward and the backward reaction.
 - Larger the initial reactant concentration for

- a second order reaction, the shorter is its half life.
- (d) When Δt is infinitesimally small, the average rate equals the instantaneous rate.
4. The activation energy for a simple chemical reaction $A \rightarrow B$ is E_a in forward direction. The activation energy for reverse reaction
- is always less than E_a
 - is always double of E_a
 - can be less than or more than E_a
 - is negative of E_a .
5. The activation energy of a reaction can be determined by
- changing the concentration of reactants
 - evaluating rate constant at standard temperature
 - evaluating rate constant at two different temperatures
 - by doubling concentration of reactants.
6. Which of the following statements is incorrect?
- The catalyst does not affect the equilibrium of a reaction.
 - Reaction with higher activation energy has higher rate constant.
 - In an exothermic reaction, the activation energy of the reverse reaction is higher than that of the forward reaction.
 - Half-life period of a first order reaction is independent of initial concentration.

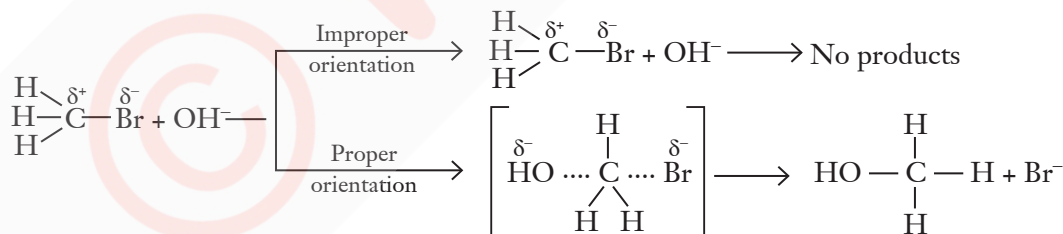
3.5 Collision Theory of Chemical Reactions

Collision Theory

- Reactions occur when molecules collide with appropriate orientation and sufficient energy, not all molecular collisions result successfully in the formation of product.
- For any successful collision :**
 - Particles must collide with sufficient energy $> E_a$.
 - They need to have correct alignment (collision geometry) to keep E_a as low as possible.
 - To account for effective collision, another factor P , called orientation factor or steric factor or probability factor is introduced.

$$k = PZ_{AB} e^{-E_a/RT}$$

where, Z_{AB} represents the collision frequency of reactants A and B .



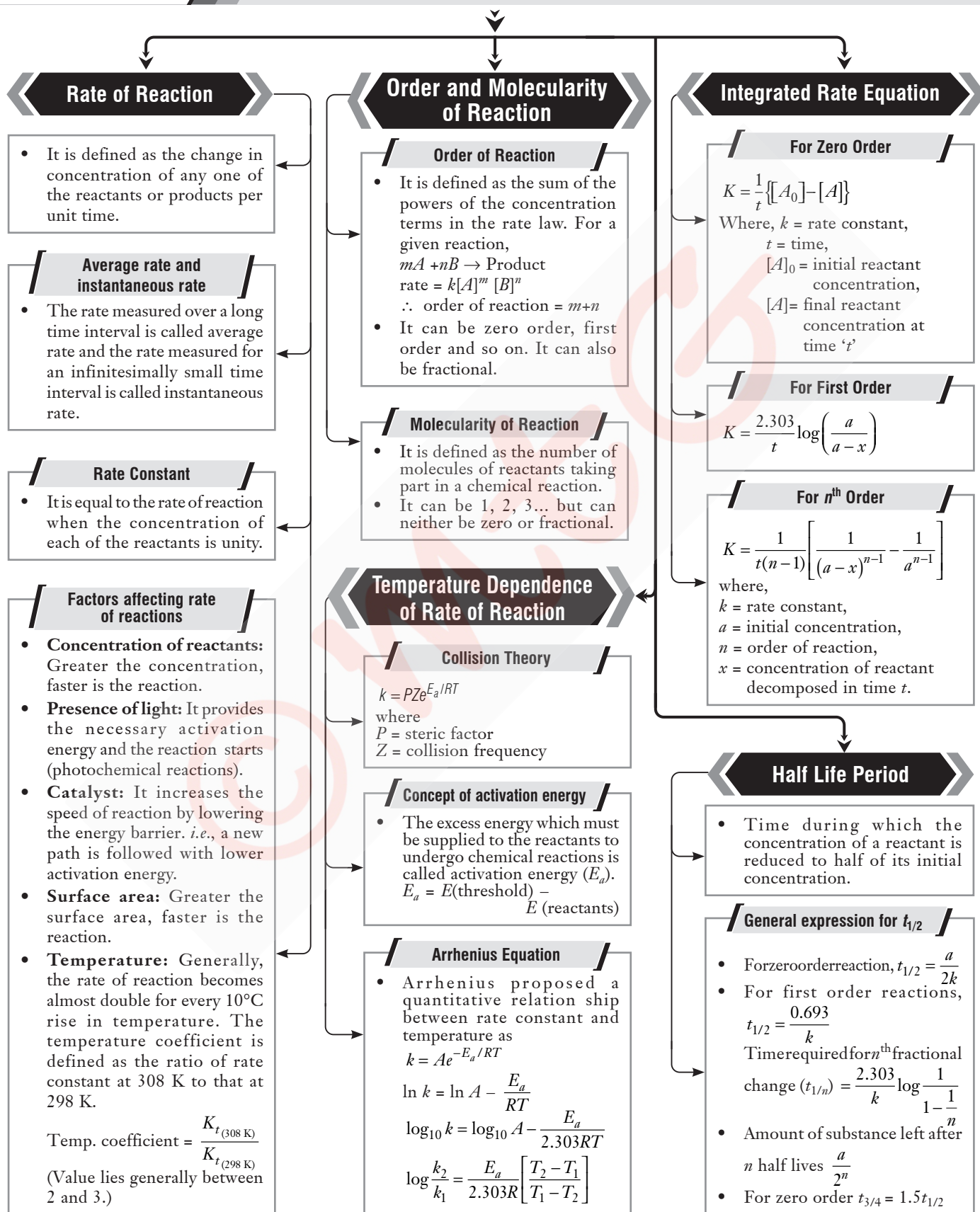
Self Test - 5

- The rate constant is given by the equation $k = PZ e^{-E_a/RT}$. Which factor should register a decrease for the reaction to proceed more rapidly?
 - T
 - Z
 - E
 - P
- Which of the following statements is incorrect about the collision theory of chemical reaction?
 - It considers reacting molecules or atoms to be hard spheres and ignores their structural features.
 - Number of effective collisions determines the rate of reaction.
 - Collision of atoms or molecules possessing sufficient threshold energy results into the product formation.
 - Molecules should collide with sufficient threshold energy and proper orientation for the collision to be effective.

CONCEPT MAP

CHEMICAL KINETICS

Chemical kinetics helps us to determine the rate of a chemical reaction and also describe the conditions by which the reactions rates can be altered. It also provides evidence for the mechanisms of chemical processes. Knowledge of reaction mechanisms is of practical use in deciding what is the most effective way to cause a reaction to occur. The word kinetics is derived from the greek word 'kinesis' meaning movement. Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction.



EXERCISE



KCET Connect

3.1 Rate of a Chemical Reaction

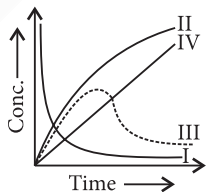
- When a chemical reaction takes place, during the course of the reaction the rate of reaction
 - keeps on increasing with time
 - remains constant with time
 - keeps on decreasing with time
 - shows irregular trend with time.

- The minus sign in rate = $-\frac{d[A]}{dt}$ indicates the _____ in concentration of the _____ with time. The rate of a reaction is always _____ quantity. The rate of reaction increases with _____ in concentration of reactants. The blanks in the question corresponds to
 - decrease, products, positive, increase
 - increase, reactants, negative, decrease
 - decrease, reactants, positive, increase
 - increase, products, positive, increase

- For a reaction $R \rightarrow P$, the concentration of a reactant changes from 0.05 M to 0.04 M in 30 minutes. What will be the average rate of reaction in minutes?
 - $4 \times 10^{-4} \text{ M min}^{-1}$
 - $8 \times 10^{-4} \text{ M min}^{-1}$
 - $3.3 \times 10^{-4} \text{ M min}^{-1}$
 - $2.2 \times 10^{-4} \text{ M min}^{-1}$

- For the reaction $A + B \rightarrow C + D$, the variation of the concentration of the reactant with time is given by the curve

- I
- II
- III
- IV



- In a reaction, $X \rightarrow Y$, the concentration of X decreases from 0.50 M to 0.38 M in 10 min. What is the rate of reaction in M s^{-1} during this interval?
 - 2×10^{-4}
 - 4×10^{-2}
 - 2×10^{-2}
 - 1×10^{-2}
- In a reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$, the concentration of HI decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in

10 minutes. What is the rate of reaction during this interval?

- $5 \times 10^{-3} \text{ M min}^{-1}$
- $2.5 \times 10^{-3} \text{ M min}^{-1}$
- $5 \times 10^{-2} \text{ M min}^{-1}$
- $2.5 \times 10^{-2} \text{ M min}^{-1}$

- In a reaction $2X \rightarrow Y$, the concentration of X decreases from 3.0 moles/litre to 2.0 moles/litre in 5 minutes. The rate of reaction is
 - 0.1 mol $\text{L}^{-1} \text{ min}^{-1}$
 - 5 mol $\text{L}^{-1} \text{ min}^{-1}$
 - 1 mol $\text{L}^{-1} \text{ min}^{-1}$
 - 0.5 mol $\text{L}^{-1} \text{ min}^{-1}$

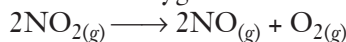
- For the reaction, $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 min. Calculate the average rate of reaction using units of time in seconds.

- 6.66×10^{-5}
- 6.6×10^{-6}
- 5.67×10^{-5}
- 7.26×10^{-6}

- In a reaction $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$, the concentration of HI decreases from 0.7 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. What is the rate of reaction during this interval?

- $1.5 \times 10^{-2} \text{ M min}^{-1}$
- $2.5 \times 10^{-3} \text{ M min}^{-1}$
- $5 \times 10^{-2} \text{ M min}^{-1}$
- $2.5 \times 10^{-2} \text{ M min}^{-1}$

- Nitrogen dioxide decomposes to nitric oxide and molecular oxygen as



The concentration - time data for the consumption of NO_2 at 300° C are as follows:

Time/s	0	100	200	300
$[\text{NO}_2]/\text{M}$	8.4×10^{-3}	5.6×10^{-3}	4.3×10^{-3}	3.0×10^{-3}

Calculate the average rate of decomposition of NO_2 .

- $-1.3 \times 10^{-5} \text{ M/s}$
- $1.3 \times 10^{-5} \text{ M/s}$
- $2.5 \times 10^{-5} \text{ M/s}$
- $-2.5 \times 10^{-5} \text{ M/s}$

- For the reaction, $2X + 3Y \rightarrow 4Z$, the rate of reaction may be represented as

- rate = $-\frac{1}{2} \frac{d[X]}{dt} = -\frac{1}{3} \frac{d[Y]}{dt} = \frac{1}{4} \frac{d[Z]}{dt}$
- rate = $-\frac{1}{2} \frac{d[X]}{dt} = -\frac{1}{3} \frac{d[Y]}{dt} = \frac{1}{4} \frac{d[Z]}{dt}$

- (c) $\text{rate} = \frac{1}{2} \frac{d[X]}{dt} = \frac{1}{3} \frac{d[Y]}{dt} = \frac{1}{4} \frac{d[Z]}{dt}$
- (d) $\text{rate} = \frac{1}{2} \frac{d[X]}{dt} = -\frac{1}{3} \frac{d[Y]}{dt} = -\frac{1}{4} \frac{d[Z]}{dt}$
12. For the reaction $4A + B \longrightarrow 2C + 2D$, which of the following statement is not correct?
- The rate of disappearance of B is one fourth of the rate of disappearance of A .
 - The rate of formation of C is one-half of the rate of consumption of A .
 - The rate of appearance of D is half of the rate of disappearance of B .
 - The rates of formation of C and D are equal.
13. Consider the reaction, $2N_2O_5 \longrightarrow 4NO_2 + O_2$. In the reaction NO_2 is being formed at the rate of $0.0125 \text{ mol L}^{-1} \text{ s}^{-1}$. What is the rate of reaction at this time?
- $0.0018 \text{ mol L}^{-1} \text{ s}^{-1}$
 - $0.0031 \text{ mol L}^{-1} \text{ s}^{-1}$
 - $0.0041 \text{ mol L}^{-1} \text{ s}^{-1}$
 - $0.050 \text{ mol L}^{-1} \text{ s}^{-1}$
14. For the reaction, $2A \longrightarrow 3C$, the reaction rate is equal to
- $-\frac{d[A]}{dt}$
 - $-\frac{1}{2} \frac{d[A]}{dt}$
 - $-\frac{1}{3} \frac{d[A]}{dt}$
 - $\frac{d[A]}{dt}$
15. In the reaction $A + 3B \longrightarrow 2C$, the rate of formation of C is
- the same as rate of consumption of A
 - the same as the rate of consumption of B
 - twice the rate of consumption of A
 - $3/2$ times the rate of consumption of B .
16. The rate expression for the following reaction in terms of rate of consumption of reactants and formation of products is
 $F_2(g) + 2ClO_2(g) \longrightarrow 2FCLO_2(g)$
- $\frac{d[F_2]}{dt}$
 - $\frac{1}{2} \frac{d[ClO_2]}{dt}$
 - $-2 \frac{d[FCLO_2]}{dt}$
 - $\frac{1}{2} \frac{d[FCLO_2]}{dt}$
17. For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, how are the rate of reaction expressions inter-related
 $\frac{d[H_2]}{dt}$ and $\frac{d[NH_3]}{dt}$?
- $-\frac{1}{3} \frac{d[H_2]}{dt} = +\frac{1}{2} \frac{d[NH_3]}{dt}$
 - $-\frac{1}{2} \frac{d[H_2]}{dt} = +\frac{1}{3} \frac{d[NH_3]}{dt}$
 - $+\frac{1}{2} \frac{d[H_2]}{dt} = -\frac{1}{3} \frac{d[NH_3]}{dt}$
 - $+\frac{1}{3} \frac{d[H_2]}{dt} = -\frac{1}{2} \frac{d[NH_3]}{dt}$
18. Nitrogen dioxide (NO_2) dissociates into nitric oxide (NO) and oxygen (O_2) as follows:
 $2NO_2 \rightarrow 2NO + O_2$
 If the rate of decrease of concentration of NO_2 is $6.0 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$. What will be the rate of increase of concentration of O_2 ?
- $3 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $6 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $1 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $1.5 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$
19. In the formation of sulphur trioxide by the Contact process,
 $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
 The rate of reaction is expressed as
 $-\frac{d(O_2)}{dt} = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ sec}^{-1}$
 The rate of disappearance of (SO_2) will be
- $5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $2.25 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $3.75 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $50.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$.
20. For the reaction $4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$, if the rate of disappearance of NH_3 is $3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$, what is the rate of formation of H_2O ?
- $5.4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $3.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $0.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
21. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ rate and rate constant are $1.02 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ and $3.4 \times 10^{-5} \text{ s}^{-1}$ respectively. The concentration of N_2O_5 in mol L^{-1} will be
- 3.4×10^{-4}
 - 3.0
 - 5.2
 - 3.2×10^{-5}
22. For the reaction,
 $5Fe^{2+}_{(aq)} + MnO_4^{-}_{(aq)} + 8H^+_{(aq)} \longrightarrow 5Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4H_2O$
 the instantaneous rate of the reaction is
- $\frac{1}{8} \frac{d[H^+]}{dt}$
 - $\frac{d[MnO_4^-]}{dt}$
 - $\frac{1}{5} \frac{d[Fe^{3+}]}{dt}$
 - $\frac{1}{5} \frac{d[Fe^{2+}]}{dt}$

23. For the reaction, $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$, the rate of reaction can be expressed in terms of time and concentration by the expression:

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

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

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

(d) $\text{Rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{O}_2]}{dt}$

24. Consider the reaction $2\text{N}_2\text{O}_4 \rightleftharpoons 4\text{NO}_2$ and given that $-\frac{d[\text{N}_2\text{O}_4]}{dt} = k$ and $\frac{d[\text{NO}_2]}{dt} = k'$, then

(a) $2k' = k$ (b) $k' = 2k$
 (c) $k' = k$ (d) none of these.

25. The rate of reaction is expressed in different ways as follows :

$$+\frac{1}{2} \frac{d[\text{C}]}{dt} = -\frac{1}{3} \frac{d[\text{D}]}{dt} = +\frac{1}{4} \frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt}$$

The reaction is

- (a) $4\text{A} + \text{B} \longrightarrow 2\text{C} + 3\text{D}$
 (b) $\text{B} + 3\text{D} \longrightarrow 4\text{A} + 2\text{C}$
 (c) $\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$
 (d) $\text{B} + \text{D} \longrightarrow \text{A} + \text{C}$
26. For a reaction $\text{P} + \text{Q} \rightarrow 3\text{R} + \text{S}$. Which of the following statements is incorrect?
- (a) Rate of disappearance of P = Rate of appearance of S
 (b) Rate of disappearance of Q = $2 \times$ Rate of appearance of R
 (c) Rate of disappearance of P = Rate of disappearance of Q
 (d) Rate of disappearance of Q = $\frac{1}{3} \times$ Rate of appearance of R

3.2 Factors Influencing Rate of a Reaction

27. According to law of mass action, rate of chemical reaction is proportional to
- (a) concentration of reactants
 (b) molar concentration of reactants
 (c) concentration of products
 (d) molar concentration of products.
28. The rate of reaction that does not involve gases does not depend upon

- (a) pressure (b) temperature
 (c) concentration (d) catalyst.

29. For the reaction, $\text{A}_2 + \text{B} + \text{C} \longrightarrow \text{AC} + \text{AB}$, it is found that tripling the concentration of A_2 triples the rate, doubling the concentration of C doubles the rate and doubling the concentration of B has no effect. What is the rate law?

(a) $k [\text{A}_2]^2 [\text{C}]$ (b) $k [\text{B}]^{1/2} [\text{C}]$
 (c) $k [\text{A}_2] [\text{C}]$ (d) $k [\text{A}_2]^3 [\text{B}]^2 [\text{C}]$

30. The rate of a gaseous reaction is given by the expression $k[\text{A}]^2[\text{B}]^3$. The volume of the reaction vessel is reduced to one half of the initial volume. What will be the reaction rate as compared to the original rate a ?

(a) $\frac{1}{8}a$ (b) $\frac{1}{2}a$
 (c) $2a$ (d) $32a$

31. In the reaction, $\text{A} + 2\text{B} \longrightarrow \text{Products}$, doubling the concentration of B (keeping the concentration of A constant) increases the rate

(a) 2 times (b) 4 times
 (c) 3 times (d) 6 times.

32. For a chemical reaction, $\text{X} \longrightarrow \text{Y}$, the rate of reaction increases by a factor of 27 when the concentration of X is increased by 3 times, the order of the reaction with respect to X is

(a) 1 (b) 3 (c) 2 (d) 2.5

33. Consider the following reaction :



How will the rate of reaction change when the concentration of A is doubled and that of B is tripled while C is taken in excess?

- (a) The rate reduces to 8 times of its original value.
 (b) The rate reduces to 12 times of its original value.
 (c) The rate increases by 8 times of its original value.
 (d) The rate increases by 12 times of its original value.

34. The rate of a gaseous reaction is given by $k [\text{A}] [\text{B}]$. If the volume occupied by the reacting gases is suddenly reduced to half the original volume, the rate of the reaction relative to the initial rate will be

(a) 1/8 (b) 1/4
 (c) 8/1 (d) 4

35. Rate of a reaction can be expressed by following rate expression, $\text{Rate} = k[A]^2[B]$, 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
36. The rate of the reaction, $A \longrightarrow \text{product}$ is $1.25 \times 10^{-2} \text{ M/s}$ when concentration of A is 0.45 M. Determine the rate constant if the reaction is second order in A .
- (a) $6.173 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
(b) $6.89 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$
(c) $5.182 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$
(d) $2.37 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$
37. The reaction, $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{SO}_3(\text{g})$ is carried out in a 1 dm^3 vessel and 2 dm^3 vessel separately. The ratio of reaction velocities will be
- (a) 1 : 8 (b) 1 : 4 (c) 4 : 1 (d) 8 : 1
38. The rate constant of a reaction depends upon
- (a) temperature of the reaction
(b) extent of the reaction
(c) initial concentration of the reactants
(d) the time of completion of reaction.
39. For the reaction $A + B \longrightarrow \text{products}$, it is found that orders of the reaction in A and B are 1 and 2 respectively. When the conc. of A is halved and that of B is doubled, the rate increases by a factor
- (a) 2 (b) 8 (c) 4 (d) 16
40. The rate law for the reaction, $2\text{NOBr}(\text{g}) \longrightarrow 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$ is rate = $k[\text{NOBr}]^2$. The rate constant for the reaction at a certain temperature is $1.62 \text{ M}^{-1} \text{ s}^{-1}$. If the concentration of NOBr at a certain time is $2.00 \times 10^{-3} \text{ M}$, what will be the rate of reaction?
- (a) $4.40 \times 10^{-6} \text{ M s}^{-1}$ (b) $4.50 \times 10^{-6} \text{ M s}^{-1}$
(c) $6.44 \times 10^{-6} \text{ M s}^{-1}$ (d) $6.48 \times 10^{-6} \text{ M s}^{-1}$
41. A reaction in which reactants (R) are converted into products (P) follows second order kinetics. If concentration of R is increased by four times, what will be the increase in the rate of formation of P ?
- (a) 9 times (b) 4 times
(c) 16 times (d) 8 times
42. The rate expression for the reaction, $A(\text{g}) + B(\text{g}) \rightarrow C(\text{g})$ is rate = $K[A]^2[B]^{1/2}$. What changes in the initial concentrations of A and B will cause the rate of reaction to increase by a factor of eight?
- (a) $[A] \times 2; [B] \times 2$ (b) $[A] \times 2; [B] \times 4$
(c) $[A] \times 1; [B] \times 4$ (d) $[A] \times 4; [B] \times 1$
43. Order of reaction is
- (a) never zero
(b) never fractional
(c) always equal to number of molecules taking part in reaction
(d) an experimentally determined quantity.
44. Consider the following reaction,
 $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$
The rate law expression, $r = k[\text{H}_2]^n$ for the above reaction. When the concentration of H_2 is doubled, the rate of reaction is found to be quadrupled. The value of n is
- (a) 0 (b) 1
(c) 2 (d) 3
45. What is the order of a reaction which has a rate expression, rate = $k[A]^{3/2}[B]^{-1}$?
- (a) $\frac{3}{2}$ (b) $\frac{1}{2}$
(c) 0 (d) 1
46. For a reaction $A + B \longrightarrow C + D$, if concentration of A is doubled without altering that of B , rate doubles. If concentration of B is increased nine times without altering that of A , rate triples. Order of the reaction is
- (a) $1\frac{1}{2}$ (b) $1\frac{1}{3}$ (c) 2 (d) 1
47. For a reaction $\text{I}^- + \text{OCl}^- \longrightarrow \text{IO}^- + \text{Cl}^-$, in an aqueous medium, the rate of the reaction is given by $\frac{d[\text{IO}^-]}{dt} = k \frac{[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$. The overall order of the reaction is
- (a) -1 (b) 1 (c) 0 (d) 2
48. The rate of an elementary reaction $A \longrightarrow B$, increases by 100 when the concentration of A is increased ten folds. The order of the reaction with respect to A is
- (a) 1 (b) 2
(c) 10 (d) 100
49. $2A \longrightarrow B + C$ 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 two times.
50. Which of the following is an example of a fractional order reaction? (All are elementary reactions.)
 (a) $X + Y \rightarrow Z$
 (b) $P + 3Q \rightarrow 2R$
 (c) $S + T \rightarrow 4Q$
 (d) $1/2 A + B \rightarrow C$
51. For the reaction, $A + B \rightarrow P$. If $[B]$ is doubled at constant $[A]$, the rate of the reaction doubles. If $[A]$ is tripled and $[B]$ is doubled, the rate of the reaction increases by a factor of 6. What is the overall order of the reaction?
 (a) 1 (b) 3 (c) 0.5 (d) 2
52. The rate of reaction, $A + B \rightarrow$ Products is given by the equation $r = k[A][B]$. If B is taken in large excess, the order of the reaction would be
 (a) 2 (b) 1
 (c) 0 (d) Unpredictable.
53. The order of reaction is decided by
 (a) temperature
 (b) mechanism of reaction as well as relative concentration of reactants
 (c) molecularity
 (d) pressure.
54. The rate of the reaction $A + 2B \rightarrow C + 2D$ is 6×10^{-4} M/s when $[A] = [B] = 0.3$ M. What is the overall order of the reaction if the rate constant at a given temperature is $2 \times 10^{-3} \text{ s}^{-1}$.
 (a) 2.0 (b) 3.0
 (c) 1.0 (d) 4.0
55. For the reaction, $aA \rightarrow xP$, when $[A] = 2.2$ mM the rate was found to be 2.4 mM sec^{-1} . On reducing concentration of A to half, the rate changes to 0.6 mM sec^{-1} . The order of reaction with respect to A is
 (a) 1.5 (b) 2.0 (c) 2.5 (d) 3.0
56. A reaction involves two reactants. The rate of reaction is directly proportional to the concentration of one of them and inversely proportional to the concentration of the other. The overall order of reaction will be
 (a) one (b) two
 (c) zero (d) none of these.
57. Calculate the order of reaction, $A \rightarrow$ Product, from the following data :

$[A]$ moles/ L	$d[\text{Product}]/dt$ (moles/L/sec)
0.003	10.0×10^{-5}
0.006	5.0×10^{-5}
0.012	2.5×10^{-5}

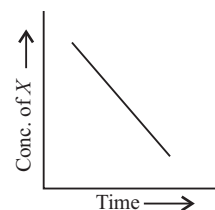
- (a) 1 (b) -2 (c) -1 (d) 2
58. The rate of reaction $A + B + C \rightarrow$ products, is given as: rate = $k[A]^{\frac{1}{2}}[B]^{\frac{1}{3}}[C]$. The order of the reaction is
 (a) 1 (b) 3
 (c) $\frac{5}{6}$ (d) $\frac{11}{6}$
59. The conversion of molecules x to y follows second order kinetics. If concentration of x is increased to three times, the rate of formation of y will
 (a) increase by three times
 (b) decrease by three times
 (c) increase by nine times
 (d) decrease by nine times.
60. The decomposition of dimethyl ether is a fractional order reaction. The rate of reaction is given by rate = $k(p_{\text{CH}_3\text{COCH}_3})^{3/2}$. If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constant?
 (a) $\text{bar min}^{-1}, \text{bar}^2 \text{ min}^{-1}$
 (b) $\text{bar min}^{-1}, \text{bar}^{-1/2} \text{ min}^{-1}$
 (c) $\text{bar}^{-1/2} \text{ min}^{-1}, \text{bar}^2 \text{ min}^{-1}$
 (d) $\text{bar min}^{-1}, \text{bar}^{1/2} \text{ min}^{-1}$
61. Match the rate law given in column I with the dimensions of rate constants given in column II and mark the appropriate choice.
- | Column I | | Column II | |
|----------|--|-----------|--|
| (A) | Rate = $k[\text{NH}_3]^0$ | (i) | $\text{mol L}^{-1} \text{ s}^{-1}$ |
| (B) | Rate = $k[\text{H}_2\text{O}_2][\text{I}^-]$ | (ii) | $\text{L mol}^{-1} \text{ s}^{-1}$ |
| (C) | Rate = $k[\text{CH}_3\text{CHO}]^{3/2}$ | (iii) | s^{-1} |
| (D) | Rate = $k[\text{C}_2\text{H}_5\text{Cl}]$ | (iv) | $\text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ |
- (a) (A) \rightarrow (iv), (B) \rightarrow (iii), (C) \rightarrow (ii), (D) \rightarrow (i)
 (b) (A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iii), (D) \rightarrow (iv)
 (c) (A) \rightarrow (ii), (B) \rightarrow (i), (C) \rightarrow (iv), (D) \rightarrow (iii)
 (d) (A) \rightarrow (i), (B) \rightarrow (ii), (C) \rightarrow (iv), (D) \rightarrow (iii)
62. The unit of rate constant for the reaction, $2\text{H}_2 + 2\text{NO} \rightarrow 2\text{H}_2\text{O} + \text{N}_2$ which has rate = $k[\text{H}_2][\text{NO}]^2$, is
 (a) $\text{mol L}^{-1} \text{ s}^{-1}$ (b) s^{-1}
 (c) $\text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ (d) mol L^{-1}

63. In a reaction $A + 2B \longrightarrow$ products, the molecularity of the reaction is
 (a) 3 (b) 2 (c) 1 (d) zero.
64. Among the following statements, the true statement is
 (a) the order of a reaction changes with the temperature
 (b) the molecularity and the order of the reaction are always equal
 (c) the molecularity and the order of the reaction can be determined experimentally
 (d) only the order and not the molecularity of a reaction can be determined experimentally.
65. For a chemical reaction,
 (a) the molecularity may be zero or fractional
 (b) the order is always equal to the molecularity
 (c) the order is always different from the molecularity
 (d) the order and the molecularity may be the same or different.
66. In a multistep reaction, the overall rate of reaction is
 (a) equal to the rate of slowest step
 (b) equal to the rate of fastest step
 (c) equal to the average rate of various steps
 (d) equal to the rate of the last step.
67. The reaction between $H_{2(g)}$ and $ICl_{(g)}$ occurs in the following steps :
 (i) $H_2 + ICl \longrightarrow HI + HCl$
 (ii) $HI + ICl \longrightarrow I_2 + HCl$
 The reaction intermediate in the reaction is
 (a) HCl (b) HI
 (c) I_2 (d) ICl
68. For a reaction, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$, the possible mechanism is
 $2NO \rightleftharpoons N_2O_2$
 $N_2O_2 + H_2 \xrightarrow{\text{slow}} N_2O + H_2O$
 $N_2O + H_2O \xrightarrow{\text{fast}} N_2 + H_2O$
 What is the rate law and order of the reaction?
 (a) Rate = $k [N_2O_2]$, order = 1
 (b) Rate = $k [N_2O_2][H_2]$, order = 2
 (c) Rate = $k [N_2O_2]^2$, order = 2
 (d) Rate = $k [N_2O_2]^2 [H_2]$, order = 3
69. Select the intermediate in the following reaction mechanism :
 $O_{3(g)} \rightleftharpoons O_{2(g)} + O_{(g)} ; O_{(g)} + O_{3(g)} \longrightarrow 2O_2$
 (a) $O_{3(g)}$ (b) $O_{(g)}$
 (c) $O_{2(g)}$ (d) none of these.

70. The reaction $A + 2B + C \longrightarrow Z$, occurs by the following mechanism :
 (i) $A + B \longrightarrow X$ (Fast)
 (ii) $X + C \longrightarrow Y$ (Slow)
 (iii) $Y + B \longrightarrow Z$ (Very fast)
 Rate law for this reaction is
 (a) $k [C]$ (b) $k [A] [B]^2 [C]$
 (c) $k [Z]$ (d) $k [X] [Y] [Z]$

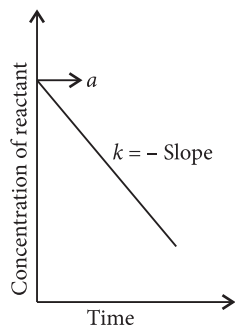
3.3 Integrated Rate Equations

71. A substance reacts with initial concentration of $a \text{ mol dm}^{-3}$ according to zero order kinetics. The time it takes for the completion of the reaction is ($k =$ rate constant)
 (a) $\frac{k}{a}$ (b) $\frac{a}{2k}$ (c) $\frac{a}{k}$ (d) $\frac{2k}{a}$
72. The reaction $X + W \rightarrow Y + Z$ would be zero order reaction when
 (a) rate remains unchanged at any concentration of Y and Z
 (b) rate of reaction doubles if concentration of Y is doubled.
 (c) rate of reaction remains same at any concentration of X and W
 (d) rate of reaction is directly proportional to square of concentration of X .
73. The rates of a certain reaction $\left(-\frac{dc}{dt}\right)$ at different times are as follows :
- | Time(s) | Rate ($\text{mol L}^{-1} \text{s}^{-1}$) |
|---------|--|
| 0 | 2.8×10^{-2} |
| 10 | 2.78×10^{-2} |
| 20 | 2.81×10^{-2} |
| 30 | 2.79×10^{-2} |
- The reaction is
 (a) first order (b) second order
 (c) zero order (d) third order.
74. The rate constant for a zero order reaction is
 (a) $k = \frac{c_0}{2t}$ (b) $k = \frac{c_0 - c_t}{t}$
 (c) $k = \ln \frac{c_0 - c_t}{2t}$ (d) $k = \frac{c_0}{c_t}$.
75. For a general reaction $X \longrightarrow Y$, the plot of conc. of X vs time is given in the figure. What is the order of the reaction and what are the units of rate constant?
 (a) Zero, $\text{mol L}^{-1} \text{s}^{-1}$



- (b) First, $\text{mol L}^{-1} \text{s}^{-1}$
 (c) First, s^{-1}
 (d) Zero, $\text{L mol}^{-1} \text{s}^{-1}$

76.



The above plot is for _____ order reaction to calculate value of rate constant.

- (a) second (b) first
 (c) zero (d) first and zero
77. For a zero order reaction, the plot of conc. of products vs time is a straight line with
 (a) +ve slope and zero intercept
 (b) -ve slope and zero intercept
 (c) +ve slope and non-zero intercept
 (d) -ve slope and non-zero intercept.
78. What is the two third of a first order reaction having $k = 5.48 \times 10^{-14} \text{s}^{-1}$?
 (a) $2.01 \times 10^{11} \text{s}$ (b) $2.01 \times 10^{13} \text{s}$
 (c) $8.08 \times 10^{13} \text{s}$ (d) $16.04 \times 10^{11} \text{s}$
79. The decomposition of a substance follows first order kinetics. If its concentration is reduced to $1/8^{\text{th}}$ of its initial value in 24 minutes, the rate constant of the decomposition process is
 (a) $\frac{1}{24} \text{min}^{-1}$
 (b) $\frac{0.692}{24} \text{min}^{-1}$
 (c) $\frac{2.303}{24} \log\left(\frac{1}{8}\right) \text{min}^{-1}$
 (d) $\frac{2.303}{24} \log\left(\frac{8}{1}\right) \text{min}^{-1}$
80. Rate constant in case of first order reaction is
 (a) inversely proportional to the concentration units
 (b) independent of concentration units
 (c) directly proportional to concentration units
 (d) inversely proportional to the square of concentration units.

81. Mathematical expression for $t_{1/4}$ i.e., when $(1/4)^{\text{th}}$ reaction is over following first order kinetics can be given by

- (a) $t_{1/4} = \frac{2.303}{k} \log 4$
 (b) $t_{1/4} = \frac{2.303}{k} \log 2$
 (c) $t_{1/4} = \frac{2.303}{k} \log \frac{4}{3}$
 (d) $t_{1/4} = \frac{2.303}{k} \log \frac{3}{4}$

82. The decomposition of dinitrogen pentoxide (N_2O_5) follows first order rate law. What will be the rate constant from the given data?

At $t = 800 \text{s}$, $[\text{N}_2\text{O}_5] = 1.45 \text{mol L}^{-1}$

At $t = 1600 \text{s}$, $[\text{N}_2\text{O}_5] = 0.88 \text{mol L}^{-1}$

- (a) $3.12 \times 10^{-4} \text{s}^{-1}$ (b) $6.24 \times 10^{-4} \text{s}^{-1}$
 (c) $2.84 \times 10^{-4} \text{s}^{-1}$ (d) $8.14 \times 10^{-4} \text{s}^{-1}$

83. A reaction is of first order when

- (a) the amount of product formed increases linearly with time
 (b) the rate decreases linearly with time
 (c) the rate is linearly related to the concentration of the reactant
 (d) the concentration of the reactant decreases linearly with time.

84. Which of the following represents the expression for $3/4^{\text{th}}$ life of a first order reaction?

- (a) $\frac{k}{2.303} \log \frac{4}{3}$ (b) $\frac{2.303}{k} \log \frac{3}{4}$
 (c) $\frac{2.303}{k} \log 4$ (d) $\frac{2.303}{k} \log 3$

85. Unit of rate constant in case of first order reaction is

- (a) inversely proportional to the concentration units
 (b) independent of concentration units
 (c) directly proportional to concentration units
 (d) inversely proportional to the square of concentration units.

86. The first order reaction was started with a decimolar solution of the reactant. After 8 minutes and 20 seconds, its concentration was found to be $M/100$. The rate constant of the reaction is

- (a) $2.303 \times 10^{-5} \text{sec}^{-1}$ (b) $2.303 \times 10^{-4} \text{sec}^{-1}$
 (c) $4.606 \times 10^{-3} \text{sec}^{-1}$ (d) $2.606 \times 10^{-4} \text{sec}^{-1}$

87. The rate constant of a first order reaction is given by

- (a) $k = 2.303 \times t \times \log_{10} \frac{a}{(a-x)}$
- (b) $\frac{k}{t} = 2.303 \log_{10} \frac{a}{(a-x)}$
- (c) $k = \frac{2.303}{t} \log_{10} \frac{1}{(a-x)}$
- (d) $k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$
88. If 60% of a first order reaction was completed in 60 minutes, 50% of the same reaction would be completed in approximately
 (a) 40 minutes (b) 50 minutes
 (c) 45 minutes (d) 60 minutes
 [log 4 = 0.60, log 5 = 0.69]
89. A reaction is 50% complete in 45 minutes and 75% complete in 90 minutes. The order of reaction is
 (a) 1 (b) 2 (c) 3 (d) 0
90. The reaction $A \longrightarrow B$ 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) 1 hour (b) 0.5 hour
 (c) 0.25 hour (d) 2 hours
91. A first order reaction is 80% complete in 10 minutes. What is the specific reaction rate per second?
 (a) 0.510 s^{-1} (b) 0.0027 s^{-1}
 (c) 0.161 s^{-1} (d) 0.2 s^{-1}
92. The rate constant of a first order reaction is $15 \times 10^{-3} \text{ s}^{-1}$. How long will 5.0 g of this reactant take to reduce to 3.0 g?
 (a) 34.07 s (b) 7.57 s
 (c) 10.10 s (d) 15 s
93. If 60% of a first order reaction was completed in 60 minutes, 30% of the same reaction would be completed in approximately
 (a) 50 minutes (b) 23.3 minutes
 (c) 60 minutes (d) 40 minutes.
94. In a first order reaction, 75% of the reactants disappeared in 1.386 hours. What is the rate constant?
 (a) $3.6 \times 10^{-3} \text{ sec}^{-1}$ (b) $2.7 \times 10^{-4} \text{ sec}^{-1}$
 (c) $72 \times 10^{-3} \text{ sec}^{-1}$ (d) $1.8 \times 10^{-3} \text{ sec}^{-1}$
95. In a first order reaction the concentration of reactant decreases from 400 mol L^{-1} to 25 mol L^{-1} in 200 seconds. The rate constant for the reaction is
 (a) 1.01386 s^{-1} (b) $2 \times 10^{-4} \text{ s}^{-1}$
 (c) $1.386 \times 10^{-2} \text{ s}^{-1}$ (d) $3.4 \times 10^{-4} \text{ s}^{-1}$
96. A radioactive isotope having a half life period of 3 days was received after 12 days. It was found that there were 3 g of the isotope in the container. The initial amount of the isotope when packed was
 (a) 36 g (b) 48 g
 (c) 12 g (d) 24 g
97. A first order reaction is 20% complete in 10 minutes. What is the specific rate constant for the reaction?
 (a) 0.0970 min^{-1} (b) 0.009 min^{-1}
 (c) 0.0223 min^{-1} (d) 2.223 min^{-1}
98. Decomposition of a compound is known to be a first order reaction. Three-fourths of the compound taken had decomposed at the end of two hours. The quantity left over at the end of the next three hours will be about
 (a) 1% (b) 2% (c) 3% (d) 4%
99. A first order reaction has a rate constant $1.15 \times 10^{-3} \text{ s}^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?
 (a) 444 s (b) 400 s
 (c) 528 s (d) 669 s
100. For the first order reaction, half-life is 14 s. The time required for the initial concentration to reduce to $\frac{1}{8}$ of its value is
 (a) 28 s (b) 42 s (c) $(14)^3 \text{ s}$ (d) $(14)^2 \text{ s}$
101. The integrated rate equation for first order reaction $A \longrightarrow$ products, is given by
 (a) $k = \frac{2.303}{t} \ln \frac{[A]_0}{[A]_t}$
 (b) $k = -\frac{1}{t} \ln \frac{[A]_t}{[A]_0}$
 (c) $k = \frac{2.303}{t} \log_{10} \frac{[A]_t}{[A]_0}$
 (d) $k = \frac{1}{t} \ln \frac{[A]_t}{[A]_0}$
102. A reaction is 50% complete in 2 hours and 75% complete in 4 hours, the order of reaction is
 (a) 0 (b) 1 (c) 2 (d) 3.
103. In a first order reaction, reactant concentration 'C' varies with time 't' as
 (a) C decreases with $\frac{1}{t}$

- (b) $\log C$ decreases with $\frac{1}{t}$
 (c) $\frac{1}{C}$ increases linearly with t
 (d) $\log C$ decreases linearly with t .

104. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is 10 times of the permissible value, after how many days it will be safe to enter the room?

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

105. Given $t_{1/2} = 3$ hours, then how many gram of a substance will remain after 18 hours from 300 gram of a substance?

- (a) 4.6 gram (b) 5.6 gram
 (c) 9.2 gram (d) 6.4 gram.

106. Thermal decomposition of a compound is 1st order reaction. If a sample of compound decomposes 50% in 120 minutes, how much time will it take for 90% decomposition?

- (a) About 240 minutes (b) About 560 minutes
 (c) About 45 minutes (d) About 400 minutes

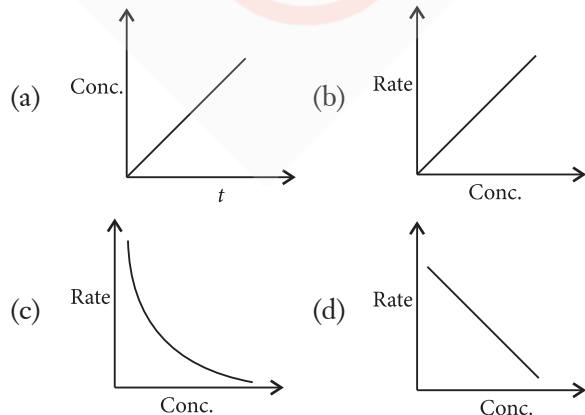
107. Rate constant for a reaction is 10^{-3} s^{-1} . Time to leave 25% reaction is

- (a) 693 s (b) 1386 s
 (c) 6930 s (d) 2029 s

108. The rate constant for a first order reaction is 60 s^{-1} . How much time will it take to reduce the initial concentration of the reactant to its $1/16^{\text{th}}$ value?

- (a) 0.046 s (b) 0.025 s
 (c) 0.098 s (d) 0.060 s

109. A graph corresponding to a first order reaction is



110. The slope of the straight line obtained by plotting rate versus concentration of reactant for a first order reaction is

- (a) $-k$ (b) $-k/2.303$
 (c) $k/2.303$ (d) k

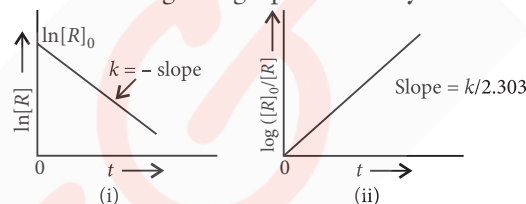
111. The slope of a graph $\ln [A]$ versus t for a first order reaction is $-2.5 \times 10^{-3} \text{ s}^{-1}$. The rate constant for the reaction will be

- (a) $5.76 \times 10^{-3} \text{ s}^{-1}$ (b) $1.086 \times 10^{-3} \text{ s}^{-1}$
 (c) $-2.5 \times 10^{-3} \text{ s}^{-1}$ (d) $2.5 \times 10^{-3} \text{ s}^{-1}$

112. A plot of $\log(a-x)$ against time t is a straight line. This indicates that the reaction is of

- (a) zero order (b) first order
 (c) second order (d) third order.

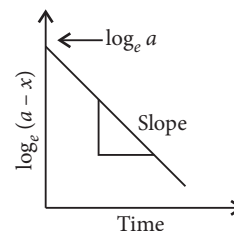
113. Observe the given graphs carefully.



Which of the given orders are shown by the graphs respectively?

- | (i) | (ii) |
|------------------|-------------|
| (a) Zero order | First order |
| (b) First order | Zero order |
| (c) First order | First order |
| (d) Second order | Zero order |

114. In the following plot, for a first order reaction, slope is equal to



- (a) $-k$ (b) $-\frac{k}{2.303}$
 (c) $-\frac{2.303}{k}$ (d) $-k \times 2.303$

115. A substance A decomposes in solution following the first order kinetics. Flask I contains 1 litre of 1 M solution of A and flask II contains 100 ml of 0.6 M solution of A . After 8 hours the concentration of A in flask I becomes 0.25 M. What will be the time for concentration of A in flask II to become 0.3 M?

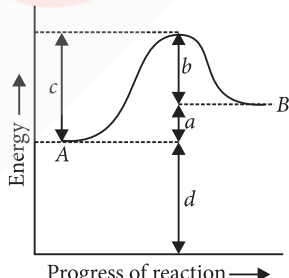
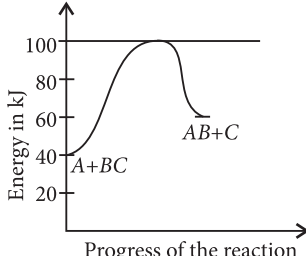
- (a) 0.4 hours
 (b) 2.4 hours
 (c) 4.0 hours
 (d) Unpredictable as rate constant is not given.

116. For a zero order reaction $A \rightarrow P$, $t_{1/2}$ is (k is rate constant)
- (a) $\frac{[A]_0}{2k}$ (b) $\frac{0.693}{k}$
 (c) $\frac{1}{k[A]_0}$ (d) $\frac{\ln 2}{[A]_0 k}$
117. The half-life period of a zero order reaction is given by
- (a) $\frac{[A]_0}{k}$ (b) $\frac{2.303k}{[A]_0}$
 (c) $\frac{[A]_0}{2k}$ (d) $\frac{2[A]_0}{k}$
118. When the concentration of a reactant in the zero order reaction is doubled, the half-life period is
- (a) halved (b) doubled
 (c) remains same (d) tripled.
119. Which of the following relation is correct for zero order reaction?
- (a) $t_{3/4} = 2t_{1/2}$ (b) $t_{3/4} = 1.5 t_{1/2}$
 (c) $t_{3/4} = \frac{1}{2}t_{1/2}$ (d) $t_{3/4} = \frac{1}{3}t_{1/2}$
120. In a first order reaction, the concentration of the reactants 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.
121. The half - life of a certain first order reaction is 60 minutes. How long will it take for 80% reaction to occur?
- (a) 139.39 minutes (b) 19.9 minutes
 (c) 199.39 hours (d) 40 minutes.
122. The half-life of a first order reaction is 10 minutes. If initial amount is 0.08 mol/litre and concentration at some instant is 0.01 mol/litre, then t is
- (a) 10 minutes (b) 30 minutes
 (c) 20 minutes (d) 40 minutes.
123. For a first order reaction, the ratio of the time for 99.9% completion of the reaction to half of the reaction to complete is
- (a) 2 (b) 4 (c) 10 (d) 8
124. The half-life period of a first order reaction is 15 minutes. The amount of substance left after one hour will be
- (a) one half (b) one fourth
 (c) one eighth (d) one sixteenth.
125. In a first-order reaction $A \rightarrow B$, if k is rate constant and initial concentration of the reactant A is 0.5 M then the half-life is
- (a) $\frac{\ln 2}{k}$ (b) $\frac{0.693}{0.5k}$
 (c) $\frac{\log 2}{k}$ (d) $\frac{\log 2}{k\sqrt{0.5}}$
126. For a first order reaction $A \rightarrow B$, the reaction rate at reactant concentration of 0.01 M is found to be $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ sec}^{-1}$. The half - life period of the reaction is
- (a) 220 seconds (b) 30 seconds
 (c) 300 seconds (d) 347 seconds.
127. If the rate constant of a first order reaction is $1.3 \times 10^{-2} \text{ min}^{-1}$, then its half-period in seconds is
- (a) 53.3 (b) 3200 (c) 1.247 (d) 0.888
128. If the half-time for a particular reaction is found to be constant and independent of the initial concentration of the reactants, then the reaction is of
- (a) first order (b) zero order
 (c) second order (d) none of these.
129. For the reaction $A \rightarrow B$, the rate law expression is, rate = $k[A]$. Which of the following statements is incorrect?
- (a) The reaction follows first order kinetics.
 (b) The $t_{1/2}$ of reaction depends on initial concentration of reactants.
 (c) k is constant for the reaction at a constant temperature.
 (d) The rate law provides a simple way of predicting the conc. of reactants and products at any time after the start of the reaction.
130. Half-life period of a first order reaction is 10 min. What percentage of the reaction will be completed in 100 min?
- (a) 25% (b) 50%
 (c) 99.9% (d) 75%
131. The rate of a first order reaction is $1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ at 0.5 M concentration of the reactant. The half-life of the reaction is
- (a) 7.53 minutes (b) 0.383 minutes
 (c) 23.1 minutes (d) 8.73 minutes.
132. What fraction of a reactant remains after 40 min if $t_{1/2}$ is 20 min for a first order reaction?
- (a) $\frac{1}{4}$ (b) $\frac{1}{2}$
 (c) $\frac{1}{8}$ (d) $\frac{1}{6}$

133. The half-life of the reaction $X \rightarrow Y$, following first order kinetics, when the initial concentration of X is 0.01 mol L^{-1} and initial rate is $0.00352 \text{ mol L}^{-1} \text{ min}^{-1}$ will be
 (a) 19.69 min. (b) 1.969 min.
 (c) 7.75 min. (d) 77.5 min.
134. The decomposition of N_2O_5 occurs as, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, and follows first order kinetics,
 (a) hence the reaction is bimolecular
 (b) the reaction is unimolecular
 (c) $t_{1/2} \propto [A]^0$
 (d) $t_{1/2} \propto [A]^2$
135. In a first order reaction, the concentration of reactant is reduced to $1/8$ of the initial concentration in 75 minutes at 298 K. What is the half-life period of the reaction in minutes?
 (a) 50 min. (b) 15 min.
 (c) 30 min. (d) 25 min.
136. The half-life of a substance in a certain enzyme-catalysed reaction is 140 s. The time required for the concentration of the substance to fall from 1.28 mg L^{-1} to 0.128 mg L^{-1} is
 (a) 465 s (b) 388 s (c) 560 s (d) 700 s
137. Half-life period of a first order reaction is 10 min. What percentage of the reaction will be completed in 20 min?
 (a) 25% (b) 50% (c) 99.9% (d) 75%
138. A first order reaction takes 40 min for 30% decomposition. What will be $t_{1/2}$?
 (a) 77.7 min (b) 52.5 min
 (c) 46.2 min (d) 22.7 min
139. The rate constant for a first order reaction is $2 \times 10^{-2} \text{ min}^{-1}$. The half-life period of reaction is
 (a) 69.3 min (b) 34.65 min
 (c) 17.37 min (d) 3.46 min
140. What will be the half-life of the first order reaction for which the value of rate constant is 200 s^{-1} ?
 (a) $3.46 \times 10^{-2} \text{ s}$ (b) $3.46 \times 10^{-3} \text{ s}$
 (c) $4.26 \times 10^{-2} \text{ s}$ (d) $4.26 \times 10^{-3} \text{ s}$
141. For a first-order reaction $P \rightarrow Q$, if k is rate constant and initial concentration of the reactant P is 1.5 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) $\frac{0.693}{0.5k}$
142. The first order rate constant for the decomposition of N_2O_5 is $6.2 \times 10^{-4} \text{ sec}^{-1}$. The $t_{1/2}$ of decomposition is
 (a) 1117.2 (b) 111.72
 (c) 223.4 (d) 160.9
143. Which of the following expressions is correct for first order reaction? (a_0 refers to initial concentration of reactant)
 (a) $t_{1/2} \propto a_0^0$ (b) $t_{1/2} \propto a_0^{-2}$
 (c) $t_{1/2} \propto a_0^{-1}$ (d) $t_{1/2} \propto a_0$
144. Which of the following is not correct?
 (a) Rate of zero order reaction depends upon initial concentration of reactant.
 (b) Rate of zero order reaction does not depend upon initial concentration of reactant.
 (c) $t_{1/2}$ of first order reaction is independent of initial concentration of reactant.
 (d) $t_{1/2}$ of zero order reaction is dependent of initial concentration of reactant.
145. The inversion of cane sugar is represented by
 $\text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6$.
 It is a
 (a) second order reaction
 (b) unimolecular reaction
 (c) pseudo-unimolecular reaction
 (d) none of these.
146. In pseudo unimolecular reactions,
 (a) both the reactants are present in low concentration
 (b) both the reactants are present in same concentration
 (c) one of the reactants is present in excess
 (d) one of the reactants is non-reactive
147. In a pseudo first order hydrolysis of ester in water, the following results were obtained.
- | t/s | 0 | 30 | 60 | 90 |
|----------------------------|------|------|------|-------|
| Ester/ mol L^{-1} | 0.55 | 0.31 | 0.17 | 0.085 |
- What will be the average rate of reaction between the time interval 30 to 60 seconds?
 (a) $1.91 \times 10^{-2} \text{ s}^{-1}$
 (b) $4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$
 (c) $1.98 \times 10^{-3} \text{ s}^{-1}$
 (d) $2.07 \times 10^{-2} \text{ s}^{-1}$

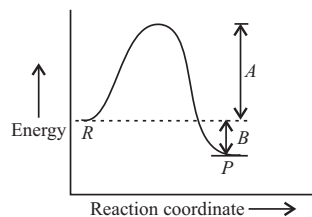
3.4 Temperature Dependence of the Rate of a Reaction

148. For every 10° rise in temperature rate of reaction
 (a) doubles (b) becomes 4 times
 (c) becomes 8 times (d) becomes 10 times

149. If the rate of a reaction at 50°C is $2.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$, then what will be rate of reaction at 80°C ? (For every 10° rise in temperature rate doubles)
- (a) 2.08×10^{-2} (b) 7.025×10^{-3}
 (c) 7.8×10^{-3} (d) None of these
150. Effect of temperature on reaction rate is given by
- (a) Claisen-Clapeyron equation
 (b) Arrhenius equation
 (c) Gibb's-Helmholtz equation
 (d) Kirchoff's equation.
151. The rate of reaction is doubled for 10°C rise of temperature. The increase in the reaction rate as a result of temperature rise from 10°C to 100°C is
- (a) 112 (b) 512
 (c) 1024 (d) 100.
152. What happens when the temperature of a solution is increased from 25°C to 65°C ?
- (a) The rate of the reaction remains unchanged and the rate constant k decreases.
 (b) The rate of the reaction increases and rate constant k decreases.
 (c) The rate of the reaction decreases and so does the rate constant k .
 (d) The rate of the reaction increases and so does the rate constant k .
153. A chemical reaction was carried out at 300 K and 280 K. The rate constants were found to be k_1 and k_2 respectively. Then
- (a) $k_2 = 4 k_1$ (b) $k_2 = 2 k_1$
 (c) $k_2 = 0.25 k_1$ (d) $k_2 = 0.5 k_1$
154. Rate constant k of a reaction is dependent on temperature as :
- $$k = A e^{-E_a/RT}$$
- k has the least value at
- (a) high T and high E_a
 (b) high T and small E_a
 (c) low T and low E_a
 (d) low T and high E_a .
155. Energy of activation of an exothermic reaction is
- (a) zero (b) negative
 (c) positive (d) can't be predicted.
156. When the activation energies of the forward and reverse reactions are equal, then
- (a) $\Delta U = 0, \Delta S = 0$ (b) $\Delta U = \infty, \Delta S = 0$
 (c) $\Delta G = 0, \Delta U = 0$ (d) only $\Delta U = 0$
157. The activation energy of exothermic reaction $A \rightarrow B$ is 80 kJ. The heat of reaction is 200 kJ mol^{-1} . The activation energy for the reaction $B \rightarrow A$ in kJ/mol will be
- (a) 80 (b) 120 (c) 280 (d) 200
158. The activation energy for the forward reaction $X \rightarrow Y$ is 80 kJ/mol and ΔH is -20 kJ/mol . Calculate the activation energy for reverse reaction.
- (a) 40 kJ/mol (b) 100 kJ/mol
 (c) 80 kJ/mol (d) 120 kJ/mol
159. For an endothermic reaction, ΔH represents the enthalpy of the reaction in kJ mol^{-1} . The minimum amount of activation energy will be
- (a) less than zero (b) equal to ΔH
 (c) less than ΔH (d) more than ΔH .
160. Consider the following reaction profile :
 For the reaction $A \rightarrow B$, the activation energy is
- 
- (a) a (b) b (c) c (d) d
161. 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 less than E_a
 (b) is always double of E_a
 (c) can be less than or more than E_a
 (d) is negative of E_a .
162. Energy profile of the reaction $A + BC \rightarrow AB + C$ is given in the figure
- 
- Which of the following statement is true?
- (a) Threshold energy of the reaction is 100 kJ.
 (b) E_f is 60 kJ mol^{-1} while E_r is 40 kJ mol^{-1} .

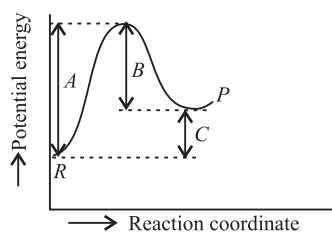
- (c) ΔH is $+ 20 \text{ kJ mol}^{-1}$ and the reaction is endothermic.
 (d) All are true.

163. The energy diagram of a reaction $P + Q \rightarrow R + S$ is given. What are A and B in the graph?



- (a) $A \rightarrow$ activation energy, $B \rightarrow$ heat of reaction
 (b) $A \rightarrow$ threshold energy, $B \rightarrow$ heat of reaction
 (c) $A \rightarrow$ heat of reaction, $B \rightarrow$ activation energy
 (d) $A \rightarrow$ potential energy, $B \rightarrow$ energy of reaction
164. For an exothermic reaction, ΔH represents the enthalpy of the reaction in kJ mol^{-1} . The minimum amount of activation energy will be
 (a) can be predicted (b) equal to ΔH
 (c) less than ΔH (d) more than ΔH .
165. The rate constant is given by the equation $k = Ae^{-E_a/RT}$. Which factor should register a decrease for the reaction to proceed more rapidly?
 (a) T (b) Z (c) A (d) E_a
166. An exothermic reaction $A \rightarrow B$ has an activation energy of 17 kJ per mole of A . The heat of the reaction is 40 kJ . Calculate the activation energy for the reverse reaction $B \rightarrow A$.
 (a) 60 kJ (b) 57 kJ
 (c) 75 kJ (d) 90 kJ
167. The rate constant, activation energy and the Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively. The value of the rate constant as $T \rightarrow \infty$ is
 (a) $2.0 \times 10^{18} \text{ s}^{-1}$ (b) $6.0 \times 10^{14} \text{ s}^{-1}$
 (c) infinity (d) $3.6 \times 10^{30} \text{ s}^{-1}$
168. For an endothermic reaction $A \rightarrow B$, the activation energy is 15 kcal mol^{-1} . The heat of reaction is 5 kJ . The activation energy for the reaction $B \rightarrow A$ is
 (a) 10 kcal mol^{-1} (b) 20 kcal mol^{-1}
 (c) 40 kcal mol^{-1} (d) $100 \text{ kcal mol}^{-1}$
169. An exothermic reaction $A \rightarrow B$ has an activation energy of $X \text{ kJ mol}^{-1}$ of A . If the energy change in the reaction is $Y \text{ kJ}$, then the activation energy of the backward reaction will be
 (a) $-X$ (b) $Y - Y$
 (c) $Y - X$ (d) $X + Y$
170. By increasing the temperature by 10°C , the rate of forward reaction at equilibrium is increased by a factor of 2. The rate of backward reaction by this increase in temperature
 (a) remains unaffected
 (b) increases by a factor greater than two
 (c) decreases by a factor lesser than two
 (d) also increases by a factor of two.
171. Arrhenius equation is
 (a) $k = Ae^{-E_a/RT}$
 (b) $k = Ae^{E_a/RT}$
 (c) $k = Ae^{-RT/E_a}$
 (d) $k = Ae^{RT/E_a}$
172. A reactant (A) forms two products
 $A \xrightarrow{k_1} B$, activation energy E_{a1}
 $A \xrightarrow{k_2} C$, activation energy E_{a2}
 If $E_{a2} = 2E_{a1}$, then k_1 and k_2 are related as
 (a) $k_1 = 2k_2e^{2E_{a1}/RT}$
 (b) $k_1 = k_2e^{2E_{a1}/RT}$
 (c) $k_2 = k_1e^{2E_{a1}/RT}$
 (d) $k_1 = Ak_2e^{2E_{a2}/RT}$
173. The activation energy in a chemical reaction is defined as,
 (a) the difference in energies of reactants and products
 (b) the sum of energies of reactants and products
 (c) the difference in energy of intermediate complex with the average energy of reactants and products
 (d) the difference in energy of intermediate complex and the average energy of reactants.
174. The activation energy necessary for a reaction, may be lowered by
 (a) decreasing the temperature
 (b) increasing the temperature
 (c) adding a catalyst
 (d) reducing the potential energy.
175. The decomposition of A into product has values of k as $4.5 \times 10^3 \text{ s}^{-1}$ at 10°C and energy of activation as 60 kJ mol^{-1} . At what temperature k would be $1.5 \times 10^4 \text{ s}^{-1}$?
 (a) 273.15 K (b) 24.19°C
 (c) 280.39 K (d) 45.29°C

176. The potential energy diagram for a reaction $X \rightarrow Y$ is given. A and C in the graph corresponding to

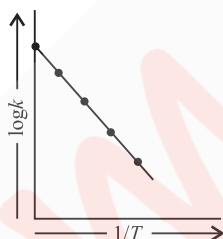


- (a) $A \rightarrow$ activation energy, $C \rightarrow \Delta H^\circ$
 (b) $A \rightarrow$ energy of reactants, $C \rightarrow$ energy of products
 (c) $A \rightarrow \Delta H^\circ$, $C \rightarrow$ activation energy
 (d) $A \rightarrow$ activation energy, $C \rightarrow$ threshold energy

177. The rate constant of a reaction

- (a) decreases with increasing E_a
 (b) decreases with decreasing E_a
 (c) is independent of E_a
 (d) decreases with increasing temperature.

178. The temperature dependence of the rate constant k is expressed as $k = Ae^{-E_a/RT}$. When a plot between $\log k$ and $1/T$ is plotted we get the graph as shown.



What is the value of slope in the graph?

- (a) $\frac{E_a}{RT}$ (b) $-\frac{E_a}{2.303R}$
 (c) $-\frac{E_a}{2.303RT} \log A$ (d) $-\frac{E_a}{2.303} \frac{R}{T}$

179. The rate constant of a reaction is shown as $k = 2.1 \times 10^{10} e^{-2700/RT}$

It means that

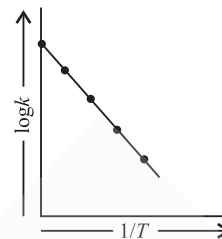
- I. $\log k$ vs $1/T$ will be a straight line with intercept on $\log k$ axis = $\log 2.1 \times 10^{10}$.
 II. Number of effective collisions are $2.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$.
 III. Half-life of a reaction increases with increase of temperature.
 IV. $\log k$ vs $1/T$ will be a straight line with slope = $-\frac{2700}{2.303R}$

Which of the above statement(s) is/are true?

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

180. The temperature dependence of the rate constant k is expressed as $k = Ae^{-E_a/RT}$.

When a plot between $\log k$ and $1/T$ is plotted we get the graph as shown.



What is the value of intercept in the graph?

- (a) $\frac{E_a}{RT}$ (b) $\log A$
 (c) $-\frac{E_a}{2.303RT} \log A$ (d) $-\frac{E_a}{2.303} \frac{R}{T}$

181. When a graph of $\log_{10} K$ against $1/T$ is plotted, for reaction, a graph with slope equal to $-1 \times 10^3 \text{ K}$ is obtained. Hence the activation energy is

- (a) $8.314 \times 10^3 \text{ J mol}^{-1}$ (b) 3.61 kJ mol^{-1}
 (c) $4.85 \times 10^3 \text{ J mol}^{-1}$ (d) 19.1 kJ mol^{-1}

182. When a graph of $\log_{10} k$ is plotted against $1/T$, the inverse of slope of the line is

- (a) $-\frac{E_a}{R}$ (b) $-\frac{2.303R}{E_a}$
 (c) $-\frac{E_a}{2.303}$ (d) $-\frac{E_a}{2.303R}$

183. Slope of the plot of $\log k$ versus $1/T$ is 5.64. Activation energy in J mol^{-1} will be

- (a) 108 (b) 98 (c) 118 (d) 138

184. A reaction rate constant is given by

$$k = 1.2 \times 10^{14} e^{-25000/RT} \text{ s}^{-1}$$

It means that

- (a) $\log k$ versus $\log T$ will give a straight line with a slope as -25000
 (b) $\log k$ versus T will give a straight line with slope as 25000
 (c) $\log k$ versus $\log 1/T$ will give a straight line with slope as -25000
 (d) $\log k$ versus $1/T$ will give a straight line

185. What is the energy of activation of a reaction if its rate doubles when the temperature is raised from 290 K to 300 K?

- (a) 12 kcal (b) 41 kcal
 (c) 13.8 kcal (d) 52 kcal.

186. The rate constants at 27°C and 67°C for the dissociation of N_2O_5 are 3.45×10^{-5} and 6.90×10^{-3} respectively. What is the activation energy for the dissociation of N_2O_5 ?

- (a) 112.3 kJ (b) 225 kJ
 (c) 448 kJ (d) 285 kJ

187. The correct expression for activation energy is,

(a) $\log_{10} \frac{k_1}{k_2} = \frac{E_a(T_1 - T_2)}{2.303R \times T_1 \times T_2}$

(b) $\log_{10} \frac{k_2}{k_1} = \frac{E_a(T_1 - T_2)}{2.303 R \times T_1 \times T_2}$

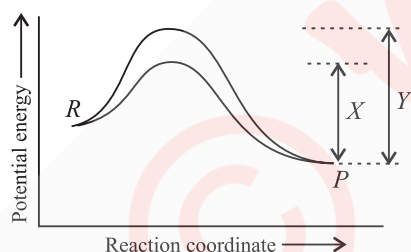
(c) $\log_{10} \frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{2.303 R \times T_1 \times T_2}$

(d) $\log_{10} \frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{R \times T_1 \times T_2}$

188. Which of the following statements about the catalyst is true?

- (a) A catalyst accelerates the rate of reaction by bringing down the energy of activation.
- (b) A catalyst does not participate in reaction mechanism.
- (c) A catalyst makes the reaction more feasible by making ΔG more negative.
- (d) A catalyst makes equilibrium constant more favourable for forward reaction.

189. The graph of the effect of catalyst on activation energy is given below. Fill up the blanks X and Y with appropriate statements.



- (a) X = energy of activation without catalyst, Y = energy of activation with catalyst
- (b) X = path of reaction with catalyst, Y = path of reaction without catalyst
- (c) X = energy of activation with catalyst, Y = energy of activation without catalyst
- (d) X = energy of endothermic reaction, Y = energy of exothermic reaction

190. When a catalyst is used in an equilibrium process,

- (a) it increases the rate of forward reaction
- (b) it decreases the rate of backward reaction
- (c) it decreases activation energy of forward process and increases activation energy of backward process

- (d) it fastens the attainment of equilibrium by lowering activation energy.

191. Which of the following statements about the catalyst is true?

- (a) A catalyst makes the reaction feasible by making ΔG more negative.
- (b) A catalyst makes equilibrium constant more favourable for forward reaction.
- (c) A catalyst accelerate rate of reaction by bringing down the activation energy.
- (d) A catalyst always increases the rate of reaction.

192. On increasing the temperature by 10 K the rate of reaction becomes double. Which of the following is the most appropriate reason?

- (a) With increase of temperature, velocities increase and hence the number of collisions is appreciably increased.
- (b) The activation energy decreases with increase of temperature.
- (c) The bonds between the atoms of the reacting molecules become weak at higher temperature.
- (d) Higher the temperature, larger is the fraction of colliding particles which can cross the energy barrier.

193. If hydrogen and oxygen are mixed and kept in the same vessel at room temperature, the reaction does not take place to form water because

- (a) activation energy for the reaction is very high at room temperature
- (b) molecules have no proper orientation to react to form water
- (c) the frequency of collisions is not high enough for the reaction to take place
- (d) no catalyst is present in the reaction mixture.

194. On increasing temperature of the reacting system by 10 degrees the rate of reaction almost doubles. The most appropriate reasons for this is

- (a) collision frequency increases
- (b) activation energy decreases by increase in temperature
- (c) the fraction of molecules having energy equal to threshold energy or more increase
- (d) the value of threshold energy decreases.

3.5 Collision Theory of Chemical Reactions

195. Rate of a general reaction $A + B \rightarrow$ products can be expressed as follows on the basis of collision theory.

$$\text{Rate} = Z_{AB} e^{-E_a/RT}$$

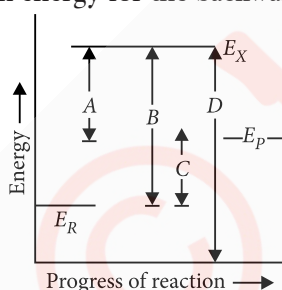
Which of the following statements is not correct for the above expression?

- Z is collision frequency and is equal to number of collisions per second per unit volume of the reaction mixture.
- $e^{-E_a/RT}$ is the fraction of molecules with kinetic energy equal to or greater than E_a .
- E_a is activation energy of the reaction.
- All the molecules which collide with one other are effective collisions.

196. The rate constant is given by the equation $k = P \cdot Z e^{-E_a/RT}$. Which factor should register a decrease for the reaction to proceed more rapidly?

- T
- Z
- E_a
- P

197. In the given diagram, E_R , E_P and E_X represent the energy of the reactants, products and activated complex respectively. Which of the following is the activation energy for the backward reaction?



- A
- B
- C
- D

198. Collision theory is applicable to

- first order reactions
- zero order reactions
- bimolecular reactions
- pseudo first order reactions.

199. For a certain reaction a large fraction of molecules has energy more than the threshold energy, still the rate of reaction is very slow. The possible reason for this could be that

- the colliding molecules could be large in size
- the colliding molecules must not be properly oriented for effective collisions

- the rate of reaction could be independent of the energy
- one of the reactants could be in excess.

200. For effective collisions, colliding molecules must have

- minimum potential energy
- sufficient kinetic energy
- sufficient potential energy
- maximum energy of activation.

201. According to collision theory of reaction rates

- every collision between reactants leads to chemical reaction
- rate of reaction is proportional to velocity of molecules
- all reactions which occur in gaseous phase are zero order reactions
- rate of reaction is directly proportional to collision frequency.

202. A chemical reaction proceeds following the formula $k = PZ e^{-E_a/RT}$. Which of the following processes will increase the rate of reaction?

- Lowering of E_a
- Lowering of P
- Lowering of Z
- Rate of reaction is independent of all the above factors.

203. According to collision theory, collision rate = Z [reactants] where Z is

- activation energy
- packing frequency
- collision frequency
- potential energy.

204. Orientation factor is directly proportional to

- collision frequency
- fraction of molecule
- rate of reaction
- threshold energy.

205. Chemical reaction occurs as a result of collisions between reacting molecules. Therefore, the reaction rate is given by

- total number of collisions occurring in a unit volume per second
- fraction of molecules which possess energy less than the threshold energy
- total number of effective collisions
- none of the above.

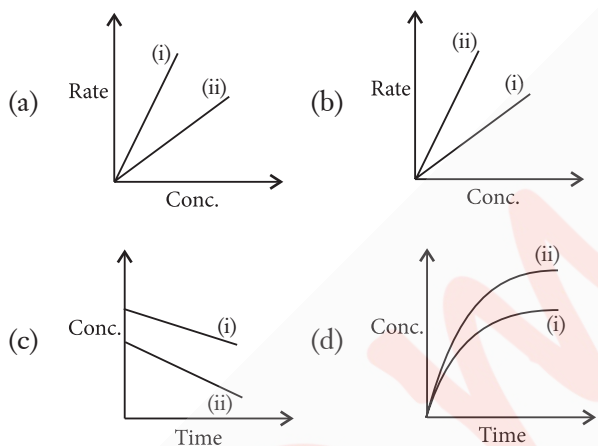


KCET Ready

1. For the reaction $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$,
if $-\frac{d[\text{NH}_3]}{dt} = k_1[\text{NH}_3]$, $\frac{d[\text{N}_2]}{dt} = k_2[\text{NH}_3]$,
 $\frac{d[\text{H}_2]}{dt} = k_3[\text{NH}_3]$

then the relation between k_1 , k_2 and k_3 is

- (a) $k_1 = k_2 = k_3$ (b) $k_1 = 3k_2 = 2k_3$
(c) $1.5k_1 = 3k_2 = k_3$ (d) $2k_1 = k_2 = 3k_3$
2. For two first order reactions, (i) $A \rightarrow$ products and (ii) $B \rightarrow$ products, k_1 and k_2 are the rate constants. The first reaction (i) is slower than the second reaction (ii). The graphical observation corresponding to this observation will be



3. A first order reaction takes 40 min for 30% decomposition. What will be $t_{1/2}$?

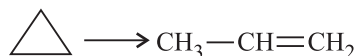
- (a) 77.7 min (b) 52.5 min
(c) 46.2 min (d) 22.7 min

4. Consider the reaction : $2\text{N}_2\text{O}_4 \rightleftharpoons 4\text{NO}_2$

If $-\frac{d[\text{N}_2\text{O}_4]}{dt} = k$ and $\frac{d[\text{NO}_2]}{dt} = k'$ then

- (a) $2k' = k$ (b) $k' = 2k$
(c) $k' = k$ (d) $k = \frac{1}{4}k'$

5. Cyclopropane rearranges to form propene



This follows first order kinetics. The rate constant is $2.714 \times 10^{-3} \text{ sec}^{-1}$. 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

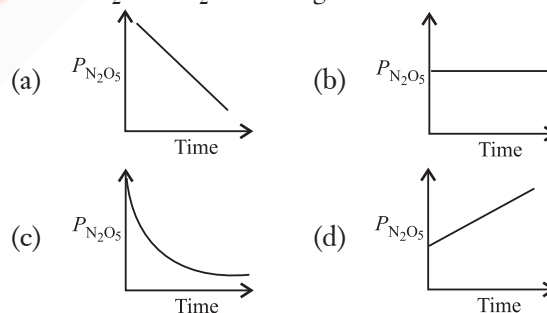
6. The rate constant, k of the reaction,
 $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ is $2.3 \times 10^{-2} \text{ sec}^{-1}$.
Which equation given below describes the change of $[\text{N}_2\text{O}_5]$ with time? $[\text{N}_2\text{O}_5]_0$ and $[\text{N}_2\text{O}_5]_t$ correspond to concentration of N_2O_5 initially and at time t .

- (a) $[\text{N}_2\text{O}_5]_t = [\text{N}_2\text{O}_5]_0 + kt$
(b) $\log_{10}[\text{N}_2\text{O}_5]_t = \log_{10}[\text{N}_2\text{O}_5]_0 - kt$
(c) $[\text{N}_2\text{O}_5]_0 = [\text{N}_2\text{O}_5]_t e^{kt}$
(d) $\ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t} = kt$

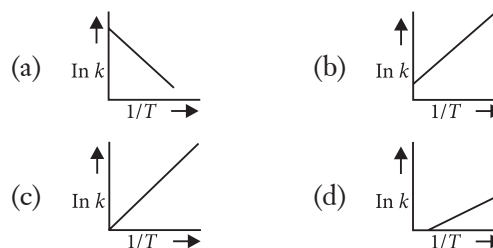
7. For a general chemical change,
 $2A + 3B \longrightarrow$ Products, the rates with respect to A is r_1 and that with respect to B is r_2 . The rates r_1 and r_2 are related as

- (a) $3r_1 = 2r_2$ (b) $r_1 = r_2$
(c) $2r_1 = 3r_2$ (d) $r_1^2 = 3r_2$

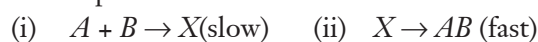
8. Which of the following graphs will show the variation of partial pressure of N_2O_5 decomposing into NO_2 and O_2 following the first order kinetics?



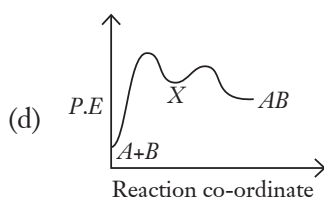
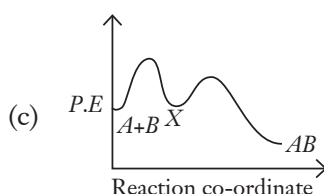
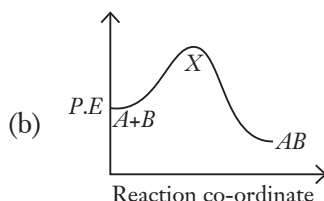
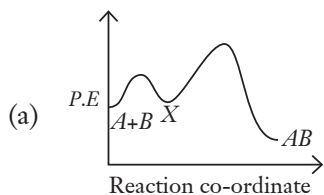
9. According to Arrhenius equation which of the following options represents the graph of $\ln k$ vs $\frac{1}{T}$?



10. For an exothermic chemical process occurring in two steps as follows :



the process of reaction can be best described by



11. The rate constant (k') of one of the reaction is found to be double than that of the rate constant (k'') of another reaction. Then the relationship between the corresponding activation energies of the two reactions (E'_a and E''_a) can be represented as

- (a) $E'_a > E''_a$ (b) $E'_a < E''_a$
(c) $E'_a = E''_a$ (d) $E'_a = 4E''_a$

12. For a given reaction, presence of catalyst reduces the energy of activation by 2 kcal at 27°C. The rate of reaction will be increased by

- (a) e^{RT} (b) $e^{-RT/2}$
(c) $e^{2/RT}$ (d) $e^{-2/RT}$

13. In the reaction $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$, the rate is expressed as

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

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

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

Relation between k_1 , k_2 and k_3 is

- (a) $2k_1 = 4k_2 = k_3$ (b) $2k_1 = k_2 = 4k_3$
(c) $2k_1 = k_2 = 2k_3$ (d) $k_1 = 4k_2 = 2k_3$

14. Which of the following factors are responsible for the increase in the rate of a surface catalysed reaction?

- (i) A catalyst provides proper orientation for the reactant molecules to react.
(ii) Heat of adsorption of reactants on a catalyst helps reactant molecules to overcome activation energy.
(iii) The catalyst increases the activation energy of the reaction.

- (a) (i) and (iii) (b) (i) and (ii)
(c) (ii) and (iii) (d) (i), (ii) and (iii)

15. The rate of first order reaction is $1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}$ 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.

16. The rate of a reaction is expressed in different ways as follows :

$$-\frac{1}{m} \frac{d[A]}{dt} = +\frac{1}{n} \frac{d[B]}{dt} = -\frac{1}{p} \frac{d[C]}{dt} = +\frac{1}{q} \frac{d[D]}{dt}$$

The reaction is

- (a) $nA + mB \longrightarrow pC + qD$
(b) $pA + qB \longrightarrow mC + nD$
(c) $pA + mB \longrightarrow nC + qD$
(d) $mA + pC \longrightarrow nB + qD$

17. For a zero order reaction, rate constant is given by

- (a) $[A]_t = kt + [A]_0$ (b) $k = t ([A]_0 - [A]_t)$
(c) $k = \frac{t}{[A]_0 - [A]_t}$ (d) $[A]_t = -kt + [A]_0$

18. A reaction is represented by $A \xrightarrow{k_1} B$ (slow) and $A + B \xrightarrow{k_2} C$ (fast) where k_1 and k_2 are the rate constants of two steps. The rate of production of C will be given by

- (a) $k_1[A][B]$ (b) $k_1[A]$
(c) $k_1k_2[A]$ (d) $k_2[A][B]$

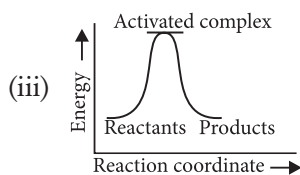
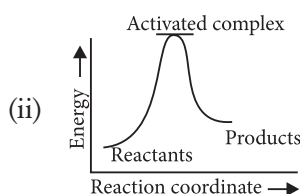
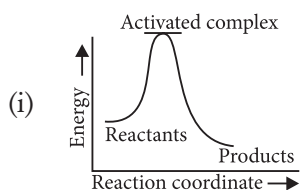
19. The incorrect order indicated against the rate of reaction : $A + B \xrightarrow{k} C$ is

- | Rate | Order |
|----------------------------------|-------|
| (a) $\frac{d[C]}{dt} = k[A]$ | 1 |
| (b) $\frac{d[C]}{dt} = k[A][B]$ | 2 |
| (c) $\frac{-d[A]}{dt} = k[A][B]$ | 1 |
| (d) $\frac{-d[A]}{dt} = k[A]$ | 1 |

20. A first order reaction takes 100 min for completion of 60% of reaction. The time required for completion of 90% of the reaction is

- (a) 150 min (b) 200 min
(c) 220.9 min (d) 251.3 min

21. Which of the following graphs represents endothermic reaction?



- (a) (i) only (b) (ii) only
(c) (iii) only (d) (i) and (ii)

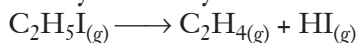
22. The half life of a first order reaction is 6.0 h. How long will it take for the concentration of reactant to decrease from 0.8 M to 0.25 M?

- (a) 9.06 h (b) 10.07 h
(c) 8.71 h (d) 5.45 h

23. Which statement is not correct?

- (a) For an endothermic reaction, heat of reaction is lesser than energy of activation.
(b) For an exothermic reaction, heat of reaction is more than energy of activation.
(c) For an exothermic reaction energy of activation is lesser in forward reaction than in backward reaction.
(d) For an endothermic reaction energy of activation is more in forward reaction than in backward reaction.

24. The first order rate constant for the decomposition of ethyl iodide by the reaction,



at 600 K is $1.60 \times 10^{-5} \text{ s}^{-1}$. Its energy of activation is 209 kJ/mol. The rate constant of the reaction at 700 K is

- (a) $5 \times 10^{-3} \text{ s}^{-1}$ (b) $7.36 \times 10^{-2} \text{ s}^{-1}$
(c) $3.5 \times 10^{-2} \text{ s}^{-1}$ (d) $6.36 \times 10^{-3} \text{ s}^{-1}$

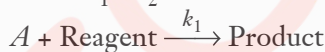
25. What is the time required for a first order reaction to be 99% complete, compared to the time taken for the reaction to be 90% complete?

- (a) There is no change.
(b) Time taken is double.
(c) Time taken is triple.
(d) The time required is half the initial value.

26. A first order reaction is 20% complete in 20 min. Time taken to complete 60% of the reaction will be

- (a) 42 min (b) 62 min
(c) 72 min (d) 82 min

27. In the following first order competing reactions where $t_1 = t_2$:



The ratio of $\frac{k_1}{k_2}$ if only 50% of B and 94% of A have been reacted is

- (a) 4.06 (b) 0.246 (c) 2.06 (d) 0.06

28. For a chemical reaction $Y_2 + 2Z \longrightarrow \text{product}$, rate controlling step is $Y + \frac{1}{2}Z \longrightarrow Q$

If the concentration of Z is doubled, the rate of reaction will

- (a) remain the same (b) become four times
(c) become $\sqrt{2}$ times (d) become double.

29. The following data pertains to reaction between A and B.

S. No.	[A] mol L ⁻¹	[B] mol L ⁻¹	Rate (mol L ⁻¹ time ⁻¹)
1.	1.0×10^{-2}	2.0×10^{-2}	2.0×10^{-4}
2.	2.0×10^{-2}	2.0×10^{-2}	4.0×10^{-4}
3.	2.0×10^{-2}	4.0×10^{-2}	8.0×10^{-4}

Which of the following inferences can be drawn from the above data?

- I. Rate constant of the reaction is 1.0×10^{-4} .
II. Rate law of the reaction is : rate = $k[A][B]$
III. Rate of reaction increases four times on doubling the concentration of both the reactants.

- (a) I, II and III (b) I and II only
(c) II and III only (d) III only

30. The half life of a first order reaction is 0.5 min at a certain temperature. Calculate the time required for 80% reactant to decompose.

- (a) 69.7 s (b) 73.5 s
(c) 45.7 s (d) 1.05 s

31. The rate constant of a reaction is shown as $k = 2.1 \times 10^{10} e^{-2700/RT}$

It means that

- I. $\log k$ vs $1/T$ will be a straight line with intercept on $\log k$ axis = $\log 2.1 \times 10^{10}$.
II. Number of effective collisions are $2.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$.
III. Half-life of a reaction increases with increase of temperature.
IV. $\log k$ vs $1/T$ will be a straight line with slope $= -\frac{2700}{2.303R}$

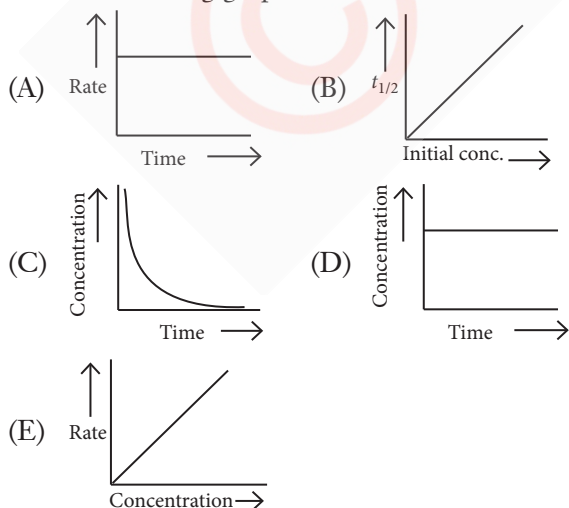
Which of the above statements are true?

- (a) I and II only (b) II and III only
(c) III and IV only (d) I and IV only

32. Which of the following statements is true?

- (a) For first order reaction, straight-line graph of $\log C$ vs t is obtained, slope = $-k/2.303$.
(b) A plot of $\log k$ vs $1/T$ gives a straight-line graph for which slope = $-E_a/2.303R$.
(c) Units of k for the first order reaction are independent of concentration units.
(d) All of these.

33. For the following graphs



Choose from the options given below, the correct one regarding order of reaction is

- (a) (B) and (D) zero order, (E) first order

- (b) (A) and (B) zero order, (E) first order
(c) (A) and (B) zero order, (C) and (E) first order
(d) (B) zero order, (C) and (E) first order.

34. In the reaction of $aA + bB + cC \longrightarrow$ Products,

- (i) if concentration of A is doubled, keeping conc. of B and C constant, the rate of reaction becomes double
(ii) if concentration of B is halved keeping conc. of A and C constant, the rate of reaction remains unaffected
(iii) if concentration of C is made 1.5 times, the rate of reaction becomes 2.25 times.

The order of reaction is

- (a) 1 (b) 2.5 (c) 3 (d) 3.5

35. In several experiments on the kinetics of reaction $A + B \longrightarrow$ products, it is observed that

- (i) On doubling the initial concentration of A , the rate was increased by four times and
(ii) On doubling the initial concentration of B , the rate was increased by two times.

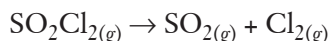
The correct statement is

- (a) the reaction is first order in A and second order in B
(b) the reaction is first order in both the reactants
(c) the rate equation is $\frac{dx}{dt} = k[A]^0[B]$
(d) Order of reaction is 3.

36. The rate constant for a first order reaction is $7.0 \times 10^{-4} \text{ s}^{-1}$. If the initial concentration of the reactant is 0.080 M, what concentration will remain after 35 minutes?

- (a) 0.0765 M (b) 0.0456 M
(c) 0.0237 M (d) 0.0184 M

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



Experiment	Time/s ⁻¹	Total pressure/atm
1	0	0.5
2	100	0.6

What is the rate of reaction when total pressure is 0.65 atm?

- (a) 0.35 atm s^{-1}
(b) $2.235 \times 10^{-3} \text{ atm s}^{-1}$
(c) $7.8 \times 10^{-4} \text{ atm s}^{-1}$
(d) $1.55 \times 10^{-4} \text{ atm s}^{-1}$

38. From the following data for the reaction between A and B ,

	$[A]$ mol L^{-1}	$[B]$ mol L^{-1}	Initial rate $\text{mol L}^{-1} \text{ s}^{-1}$
I	2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}
II	5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}
III	1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}

the order of reaction with respect to A is 2 and with respect to B is 1.

Using the value of activation energy 55.3 kJ mol^{-1} , calculate the pre-exponential factor.

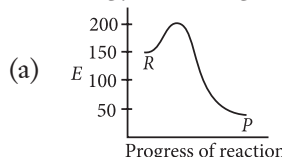
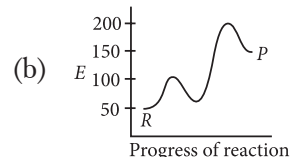
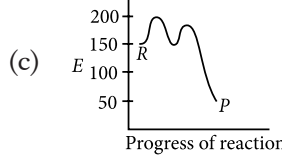
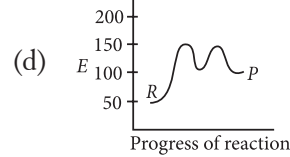
Given $T = 27^\circ\text{C}$.

- (a) 2.280×10^{18} (b) 1.140×10^{18}
(c) 2.280×10^{15} (d) 1.140×10^{15}
39. Hydrolysis of cane sugar in presence of acid is a first order reaction with half life time of 4 hours. What fraction of sucrose undergoes hydrolysis in 11 hrs?
- (a) 0.9345 (b) 0.6122
(c) 0.8511 (d) 0.412
40. A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C . If the reaction is allowed for 10 hours, what percentage of the initial concentration would have changed in the product?
- (a) 0.052% (b) 52%
(c) 5.20% (d) 2.6%
41. Which of the following statements is not correct?
- (a) For a zero order reaction, $t_{1/2}$ is proportional to initial concentration.
(b) The relationship of variation of rate constant with temperature is given by

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

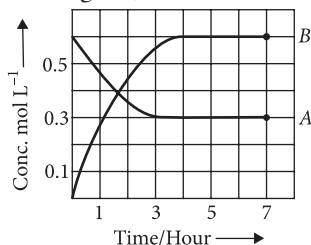
- (c) The unit of rate constant for a reaction is $\text{mol}^{1-n} \text{L}^{n-1} \text{s}^{-1}$ where n is order of the reaction.
(d) The unit of rate of reaction changes with order of reaction.
42. In acidic medium, the rate of reaction between $[\text{BrO}_3^-]$ and $[\text{Br}^-]$ ions is given by the expression
- $$-\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$
- It means
- (i) rate constant of the reaction depends upon the concentration of H^+ ions
(ii) rate of reaction is independent of the concentration of acid added
(iii) the change in pH of the solution will affect the rate of reaction

(iv) doubling the concentration of H^+ ions will increase the reactions rate by 4 times.

- (a) Only (ii) (b) Only (iii)
(c) Only (i) and (ii) (d) Only (iii) and (iv)
43. Time required for 99.9% completion of a first order reaction is nearly
- (a) 10 times that required for 25% of the reaction
(b) 10 times that required for 50% of the reaction
(c) 20 times that required for 50% of the reaction
(d) 100 times that required for 90% of the reaction.
44. In a first order reaction $A \longrightarrow B$, 60% of the given sample of compound decomposes in 45 minutes. What is the half life of the reaction?
- (a) 34 min (b) 56 min
(c) 48 min (d) 27 min
45. In a hypothetical reaction $X \longrightarrow Y$, the activation energy for the forward and backward reactions are 15 and 9 kJ mol^{-1} respectively. The potential energy of X is 10 kJ mol^{-1} . Which of the following statements is/are correct?
- (i) The threshold energy of the reaction is 25 kJ mol^{-1} .
(ii) The potential energy of Y is 16 kJ mol^{-1} .
(iii) Heat of reaction is 6 kJ mol^{-1} .
(iv) The reaction is endothermic.
- (a) Only (i) (b) Only (i) and (ii)
(c) Only (ii) and (iii) (d) All are correct.
46. An exothermic chemical reaction proceeds by two stages.
- Reactants $\xrightarrow{\text{stage 1}}$ Intermediate $\xrightarrow{\text{stage 2}}$ Products
The activation energy of state 1 is 50 kJ mol^{-1} . The overall enthalpy change for the reaction is -100 kJ mol^{-1} . Which diagram could represent the energy level diagram for the reaction?
- (a)  (b) 
- (c)  (d) 
47. The energy of activation for a certain second order reaction is 85.2 kJ mol^{-1} and its frequency factor is $3.1 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$ at 310 K. Calculate the rate constant of the reaction. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

- (a) $13.72 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$
 (b) $1.372 \text{ L mol}^{-1} \text{ s}^{-1}$
 (c) $1.592 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$
 (d) $1.372 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$

48. The progress of a reaction $A \rightleftharpoons nB$, with time is presented in the figure, determine the value of n .



- (a) 1 (b) 2 (c) 3 (d) 4
49. A first order reaction $A \rightarrow B$, requires activation energy of 70 kJ mol^{-1} . When a 20% solution of A was kept at 25°C for 20 min. 25% decomposition takes place. What will be the percent decomposition at the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains

constant in this range of temperature.

- (a) 39.08% (b) 32.83%
 (c) 67.17% (d) 60.92%

50. Fill up the following with suitable terms.

- (i) Activation energy = Threshold energy – _____
 (ii) Half-life period of zero order reaction = _____
 (iii) Average rate of reaction = _____
 (iv) Instantaneous rate of reaction = _____

	(i)	(ii)	(iii)	(iv)
(a) Potential energy	$\frac{0.693}{k}$	$\frac{dx}{dt}$	$\frac{\Delta[A]}{\Delta t}$	$\frac{\Delta[A]}{\Delta t}$
(b) Energy of reactants	$\frac{1}{k}$	$\frac{\Delta[A]}{\Delta t}$	$\frac{dx}{dt}$	$\frac{dx}{dt}$
(c) Energy of reaction	$\frac{\log k}{t}$	$\frac{\Delta[A]}{\Delta t}$	$\frac{dx}{dt}$	$\frac{dx}{dt}$
(d) Average kinetic energy of reactants	$\frac{a}{2k}$	$\frac{\Delta[A]}{\Delta t}$	$\frac{dx}{dt}$	$\frac{dx}{dt}$



KCET Exam Archive

10 Years' PYQs (2014-2023)

1. $A_{(g)} \xrightarrow{\Delta} P_{(g)} + Q_{(g)} + R_{(g)}$, follows first order kinetics with a half-life of 69.3 s at 500°C . Starting from the gas 'A' enclosed in a container at 500°C and at a pressure of 0.4 atm, the total pressure of the system after 230 s will be
 (a) 1.15 atm (b) 1.32 atm
 (c) 1.22 atm (d) 1.12 atm (2014)
2. 100 cm^3 of 1 M CH_3COOH was mixed with 100 cm^3 of 2 M CH_3OH to form an ester. The change in the initial rate if each solution is diluted with equal volume of water would be
 (a) 4 times (b) 0.25 times
 (c) 2 times (d) 0.5 times. (2015)
3. In a first order reaction, the concentration of the reactant is reduced to 12.5% in one hour. When was it half completed?
 (a) 20 min (b) 15 min
 (c) 3 hr (d) 30 min (2015)
4. Half-life period of a first order reaction is 10 min. Starting with initial concentration 12 M, the rate after 20 min is
 (a) $0.693 \times 3 \text{ M min}^{-1}$
 (b) $0.0693 \times 4 \text{ M min}^{-1}$
 (c) $0.0693 \text{ M min}^{-1}$
 (d) $0.0693 \times 3 \text{ M min}^{-1}$ (2015)
5. The half-life period of a first order reaction is 60 minutes. What percentage will be left over after 240 minutes?
 (a) 6.25% (b) 4.25%
 (c) 5% (d) 6% (2016)
6. For a chemical reaction, $mA \rightarrow xB$, the rate law is $r = k[A]^2$. If the concentration of A is doubled, the reaction rate will be
 (a) doubled
 (b) quadrupled
 (c) increased by 8 times
 (d) unchanged. (2016)
7. $3A \rightarrow 2B$, rate of reaction, $+\frac{d[B]}{dt}$ is equal to
 (a) $-\frac{3}{2} \frac{d[A]}{dt}$ (b) $-\frac{2}{3} \frac{d[A]}{dt}$
 (c) $+2 \frac{d[A]}{dt}$ (d) $-\frac{1}{3} \frac{d[A]}{dt}$ (2016)

8. The activation energy of a chemical reaction can be determined by
- evaluating rate constants at two different temperatures
 - changing the concentration of reactants
 - evaluating the concentration of reactants at two different temperatures
 - evaluating rate constant at standard temperature. (2016)
9. For a reaction $\frac{1}{2}A \longrightarrow 2B$, rate of disappearance of A is related to rate of appearance of B by the expression
- $\frac{-d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$
 - $\frac{-d[A]}{dt} = 4 \frac{d[B]}{dt}$
 - $\frac{-d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$
 - $\frac{-d[A]}{dt} = \frac{d[B]}{dt}$ (2017)
10. Which of the following statements is in accordance with the Arrhenius equation?
- Rate of a reaction increases with increase in temperature.
 - Rate of reaction does not change with increase in activation energy.
 - Rate constant decreases exponentially with increase in temperature.
 - Rate of a reaction increases with decrease in activation energy. (2017)
11. Which of the following statements is incorrect?
- Molecularity is only applicable for elementary reaction.
 - The rate law for any reaction cannot be determined experimentally.
 - Bimolecular reactions involve simultaneous collision between two species.
 - Complex reactions have fractional order. (2017)
12. For the reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the rate of disappearance of O_2 is $2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. The rate of appearance of SO_3 is
- $2 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $1 \times 10^{-1} \text{ mol L}^{-1} \text{ s}^{-1}$
 - $6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ (2018)
13. The temperature coefficient of a reaction is 2. When the temperature is increased from 30°C to 90°C , the rate of reaction is increased by
- 150 times
 - 410 times
 - 72 times
 - 64 times. (2018)
14. The value of rate constant of pseudo first order reaction
- depends only on temperature
 - depends on the concentration of reactants present in small amounts
 - depends on the concentration of reactants present in excess
 - is independent of the concentration of reactants. (2018)
15. The plot of $t_{1/2}$ vs $[R]_0$ for a reaction is a straight-line parallel to x -axis. The unit for the rate constant of this reaction is
- $\text{mol L}^{-1} \text{ s}$
 - $\text{mol L}^{-1} \text{ s}^{-1}$
 - $\text{L mol}^{-1} \text{ s}^{-1}$
 - s^{-1} (2019)
16. Which is a wrong statement?
- Rate constant, $k = \text{Arrhenius constant } A : \text{if } E_a = 0$
 - $e^{-E_a/RT}$ gives the fraction of reactant molecules that are activated at the given temperature.
 - $\ln k$ vs $\frac{1}{T}$ plot is a straight line.
 - Presence of catalyst will not alter the value of E_a . (2019)
17. 1 L of 2 M CH_3COOH is mixed with 1 L of 3 M $\text{C}_2\text{H}_5\text{OH}$ to form an ester. The rate of the reaction with respect to the initial rate when each solution is diluted with an equal volume of water will be
- 0.25 times
 - 2 times
 - 0.5 times
 - 4 times. (2019)
18. The time required for 60% completion of a first order reaction is 50 min. The time required for 93.6% completion of the same reaction will be
- 83.8 min
 - 50 min
 - 150 min
 - 100 min. (2020)
19. For an elementary reaction, $2A + 3B \rightarrow 4C + D$ the rate of appearance of C at time ' t ' is $2.8 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$. Rate of disappearance of B at ' t ', t will be
- $\frac{3}{4}(2.8 \times 10^{-3}) \text{ mol L}^{-1} \text{ s}^{-1}$

- (b) $2(2.8 \times 10^{-3}) \text{ mol L}^{-1} \text{ s}^{-1}$
 (c) $\frac{1}{4}(2.8 \times 10^{-3}) \text{ mol L}^{-1} \text{ s}^{-1}$
 (d) $\frac{4}{3}(2.8 \times 10^{-3}) \text{ mol L}^{-1} \text{ s}^{-1}$ (2020)
20. The rate constant of a reaction is given by $k = PZe^{-E_a/RT}$ under standard notation. In order to speed up the reaction, which of the following factors has to be decreased?
 (a) Both Z and T (b) E_a
 (c) T (d) Z (2020)
21. For a reaction $A + 2B \rightarrow \text{Products}$, when concentration of B alone is increased, half life remains the same. If concentration of A alone is doubled, rate remains the same. The unit of rate constant for the reaction is
 (a) s^{-1} (b) $\text{L mol}^{-1} \text{ s}^{-1}$
 (c) $\text{mol L}^{-1} \text{ s}^{-1}$ (d) atm^{-1} (2021)
22. If the rate constant for a first order reaction is k , the time(t) required for the completion of 99% of the reaction is given by
 (a) $t = \frac{4.606}{k}$ (b) $t = \frac{2.303}{k}$
 (c) $t = \frac{0.693}{k}$ (d) $t = \frac{6.909}{k}$ (2021)
23. The rate of a gaseous reaction is given by the expression, $k[A][B]^2$. If the volume of vessel is reduced to one half of the initial volume, the reaction rate as compared to original rate is
 (a) $\frac{1}{16}$ (b) $\frac{1}{8}$
 (c) 8 (d) 16 (2021)
24. Higher order (> 3) reactions are rare due to
 (a) shifting of equilibrium towards reactants due to elastic collisions
 (b) loss of active species on collision
 (c) low probability of simultaneous collision of all reacting species
 (d) increase in entropy as more molecules are involved. (2021)
25. A first order reaction is half completed in 45 min. How long it need 99.9% of the reaction to be completed?
 (a) 10 hours (b) 20 hours
 (c) 5 hours (d) 7.5 hours (2022)
26. The rate of the reaction:
 $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$
 is given by the equation
 $\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{NaOH}]$
 If concentration is expressed in mol L^{-1} , the unit of k is
 (a) $\text{L mol}^{-1} \text{ s}^{-1}$ (b) s^{-1}
 (c) $\text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ (d) $\text{mol L}^{-1} \text{ s}^{-1}$ (2022)
27. For n^{th} order of reaction, half-life period is directly proportional to
 (a) a^{n-1} (b) a^{1-n}
 (c) $\frac{1}{a^{n-1}}$ (d) $\frac{1}{a^{1-n}}$ (2022)
28. Half-life of a reaction is found to be inversely proportional to the fifth power of its initial concentration, the order of reaction is
 (a) 5 (b) 6 (c) 3 (d) 4 (2022)
29. In which one of the following reactions, rate constant has the unit $\text{mol L}^{-1} \text{ s}^{-1}$?
 (a) Acid catalysed hydrolysis of $\text{CH}_3\text{COOCH}_3$
 (b) $\text{CHCl}_3 + \text{Cl}_2 \longrightarrow \text{CCl}_4 + \text{HCl}$
 (c) $2\text{NO}_{(g)} + \text{O}_{2(g)} \longrightarrow 2\text{NO}_{2(g)}$
 (d) Decomposition of HI on the surface of gold (2023)
30. For a reaction, the value of rate constant at 300 K is $6.0 \times 10^5 \text{ s}^{-1}$. The value of Arrhenius factor A at infinitely high temperature is
 (a) $6 \times 10^5 \times e^{-E_a/300R}$ (b) $e^{-E_a/300R}$
 (c) $\frac{6 \times 10^5}{300}$ (d) 6×10^5 (2023)
31. The rate constants k_1 and k_2 for two different reactions are $10^{16} \times e^{-2000/T}$ and $10^{15} \times e^{-1000/T}$ respectively. The temperature at which $k_1 = k_2$ is
 (a) $\frac{2000}{2.303} \text{ K}$ (b) 2000 K
 (c) $\frac{1000}{2.303} \text{ K}$ (d) 1000 K (2023)

Hints & Explanations

Self Test - 1

- (b)
- (c) : $-\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt}$
 $\frac{d[\text{N}_2\text{O}_5]}{dt} = -\frac{2}{4} \times 0.0072 = -0.0036 \text{ mol L}^{-1} \text{ s}^{-1}$
- (c) : For this reaction,

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

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

$$\Rightarrow -\frac{d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$$
- (d) : The rate of disappearance of SO_2 and the rate of formation of SO_3 are same.
- (d) : $\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$ or $-\frac{d[\text{H}_2]}{dt} = \frac{3}{2} \times \frac{d[\text{NH}_3]}{dt}$

Self Test - 2

- (b)
- (c) : $t_{1/2} \propto [A_0]$ for zero order reaction
 If A_0 becomes $\left[\frac{1}{4} A_0\right]$ then, $t_{1/2}$ also becomes $\left(\frac{1}{4}\right)^{\text{th}}$.
- (a) : Greater the value of k , faster is the reaction.
- (a) : $2A \rightarrow A_2$
 Rate of formation of dimer = $k[A]^2$

$$k = \frac{\text{Rate of formation of dimer}}{[A]^2}$$

$$k = \frac{9.1 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.01 \text{ mol L}^{-1})^2} = 9.1 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$$
- (a) : For second order, rate constant

$$= \frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{ L s}^{-1}$$
 For first order, rate constant = $\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{\text{mol L}^{-1}} = \text{s}^{-1}$
- (c) : Rate = $k [\text{concentration}]^n$
 if $[\text{concentration}]^n = 1$, rate = k
- (d) : $2\text{H}_2\text{S} + \text{O}_2 \longrightarrow \text{Product}$
 Rate = $k p_{\text{H}_2\text{S}}^2 \times p_{\text{O}_2} = x$
 On increasing the pressure three fold
 Rate = $k (3p_{\text{H}_2\text{S}})^2 \times 3p_{\text{O}_2}$

$$= k \times 9 p_{\text{H}_2\text{S}}^2 \times 3p_{\text{O}_2}$$

$$= k \times 27 \times p_{\text{H}_2\text{S}}^2 \times p_{\text{O}_2} = 27x$$
 Hence, rate will increase 27 times.

- (a) : $X + Y \rightarrow Z$
 Rate $\propto [X]$; hence order of reaction = 1
 Molecularity of reaction = 2

- (c) : For a second order reaction, $\frac{dx}{dt} = k[A]^2$
 $\frac{\text{conc.}}{\text{time}} = k[\text{conc.}]^2$
 $\frac{\text{mol L}^{-1}}{\text{s}} = k \text{ mol L}^{-1} \times \text{mol L}^{-1}$
 $k = \text{L mol}^{-1} \text{ s}^{-1}$

- (b) : Order of a reaction cannot be obtained from the balanced chemical equation of the reaction. It is an experimentally determined quantity.

Self Test - 3

- (c) : Given : $t = 40 \text{ min}$, $[X]_0 = 0.1 \text{ M}$, $[X] = 0.025 \text{ M}$

$$\therefore k = \frac{2.303}{t} \log \frac{0.1}{0.025}$$

$$= \frac{2.303}{40} \times \log 4 = \frac{2.303}{40} \times 2 \log 2$$

$$= \frac{2.303 \times 2 \times 0.3010}{40} = 0.03467 \text{ min}^{-1}$$

$$\therefore \text{Rate} = k [X]$$

$$= (0.03467 \times 0.01) \text{ M min}^{-1}$$

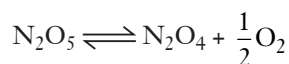
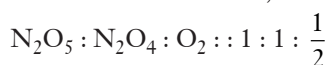
$$= 3.467 \times 10^{-4} \text{ M min}^{-1} \approx 3.47 \times 10^{-4} \text{ M min}^{-1}$$
- (a) : $[R] = [R_0] - kt$
 For completion of reaction, $[R] = 0$
 or $t = \frac{[R_0]}{k}$
- (c) : For n^{th} order reaction, $t_{1/2} \propto [A_0]^{1-n}$
 For 2nd order, $t_{1/2} \propto [A_0]^{-1}$ i.e., $t_{1/2} \propto \frac{1}{[A_0]}$.
- (c) : $r_1 = k[A]^1$, $r_2 = k[A]^2$, $r_3 = k[A]^3$
 If $[A] > 1 \text{ M}$; then $r_3 > r_2 > r_1$
- (a) : $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{480} = 1.44 \times 10^{-3} \text{ s}^{-1}$
- (a) : For zero order reaction, $t = \frac{1}{k} \{[A]_0 - [A]\}$
 When reaction is complete, $[A] = 0$
 Hence, $t = \frac{[A]_0}{k} = \frac{a}{k}$
- (a) : $t = \frac{2.303}{k} \log \frac{[R_0]}{[R]} = \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$

$$= 2.00 \times 10^3 \log 1.667 = 2 \times 10^3 \times 0.2219 = 444 \text{ s}$$
- (b) : $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10}$
 Amount left after n half-lives, $0.01 = \frac{0.08}{2^n}$

$$2^n = \frac{0.08}{0.01} = 8, n = 3$$

then, total time = $3 \times 10 = 30$ minutes.

9. (a) : As at the completion of reaction 35 mL of O_2 is formed, hence 70 mL of N_2O_5 is present initially as from the reaction we can see that,



Initial	70 mL	0	0
After 15 min.	70-18 mL	18 mL	9 mL

For first order reaction

$$k = \frac{1}{t} \ln \frac{a}{a-x} = \frac{1}{15} \ln \frac{70}{52} \quad \text{or} \quad \frac{1}{15} \ln \frac{35}{26}$$

10. (b)

Self Test - 4

1. (c) : ΔH° of the reaction is the difference of energy of products and reactants.

2. (d) : Increase in temperature increases the rate of both forward and backward reaction by equal factor to bring the equilibrium faster.

3. (a) : $E_f \neq E_r$

4. (c) : Activation energy can be same or different for forward and backward reaction.

5. (c) : The activation energy of a reaction can be determined by evaluating rate constant at two different temperatures by using the following expression :

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

6. (b) : Higher the activation energy, lower is the rate constant.

Self Test - 5

1. (a) : Lower the activation energy, faster is the reaction.

2. (c) : Not only sufficient threshold energy of colliding atoms or molecules but also the proper orientation for the collision is required for the formation of products.

KCET Connect

1. (c) : Rate of reaction \propto conc. of reactants

As the reaction proceeds, concentration of the reactants decreases hence the rate also keeps on decreasing with time.

2. (c)

$$3. (c) : \text{Average rate} = -\frac{\Delta[R]}{\Delta t} = -\frac{([R]_2 - [R]_1)}{t_2 - t_1}$$

$$= -\frac{(0.04 - 0.05)}{30} = \frac{0.01}{30} = 3.3 \times 10^{-4} \text{ M min}^{-1}$$

4. (a) : Concentration of reactants decreases with time.

$$5. (a) : \text{Rate of reaction} = \frac{\Delta[X]}{\Delta t}$$

$$\Delta[X] = X_i - X_f = 0.50 - 0.38 = 0.12 \text{ M}$$

$$\text{Rate} = \frac{0.12}{10 \times 60} = 2 \times 10^{-4} \text{ M s}^{-1}$$

$$6. (a) : \text{Average rate} = -\frac{1}{2} \frac{\Delta[R]}{\Delta t} = -\frac{1}{2} \times \frac{0.4 - 0.5}{10}$$

$$= \frac{1}{2} \times \frac{0.1}{10} = 5 \times 10^{-3} \text{ M min}^{-1}$$

$$7. (a) : \text{Rate} = -\frac{1}{2} \frac{\Delta[X]}{\Delta t}$$

$$= -\frac{1}{2} \frac{(3-2)}{5} = -0.1 \text{ mol L}^{-1} \text{ min}^{-1}$$

Negative sign signifies the decrease in concentration.

8. (b) : For the reaction $R \rightarrow P$

Average rate of reaction

$$= \frac{\text{Change in concentration of reactant}}{\text{Time taken}}$$

$$= \frac{-\Delta[R]}{t} = \frac{[R_2] - [R_1]}{t}$$

Where, change in concentration of reactant,

$$\Delta[R] \text{ or } [R_2] - [R_1] = [0.02 - 0.03]$$

Time, $t = 25$ min

$$= -\frac{(0.02 - 0.03) \text{ M}}{(25 \times 60) \text{ s}} = -\frac{(-0.01) \text{ M}}{(1500) \text{ s}}$$

$$= 6.66 \times 10^{-6} \text{ Ms}^{-1} \quad (\because \text{M} = \text{mol L}^{-1})$$

$$9. (a) : \text{Average rate} = -\frac{1}{2} \frac{\Delta[R]}{\Delta t} = -\frac{1}{2} \times \frac{0.4 - 0.7}{10}$$

$$= \frac{1}{2} \times \frac{0.3}{10} = 1.5 \times 10^{-2} \text{ M min}^{-1}$$

10. (b) : Average rate of decomposition of NO_2

$$= -\frac{\Delta[NO_2]}{\Delta t} = -\frac{3.0 \times 10^{-3} \text{ (M)} - 4.3 \times 10^{-3} \text{ (M)}}{300 \text{ (s)} - 200 \text{ (s)}}$$

$$= 1.3 \times 10^{-5} \text{ M/s}$$

$$11. (b) : \text{Rate} = -\frac{1}{2} \frac{d[X]}{dt} = -\frac{1}{3} \frac{d[Y]}{dt} = \frac{1}{4} \frac{d[Z]}{dt}$$

12. (c) : The rate of appearance of D is double the rate of disappearance of B .

$$13. (b) : \text{Rate} = \frac{1}{4} \frac{d[NO_2]}{dt} = \frac{1}{4} \times 0.0125 = 0.0031 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$14. (b) : -\frac{1}{2} \frac{d[A]}{dt}$$

$$15. (c) : \text{Rate} = -\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt}$$

$$16. (d) : \text{Rate of consumption of } F_2 \text{ at time } t = -\frac{d[F_2]}{dt}$$

$$\text{Rate of consumption of } ClO_2 \text{ at time } t = -\frac{d[ClO_2]}{dt}$$

$$\text{Rate of formation of } FClO_2 \text{ at time } t = \frac{d[FClO_2]}{dt}$$

$$\text{Rate of reaction at time } t = -\frac{d[\text{F}_2]}{dt} = -\frac{1}{2} \frac{d[\text{ClO}_2]}{dt} = \frac{1}{2} \frac{d[\text{FClO}_2]}{dt}$$

17. (a)

18. (a) : For the reaction, $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$

$$\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$$

$$-\frac{d[\text{NO}_2]}{dt} = 6 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{d[\text{O}_2]}{dt} = 3 \times 10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$$

19. (a) : $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$

Rate of formation or disappearance are related

$$\therefore -\frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{SO}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

$$-2.5 \times 10^{-4} = -\frac{1}{2} \frac{d[\text{SO}_2]}{dt}$$

$$\frac{d[\text{SO}_2]}{dt} = 5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$20. (a) : -\frac{1}{4} \frac{d[\text{NH}_3]}{dt} = +\frac{1}{6} \frac{d[\text{H}_2\text{O}]}{dt}$$

$$\frac{d[\text{H}_2\text{O}]}{dt} = \frac{6}{4} \times 3.6 \times 10^{-3} = 5.4 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

$$21. (b) : [\text{N}_2\text{O}_5] = \frac{\text{Rate}}{k} = \frac{1.02 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{3.4 \times 10^{-5} \text{ s}^{-1}} = 3 \text{ mol L}^{-1}$$

$$22. (c) : \frac{1}{5} \frac{d[\text{Fe}^{3+}]}{dt}$$

23. (b) : For $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, the rate of reaction can be expressed as

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

24. (b) : $2\text{N}_2\text{O}_4 \rightleftharpoons 4\text{NO}_2$

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_4]}{dt} = +\frac{1}{4} \frac{d[\text{NO}_2]}{dt}$$

$$\frac{1}{2} k = \frac{1}{4} k' \Rightarrow k' = 2k$$

25. (b) : Minus signs are for reactants and positive signs for product. Dividing numbers are the coefficients.

26. (b) : Rate of disappearance of $Q = \frac{1}{3} \times$ rate of appearance of R

27. (b) : According to law of mass action, rate of chemical reaction is proportional to molar concentration of reactants.

28. (a) : Only gaseous reactions depend upon pressure. Non-gaseous reactions have no effect of pressure.

29. (c) : Given : $A_2 + B + C \rightarrow AC + AB$

The rate law may be represented as,

$$\text{Rate} = k[A_2]^x[B]^y[C]^z$$

Let $[A_2]_1$, $[B]_1$ and $[C]_1$ represent initial concentrations and $[A_2]_2$, $[B]_2$ and $[C]_2$ represent final concentrations, and let R_1 and R_2 be initial and final rates of the reaction when the concentrations are changed.(i) If $[A_2]_2 = 3[A_2]_1$, $R_2 = 3R_1$

$$\frac{R_2}{R_1} = \frac{k[A_2]_2^x[B]_2^y[C]_2^z}{k[A_2]_1^x[B]_1^y[C]_1^z}$$

If the concentrations of B and C remain constant, then

$$\frac{R_2}{R_1} = \frac{(3[A_2]_1)^x}{[A_2]_1} = 3^x$$

$$\therefore \frac{3R_1}{R_1} = 3^x$$

$$\therefore 3 = 3^x \therefore x = 1$$

(ii) $[B]_2 = 2[B]_1$, $R_2 = R_1$ The concentrations of A and C remain constant.

$$\therefore \frac{R_2}{R_1} = \frac{[B]_2^y}{[B]_1^y} = \frac{(2[B]_1)^y}{[B]_1} = 2^y$$

$$\therefore 1 = 2^y \therefore y = 0$$

(iii) If $[C]_2 = 2[C]_1$, $R_2 = 2R_1$

$$\therefore \frac{R_2}{R_1} = \frac{[C]_2^z}{[C]_1^z} = \frac{(2[C]_1)^z}{[C]_1} = 2^z$$

$$\therefore \frac{2R_1}{R_1} = 2^z \therefore z = 1$$

Hence, the rate law is :

$$\text{Rate} = k[A_2]^x[B]^y[C]^z = k[A_2]^1[B]^0[C]^1 = k[A_2][C]$$

30. (d) : Rate = $k[A]^2[B]^3 = a$

When volume is reduced to one half then conc. of reactants will be doubled.

$$\text{Rate} = k[2A]^2[2B]^3 = 32k[A]^2[B]^3 = 32a$$

31. (b) : (Rate) $_1 = k[A]^x[B]^y$

$$(\text{Rate})_2 = k[A]^x[2B]^y$$

(Rate) $_2 = 2^y$ for an elementary process, the coefficient (Rate) $_1$ in front of the reactant is the order with respect to the reactant. $\therefore y = 2$.

$$\therefore (\text{Rate})_2 = (\text{Rate})_1 \times (2)^2 = 4 \times (\text{Rate})_1$$

 \therefore Rate should increase 4 times.32. (b) : Initially rate (r_1) = $k[X]^n$... (i)(let n be the order of reaction)

$$\text{Then, } r_1 \times 27 = k[3X]^n$$

... (ii)

Dividing eqn. (ii) by eqn. (i)

$$27 = [3]^n$$

$$\therefore n = 3$$

Thus, order of reaction is 3.

33. (d) : $2A + B + C \rightarrow$ Products

$$r_1 = k[A]^2[B]$$

 \therefore C is taken in excess, rate does not depend upon C

$$r_2 = k[2A]^2[3B]$$

$$\Rightarrow r_2 = 12k[A]^2[B]$$

$$\frac{r_2}{r_1} = \frac{12k[A]^2[B]}{k[A]^2[B]}$$

$$r_1 = k[A]^2[B]$$

$$\Rightarrow r_2 = 12r_1$$

34. (d) : Given $r_1 = k [A]^x [B]^y$... (i)

On reducing the original volume to half, the concentrations of reactants A and B will be doubled.

Let the new rate be r_2 . Then,

$$r_2 = k[2A]^x [2B]^y$$

$$\text{or } r_2 = k \times 4^x [A]^x [B]^y \quad [\because x = y = 1] \quad \dots \text{ (ii)}$$

or $r_2 = 4r_1$ The rate will become four times relative to the initial rate.

35. (c) : Given, $R_1 = k[A]^2 [B]$
According to question, $R_2 = k[3A]^2 [2B]$
 $= k \times 9 [A]^2 \times 2 [B]$

$$= 18 \times k [A]^2 [B] = 18 R_1$$

36. (a) : For second order, rate law is, $R = k [A]^2$

$$\therefore k = \frac{R}{[A]^2} = \frac{1.25 \times 10^{-2}}{(0.45)^2} = 6.173 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$$

37. (d) : Rate (r_1) = $k[\text{SO}_2]^2 [\text{O}_2]$ in 1 dm³ vessel
(Law of mass action)

In 2 dm³ vessel *i.e.*, double volume, concentration becomes half.

$$\text{Rate}(r_2) = k \left[\frac{1}{2} \text{SO}_2 \right]^2 \left[\frac{1}{2} \text{O}_2 \right] = \frac{1}{8} k [\text{SO}_2]^2 [\text{O}_2] = \frac{1}{8} r_1$$

$$r_1 = 8 r_2, \text{ i.e., } 8 : 1$$

38. (a) : Rate constant of a reaction depends on its temperature.

39. (a) : For the reaction, $A + B \longrightarrow$ products, the rate law is

$$\frac{dx}{dt} = r_1 = k[A][B]^2 \quad \dots \text{ (i)}$$

$$r_2 = k \left[\frac{1}{2} A \right] [2B]^2 \quad \dots \text{ (ii)}$$

$$\text{or } r_2 = k \frac{1}{2} \times 2^2 k[A][B]^2 \quad \dots \text{ (iii)}$$

Dividing (iii) by (i)

$$\frac{r_2}{r_1} = \frac{2k[A][B]^2}{k[A][B]^2} = 2 \quad (\because r_2 = 2r_1)$$

40. (d) : Rate = $k[\text{NOBr}]^2$
 $k = 1.62 \text{ M}^{-1} \text{ s}^{-1}$, $[\text{NOBr}] = 2.00 \times 10^{-3} \text{ M}$
Hence, rate = $1.62 (\text{M}^{-1} \text{ s}^{-1}) \times (2 \times 10^{-3})^2 (\text{M}^2)$
 $= 6.48 \times 10^{-6} \text{ M s}^{-1}$

41. (c) : $R \rightarrow P$

For a second order reaction, rate = $k[R]^2$
If conc. of R is increased by four times, rate = $k[4R]^2$
Hence the rate of formation of P increases by 16 times.

42. (b) : Rate (r_1) = $k[A]^2 [B]^{1/2}$

If $[A]$ is doubled and $[B]$ is increased four times,

$$\text{Rate} = k[2A]^2 [4B]^{1/2} = 4 \times 2k[A]^2 [B]^{1/2} = 8 r_1$$

43. (d)

44. (c) : $r = k [\text{H}_2]^n$... (i)

On doubling the concentration of H_2 ,
 $4r = k [2\text{H}_2]^n$ (ii)

On dividing equation (ii) by (i), we get,

$$4 = 2^n$$

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

$$\Rightarrow n = 2$$

45. (b) : $\frac{3}{2} - 1 = \frac{1}{2}$

46. (a) : Order of reaction with respect to A ,

$$\text{Rate } (r_1) \propto [A]^n$$

On doubling concentration of $[A]$,

$$\text{Rate } (r_2) = 2r_1 \propto [2A]^n$$

Thus, $n = 1$

Order of reaction with respect to B ,

$$\text{Rate } (r_1) \propto [B]^m$$

On increasing concentration of $[B]$ nine times,

$$\text{Rate } (r_2) = 3r_1 \propto [9B]^m$$

Thus, $n = 1/2$.

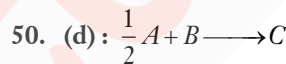
$$\text{Overall order of reaction} = 1 + \frac{1}{2} = 1 \frac{1}{2}$$

$$47. \text{ (b) : } \frac{d[\text{IO}^-]}{dt} = k \frac{[\text{I}^-][\text{OCl}^-]^2}{[\text{OH}^-]^2}$$

$$\text{Order of reaction} = 1 + 1 - 1 = 1$$

48. (b)

49. (b) : Zero order reaction is independent of concentration of reactant.



$$\text{Rate} = k[A]^{1/2} [B]^1$$

Order = 1.5

51. (d) : The rate law of the reaction is of the form,

$$\text{rate}_1 = k[A]^x [B]^y$$

If $[B]$ is doubled at constant $[A]$, the new rate law is

$$\text{rate}_2 = k[A]^x [2B]^y$$

$$\text{Hence, } \frac{\text{rate}_2}{\text{rate}_1} = \frac{k[A]^x [B]^y 2^y}{k[A]^x [B]^y} = 2^y$$

$$\text{But } \frac{\text{rate}_2}{\text{rate}_1} = 2 \text{ because rate}_2 \text{ is twice of rate}_1$$

Thus, $2 = 2^y$ and hence $y = 1$

If $[B]$ doubled and $[A]$ is tripled, the rate law becomes

$$\text{rate}_3 = k [3A]^x [2B]^y \text{ and } \text{rate}_3 = 6 \text{ rate}_1$$

$$\text{Therefore, } \frac{\text{rate}_3}{\text{rate}_1} = \frac{k \times 3^x [A]^x \times 2^y [B]^y}{k[A]^x [B]^y} = 3^x \times 2^y$$

$$\text{Now, because } \frac{\text{rate}_3}{\text{rate}_1} = 6 \text{ and } y = 1$$

$$6 = 2 \times 3^x \text{ or } 3 = 3^x \text{ and hence } x = 1.$$

It follows that the reaction is first order with respect to A and B each and second order overall.

52. (b) : $r = k[A][B]$

If B is in large excess then rate becomes independent of $[B]$ and will depend only on $[A]$.

$$r = k[A]$$

\therefore Order of reaction = 1

53. (b) : Mechanism of reaction as well as relative concentration of reactants decide that how many

concentration terms affect the rate of reaction *i.e.*, order of reaction.

54. (c) : The rate law for the reaction is of the form,

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

rate = 6×10^{-4} M/s, $k = 2 \times 10^{-3}$ s⁻¹, $[A] = [B] = 0.3$ M.
Hence, 6×10^{-4} (M/s) = 2×10^{-3} (s⁻¹) \times (0.3 M)^x (0.3 M)^y

$$\text{or } \frac{6 \times 10^{-4} (\text{M/s})}{2 \times 10^{-3} (\text{s}^{-1})} = (0.3)^{x+y} (\text{M}^{x+y})$$

$$\text{or } 0.3 (\text{M}) = (0.3)^{x+y} (\text{M})^{x+y}$$

It follows that $x + y = 1$. Hence, the overall order of the reaction is 1.

55. (b) : Rate = k [concentration]ⁿ

$$r_1 = 2.4 = k [2.2]^n \quad \dots(i)$$

$$r_2 = 0.6 = k \left[\frac{1}{2} \times 2.2 \right]^n \quad \dots(ii)$$

On solving equations (i) and (ii),
 $n = 2$, *i.e.*, 2nd order reaction.

56. (c) : Rate \propto [Conc.] \times $\frac{1}{[\text{Conc.}]}$

i.e., Rate \propto [Conc.]⁰. Hence, order = 0

57. (c) : From 1st reading,

$$\text{rate} = 10.0 \times 10^{-5} = k[0.003]^n \quad \dots(i)$$

(where, n is order of reaction)

From 2nd reading,

$$\text{rate} = 5.0 \times 10^{-5} = k[0.006]^n \quad \dots(ii)$$

Dividing eqn. (i) by (ii),

$$\frac{10.0 \times 10^{-5}}{5.0 \times 10^{-5}} = \frac{k[0.003]^n}{k[0.006]^n}$$

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

$$58. (d) : \frac{1}{2} + \frac{1}{3} + 1 = \frac{11}{6}$$

59. (c) : For second order kinetics,

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

so make two equation first by taking initial rate and concentration, second by taking tripled concentration and unknown rate (r'). Compare them to find a relation between r and r' .

For the reaction, $x \longrightarrow y$

$$\text{Reaction rate } (r) = k [x]^2 \quad \dots (i)$$

If the concentration of x is increased three times, then

$$\text{Reaction rate } (r') = k [x]^2 = k \times [3x]^2 \quad \dots (ii)$$

On dividing equation (ii), we get

$$\frac{r'}{r} = \frac{k \times [9x^2]}{k \times [x^2]} = 9$$

It means that the rate of formation of y will increase by nine times.

60. (b) : In terms of pressure,

$$\text{Rate} = k (p_{\text{CH}_3\text{COCH}_3})^{3/2}$$

$$\text{Units of rate} = \text{bar min}^{-1}$$

$$\begin{aligned} \text{Units of rate constant} &= \frac{\text{rate}}{(p_{\text{CH}_3\text{COCH}_3})^{3/2}} \\ &= \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2} \text{ min}^{-1} \end{aligned}$$

61. (d)

62. (c) : Unit of rate constant for the reaction is

$$k = \frac{\text{rate}}{[\text{H}_2][\text{NO}]^2} = \frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})^2} = \text{mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

63. (a) : Molecularity of the reaction $A + 2B \longrightarrow P$, is $1 + 2 = 3$, as one molecule of reactant A and two molecules of reactant B collide with each other.

64. (d)

65. (d)

66. (a) : Slowest step is the rate determining step.

67. (b)

68. (b) : The slowest step of the reaction is rate determining step.



$$\text{Rate of reaction} = k[\text{N}_2\text{O}_2][\text{H}_2]$$

Hence, order of reaction = 2

69. (b) : The intermediate species is one which is formed and used up during the course of reaction.

70. (a) : Slow step is the rate determining step of the reaction. Only in step (ii), the reactant 'C' is involved in the slow step of the reaction.

71. (c) : $x = k \times t$

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

Time for completion of reaction (when $x = a$), *i.e.*, $t = \frac{a}{k}$

72. (c) : Rate of a zero order reaction is independent of the concentration of reactants.

73. (c) : The study of the data shows that the rate of reaction does not vary with time. It is characteristic of a zero order reaction.

74. (b) : For zero order reaction integrated rate equation is

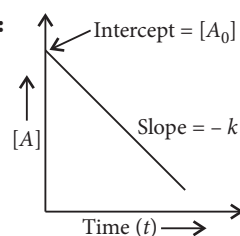
$$k = \frac{c_0 - c_t}{t}$$

75. (a) : For a zero order reaction, rate = $k = \frac{dx}{dt}$

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

76. (c)

77. (d) :



78. (b) : For two-third of a reaction,

$$[A]_0 = a, [A]_t = \frac{a}{3}$$

$$t_{2/3} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t}$$

$$= \frac{2.303}{k} \log \frac{a}{\frac{a}{3}} = \frac{2.303}{k} \log 3$$

$$t_{2/3} = \frac{2.303 \times 0.4771}{5.48 \times 10^{-14}} = 2.01 \times 10^{13} \text{ s}$$

79. (d) : First order rate constant

$$k = \frac{2.303}{t} \log \frac{a}{a-x}; a = 1; a-x = 1/8$$

$$k = \frac{2.303}{24} \log \left(\frac{1}{1/8} \right) \text{ min}^{-1}$$

$$\text{or } k = \frac{2.303}{24} \log \left(\frac{8}{1} \right) \text{ min}^{-1}$$

80. (b) : In case of first order reaction rate constant
(k) = sec⁻¹

$$81. (c) : t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$\text{If } t = t_{1/4}; x = a/4$$

$$\therefore t_{1/4} = \frac{2.303}{k} \log \frac{a}{(a-a/4)} = \frac{2.303}{k} \log \frac{4}{3}$$

$$82. (b) : k = \frac{2.303}{(t_2 - t_1)} \log \frac{[A_1]}{[A_2]}$$

$$k = \frac{2.303}{(1600 - 800)} \log \frac{1.45}{0.88} = \frac{2.303}{800} \times 0.2169$$

$$= 6.24 \times 10^{-4} \text{ s}^{-1}$$

83. (c) : For a 1st order reaction, rate \propto conc.

$$84. (c) : t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$\text{for } \frac{3}{4} \text{ th life, } x = \frac{3a}{4}$$

$$t_{3/4} = \frac{2.303}{k} \log \frac{a}{a-3a/4} = \frac{2.303}{k} \log 4.$$

85. (b) : In case of first order reaction, rate constant, $k = \text{s}^{-1}$.

$$86. (c) : k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$t = 8 \text{ minutes } 20 \text{ seconds} = 8 \times 60 + 20 = 500 \text{ seconds}$$

$$a = \frac{1}{10} \text{ M}$$

$$(a-x) = \frac{1}{100} \text{ M}$$

$$k = \frac{2.303}{500} \log \frac{1/10}{1/100} = 4.606 \times 10^{-3} \text{ sec}^{-1}$$

$$87. (d) : k = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

$$88. (c) : k = \frac{2.303}{60 \text{ min}} \log \frac{a}{a-0.6a} = \frac{2.303}{60} \log \frac{1}{0.4}$$

$$= 0.0153 \text{ min}^{-1}$$

$$\text{For } 50\% \text{ completion, } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0153 \text{ min}^{-1}}$$

$$= 45.3 \text{ min} = 45 \text{ min}$$

89. (a) : As $t_{75\%} = 2 \times t_{50\%}$, the order of the reaction is one.

$$90. (a) : \text{In case I, fraction of } A \text{ reacted} = \frac{0.6}{0.8} = \frac{3}{4}$$

$$\text{In case II, fraction of } A \text{ reacted} = \frac{0.675}{0.9} = \frac{3}{4}$$

For a first order reaction, time taken for the same fraction of reaction is independent of initial concentration.

91. (b) : Given, $a = 100$, $x = 80$, when $t = 10$ min.

Substituting these values in the first order rate equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x}, \text{ we get}$$

$$k = \frac{2.303}{10 \times 60} \log \frac{100}{100-80}$$

$$= \frac{2.303}{10 \times 60} \log 5 = \frac{2.303}{600} \times 0.6989$$

$$k = 0.00268 \text{ s}^{-1} \approx 0.0027 \text{ s}^{-1}$$

$$92. (a) : t = \frac{2.303}{k} \log \frac{a}{a-x}$$

$$\text{or } t = \frac{2.303}{15 \times 10^{-3}} \log \frac{5}{3} = 34.07 \text{ s}$$

93. (b) : For 60% completion, $a = 100$ and $a-x = 40$ and time, $t = 60$ min

$$\therefore k = \frac{2.303}{60} \log \frac{100}{40} = \frac{2.303}{60} \log 2.5 = 0.0153$$

$$t_{30\%} = \frac{2.303}{0.0153} \log \frac{100}{70} = 23.3 \text{ minutes}$$

$$94. (b) : k = \frac{2.303}{1.386 \times 60 \times 60} \log \frac{100}{100-75}$$

$$= \frac{2.303}{1.386 \times 3600} \log 4 = 2.7 \times 10^{-4} \text{ sec}^{-1}.$$

(Time 1.386 hours need to be changed to seconds)

95. (c) : For first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{200} \log \frac{400}{25}$$

$$= \frac{2.303}{200} \times 1.204 = 0.01386 \text{ s}^{-1} = 1.386 \times 10^{-2} \text{ s}^{-1}$$

96. (b) : Amount of substance left after n half lives = $\frac{[A]_0}{2^n}$
Number of half lives = 4

[12 days = 4 half lives if $t_{1/2} = 3$ days]

$$\therefore [A]_0 = 3 \times 2^n = 3 \times 2^4 = 48 \text{ g}$$

$$97. (c) : a-x = \frac{80}{100} \times a = 0.8a, t = 10 \text{ min}$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{10} \log \frac{a}{0.8a}$$

$$k = 0.2303 \log \frac{10}{8} = 0.2303(1-0.9030)$$

$$= 0.2303 \times 0.0970 = 0.0223 \text{ min}^{-1}$$

98. (c) : 3/4 or 75% completion from 100 \rightarrow 50 \rightarrow 25 in 2 hours. Time means $t_{1/2} = 1$ hour.

$$k = \frac{0.693}{1} \text{ hour}^{-1}$$

After 3 more hours total time will be 5 hours.

$$5 = \frac{2.303}{0.693} \log \frac{100}{x}$$

$$\text{or } \log \frac{100}{x} = \frac{5 \times 0.693}{2.303}; x \Rightarrow 3.16 \approx 3\%$$

$$99. \text{ (a) : } t = \frac{2.303}{k} \log \frac{R_0}{R} = \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$$

$$= 2.00 \times 10^3 \log 1.667 = 2 \times 10^3 \times 0.2219 = 444 \text{ s}$$

100. (b) : For initial concentration to reduce to $\frac{1}{8}$, no. of half lives = 3.

$$101. \text{ (b) : } k = -\frac{1}{t} \ln \frac{[A]_t}{[A]_0}$$

102. (b) : $t_{50\%} = 2$ hours, $t_{75\%} = 4$ hours

if 1st order then, $t_{75\%} = 2 \times t_{50\%}$

$4 = 2 \times 2$, hence, 1st order reaction.

103. (d) : For a first order reaction

$$\frac{k.t}{2.303} = \log[C]_0 - \log[C]$$

$$\text{or, } \log[C] = \log[C]_0 - \frac{k.t}{2.303}$$

Plot of $\log [C]$ vs t is a straight line with negative slope.

Hence, $\log [C]$ decreases linearly with ' t '.

104. (d) : A radioactive disintegration reaction is always of 1st order. $[A]_0 = 10[A]$; $t_{1/2} = 30$ days

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{30}$$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} = \frac{2.303}{0.693} \times 30 \times \log \frac{10[A]}{[A]}$$

$$= 99.7 \approx 100 \text{ days}$$

$$105. \text{ (a) : Number of half-lives} = \frac{18}{3} = 6$$

$$\text{Amount left after } n \text{ half-lives} = \frac{[A_0]}{2^n}$$

$$\text{Thus, amount left} = \frac{300}{2^6} = 4.6 \text{ g.}$$

106. (d) : Given $t_{1/2} = 120$ min

$$\therefore k = \frac{0.693}{120} \text{ min}^{-1}$$

Now for 90% completion

$$k = \frac{2.303}{t} \log \frac{a}{0.1a} = \frac{2.303}{t}$$

Comparing (i) and (ii)

$$\frac{0.693}{120} = \frac{2.303}{t}$$

$$t = \left[\frac{2.303 \times 120}{0.693} \right] \text{ min} = 398.78 \text{ min} \approx 400 \text{ min.}$$

107. (b) : Where, $k = \text{rate constant} = 10^{-3} \text{ s}^{-1}$

$a = \text{initial amount} = 100$

$a - x = \text{amount left after time } t = 25$

$t = \text{time to leave } 25\% \text{ reaction}$

$$\therefore t = \frac{2.303}{10^{-3}} \log \frac{100}{25} = \frac{2.303}{10^{-3}} \log 4$$

$$\frac{2.303 \times 0.6020}{10^{-3}} = 1386 \text{ s}$$

$$108. \text{ (a) : } t = \frac{2.303}{k} \log 16$$

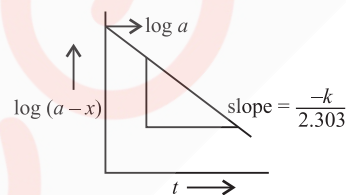
$$\Rightarrow t = \frac{2.303}{60} \times 1.204 = 0.046 \text{ s}$$

109. (b)

110. (d)

111. (d) : Slope of the graph $\ln [A]_t$ vs t will be equal to $-k$ hence, the value of rate constant is $2.5 \times 10^{-3} \text{ s}^{-1}$

112. (b) : First order reaction gives a straight line plot of $\log (a - x)$ and time.



113. (c)

114. (b)

115. (c) : For flask I

$$k = \frac{2.303}{8} \log \frac{1}{0.25} = \frac{2.303}{8} \log 4 = \frac{2.303}{8} \times 0.6021$$

For flask II

$$t = \frac{2.303}{k} \log \frac{0.6}{0.3} = \frac{2.303 \times 8}{2.303 \times 0.6021} \times 0.3010 = 4 \text{ hours}$$

Alternatively,

From concentration 0.6 M to 0.3 M it means $t_{1/2}$ has been asked. Then

$$t_{1/2} = \frac{0.693 \times 8}{2.303 \times 0.6021} = 4 \text{ hours.}$$

$$116. \text{ (a) : For zero order reaction, } t_{1/2} = \frac{[A]_0}{2k}$$

117. (c)

118. (b) : For zero order reaction, $t_{1/2} \propto a$.

119. (b)

$$120. \text{ (c) : } 100 \xrightarrow{\frac{t_{1/2}}{2} \text{ hr}} 50 \xrightarrow{\frac{t_{1/2}}{2} \text{ hr}} 25, \text{ Thus } t_{1/2} = 1/2 \text{ hr}$$

$$\dots \text{ (ii) } 121. \text{ (a) : } k = \frac{0.693}{t_{1/2}} = \frac{0.693}{60}$$

Time taken for 80% reaction to occur

$$t = \frac{2.303}{k} \log \frac{a}{a-x} = \frac{2.303 \times 60}{0.693} \log \frac{100}{100-80}$$

$$= \frac{2.303 \times 60}{0.693} \log 5 = 139.39 \text{ minutes}$$

$$122. (b) : k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10}$$

$$t = \frac{2.303}{k} \log \frac{0.08}{0.01} = \frac{2.303 \times 10}{0.693} \log 8 = 30 \text{ minutes}$$

Alternatively,

$$\text{Amount left after } n \text{ half-lives, } 0.01 = \frac{0.08}{2^n}$$

$$2^n = \frac{0.08}{0.01} = 8$$

$$n = 3$$

Then, total time = $3 \times 10 = 30$ minutes

$$123. (c) : t_{90.9\%} = 10 \text{ half lives.}$$

$$124. (d) : \text{Half-lives} = n = \frac{1}{t_{1/2}} = \frac{1 \text{ hr}}{15 \text{ min}} = \frac{60}{15} = 4$$

$$\text{Amount left after } n \text{ half lives} = \frac{[A]_0}{2^n} = \frac{[A]_0}{2^4} = \frac{[A]_0}{16}$$

125. (a) : Half-life of a first order reaction does not depend upon initial concentration.

126. (d) : Rate = $k[\text{concentration}]^n$

$$k = \frac{2.0 \times 10^{-5}}{0.01} = 2 \times 10^{-3} \text{ sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2 \times 10^{-3}} = 347 \text{ seconds}$$

$$127. (b) : t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.3 \times 10^{-2}}$$

$$= 53.30 \text{ minutes} = 3198.46 \text{ s} \approx 3200 \text{ s}$$

128. (a) : For n^{th} order reaction,

$$t_{1/2} \propto \frac{1}{a^{(n-1)}} \text{ where } n = \text{order of reaction.}$$

$$i.e. \text{ If } n = 1, t_{1/2} \propto \frac{1}{a^{1-1}} \Rightarrow t_{1/2} \propto \frac{1}{a^0}$$

i.e. independent of initial concentration.

$$\text{For first order reaction, } t_{1/2} = \frac{0.693}{k}.$$

129. (b) : As it is a reaction of 1st order, $t_{1/2}$ does not depend

$$\text{upon initial conc. as } t_{1/2} = \frac{0.693}{k}$$

$$130. (c) : \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\frac{0.693}{10} = \frac{2.303}{100} \log \frac{100}{100-x} \Rightarrow x = 99.9 \%$$

131. (c) : Rate = $k[\text{concentration}]$

$$k = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^{-2}} = 23.1 \text{ minutes}$$

$$132. (a) : 1 \xrightarrow[20 \text{ min}]{t_{1/2}} \frac{1}{2} \xrightarrow[20 \text{ min}]{t_{1/2}} \frac{1}{4}$$

$$133. (b) : \frac{dx}{dt} = k[X] \text{ (For a first order reaction)}$$

$$0.00352 = k \times 0.01 \Rightarrow k = 0.352$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.352} = 1.969 \text{ min.}$$

134. (c) : For first order reaction, half life is independent of concentration.

135. (d) : Let $a = 1, a - x = 1/8, t = 75$ min.

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

For first order reaction,

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693 \times 75}{2.303 \times 0.903} = 24.99 \approx 25 \text{ min.}$$

$$136. (a) : k = \frac{0.693}{t_{1/2}} \text{ and } k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\text{So, } \frac{0.693}{140} = \frac{2.303}{t} \log \frac{1.28}{0.128} \Rightarrow t = 465 \text{ s}$$

$$137. (d) : \frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\frac{0.693}{10} = \frac{2.303}{20} \log \frac{100}{100-x} \Rightarrow x = 75\%$$

138. (a) : 30% decomposition means $X = 30\%$ of R_0
or $R = R_0 - 0.3R_0 = 0.7R_0$

$$\text{For first order, } k = \frac{2.303}{t} \log \frac{R_0}{R}$$

$$= \frac{2.303}{40} \log \frac{10}{7} \text{ min}^{-1} = 8.918 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3} \text{ min}^{-1}} = 77.7 \text{ min}$$

$$139. (b) : t_{1/2} = \frac{0.693}{k} = \frac{0.693}{2 \times 10^{-2}} = 34.65 \text{ min}$$

$$140. (b) : t_{1/2} = \frac{0.693}{k} = \frac{0.693}{200} = 3.46 \times 10^{-3} \text{ s}$$

141. (c) : For a 1st order kinetics,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

$$\text{At } t_{1/2}, k = \frac{2.303}{t_{1/2}} \log_{10} \frac{a}{a-\frac{a}{2}}$$

$$\text{or } t_{1/2} = \frac{2.303}{k} \log_{10} 2 = \frac{\ln 2}{k}$$

$$142. (a) : t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.2 \times 10^{-4}} = 1117.2 \text{ seconds.}$$

143. (a) : $t_{1/2}$ for first order reaction is independent of initial concentration $\therefore t_{1/2} \propto a_0^0$.

144. (a)

145. (c) : Inversion of cane sugar is a particular example of pseudo-unimolecular reaction.

146. (c) : When one of the reactants is in excess the reaction behaves as a first order reaction.

147. (b) : Average rate during the time interval 30-60 s.

$$\text{Rate} = -\frac{C_2 - C_1}{t_2 - t_1} = -\frac{(0.17 - 0.31)}{60 - 30} = \frac{0.14}{30}$$

$$= 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

148. (a)

149. (a) : For every 10° rise in temperature rate of reaction double.

$\therefore 30^\circ$ rise in temperature means $2 \times 2 \times 2 = 8$ times rate.

$$\frac{r_{\text{new}}}{r_{\text{old}}} = 8$$

$$\text{New rate} = 2.6 \times 10^{-3} \times 8 = 20.8 \times 10^{-3}$$

$$= 2.08 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$$

150. (b) : Arrhenius equation gives a quantitative idea about effect of temperature on reaction rates.

151. (b) : Rise of temperature = $100 - 10 = 90^\circ\text{C}$ i.e. 9×10 .
For $n \times 10^\circ$ increase of temperature rate increases 2^n times.
Thus, increase in rate = $2^9 = 512$.

152. (d) : Rate \propto rate constant

153. (c) : For every 10°C rise of temperature rate constant becomes double. Thus for 20°C rise (280 K to 300 K) rate constant becomes four times.

$$\text{i.e. } k_1 = 4k_2 \text{ or } k_2 = \frac{1}{4}k_1 = 0.25 k_1$$

154. (d) : We have, the Arrhenius equation,

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

k becomes least when T is low and E_a is high.

155. (c) : Activation energy is always positive.

156. (d)

$$157. (c) : \Delta H = E_f - E_b$$

$$-200 = 80 - E_b$$

$$E_b = 200 + 80 = 280 \text{ kJ/mol}$$

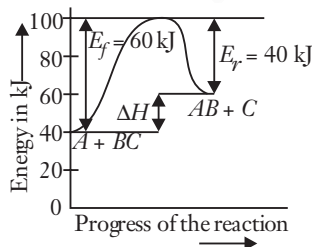
158. (b) : Activation energy of reverse reaction
= $E_{a(f)} - (\Delta H) = 80 \text{ kJ/mol} - (-20 \text{ kJ/mol})$
= $(80 + 20) \text{ kJ/mol} = 100 \text{ kJ/mol}$

159. (d) : For endothermic reaction, the minimum amount of activation energy will be more than ΔH .

160. (c) : Activation energy is the extra energy that the reactants must acquire in order to give products, on collisions.

161. (c) : Activation energy can be same or different for both forward and backward reactions.

162. (d) :



From this energy profile it is clear that :

Threshold energy of the reaction = 100 kJ; average energy of reactants = 40 kJ.

Energy of activation of forward reaction,

$$E_f = 100 - 40 = 60 \text{ kJ}$$

Heat of reaction,

$$\Delta H = \text{Energy of products} - \text{Energy of reactants}$$

$$= 60 - 40 = 20 \text{ kJ (Endothermic reaction)}$$

Energy of activation of reverse reaction,

$$E_r = \text{Threshold energy} - \text{Average energy of products}$$

$$= 100 - 60 = 40 \text{ kJ.}$$

163. (a)

164. (a) : cannot be predicted

165. (d)

$$166. (b) : E_{a(\text{forward})} + \Delta E = E_{a(\text{reverse})}$$

$$17 + 40 = E_{a(\text{reverse})}$$

$$E_{a(\text{reverse})} = 57 \text{ kJ}$$

$$167. (b) : k = Ae^{-E_a/RT} \text{ As } T \longrightarrow \infty$$

$$k = A = 6.0 \times 10^{14} \text{ s}^{-1}$$

$$168. (a) : \Delta H = E_a - E_a^r \therefore +5 = 15 - E_a^r \therefore E_a^r = 10$$

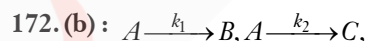
169. (d) : Activation energy (E_a) of backward reaction for an exothermic reaction.

$$= E_a \text{ of forward reaction} + \text{heat of reaction}$$

$$= X + Y.$$

170. (d) : Increase in temperature increases the rate of both forward and backward reactions by equal factor to bring the equilibrium faster.

171. (a)



By Arrhenius equation

$$k_1 = Ae^{-E_{a1}/RT}$$

$$\text{and } k_2 = Ae^{-E_{a2}/RT} \text{ (A is Arrhenius constant)}$$

$$\text{(Given, } E_{a2} = 2E_{a1}\text{)}$$

$$\therefore k_2 = Ae^{-2E_{a1}/RT}$$

$$\frac{k_1}{k_2} = \frac{Ae^{-E_{a1}/RT}}{Ae^{-2E_{a1}/RT}} = e^{2E_{a1}/RT}$$

$$\therefore k_1 = k_2 e^{2E_{a1}/RT}$$

173. (d)

174. (c) : A catalyst lowers the activation energy.

175. (b) : According to Arrhenius equation

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \times \frac{T_2 - T_1}{T_1 T_2}$$

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{(60000 \text{ J mol}^{-1})}{2.303 \times (8.314 \text{ J mol}^{-1})} \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$\log 3.333 = 3133.62 \left(\frac{T_2 - 283}{283 T_2} \right)$$

$$T_2 = 297.19 \text{ K} = (297.19 - 273.0) = 24.19^\circ\text{C}$$

$$\text{Temperature} = 24.19^\circ\text{C}$$

176. (a) : ΔH° is the difference in energy of reactants and products.

Activation energy is the minimum energy of a reaction at which activated complex is formed.

177. (a) : According to Arrhenius equation rate constant decreases with increasing E_a .

178. (b)

$$179. (d) : k = 2.1 \times 10^{10} e^{-2700/RT}$$

$$\ln k = \ln 2.1 \times 10^{10} + \ln e^{-2700/RT}$$

$$\ln k = \ln 2.1 \times 10^{10} - \frac{2700}{RT}$$

$$\log k = \log 2.1 \times 10^{10} - \frac{2700}{2.303RT}$$

$$\log k = -\frac{2700}{2.303R} \frac{1}{T} + \log 2.1 \times 10^{10}$$

On comparing it with straight line equation $y = mx + c$, we get

$$\therefore m \text{ (slope)} = -\frac{2700}{2.303R}$$

$$\text{and } C = \log 2.1 \times 10^{10}$$

180. (b)

$$181. (d) : \text{Slope} = \frac{-E_a}{2.303R}$$

$$\Rightarrow -1 \times 10^3 = \frac{-E_a}{2.303R}$$

$$\Rightarrow E_a = 2.303 \times 8.314 \times 10^3 = 19.1 \text{ kJ mol}^{-1}$$

182. (b)

$$183. (a) : \text{slope} = -\frac{E_a}{2.303R}$$

$$-5.64 = -\frac{E_a}{2.303R}$$

$$\therefore E_a = 5.64 \times 2.303 \times 8.314$$

$$= 107.9898 \approx 108 \text{ J mol}^{-1}$$

$$184. (d) : k = 1.2 \times 10^{14} e^{-25000/RT} \text{ s}^{-1}$$

$$\log k = \log(1.2 \times 10^{14}) - \frac{25000}{RT}$$

$$\text{slope} = -\frac{25000}{R}$$

$$185. (a) : \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log 2 = \frac{E_a}{2.303 \times 2} \left[\frac{300 - 290}{290 \times 300} \right]$$

$$(k_2 = 2k_1, R = 2 \text{ cal/K/mole})$$

$$E_a = 12062 \text{ calories} \approx 12 \text{ kcal.}$$

$$186. (a) : \log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \times \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\log \left(\frac{6.90 \times 10^{-3}}{3.45 \times 10^{-5}} \right) = \frac{E_a}{2.303 \times 8.314} \times \frac{40}{300 \times 340}$$

$$\therefore E_a = \frac{2.303 \times 8.314 \times 300 \times 340 \times \log 200}{40} = 112.34 \text{ kJ}$$

$$187. (c) : \log_{10} \frac{k_2}{k_1} = \frac{E_a(T_2 - T_1)}{2.303 R \times T_1 \times T_2}$$

188. (a) : A catalyst brings down the energy of activation.

189. (c) : Energy of activation is lowered when a catalyst is used.

190. (d) : The equilibrium is attained faster in case of reaction in which catalyst is used as it lowers the activation energy.

191. (c)

192. (d)

193. (a)

194. (c)

195. (d) : Only those collisions in which molecules collide to get sufficient energy, called threshold energy and proper orientation are effective collisions. Rest of the molecules collide and bounce back.

196. (c) : E_a is activation energy. Lower activation energy favours the reaction.

197. (a) : For backward reaction, activation energy is from product to activated complex.

198. (c) : Collision theory is applicable to bimolecular reactions only because three or more molecules can't collide effectively.

199. (b) : Apart from energy considerations, the colliding molecules should have proper orientation for effective collisions.

200. (b)

201. (d) : The increase in collision frequency brings an increase in effective collisions and thus rate of reaction increases.

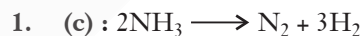
202. (a) : Lowering of E_a , raises the value of k .

203. (c)

204. (c)

205. (c) : More is the number of effective collisions more will be reaction rate.

KCET Ready



$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\frac{1}{2} k_1 [\text{NH}_3] = k_2 [\text{NH}_3] = \frac{1}{3} k_3 [\text{NH}_3]$$

$$1.5k_1 = 3k_2 = k_3$$

2. (b)

3. (a) : 30% decomposition means $X = 30\%$ of R_0

$$\text{or } R = R_0 - 0.3R_0 = 0.7R_0$$

$$\text{For first order, } k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

$$= \frac{2.303}{40} \log \frac{10}{7} \text{ min}^{-1} = 8.918 \times 10^{-3} \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3} \text{ min}^{-1}} = 77.7 \text{ min}$$

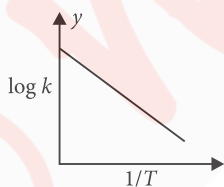


$$\text{Rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_4]}{dt} = +\frac{1}{4} \frac{d[\text{NO}_2]}{dt} \text{ or } \frac{1}{2} k = \frac{1}{4} k'$$

$$\text{or } k' = 2k$$

$$5. (b) : k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

($a-x$) is the concentration left after 100 sec.



$$2.714 \times 10^{-3} = \frac{2.303}{100} \log \frac{0.29}{(a-x)}$$

$$\Rightarrow \frac{0.27}{2.303} = \log \frac{0.29}{(a-x)} \Rightarrow 0.117 = \log \frac{0.29}{(a-x)}$$

$$\Rightarrow (a-x) = 0.22 \text{ M}$$

$$6. \text{ (d): } k = \frac{1}{t} \ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

$$kt = \ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]_t}$$

7. (a): For the reaction $2A + 3B \longrightarrow \text{Products}$;

$$-\frac{1}{2} \frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt}$$

$$\text{Given: } -\frac{d[A]}{dt} = r_1; -\frac{d[B]}{dt} = r_2$$

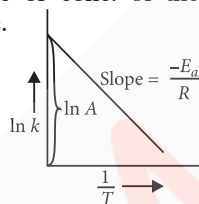
$$\text{or } \frac{1}{2} r_1 = \frac{1}{3} r_2 \text{ or } 3r_1 = 2r_2$$

8. (c): For first order, partial pressure or conc. of the reactant decreases exponentially with time.

9. (a): Arrhenius equation, $k = Ae^{-E_a/RT}$

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

This equation is of the form, $y = mx + c$,
i.e., the equation of a straight line.



10. (c): First step is slow (require large activation energy) second step is fast (less activation energy) and overall reaction is exothermic. So, product energy level should be less as compared to reactants.

11. (b): As $k' > k''$.

Greater the rate constant, lesser is the activation energy.

$$\therefore E'_a < E''_a$$

$$12. \text{ (c): } k_1 = Ae^{-E_a/RT}$$

$$k_2 = Ae^{-[E_a-2]/RT}$$

$$\frac{k_2}{k_1} = \frac{e^{-\frac{[E_a-2]}{RT}}}{e^{-\frac{E_a}{RT}}} = e^{-\frac{[E_a-2]}{RT} + \frac{E_a}{RT}} = e^{\frac{2}{RT}}$$

$$13. \text{ (b): Rate} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$

$$\text{Rate} = -\frac{1}{2} k_1 [\text{N}_2\text{O}_5] = \frac{1}{4} k_2 [\text{N}_2\text{O}_5] = k_3 [\text{N}_2\text{O}_5]$$

On dividing all the terms by $[\text{N}_2\text{O}_5]$ and multiplying by 4 we get, $2k_1 = k_2 = 4k_3$

14. (b): The catalyst decreases the activation energy of the reaction and thus increases the rate of reaction.

15. (b): For the first order reaction,

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

Given that,

$$\frac{dx}{dt} = 1.5 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} \text{ and}$$

$$[A] = 0.5 \text{ M}$$

$$\therefore 1.5 \times 10^{-2} = k \times 0.5$$

$$\therefore k = \frac{1.5 \times 10^{-2}}{0.5} = 3 \times 10^{-2} \text{ min}^{-1}$$

For first order reaction,

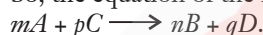
$$\text{Half-life period } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{3 \times 10^{-2}} = 23.1 \text{ min}$$

16. (d): A and C are reactants as their concentration falls with time hence, (minus sign).

B and D are the products of the reaction because their concentration increases with time hence (plus sign).

m and p are the stoichiometric coefficients of A and C while n and q are the coefficients of products B and D .

So, the equation of the reaction becomes:



17. (d)

18. (b): The slow step $A \xrightarrow{k_1} B$, is the rate determining step of the reaction, Hence, rate of production of C , i.e.,

$$\frac{d[C]}{dt} = k_1[A].$$

19. (c): According to the expression $\frac{-d[A]}{dt} = k[A][B]$ the order of reaction should be two.

20. (d): For the first order reaction, $k = \frac{2.303}{t} \log \frac{C_0}{C_t}$

Case I:

$$C_0 = 100 \text{ M}, C_t = 100 - 60 = 40, t = 100 \text{ min}$$

$$k = \frac{2.303}{100} \times \log \frac{100}{40}$$

$$k = \frac{2.303 \times 0.3979}{100} \quad \dots (i)$$

Case II:

$$C_0 = 100 \text{ M}, C_t = 100 - 90 = 10 \text{ M}$$

$$t = \frac{2.303}{k} \log \frac{100}{10}$$

$$= \frac{2.303 \times 100}{2.303 \times 0.3979} = 251.3 \text{ min}$$

... Substituting k from (i)

21. (b): For an endothermic reaction,

$$E_{a(\text{products})} < E_{a(\text{reactants})}$$

$$\Delta H_{(\text{products})} > \Delta H_{(\text{reactants})}$$

22. (b): First we calculate the rate constant from $t_{1/2}$,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{6(\text{h})} = 0.1155 \text{ h}^{-1}$$

$$\text{Now, } t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$$

$$[A]_0 = 0.8 \text{ M}, [A]_t = 0.25 \text{ M}, k = 0.1155 \text{ h}^{-1}$$

$$\text{Hence, } t = \frac{2.303}{0.1155 \text{ h}^{-1}} \log_{10} \frac{0.8(\text{M})}{0.25(\text{M})}$$

$$= \frac{2.303}{0.1155 \text{ h}^{-1}} \log_{10} 3.2 = \frac{2.303 \times 0.5051}{0.1155} \text{ h} = 10.07 \text{ h}$$

23. (b): For an exothermic reaction $E_a > \Delta E$. However, rest all are true. We have

$$E_{a(f)} = E_{\text{Threshold}} - E_{\text{Reactant}}$$

$$E_{a(b)} = E_{\text{Threshold}} - E_{\text{Product}}$$

$$\text{Thus, } E_{a(f)} - E_{a(b)} = E_{\text{Product}} - E_{\text{Reactant}} = \Delta E$$

If $\Delta E = -ve$ then $E_{a(f)} < E_{a(b)}$

If $\Delta E = +ve$ then $E_{a(b)} < E_{a(f)}$

24. (d): We know that

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

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

$$= \log(1.60 \times 10^{-5}) + \frac{209000 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J mol}^{-1} \text{K}^{-1}}$$

$$\left[\frac{1}{600 \text{ K}} - \frac{1}{700 \text{ K}} \right]$$

$$\log k_2 = -4.796 + 2.599 = -2.197$$

$$k_2 = 6.36 \times 10^{-3} \text{ s}^{-1}$$

$$25. (b): t_{99\%} = \frac{2.303}{k} \log \frac{100}{100-99} \quad \dots(i)$$

$$t_{90\%} = \frac{2.303}{k} \log \frac{100}{100-90} \quad \dots(ii)$$

$$\text{Dividing equation (i) by (ii), } \frac{t_{99\%}}{t_{90\%}} = \frac{\log 100}{\log 10} = 2$$

$$\therefore t_{99\%} = 2 \times t_{90\%}$$

$$26. (d): k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$k = \frac{2.303}{20} \log \frac{100}{100-20}$$

$$= \frac{2.303}{20} \log \frac{100}{80} = \frac{2.303}{20} \times 0.0969 = 0.01115 \text{ min}^{-1}$$

$$k = \frac{2.303}{t_{60\%}} \log \frac{100}{100-60} = 0.01115$$

$$\Rightarrow t_{60\%} = \frac{2.303}{0.01115} \times 0.3979 = 82 \text{ min}$$

$$27. (a): k_2 = \frac{2.303}{t_2} \log \frac{100}{50} \text{ for } 50\% \text{ of } B \text{ reacted}$$

$$k_1 = \frac{2.303}{t_1} \log \frac{100}{6} \text{ for } 94\% \text{ of } A \text{ reacted}$$

$$\therefore \frac{k_2}{k_1} = \frac{t_1}{t_2} \times \frac{0.3010}{1.2218}$$

Since $t_2 = t_1$, because 50% B has reacted when 94% A has reacted.

$$\therefore \frac{k_2}{k_1} = \frac{0.3010}{1.2218} = 0.246 \text{ and } \frac{k_1}{k_2} = 4.06$$

$$28. (c): \text{Rate}_1 = k[Y][Z]^{\frac{1}{2}}$$

$$\text{Rate}_2 = k[Y][2Z]^{\frac{1}{2}}$$

$$\therefore \frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[Y][2Z]^{\frac{1}{2}}}{k[Y][Z]^{\frac{1}{2}}} = (2)^{\frac{1}{2}} = \sqrt{2}$$

$$29. (c): \text{Rate law: Rate} = k[A]^x [B]^y$$

Doubling $[A]$, rate is doubled. Hence, $x = 1$

Similarly, $y = 1$

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

$$k = \frac{\text{rate}}{[A][B]} = \frac{2.0 \times 10^{-4}}{1 \times 10^{-2} \times 2 \times 10^{-2}} = 1$$

$$\frac{(\text{rate})_2}{(\text{rate})_1} = \frac{k(2[A])(2[B])}{k[A][B]} = 4$$

$$30. (a): k = \frac{0.693}{t_{1/2}} = \frac{0.693}{0.5(\text{min})} = 1.386 \text{ min}^{-1}$$

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

$$\text{or } t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$$

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

$$\text{Hence, } t = \frac{2.303}{1.386(\text{min}^{-1})} \log_{10} \frac{100}{20}$$

$$= \frac{2.303}{1.386(\text{min}^{-1})} \log_{10} 5 = \frac{2.303}{1.386(\text{min}^{-1})} \times 0.699$$

$$= 1.162 \text{ min} = 69.7 \text{ s}$$

$$31. (d): k = 2.1 \times 10^{10} e^{-2700/RT}$$

$$\ln k = \ln 2.1 \times 10^{10} + \ln e^{-2700/RT}$$

$$\ln k = \ln 2.1 \times 10^{10} - \frac{2700}{RT}$$

$$\log k = \log 2.1 \times 10^{10} - \frac{2700}{2.303RT}$$

$$\log k = -\frac{2700}{2.303RT} + \log 2.1 \times 10^{10}$$

On comparing it with straight line equation $y = mx + c$, we get

$$\therefore m \text{ (slope)} = -\frac{2700}{2.303R} \text{ and } C = \log 2.1 \times 10^{10}$$

$$32. (d): \log k = -\frac{E_a}{2.303RT} + \log A$$

$$\text{Straight line with slope} = -\frac{E_a}{2.303R}$$

$$\text{First order reaction, } k = \frac{2.303}{t} \log \frac{C}{C-x}$$

$$\therefore \text{Straight line with slope} = -\frac{k}{2.303}$$

Units of k for the first order reaction are independent of concentration units.

33. (b): Graph (A) is for zero order reaction as the rate remains constant at any time.

Graph (B) is for zero order reaction.

$$\text{According to the formula, } t_{1/2} = \frac{a}{2k}$$

$$\text{So, } t_{1/2} \propto a$$

Graph (E) is for 1st order reaction as the rate of reaction is directly proportional to concentration.

$$\text{According to the equation, } r = k[A]_t$$

$$\Rightarrow r \propto [A]_t$$

34. (c) : (i) $R \propto [A]$ (ii) $R \propto [B]^0$ (iii) $R \propto [C]^2$

$$\text{Rate} \propto [A] [B]^0 [C]^2$$

\therefore Overall order = 3.

35. (d): The rate law of the reaction $A + B \longrightarrow$ Products, as determined from its kinetics is,

$$\frac{dx}{dt} = k[A]^2[B].$$

So, the overall order of the reaction is $2 + 1 = 3$.

36. (d) : $k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$

or $\log_{10} \frac{[A]_0}{[A]_t} = \frac{k \times t}{2.303}$

$k = 7.0 \times 10^{-4} \text{ s}^{-1}$, $t = 35 \text{ min} = 2100 \text{ s}$, $[A]_0 = 0.08 \text{ M}$

Hence,

$$\log \frac{0.08(\text{M})}{[A]_t} = \frac{7.0 \times 10^{-4} (\text{s}^{-1}) \times 2100(\text{s})}{2.303} = 0.6383$$

and $\frac{0.08(\text{M})}{[A]_t} = \text{antilog}(0.6383) = 4.35$

It follows that $[A]_t = \frac{0.08(\text{M})}{4.35} = 0.0184 \text{ M}$

The concentration that remains after 35 min is 0.0184 M.

37. (c) : $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$

Initial pressure p_0 0 0

Pressure at time t $p_0 - p$ p p

Let initial pressure, $p_0 \propto R_0$

Pressure at time t , $P_t = p_0 - p + p + p = p_0 + p$

Pressure of reactants at time t , $p_0 - p = 2p_0 - P_t \propto R$

$$k = \frac{2.303}{t} \log \frac{p_0}{2p_0 - P_t}$$

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

$$= 2.2318 \times 10^{-3} \text{ s}^{-1}$$

Pressure of SO_2Cl_2 at time t ($p_{\text{SO}_2\text{Cl}_2}$)

$$= 2p_0 - P_t = 2 \times 0.50 - 0.65 \text{ atm} = 0.35 \text{ atm}$$

Rate at that time = $k \times p_{\text{SO}_2\text{Cl}_2}$

$$= (2.2318 \times 10^{-3}) \times (0.35) = 7.8 \times 10^{-4} \text{ atm s}^{-1}$$

38. (b) : From experiment 1, we have

$$\text{Rate} = k(2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})$$

$$k = \frac{5.0 \times 10^{-4}}{(2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})} = 2.67 \times 10^8 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

$$\log k = -\frac{E_a}{2.303 R} \times \frac{1}{T} + \log A$$

$$\log 2.67 \times 10^8 = -\frac{55.3 \times 10^3}{2.303 \times 8.314} \times \frac{1}{300} + \log A$$

or $\log A = 18.057 \Rightarrow A = 1.140 \times 10^{18}$

39. (c) : $k = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$

$$\therefore \frac{0.693}{t_{1/2}} = \frac{2.303}{11} \log_{10} \left(\frac{a}{a-x} \right)$$

$$\therefore \frac{0.693}{4} = \frac{2.303}{11} \log_{10} \left(\frac{a}{a-x} \right)$$

$$\therefore \log_{10} \left(\frac{a}{a-x} \right) = \frac{0.693 \times 11}{2.303 \times 4} = 0.827$$

$$\therefore \frac{a}{a-x} = \text{Antilog}(0.827)$$

$$\left(\frac{a-x}{a} = \text{fraction remaining unhydrolysed} \right)$$

$$\therefore 1 - \left(\frac{a-x}{a} \right) = \text{fraction hydrolysed.}$$

$$\therefore \text{Fraction of sucrose that undergoes hydrolysis} = 1 - 0.1489 = 0.8511$$

40. (c) : For a first order reaction,

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

Given : $t = 10 \times 60 \times 60 \text{ sec}$

Let initial concentration (a) be 1,

$$\text{Then, } k = \frac{2.303}{10 \times 60 \times 60} \log \frac{1}{(1-x)}$$

On putting value of $k = 1.5 \times 10^{-6} \text{ s}^{-1}$, we get

$$\Rightarrow \log \frac{1}{(1-x)} = 0.0234 \quad \text{or} \quad \frac{1}{(1-x)} = 1.055$$

On putting value of $k = 1.5 \times 10^{-6} \text{ s}^{-1}$, we get

$$\text{or } x = \frac{1.055 - 1}{1.055} = 0.052 \text{ i.e., } 0.052 \times 100 = 5.2\%$$

41. (d) : The unit of rate of reaction is $\text{mol L}^{-1} \text{ s}^{-1}$. It does not change with order.

42. (d) : (i) is wrong because rate constant does not depend upon the concentrations of the reactants.

(ii) is wrong because rate depends upon $[\text{H}^+]^2$

(iii) is correct because change in pH means change in $[\text{H}^+]$ ions

(iv) is correct because rate $\propto [\text{H}^+]^2$.

43. (b) : For first order reaction, $t = \frac{2.303}{k} \log \frac{a}{a-x}$

$$t_{99.9} = \frac{2.303}{k} \log \frac{100}{100 - 99.9} = \frac{2.303}{k} \times 3$$

$$t_{50} = \frac{2.303}{k} \log \frac{100}{50} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.301$$

$$\frac{t_{99.9}}{t_{50}} = 10 \text{ approx.}$$

44. (a) : First we calculate rate constant of the reaction.

$$k = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]_t}$$

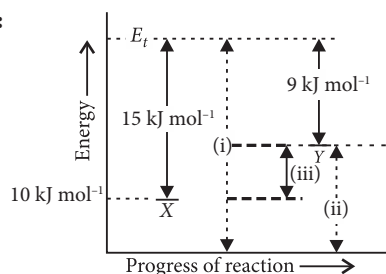
$$[A]_0 = 100, [A]_t = 100 - 60 = 40, t = 45 \text{ min}$$

$$\text{Hence, } k = \frac{2.303}{45(\text{min})} \log_{10} \frac{100}{40} = \frac{2.303}{45(\text{min})} \times \log_{10} 2.5$$

$$= \frac{2.303}{45(\text{min})} \times 0.3979 = 0.0204 \text{ min}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0204(\text{min}^{-1})} = 34 \text{ min}$$

45. (d) :



46. (c) :

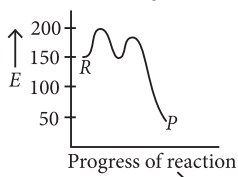


Diagram (c) represents exothermic reaction with $E_a = 200 - 150 = 50 \text{ kJ mol}^{-1}$ and $\Delta H = 50 - 150 = -100 \text{ kJ mol}^{-1}$

47. (d) : The logarithmic form of Arrhenius equation is

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\text{or } \log_{10} \frac{A}{k} = \frac{E_a}{2.303RT}$$

$E_a = 85.2 \text{ kJ mol}^{-1} = 85.2 \times 10^3 \text{ J mol}^{-1}$, $T = 310 \text{ K}$,
 $A = 3.1 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$

$$\text{Hence, } \log_{10} \frac{3.1 \times 10^{11}}{k} = \frac{85.2 \times 10^3}{2.303 \times 8.314 \times 310} = 14.354$$

$$\text{That is } \frac{3.1 \times 10^{11}}{k} = \text{antilog}(14.354) = 2.26 \times 10^{14}$$

$$\text{and } k = \frac{3.1 \times 10^{11}}{2.26 \times 10^{14}} = 1.372 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

48. (b) : From the graph we can see that in 4 hours (1 to 5) concentration of A decreases to 0.3 M from 0.5 M whereas concentration of B increases to 0.6 M from 0.2 M. Loss of conc. of A in 4 hours = $(0.5 - 0.3) = 0.2 \text{ M}$. Gain in concentration of B in 4 hours = $(0.6 - 0.2) = 0.4 \text{ M}$. So, the increase in concentration of 'B' in the same time (4 hours) is twice the decrease in concentration of 'A'.

Thus, $n = 2$.49. (c) : Given : $a = 100$, $(a - x) = 100 - 25 = 75$; $t = 20 \text{ min}$

Using the relation

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

we get

$$\text{At } 25^\circ\text{C} (298 \text{ K}); k_1 = \frac{2.303}{20} \log \frac{100}{75} = 0.014386 \text{ min}^{-1}$$

At $40^\circ\text{C} (313 \text{ K}); k_2 = ?$

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

$$\therefore \log \frac{k_2}{0.014386} = \frac{70 \times 10^3}{2.303 \times 8.314} \times \left(\frac{313 - 298}{298 \times 313} \right)$$

$$\text{or } \frac{k_2}{0.014386} = 3.864 \text{ or } k_2 = 0.0556$$

Now, for % age decomposition at $40^\circ\text{C} (313 \text{ K})$ Given, $a = 100$, $(a - x) = (100 - x)$; $t = 20 \text{ min}$; $k = 0.0556$

$$\text{Thus, } k_{313} = \frac{2.303}{20} \log \frac{100}{(100-x)}$$

$$0.0556 = \frac{2.303}{20} \log \frac{100}{(100-x)} \Rightarrow x = 67.169 \text{ or } 67.17\%$$

50. (d)

KCET Exam Archive1. (d) : $t_{1/2} = 69.3 \text{ s}$, $t = 230 \text{ s}$, $a = 0.4 \text{ atm}$

For first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{69.3} = 0.01 \text{ s}^{-1}$$

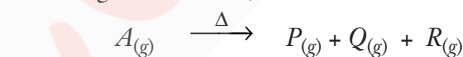
$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{230} \log \frac{0.4}{0.4-x}$$

$$0.01 = \frac{2.303}{230} \log \frac{0.4}{0.4-x} = 0.01 \log \frac{0.4}{0.4-x}$$

$$\frac{0.01}{0.01} = \log \frac{0.4}{0.4-x} \Rightarrow 1 = \log \frac{0.4}{0.4-x}$$

$$\text{Antilog of } 1 = \frac{0.4}{0.4-x} \Rightarrow 10 = \frac{0.4}{0.4-x} \Rightarrow x = 0.36$$

For the given reaction,



Initial	0.4	0	0	0
Final	$0.4 - 0.36$	0.36	0.36	0.36

Total pressure = $(0.4 - 0.36) + (3 \times 0.36) = 1.12 \text{ atm}$ 2. (b) : $\text{CH}_3\text{COOH} + \text{CH}_3\text{OH} \longrightarrow \text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$

$$r_1 = k[\text{CH}_3\text{COOH}][\text{CH}_3\text{OH}] = k(1)(2) = 2k$$

When solution is diluted with equal volume of water, concentration is reduced to half.

$$\therefore r_2 = k\left(\frac{1}{2}\right)\left(\frac{2}{2}\right) = \frac{k}{2}$$

$$\frac{r_1}{r_2} = \frac{2k}{k/2} = 4 \Rightarrow r_2 = \frac{r_1}{4} = 0.25 r_1$$

3. (a) : For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{60} \log \frac{100}{12.5} = 0.0346 \text{ min}^{-1}$$

$$\text{Now } t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0346} = 20 \text{ min}$$

4. (d) : $12 \text{ M} \xrightarrow{t_{1/2}} 6 \text{ M} \xrightarrow{t_{1/2}} 3 \text{ M}$

Initial conc.

 $t_{1/2} = 10 \text{ min}$

$$k = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}$$

As $t_{1/2}$ is 10 min, after 20 minutes the concentration will be 3 M.Hence, Rate = $0.0693 \times 3 \text{ M min}^{-1}$

$$5. \quad (\text{a}) : t_{1/2} = \frac{0.693}{k} \Rightarrow \frac{0.693}{t_{1/2}} = k \Rightarrow \frac{0.693}{60} = k$$

$$k = 0.01155 \text{ min}^{-1}$$

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

Let the initial amount (a) be 100.

$$0.01155 \text{ min}^{-1} = \frac{2.303}{240 \text{ min}} \log \left(\frac{100}{a-x} \right)$$

$$\frac{0.01155 \text{ min}^{-1} \times 240 \text{ min}}{2.303} = \log \left(\frac{100}{a-x} \right)$$

$$1.204 = \log 100 - \log (a-x)$$

$$1.204 = 2 - \log (a-x)$$

$$\log (a-x) = 2 - 1.204$$

$$\log (a-x) = 0.796$$

$$\text{or } (a-x) = 6.25\%$$

$$6. \quad (\text{b}) : r = k[A]^2$$

When concentration of A is doubled,

$$r = k[2A]^2 \Rightarrow r = 4k[A]^2$$

$$7. \quad (\text{b}) : -\frac{1}{3} \frac{d[A]}{dt} = +\frac{1}{2} \frac{d[B]}{dt}$$

$$-\frac{2}{3} \frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

$$8. \quad (\text{a}) : \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$9. \quad (\text{a}) : \frac{1}{2} A \longrightarrow 2B$$

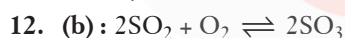
$$-\frac{1}{1/2} \frac{d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt}$$

$$\text{or } -\frac{2d[A]}{dt} = \frac{1}{2} \frac{d[B]}{dt} \Rightarrow \frac{-d[A]}{dt} = \frac{1}{4} \frac{d[B]}{dt}$$

10. (a, d) : According to Arrhenius equation,
 $k = A e^{-E_a/RT}$

On increasing temperature and decreasing activation energy (E_a), rate of reaction increases.

11. (b) : The rate law for any reaction cannot be determined theoretically but it is determined experimentally.



Rate of reaction

$$= -\frac{1}{2} \frac{d[\text{SO}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

$$\frac{-d[\text{O}_2]}{dt} = +\frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

$$2 \times 10^{-4} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

$$\frac{d[\text{SO}_3]}{dt} = 2 \times 2 \times 10^{-4} = 4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

13. (d) : Temperature coefficient 2 means rate of reaction doubles at every 10°C rise in temperature.

$$\text{Thus, } \frac{k_{90^\circ\text{C}}}{k_{30^\circ\text{C}}} = 2^6 = 64$$

14. (a)

15. (d) : Plot of $t_{1/2}$ vs $[R]_0$ for a reaction is a straight line parallel to x -axis, means $t_{1/2}$ is independent of $[R]_0$ hence, the reaction is first order.

\therefore Unit of rate constant = s^{-1}

16. (d)



$$r_i = k[2 \text{ M}][3 \text{ M}] \quad \dots(\text{i})$$

$$r_f = k \left[\frac{2 \text{ M}}{2} \right] \left[\frac{3 \text{ M}}{2} \right] \quad \dots(\text{ii})$$

On dividing (ii) by (i), we get

$$\frac{r_f}{r_i} = \frac{k[M] \left[\frac{3}{2} M \right]}{k[2 \text{ M}][3 \text{ M}]} = 0.25$$

\therefore The rate of reaction becomes 0.25 times of initial rate.

18. (c) : For first order reaction,

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

where, a = initial concentration of the reactant, $a-x$ = concentration of the reactant after time, t .

For 60% completion of reaction,

$$k = \frac{2.303}{50} \log \frac{100}{40}$$

$$k = \frac{2.303}{50} \times 0.397 = 0.0183$$

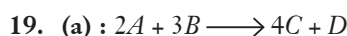
For 93.6% completion of reaction,

$$k = \frac{2.303}{t} \log \frac{100}{6.4}$$

$$0.0183 = \frac{2.303}{t} \log \frac{100}{6.4}$$

$$t = \frac{2.303}{0.0183} \times 1.193$$

$$t = 150 \text{ min}$$



$$-\frac{1}{3} \frac{d[B]}{dt} = +\frac{1}{4} \frac{d[C]}{dt}$$

$$-\frac{d[B]}{dt} = \frac{3}{4} \frac{d[C]}{dt} = \frac{3}{4} (2.8 \times 10^{-3}) \text{ mol L}^{-1} \text{ s}^{-1}$$

$$20. \quad (\text{b}) : k = PZ e^{-E_a/RT}$$

$$\log k = \log (PZ) - \frac{E_a}{RT}$$

For k to increase, $-\frac{E_a}{RT}$ should be small and that is possible only when E_a is less or T is more. So, for the reaction to speed up rapidly E_a should decrease.

21. (a) : As $[B]$ increase, $t_{1/2}$ remains same *i.e.*, 1st order with respect to B .

On doubling concentration of A , rate remains same, so it is zero order w.r.t. A .

$$\text{Rate} = k[A]^0[B]^1$$

Overall order = 1

\therefore Units of $k = \text{s}^{-1}$

$$22. \text{ (a) : } t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$$= \frac{2.303}{k} \log \left(\frac{100}{1} \right) = \frac{4.606}{k}$$

$$23. \text{ (c) : } R = k[A]^1[B]^2$$

Volume is reduced to half means pressure is doubled.

$$R' = k[2A][2B]^2$$

$$R' = k[A][B]^2 \times 8$$

$$R' = 8R$$

\therefore Rate of reaction becomes 8 times the initial rate.

24. (c) : Higher order reactions are rare because there is low probability of simultaneous collisions of all reacting species, so the number of effective collisions becomes very less (negligible).

25. (d) : For first order reaction,

$$t_{1/2} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{t_{1/2}} = \frac{0.693}{45} \text{ min}^{-1}$$

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

$$\frac{0.693}{45} = \frac{2.303}{t} \log \left(\frac{100}{0.1} \right) = \frac{2.303 \times 3}{t}$$

$$t = \frac{2.303 \times 3 \times 45}{0.693} \text{ min} = 448.6 \text{ min} = \frac{448.6}{60} \text{ hours}$$

$$= 7.5 \text{ hours}$$

26. (a) : The rate of the given reaction is expressed in $\text{mol L}^{-1} \text{s}^{-1}$. Hence,

$$\text{mol L}^{-1} \text{s}^{-1} = k [\text{mol L}^{-1}]^2$$

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

27. (b, c) : For n^{th} order reaction,

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

28. (b) : For n^{th} order : $t_{1/2} \propto \frac{1}{a^{n-1}} \propto \frac{1}{a^5}$

$$n - 1 = 5 \Rightarrow n = 5 + 1 = 6$$

29. (d) : $\text{mol L}^{-1} \text{s}^{-1}$ is the unit of zero order rate constant. Decomposition of HI on gold surface is a zero order reaction.

30. (d) : $k = Ae^{-E_a/RT}$ (Arrhenius equation)

$$A = ke^{E_a/RT}$$

$$\text{at } T = \infty, \frac{1}{T} = 0$$

$$\therefore A = k$$

$$A = 6 \times 10^5$$

31. (c) : Let the temperature be T' .

At T' , $k_1 = k_2$

$$10^{16} \times e^{-2000/T'} = 10^{15} \times e^{-1000/T'}$$

$$\text{or } \frac{e^{-1000/T'}}{e^{-2000/T'}} = 10 \text{ or } e^{\left(\frac{2000}{T'} - \frac{1000}{T'} \right)} = 10$$

$$\text{or } e^{\left(\frac{1000}{T'} \right)} = 10 \text{ or } \frac{1000}{T'} = \ln 10$$

$$\text{or } T' = \frac{1000}{\ln 10} = \frac{1000}{2.303 \log 10} = \frac{1000}{2.303} \text{ K}$$



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