11

Chemical Kinetics

The chapter deals with the rate and mechanism of chemical reactions. There are several reactions which take place instantaneously (*e.g.*, ionic reactions) for which rate cannot be determined. On the other hand, some reactions occur so slowly (*e.g.*, rusting of iron) for which rate determination is of no use. In between these two extremes, many molecular reactions occur with considerable rate for which rate determination is made. In a reaction of this type if, taking place in steps, the slow step reaction decides the rate of reaction.

$$R - Cl + KOH \longrightarrow ROH + KCl$$

$$R - Cl \xrightarrow[\text{Slow}]{} R^+ + Cl^- \xrightarrow[\text{Fast}]{OH^-} ROH$$

In chemical kinetics, reactions which occur in single step are simple or **elementary reactions** and those which take place in two or more steps are termed as complex reactions. For **elementary reactions,** order of reaction and molecularity are generally same.

The rate of reaction : Consider a reaction

$$A \longrightarrow \text{Product}$$

	A	Product
$t = 0$	a mole	0
$t = t$	$(a - X)$ mole	
$t = (t + dt)$	$(a - X - dX)$ mole	

Like other ways to define rate say change in position in unit time, the rate of reaction may also be given as,

$$\text{Rate} = \frac{\text{mole of reactant used}}{\text{time required for this change}} = \frac{X}{t} \qquad \ldots(1)$$

However, as we know, rate of a reaction continuously decreases with time and thus, Eq. (1) simply reveals average rate of reaction and it is not advised to take this equation in account for instantaneous rate of reaction, *i.e.*, rate of reaction at any time.

To obtain instantaneous rate, one should consider the average rate when time interval is smallest say dt (*i.e.*, when dt approaches to zero). Therefore, consider an infinitesimally small time dt in which dX mole of reactant are used.

Then, $\quad \text{Rate of formation of product} = \frac{dX}{dt}$

or $\quad \text{Rate of decomposition of reactant} = -\frac{dC_A}{dt}$

when dC_A is concentration of reactant used in time dt; the negative sign indicates for decreasing trend of rate with time.

Furthermore, consider a reaction,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

It is clear from the reaction that rate of decomposition for N_2O_5 is twice as fast as the rate of formation of O_2 and therefore,

$$\text{Instantaneous rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

$$\text{Average rate} = -\frac{1}{2}\frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

If $\Delta t \rightarrow 0$, the average rate changes to instantaneous rate.

where, $-\frac{d}{dt}[N_2O_5]$ is rate of decomposition of N_2O_5

$\frac{+d[NO_2]}{dt}$ is rate of formation of NO_2

$\frac{d[O_2]}{dt}$ is rate of formation of O_2

In general, we can write for

$$n_1A + n_2B + \cdots\cdots \longrightarrow m_1Z + m_2Y + \cdots\cdots$$

$$\text{Rate of reaction} = -\frac{1}{n_1}\frac{d[A]}{dt} = -\frac{1}{n_2}\frac{d[B]}{dt} = \ldots$$

$$= \frac{1}{m_1}\frac{d[Z]}{dt} = \frac{1}{m_2}\frac{d[Y]}{dt} = \ldots\ldots$$

Factors influencing rate of reaction :

(1) Conc. of reactant, (2) Temperature, (3) Pressure, (4) Surface area of reactant, (5) Exposure to light, (6) Presence of catalyst, (7) Order of reaction.

Unit of rate : $\quad \text{Rate} = \frac{dx}{dt}$

$$\therefore \text{ Unit of rate} = \frac{\text{unit of concentration}}{\text{unit of time}} = \text{mol litre}^{-1}\text{time}^{-1}$$

Rate constant and its variation with temperature : Rate constant is a characteristic constant for a given reaction and is defined as the rate of reaction when concentration of reactant is unity.

i.e., $\quad \text{Rate} = K(a - x) \quad \because (a - x) = 1 \quad \therefore \text{rate} = K$

The rate constant K varies only with temperature and is expressed as,

$$2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R} \frac{[T_2 - T_1]}{T_1 T_2}$$

for two temperature limits

or $\quad K = Ae^{-E_a/RT}$ **for one temperature**

where E_a is energy of activation, T is temperature in Kelvin, A is frequency factor; R is molar gas constant.

NOTE : (1) Put R in the units in which E_a is given or desired.

(2) Temperature coefficient : The ratio of rate constant for each 10°C rise in temperature preferably 25°C and 35°C, *i.e.*, $K_{35}/K_{25} \approx 2 \sim 3$.

Unit of rate constant : Varies with order of reaction.

$$\text{Rate} = K\,[\text{Reactant}]^n$$

$$\therefore \quad K = \frac{\text{rate}}{[\text{Reactant}]^n} = \frac{\text{mol litre}^{-1}\text{time}^{-1}}{(\text{mol litre}^{-1})^n}$$

Unit of $\quad K = \text{mol}^{1-n}\,\text{litre}^{n-1}\,\text{time}^{-1}$

where n is order of reaction.

Molecularity and order of reaction:

	Molecularity of reaction	Order of reaction
1.	It is defined as the no. of molecules of reactant taking part in a chemical reaction. *e.g.*, $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ $\therefore \quad m = 1$	It is defined as the no. of molecules of reactants whose concentration determines the rate of reaction. $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ and rate $= K[NH_4NO_2]$ $\therefore$ O.R. = 1
2.	It can neither be zero nor fractional.	It may be zero, fractional or integer.
3.	It is derived from mechanism of reaction.	It is derived from rate expression.
4.	It is theoretical value.	It is experimental value.
5.	Reactions with molecularity ≥ 4 are rare.	Reactions with O.R. ≥ 4 are also rare.
6.	Molecularity is independent of pressure and temperature.	O.R. depends upon pressure and temperature.

Salient features for determination of order of reaction:

(1) The rate expression is directly given, *i.e.*,

$$2NO + O_2 \longrightarrow 2NO_2$$

and $\quad \text{Rate} = K[NO]^2[O_2]^1 \quad \therefore \text{ O.R.} = 2 + 1 = 3$

i.e., O.R. is also defined as sum of powers raised on concentration terms in order to write rate expression.

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

and $\quad \text{Rate} = K[CH_3COOC_2H_5]^1[H_2O]^0$

$$\therefore \text{ O.R.} = 1 + 0 = 1$$

(2) The problem is provided up in form of language, *i.e.*,

$$2A + B \longrightarrow \text{Product and Given}$$

A shows first order kinetics and B shows zero order kinetics.

$\therefore \quad \text{O.R.} = 1 + 0 = 1 \quad$ and $\quad \text{rate} = K[A]^1[B]^0$

(3) Either of reactant is mentioned as excess, *i.e.*,

(a) $\quad 2A + \underset{\text{excess}}{B} \longrightarrow \text{Products}$

$\therefore \quad \text{O.R.} = 2 + 0 = 2 \quad$ and $\quad \text{rate} = K[A]^2[B]^0$

(b) $\quad \underset{\text{excess}}{2A} + B \longrightarrow \text{Products}$

$\therefore \quad \text{O.R.} = 0 + 1 = 1 \quad$ and $\quad \text{rate} = K[A]^0[B]^1$

(4) Experimental data is given :

(a) Case I : Rate is given using different conc. of A and B at same temperature.

Given that,	$[A]$	$[B]$	Rate
	a_1	b_1	r_1
	a_2	b_2	r_2
	a_3	b_3	r_3

$$\therefore \quad r_1 = K[a_1]^m[b_1]^n$$

$$r_2 = K[a_2]^m[b_2]^n$$

$$r_3 = K[a_3]^m[b_3]^n$$

where m and n are order for A and B respectively

Solve these to get m and n

$\therefore \quad \text{O.R.} = (m + n)$

(b) Case II : Half-life period $(t_{1/2})$ and initial concentration (a) are given.

Half-life period : Time to complete half of the reaction

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

when n is order of reaction;

(c) Case III : Characteristic study of experimental facts about a reaction.

(5) The given reaction is pseudo unimolecular or pseudo bimolecular.

Pseudo unimolecular reactions:

Reactions with O.R. = 1 but Molecularity ≥ 2

O.R. = 1, molecularity = 2 for reaction given below:

e.g., $CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$

$C_{12}H_{22}O_{11} + H_2O \rightleftharpoons C_6H_{12}O_6 + C_6H_{12}O_6$

Pseudo bimolecular reactions:

Reactions with O.R. = 2 but Molecularity ≥ 3

(6) Unit of rate constant is given :

Unit of $K = (\text{mol})^{1-n}\,(\text{litre})^{n-1}\,\text{time}^{-1}$

Types of order of reactions :

(I) Zero order reaction :

for $\quad A \rightarrow \text{Product}$

at $t = 0 \quad C_0$

at $t = t \quad C_A$

$$\text{Rate} = K[\text{Reactant}]^0$$

i.e., $\quad \frac{dx}{dt} = K$

On integrating,

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

or $\quad -\frac{dC_A}{dt} = K[C_A]^0$

on integrating $-C_A = Kt + C$

at $\quad t = 0,\ C_A = C_0$

$\therefore \quad C = -C_0$

$\therefore \quad Kt = C_0 - C_A$

Characteristics : (1) Rate remains constant through out the course of reaction.

(2) Unit of rate constant = mol $\text{litre}^{-1}\text{time}^{-1}$.

(3) Half-life period : $t_{1/2} \propto (a)$, where a is initial concentration.

(II) I order reaction :

Rate $= K[C]^1$ | for $A \rightarrow$ Product

i.e., $\frac{dx}{dt} = K[C]^1 = K[a-x]^1$ | a at $t = 0$; $(a-x)$ at $t = t$

On integrating, we get $K \times t = 2.303 \log_{10} \frac{a}{a-x}$

Characteristics : (1) Rate continuously decreases with time.

(2) Unit of rate constant : Time^{-1}

(3) Half-life period : $t_{1/2} \propto (a)^0$

i.e., half-life for I order is independent of initial concentration.

(III) II order reaction :

Case I : If one reactant or two reactants with same initial concentration;

$$\begin{array}{llll} \text{For} & A & \longrightarrow & \text{Products} \\ & a & & \text{at } t=0 \\ & (a-x) & & \text{at } t=t \end{array}$$

$$\text{Rate} = K[C]^2 \quad \text{or} \quad \frac{dx}{dt} = K(a-x)^2$$

On integrating, we get $K \times t = \frac{1}{a}\frac{x}{(a-x)}$

Case II : If reactants are two and initial concentrations are different;

$$\begin{array}{lllll} \text{For} & A & + & B & \longrightarrow \text{Products} \\ \text{at } t=t & (a-x) & & (b-x) & \end{array}$$

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

$$\frac{dx}{dt} = K(a-x)(b-x)$$

On integrating, we get $K \times t = \frac{2.303}{(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

Characteristics : (1) Rate continuously decreases with time.

(2) Unit of rate constant : $\text{mol}^{-1}\text{litre}^{1}\text{time}^{-1}$

(3) Half-life period : $t_{1/2} \propto (a)^{-1}$ or $t_{1/2} \propto 1/a$

Salient features of rate constant and half-life period :

Order of reaction	Half-life	Unit of rate constant
0	$t_{1/2} \propto a$	mol $\text{litre}^{-1}\text{time}^{-1}$
1	$t_{1/2} \propto (a)^0$	time^{-1}
2	$t_{1/2} \propto (a)^{-1}$	$\text{mol}^{-1}\text{litre}^{1}\text{time}^{-1}$
3	$t_{1/2} \propto (a)^{-2}$	$\text{mol}^{-2}\text{litre}^{2}\text{time}^{-1}$
n	$t_{1/2} \propto (a)^{1-n}$	$\text{mol}^{1-n}\text{litre}^{n-1}\text{time}^{-1}$

Experimental methods to determine order of reaction:

(1) By integration method : The experiments are carried out between the required amounts of reactants and products formed are analysed in terms of values as desired in various integrated forms of order of reactions. Using experimental values, rate constant is obtained by using different order rate equations. The one which gives most constant value for rate constant suggests the order of reaction. This is also known as **hit and trial method.** Most of the numericals are based on this method.

(2) Graphical method : Experiments are made to obtain the rates of reactions at different intervals using different amounts of reactants. Now the rates are plotted against $(a-x)^n$ values. The nature of graph suggests order of reaction. In I order reaction straight line is obtained when rate is plotted against $(a-x)$. In zero order reaction a straight line parallel to X-axis is formed.

(3) Time required to complete a definite fraction : As we have,

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

where n is order of reaction. Experiments are made to study the time required for a definite fraction to be completed using different amounts of reactants and then use of $t_{1/m} \propto (a)^{1-n}$ gives order.

(4) Isolation method : In this method, all the reactants except one are taken in very large excess and order is determined using either of the above methods. Different experiments are made using one by one reactant in small amount and rest all in excess. The sum of all the orders of reactants give order for reaction.

Reversible elementary reactions :

For reversible reaction $A \rightleftharpoons B$

Rate of reaction $= K_f[A] - K_b[B]$ ...(A)

First order opposed by first order :

$$\begin{array}{lll} & A \underset{K_p}{\overset{K_f}{\rightleftharpoons}} & B \\ t=0 & [A]_0 & 0 \\ t=t & [A]_0 - X & X \\ t=eq. & [A]_0 - X_{eq.} & X_{eq.} \end{array}$$

We can integrate Eq. (A) to have

$$t = \frac{2.303}{(K_f + K_b)} \log\left[\frac{X_{eq.}}{X_{eq.} - X}\right]$$

If $[B] = [B]_0$ at $t = 0$,

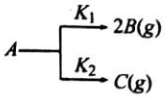
then $t = \frac{2.303}{K_f}\left[\frac{[B]_0 + X_{eq.}}{[A]_0 + [B]_0}\right] \log\left[\frac{X_{eq.}}{X_{eq.} - X}\right]$.

• NUMERICAL PROBLEMS •

1. The reaction $2NO + Br_2 \longrightarrow 2NOBr$, obeys the following mechanism.
   (i) $NO + Br_2 \overset{\text{Fast}}{\rightleftharpoons} NOBr_2$
   (ii) $NOBr_2 + NO \xrightarrow{\text{Slow}} 2NOBr$
   Suggest the rate expression.
2. The thermal decomposition of N_2O_5 occurs in the following steps:
   Step I $N_2O_5 \xrightarrow{\text{Slow}} NO_2 + NO_3$
   Step II $N_2O_5 + NO_3 \xrightarrow{\text{Fast}} 3NO_2 + O_2$
   Overall reaction is $2N_2O_5 \longrightarrow 4NO_2 + O_2$
   Suggest the rate expression.
3. For the reaction $2NO_2 + F_2 \longrightarrow 2NO_2F$, the experimental rate law is $r = K[NO_2][F_2]$. Propose the mechanism of reaction.
4. The reaction $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$ has experimental data that rate $= K[NO_2Cl]$. Propose the mechanism.
5. The decomposition of A and B obeys I order with half-life 54.0 and 18.0 minutes respectively. If $[A]_0 = [B]_0$ then after how much time the ratio of concentration of A and B will be 4 : 1 and 1 : 4 respectively.
6. From the concentrations of R at different times given below, calculate the average rate of the reaction : $R \rightarrow P$ during different intervals of time.

t/s	0	5	10	20	30
$10^3 \times [R]/\text{mol L}^{-1}$	160	80	40	10	2.5

7. The initial concentration of $[I^-]_0$ and $[ClO^-]_0$ are 0.075 M and 0.125 M to carry out a reaction :
   $$ClO^- + I^- \longrightarrow Cl^- + IO^-$$
   and rate $= K[ClO^-][I^-]$. Derive the rate expression in terms of concentration of ClO^- alone at any time.
8. The net rate of reaction for the change :
   $[Cu(NH_3)_4]^{2+} + H_2O \rightleftharpoons [Cu(NH_3)_3H_2O]^{2+} + NH_3$ is,
   $$\frac{dx}{dt} = 2.0 \times 10^{-4}[Cu(NH_3)_4]^{2+} - 3.0 \times 10^{5}[Cu(NH_3)_3H_2O]^{2+}[NH_3]$$ calculate :
   (i) Rate expression for forward and backward reactions.
   (ii) The ratio of rate constant for forward and backward reactions.
   (iii) The direction of reaction in which the above reaction will be more predominant.
9. Gas $A(g)$ shows two parallel path I order reaction as:



   The initial pressure of $A(g)$ in a container of volume V litre is 1 atm. After 10 sec the pressure becomes 1.4 atm and after ∞ time it becomes 1.5 atm. Calculate K_1 and K_2.
10. For a reversible reaction $A \rightleftharpoons B$, if pre-exponential factor is same for both forward and backward reaction, show that $K_C = e^{-\Delta H/RT}$, where ΔH is heat of reaction.
11. The rate constant of a reaction is $1.5 \times 10^7 \text{sec}^{-1}$ at 50°C and $4.5 \times 10^7 \text{sec}^{-1}$ at 100°C. Evaluate the Arrhenius parameters A and E_a. **(IIT 1998)**
12. The specific rate constant for the decomposition of formic acid is $5.5 \times 10^{-4} \text{sec}^{-1}$ at 413 K. Calculate the specific rate constant at 458 K, if the energy of activation is 2.37×10^4 cal mol^{-1}.
13. For a reaction $A_2 + B_2 \longrightarrow 2AB$, evaluate the energy of activation from the following data :

T (in K)	$\frac{1}{T}(K^{-1})$	$\log_{10} K$
500	2×10^{-3}	3.0
200	5×10^{-3}	2.0

14. Calculate the rate constant and half-life period for first order reaction having the activation energy 39.3 kcal mol^{-1} at 300°C and the frequency constant $1.11 \times 10^{11} \text{sec}^{-1}$.
15. A reaction proceeds five times more at 60°C as it does at 30°C. Estimate energy of activation.
16. For two first order reactions having same concentration of A and B at $t = 0$, use the given data to calculate the temperature at which both occurs with same rate.
   Reaction I $A \longrightarrow Z$; $K_1 = 10^{16} e^{\left(-\frac{3000}{T}\right)}$
   Reaction II $B \longrightarrow Y$; $K_2 = 10^{15} e^{\left(-\frac{2000}{T}\right)}$
17. The rate constant of a reaction increases by 7% when its temperature is raised from 300 K to 310 K, while its equilibrium constant increases by 3%. Calculate the activation energy of the forward and reverse reactions.
18. For the reaction $A \rightleftharpoons B$, ΔE for the reaction is -33.0 kJ mol^{-1}. Calculate:
   (a) equilibrium constant K_C for the reaction at 300 K.
   (b) if E_f and E_b are in the ratio 20 : 31, calculate E_f, E_b at 300 K.
   Assuming pre-exponential factor same for forward and backward reactions.
19. The rate of decomposition for methyl nitrite and ethyl nitrite can be given in terms of rate constant (in sec^{-1}) K_1 and K_2 respectively. The energy of activations for the two reactions are 152.30 kJ mol^{-1} and 157.7 kJ mol^{-1} as

well as frequency factors are 10^{13} and 10^{14} respectively for the decomposition of methyl and ethyl nitrite. Calculate the temperature at which rate constant will be same for the two reactions.

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

21. 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 minute, 25% decomposition took place. What will be the per cent decomposition in the same time in a 30% solution maintained at 40°C? Assume that activation energy remains constant in this range of temperature. **(IIT 1993)**

22. A given sample of milk turns sour at room temperature (20°C) in 64 hour. In a refrigerator at 3°C, milk can be stored three times as long before it sours. Estimate (a) the activation energy for souring of milk, (b) how long it take milk to sour at 40°C?

23. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 s^{-1}$, calculate its rate constant at 318 K and also the energy of activation. **(IIT 1997)**

24. Calculate the factor by which the rate of I order reaction is increased for a temperature rise of 10°C from 25°C to 35°C. The energy of activation is 35 kcal mol^{-1}.

25. A Ist order reaction is 50% complete in 30 minute at 27°C and in 10 minute at 47°C. Calculate the :

(a) rate constant for reaction at 27°C and 47°C.

(b) energy of activation for the reaction.

(c) energy of activation for the reverse reaction if heat of reaction is -50 kJ mol^{-1}.

26. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 minute. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C. **(IIT 1995)**

27. The energy of activation for a reaction is 100 kJ mol^{-1}. Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C; other things being equal?

28. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction, if the catalyst lowers the activation energy barrier by 20 kJ mol^{-1}. **(IIT 2000)**

29. The rate constant for the first order decomposition of a certain reaction is given by the equation,

$$\ln K(\sec^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$$

Calculate :

(a) the energy of activation.

(b) the rate constant at 500 K.

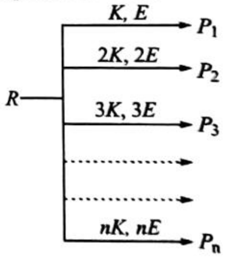
(c) at what temperature will its half-life period be 256 minute? **(IIT July 1997)**

30. For $A + B \longrightarrow C + D$; $\Delta H = 20$ kJ mol^{-1}; the activation energy of the forward reaction is 85 kJ/mol. Calculate activation energy of the reverse reaction.

31. Two reactions (I) $A \rightarrow$ Products (II) $B \rightarrow$ Products follow first order kinetics. The rate of the reaction (I) is doubled when temperature is raised from 300 K to 310 K. The half-life for this reaction at 310 K is 30 minute. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (II) is half that of reaction (I) calculate the rate constant of reaction (II) at 300 K. **(IIT 1992)**

32. In the Arrhenius equation for a certain reaction, the values of A and E_a (energy of activation) are 4×10^{13} sec^{-1} and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half-life period be 10 minute? **(IIT 1990)**

33. A compound (R) undergoes parallel path reactions involving n steps as shown below :



Where K and E represents rate constant and energy of activations. Calculate the overall rate constant and overall energy of activation.

34. Two I order reactions having same reactant concentrations proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C.

35. The decomposition of ammonia on platinum surface follow the change,

$$2NH_3 \longrightarrow N_2 + 3H_2$$

(a) What does $\frac{-d[NH_3]}{dt}$ denote?

(b) What does $\frac{d[N_2]}{dt}$ and $\frac{d[H_2]}{dt}$ denote?

(c) If the decomposition is zero order then what are the rate of production of N_2 and H_2, if $K = 2.5 \times 10^{-4}\ M\ s^{-1}$?

(d) If the rate obeys $-\frac{d[NH_3]}{dt}=\frac{K_1[NH_3]}{1+K_2[NH_3]}$, what will be the order for decomposition of NH_3, if (i) $[NH_3]$ is very very less and (ii) $[NH_3]$ is very very high? K_1 and K_2 are constants.

36. Dinitrogen pentaoxide decomposes as follows :

$$N_2O_5 \longrightarrow 2NO_2+\frac{1}{2}O_2. \text{ If,}$$

$$\frac{-d[N_2O_5]}{dt}=K_1[N_2O_5]$$

$$\frac{d[NO_2]}{dt}=K_2[N_2O_5]$$

$$\frac{d[O_2]}{dt}=K_3[N_2O_5]$$

Derive a relation between K_1, K_2 and K_3.

37. The decomposition of ozone occurs as $2O_3(g)\rightarrow 3O_2$, following the rate law :

$$-\frac{d[O_3]}{dt}=K\frac{[O_3]^2}{[O_2]}$$

what are the units of rate and rate constant?

38. The rate law has the form; rate $=K[A][B]^{3/2}$, can the reaction be an elementary process?

39. For the chemical reaction,

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

the rate expression is rate $=K[Br^-][BrO_3^-][H^+]^2$, calculate:

(a) order of reaction.

(b) apparent molecularity of reaction.

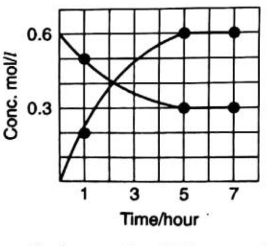
40. In a reaction, $2A\rightarrow$ Products, the concentration of A decreases from 0.5 mol litre^{-1} to 0.4 mol litre^{-1} in 10 minute. Calculate average rate during this interval.

41. The progress of the reaction $A \rightleftharpoons nB$ with time is presented in the figure. Determine :

(i) the value of n,

(ii) the equilibrium constant, K and

(iii) the initial rate of conversion of A. **(IIT 1994)**



42. A 22.4 litre flask contains 0.76 mm of ozone at 25°C. Calculate:

(i) the concentration of oxygen atom needed so that the reaction $O+O_3\rightarrow 2O_2$ having rate constant equal to 1.5×10^7 litre mol^{-1}sec^{-1} can proceed with a rate of 0.15 mol litre^{-1}sec^{-1}.

(ii) the rate of formation of oxygen under this condition.

43. The rate constant for the reaction :

$$CO_2+OH^- \longrightarrow HCO_3^-$$

in the aqueous solution is 4×10^{-3} litre mol^{-1} sec^{-1}. Calculate the number of mole of CO_2 and OH^- used up per second when $[CO_2]$ and $[OH^-]$ are 10^{-6} and 10^{-3} mol litre^{-1}. Also predict the mole of HCO_3^- formed per second.

44. For a reaction $3A \longrightarrow$ Products, it is found that the rate of reaction doubles, if concentration of A is increased four times, calculate order of reaction.

45. The rate of a reaction starting with initial concentration of $2\times10^{-3}M$ and $1\times10^{-3}M$ are equal to $2.40\times10^{-4}\ Ms^{-1}$ and $0.60\times10^{-4}\ M\ sec^{-1}$ respectively. Calculate the order of reaction w.r.t. reactant and also the rate constant.

46. The reaction $2A+B+C \longrightarrow D+2E$ is found to be I order in A, II order in B and zero order in C.

(a) Write rate expression.

(b) What is the effect on rate on increasing the conc. of A, B and C two times?

47. For $2A+B+\underset{\text{(excess)}}{C} \longrightarrow$ Products, calculate the :

(a) rate expression.

(b) units of rate and rate constant.

(c) effect on rate, if concentration of A is doubled and of B is tripled.

48. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which reaction should be the fastest and is this true for all ranges of concentrations?

49. Find the order of reaction for the rate expression rate $=K[A][B]^{2/3}$. Also suggest the units of rate and rate constant for this expression.

50. The rate law of a chemical reaction given below :

$$2NO+O_2 \longrightarrow 2NO_2$$

is given as rate $=K[NO]^2[O_2]$. How will the rate of reaction change, if the volume of reaction vessel is reduced to 1/4th of its original value?

51. Calculate the order of reaction for which rate becomes half if volume of container having same amount of reactant is doubled. (Assume gaseous phase reaction)

52. The rate of a reaction is given by $\frac{dx}{dt}=\frac{K(a-x)}{1+bx}$, where a is the initial concentration of the reactant and K, b are constants. x is the concentration of product at time t. What is half-life of this reaction?

53. The rate of a first order reaction is 0.04 mol litre^{-1}sec^{-1} at 10 minute and 0.03 mol litre^{-1} at 20 minute after initiation. Find the half-life of the reaction. **(IIT 2001)**

54. The rate law for the following reaction;

Ester $+ H^+ \longrightarrow$ Acid + Alcohol, is $\frac{dx}{dt} = K$ (ester) $[H_3O^+]^0$

What would be the effect on rate if :

(a) concentration of ester is doubled?

(b) concentration of H^+ ion is doubled?

55. The rate of change in concentration of C in the reaction $2A + B \longrightarrow 2C + 3D$ was reported as 1.0 mol litre^{-1} sec^{-1}. Calculate the reaction rate as well as rate of change of concentration of A, B and D.

56. Write the rate law expression and find the rate constant of the reaction $A + B \rightarrow$ Product. Also calculate half-life period. **(IIT 2004)**

$[A_0]$ mol litre^{-1}	$[B_0]$ mol litre^{-1}	Rate $[R_0]$ mol litre^{-1}sec^{-1}
0.1	0.2	0.05
0.2	0.2	0.10
0.1	0.1	0.05

57. For the reaction $A + B \longrightarrow C$, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M, the observed initial rate of formation of C is 1×10^{-4} mol litre^{-1}minute^{-1}. In the second experiment when the initial concentrations of A and B are 0.1 M and 0.3 M, the initial rate is 9.0×10^{-4}mol litre^{-1}minute^{-1}. In the third experiment when the initial concentrations of both A and B are 0.3M, the initial rate is 2.7×10^{-3} mol litre^{-1}minute^{-1}.

(a) Write rate law for this reaction.

(b) Calculate the value of specific rate constant for this reaction. **(Roorkee 1987)**

58. For the reaction, $2NO + H_2 \rightarrow N_2O + H_2$, the value of $-\frac{dP}{dt}$ was found to be 1.5 Pa s^{-1} for a pressure of 359 Pa of NO and 0.25 Pa s^{-1} for a pressure of 152 Pa of NO. The pressure of H_2 being constant. If pressure of NO was kept constant, the value of $-\frac{dP}{dt}$ was found 1.60 Pa s^{-1} for a pressure of H_2 289 Pa and 0.79 Pa s^{-1} for a pressure of 147 Pa of H_2. Calculate the order of reaction.

59. The data given below are for the reaction of NO and Cl_2 to form NOCl at 295 K.

$[Cl_2]$	[NO]	Initial rate (mol litre^{-1}sec^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order with respect to NO and Cl_2 in the reaction?

(b) Write the rate expression.

(c) Calculate the rate constant.

(d) Determine the reaction rate when conc. of Cl_2 and NO are 0.2 M and 0.4 M respectively. **(Roorkee 1993)**

60. The following data are for the reaction $A + B \longrightarrow$ Products:

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

(a) What is the order with respect to A and B for the reaction?

(b) Calculate the rate constant.

(c) Determine the reaction rate when the concentrations of A and B are 0.2 M and 0.35 M respectively. **(Roorkee 1995)**

61. The chemical reaction between $K_2C_2O_4$ and $HgCl_2$ is,

$$2HgCl_2 + K_2C_2O_4 \longrightarrow 2KCl + 2CO_2 + Hg_2Cl_2$$

The weights of Hg_2Cl_2 precipitated from different solutions in given time are as:

Time	$HgCl_2$ (mol litre^{-1})	$K_2C_2O_4$ (mol litre^{-1})	Hg_2Cl_2 formed (mol litre^{-1})
60	0.0418	0.404	0.0032
65	0.0836	0.404	0.0068
120	0.0836	0.202	0.0031

Calculate order of reaction.

62. For a gaseous reaction $2A + B_2 \longrightarrow 2AB$, the following rate data were obtained.

Rate of disappearance of B_2	mol litre^{-1}	
	$[A]$	$[B_2]$
1.8×10^{-3}	0.015	0.15
1.08×10^{-2}	0.090	0.15
5.4×10^{-3}	0.015	0.45

Calculate : (a) the rate constant, (b) rate of formation of AB when,

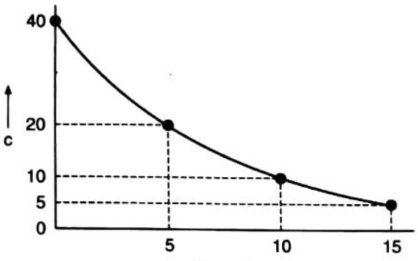
$$[A] = 0.02 \text{ and } [B_2] = 0.04$$

63. For a reaction at 800°C, $2NO + 2H_2 \rightarrow N_2 + 2H_2O$, the following data were obtained.

	$[NO] \times 10^{-4}$ mol litre^{-1}	$[H_2] \times 10^{-3}$ mol litre^{-1}	$-\frac{1}{2}d[NO]/dt \times 10^{-4}$ mol litre^{-1}min^{-1}
(i)	1.5	4.0	4.4
(ii)	1.5	2.0	2.2
(iii)	0.5	2.0	0.24

What is the order of this reaction with respect to NO and H_2? Also calculate rate constant.

64. For a reaction a graph was plotted between reactant concentration *C* and time *t* as shown in figure.



Identify the order of the reaction with respect to the reactant. Can the concentration of the reactant be theoretically zero after infinite time?

65. In the decomposition of N_2O_5, the plot between the reciprocal of concentration of the reactant and the time was found to be linear as shown in figure. Determine the order of reaction.

66. What will be the initial rate of a reaction if its rate constant is $10^{-3}\ \text{min}^{-1}$ and the concentration of reactant is 0.2 mol dm^{-3}? How much of reactant will be converted into products in 200 minute? **(Roorkee 1992)**

67. 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 the reaction after 1 hr. **(IIT 1999)**

68. A substance reacts according to I order kinetics and rate constant for the reaction is $1 \times 10^{-2}\ \text{sec}^{-1}$. If its initial concentration is 1 *M*,

(a) What is initial rate?

(b) What is rate after 1 minute? **(Roorkee 1993)**

69. Show that for a first order reaction, time required for 99% completion is twice for the time required for the completion of 90% of the reaction.

70. Show that $t_{1/2} / t_{3/4}$ for n^{th} order reaction is a function of '*n*' alone. $t_{3/4}$ is the time required for concentration to become 1/4 of original concentration.

71. In a reaction, the decrease in reactant's concentration is 20% in 20 minute and 40% in 40 minute. Calculate order of reaction and rate constant.

72. The rate of a certain reaction depends on concentration according to the equation :

$-\frac{dC}{dt} = \frac{K_1 C}{1 + K_2 C}$, what will be the order of reaction, where (a) concentration is very very high, (b) very very low?

73. The rate expression for a reaction is $\frac{-dC}{dt} = \frac{\alpha \cdot C}{1 + \beta C}$ where $\alpha, \beta > 0$. Calculate the $t_{1/2}$ for this reaction.

74. For a homogeneous gaseous phase reaction : $2A \rightarrow 3B + C$, the initial pressure of reactant was P° while pressure at time '*t*' was *P*. Find the pressure after time $2t$. Assume I order reaction.

75. If a reaction $A \longrightarrow$ Products, the concentrations of reactant *A* are $C_0, aC_0, a^2C_0, a^3C_0, \ldots$ after time interval, $0, t, 2t, 3t, \ldots$ where *a* is constant. Given $0 < a < 1$. Show that the reaction is of I order. Also calculate the relation in *K*, *a* and *t*.

76. Starting with one mole of a compound *A*, it is found that the reaction is 3/4 completed in 1 hour. Calculate the rate constant if the reaction is of:

(a) I order.

(b) II order.

77. The half time of first order decomposition of nitramide is 2.1 hour at 15°C.

$$NH_2NO_2(aq.) \longrightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate:

(i) time taken for NH_2NO_2 is decompose 99%.

(ii) volume of dry N_2O produced at this point measured at STP. **(Roorkee 1994)**

78. In I order reaction, the concentrations of reactants 10 and 20 minute after the beginning of reaction corresponds to 13.8 and 8.25 (arbitrary units). Calculate the initial concentrations of the reactants and the velocity constant.

79. Catalytic decomposition of nitrous oxide by gold at 900°C at an initial pressure of 200 mm was 50% in 53 minute and 73% in 100 minute. **(Roorkee 1990)**

(a) What is the order of reaction?

(b) Calculate velocity constant.

(c) How much will it decompose in 100 minute at the same temperature but at an initial pressure of 600 mm?

80. The decomposition of N_2O_5 according to equation $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ is a first order reaction. After 30 minute from start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of reaction. **(IIT 1991)**

81. At 100°C, a gaseous reaction $A \longrightarrow B + 2C$; is observed to be of I order. On starting with pure *A*, at the end of 14 minute, the total pressure was found to be 264 mm of Hg. After a long time the total pressure of the system was 450 mm of Hg. Calculate :

(a) initial pressure of *A*.

(b) rate constant of reaction.

(c) half-life period of reaction.

82. Arsine decomposes on heating to give As and H_2. The decomposition studied at constant volume and temperature gives the following data.

T in hr.	0	5.5	6.5	8
P in atm.	0.9654	1.06	1.076	1.1

Calculate velocity constant, assuming first order reaction.

83. The half-life period and initial concentration for a reaction are as follows. What is order of reaction?

Initial concentration	350	540	158
$t_{1/2}$	425	275	941

84. The inversion of cane sugar proceeds with constant half-life of 500 minute at pH = 5 for any concentration of sugar. However, if pH = 6, the half-life changes to 50 minute. Derive the rate law for inversion of cane sugar.

85. Hydrogenation of vegetable ghee at 25°C reduces the pressure of H_2 from 2 atm to 1.2 atm in 50 minute. Calculate the rate of reaction in terms of change of :

(a) pressure per minute.

(b) molarity per second.

86. The following data were obtained for the decomposition of NO in contact with gold surface at 900°C. Find the O.R.

Time (in minute)	15	30	45	65	80
% decomposition	17	32	44.5	57	65

87. Ethylene is produced by :

$$\underset{\text{Cyclobutane}}{C_4H_8} \xrightarrow{\Delta} 2C_2H_4$$

The rate constant is $2.48 \times 10^{-4} \text{sec}^{-1}$. In what time will the molar ratio of the ethylene to cyclobutane in reaction mixture attain the value (a) 1, (b) 100?

88. A drop of solution (volume 0.05 mL) contains 3.0×10^{-6} mole of H^+. If the rate constant of disappearance of H^+ is $1.0 \times 10^7 \text{mol litre}^{-1}\text{sec}^{-1}$. How long would it take for H^+ in drop to disappear?

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

(a) The rate constant.

(b) Pressure of Cl_2O_7 after 100 sec.

90. While studying the decomposition of $N_2O_5(g)$ it is observed that a plot of logarithm of its partial pressure *versus* time is linear. What kinetic parameter can be obtained from this?

91. The following data represent for the decomposition of NH_4NO_2 in aqueous solution.

Time in minute	10	15	20	25	∞
Volume of N_2 (in mL)	6.25	9.0	11.40	13.65	33.05

(a) Show that reaction is of I order.

(b) Calculate velocity constant.

92. Derive O.R. for the decomposition of H_2O_2 from the following data.

Time in minute	0	10	20	30
Volume of $KMnO_4$ needed for H_2O_2	25	16	10.5	7.09

93. Derive the O.R. for decomposition of H_2O_2 from the following data.

Time in minute	10	15	20	25	∞
Volume of O_2 given by H_2O_2	6.30	8.95	11.40	13.5	35.75

94. The kinetics of hydrolysis of methyl acetate in excess dilute HCl at 25°C were followed by withdrawing 2 mL of the reaction mixture at intervals of (t), adding 50 mL water and titrating with baryta water. Determine the velocity constant of hydrolysis.

t (in minute)	0	75	119	259	∞
Titre value (in mL)	19.24	24.20	26.60	32.23	42.03

95. In the inversion of cane sugar in presence of an acid, the following polarimeter readings are obtained.

Time in minute	0	30	90	230	∞
Rotation in degree	+46.75	+41.0	+30.75	+12.75	−18.75

Calculate rate constant.

96. The gas phase decomposition of dimethyl ether follows first order kinetics,

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500°C and has a half-life of 14.5 minute. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 minute? Assume ideal gas behaviour. **(IIT 1993)**

97. The reaction $A + OH^- \longrightarrow$ Products, obeys rate law expression as,

$$\frac{-d[A]}{dt} = k[A][OH^-]$$

If initial concentrations of $[A]$ and $[OH^-]$ are 0.002 M and 0.3 M respectively and if it takes 30 sec for 1% A to react at 25°C, calculate the rate constant for the reaction.

98. For the non-equilibrium process, $A + B \rightarrow$ Products, the rate is first order with respect to A and second order reaction with respect to B. If 1.0 mole each of A and B are introduced into 1 litre vessel and the initial rate were 1.0×10^{-2} mol/litre-sec, calculate the rate when half of the reactants have been used.

99. Two reactants A and B separately shows two chemical reactions. Both reactions are made with same initial concentration of each reactant. Reactant A follows first order kinetics whereas reactant B follows second order kinetics. If both have same half-lives, compare their rates (a) at the start of reaction (b) after the lapse of one half-life.

100. A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as:

$$CH_3OCH_3(g) \longrightarrow CH_4(g) + CO(g) + H_2(g)$$

The rate constant of decomposition is $4.78 \times 10^{-3}\ \text{min}^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hour of initiation of decomposition. Assume composition of gas present and gas diffused remains same.

101. Some $PH_3(g)$ is introduced into a flask at 600°C containing an inert gas. PH_3 proceeds to decompose into $P_4(g)$ and $H_2(g)$ and the reaction goes to completion. The total pressure is given below as a function of time. Find the order of the reaction and calculate the rate constant. **(Roorkee 2001)**

Time (sec.)	0	60	120	∞
P (mm Hg)	262.40	272.90	275.51	276.40

102. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volume was left open. Due to this some H_2O_2 decomposed. To determine the new volume strength after 6 hr, 10 mL of this solution was diluted to 100 mL. 10 mL of this diluted solution was titrated against 25 mL of 0.25 M $KMnO_4$ acidified solution. Calculate the rate constant for the decomposition of H_2O_2.

103. A certain reaction B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing agent which reacts only with B^{n+} and $B^{(n+4)+}$. In the process it converts B^{n+} to $B^{(n+2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$, the volume of reagent consumed is 25 mL and at $t = 10$ minute, the volume used is 32 mL. Calculate the rate constant for the conversion of B^{n+} of $B^{(n+4)+}$ assuming it to be a first order reaction.

104. The reaction $CH_3COF + H_2O \rightarrow CH_3COOH + HF$ has been studied under the following initial conditions,

Case I	Case II
$[H_2O]_0 = 1.0\,M$	$[H_2O]_0 = 0.02\,M$
$[CH_3COF]_0 = 0.01\,M$	$[CH_3COF]_0 = 0.80\,M$

The variation of concentration with time were noted as:

Case I :		**Case II :**	
t/min	$[CH_3COF]$	t/min	$[H_2O]$
0	0.01000	0	0.0200
10	0.00857	10	0.0176
20	0.00735	20	0.0156
40	0.00540	40	0.0122

Determine the order of reaction and rate constant of reaction.

105. Two second order reactions given below having identical frequency factors :

(i) $A \longrightarrow$ Product

(ii) $B \longrightarrow$ Product

The E_a for first reaction is 10.46 kJ/mol^{-1} more than that of B. At 100°C, the reaction (i) is 30% completed after 60 minute when initial concentration of A is 0.1 mol dm^{-3}. How long will it take for reaction (ii) to reach 70% completion at the same temperature if initial concentration of B is 0.05 mol litre^{-1}?

106. The reaction : $OCl^- + I^- \xrightarrow{OH^-} OI^- + Cl^-$ takes place in following steps:

(i) $OCl^- + H_2O \underset{K_2}{\overset{K_1}{\rightleftharpoons}} HOCl + OH^-$ (fast)

(ii) $I^- + HOCl \xrightarrow{K_3} HOI + Cl^-$ (slow)

(iii) $OH^- + HOI \underset{K_2'}{\overset{K_1'}{\rightleftharpoons}} H_2O + OI^-$ (fast)

Write the rate expression in terms of rate of consumption of I^-.

107. The reaction : $CO + Cl_2 \longrightarrow COCl_2$ has the following mechanism. Derive the rate expression:

(i) $Cl_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast)

(ii) $Cl + CO \underset{K_2'}{\overset{K_1'}{\rightleftharpoons}} COCl$ (fast)

(iii) $COCl + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

108. What will be the order of reaction given below?

$$NH_4CNO \longrightarrow NH_2CONH_2$$

The reaction is completed in three steps as:

(i) $NH_4CNO \rightleftharpoons NH_4NCO$ (fast equilibrium)

(ii) $NH_4NCO \rightleftharpoons NH_3 + H{-}N{=}C{=}O$ (fast equilibrium)

(iii) $NH_3 + H{-}N{=}C{=}O \longrightarrow NH_2CONH_2$ (slow)

109. For the reversible reaction in equilibrium : $A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$.

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

110. For a reversible first order reaction,

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B;\ K_f = 10^{-2}\text{sec}^{-1}$$

and $\dfrac{B_{eq.}}{A_{eq.}} = 4$; If $A_0 = 0.01\ ML^{-1}$ and $B_0 = 0$, what will be concentration of B after 30 sec?

111. 8 mole of an element undergoes decomposition in three parallel path following I order reaction giving three new elements B, C and D with rate constant 2×10^{-3}, 3×10^{-3} and 1.93×10^{-3} sec^{-1} respectively. What will be the mole of B after 100 sec.

112. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate(II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is : **[JEE (Advanced II) 2015]**

SOLUTIONS (Numerical Problems)

1. The rate expression is derived by (ii) step of mechanism, a slower step, thus,

$$\text{rate} = K[\text{NOBr}_2][\text{NO}] \quad \ldots(1)$$

However, NOBr_2 is an intermediate and thus its concentration should be replaced from Eq. (1)

For step (1), equilibrium constant $K_C = \dfrac{[\text{NOBr}_2]}{[\text{NO}][\text{Br}_2]}$

$$\therefore \quad [\text{NOBr}_2] = K_C[\text{NO}][\text{Br}_2] \quad \ldots(2)$$

Thus, by Eqs. (1) and (2)

$$\text{rate} = K \cdot K_C[\text{NO}]^2[\text{Br}_2]$$

$$\text{rate} = \mathbf{K'[NO]^2[Br_2]}$$

2. From the slow step, we can have

$$\text{rate} = \mathbf{K[N_2O_5]}$$

3. The rate $= K[NO_2][F_2]$ implies that slow step of reaction involves only one molecule of each reacting species, thus we can have the mechanism as :

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

$$NO_2 + F \xrightarrow{\text{Fast}} NO_2F$$

$$\therefore \text{Overall reaction is } 2NO_2 + F_2 \longrightarrow 2NO_2F$$

4.

$$NO_2Cl \xrightarrow{\text{Slow}} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{\text{Fast}} NO_2 + Cl_2$$

$$\text{Overall reaction is } 2NO_2Cl \longrightarrow 2NO_2 + Cl_2$$

5.

$$[A]_t = [A]_0 \cdot e^{-K_1t}$$

$$[B]_t = [B]_0 \cdot e^{-K_2t}$$

$$\therefore \quad \frac{[A]_t}{[B]_t} = e^{(-K_1+K_2)\cdot t}$$

$$4 = e^{(K_2-K_1)\cdot t} \qquad \text{if } \frac{[A]_t}{[B]_t} = 4$$

or $(K_2 - K_1)\cdot t = \ln 4$

$$\therefore \quad t = \frac{\ln 4}{K_2 - K_1} = \frac{1.386}{\frac{0.693}{18} - \frac{0.693}{54}} = \mathbf{54\ minute}$$

$\dfrac{[A]_t}{[B]_t} = \dfrac{1}{4}$ is not possible because B decays fastly.

6. Average rate $= -\dfrac{[R_2 - R_1]\times 10^{-3}}{[t_2 - t_1]}$

$$\text{After 5 sec } r_1 = -\frac{[80-160]\times 10^{-3}}{5} = \mathbf{16\times 10^{-3}\ ms^{-1}}$$

$$\text{After 10 sec } r_2 = -\frac{[40-80]\times 10^{-3}}{5} = \mathbf{8\times 10^{-3}\ ms^{-1}}$$

$$\text{After 20 sec } r_3 = -\frac{[10-40]\times 10^{-3}}{10} = \mathbf{3\times 10^{-3}\ ms^{-1}}$$

$$\text{After 30 sec } r_4 = -\frac{[2.5-10]\times 10^{-3}}{10} = \mathbf{0.75\times 10^{-3}\ ms^{-1}}$$

7. The reaction suggest that 1 mole of ClO^- reacts with 1 mole of I^- at any time. Thus, at any time after the reaction begins

$$\Delta[I^-] = 0.075 - [I^-]_{\text{left}}$$

$$\Delta[ClO^-] = 0.125 - [ClO^-]_{\text{left}}$$

Also $\quad \Delta[I^-] = \Delta[ClO^-] \qquad (\because 1:1 \text{ ratio})$

$$\therefore \quad 0.075 - [I^-]_{\text{left}} = 0.125 - [ClO^-]_{\text{left}}$$

$$\text{or} \quad [I^-]_{\text{left}} = [ClO^-]_{\text{left}} - 0.050$$

$$\text{Rate at any time} = K[ClO^-]_{\text{left}} \times [I^-]_{\text{left}}$$

$$= K[ClO^-]_{\text{left}} \times ([ClO^-]_{\text{left}} - 0.050)$$

8. (i) Rate of forward reaction

$$= \mathbf{2.0\times 10^{-4}[Cu(NH_3)_4]^{2+}[H_2O]}$$

Rate of backward reaction

$$= \mathbf{3.0\times 10^{5}[Cu(NH_3)_3H_2O]^{2+}[NH_3]}$$

(ii) Also, $\quad K_f = 2.0\times 10^{-4}$

$$K_b = 3.0\times 10^{5}$$

$$\frac{K_f}{K_b} = \frac{2.0\times 10^{-4}}{3.0\times 10^{5}} = \mathbf{6.6\times 10^{-10}}$$

(iii) More predominant reaction is **backward reaction.**

9.

$$\frac{-d[B]}{dt} = K_1[A]$$

$$\frac{-d[C]}{dt} = K_2[A]$$

$$\therefore \quad \frac{[B]}{[C]} = \frac{K_1}{K_2}$$

Let after ∞ time pressure equivalent to P' shows dissociation to B and $1-P'$ to C

$$\therefore \quad 2P' + 1 - P' = 1.5$$

$$\therefore \quad P' = 0.5 \text{ atm}$$

$$\therefore \quad \frac{K_1}{K_2} = \frac{2P'}{1-P'} = \frac{1}{0.5} = 2$$

i.e., 2 : 1 is the ratio for the decomposition to $B : C$.

$$\text{Now,} \quad \begin{array}{ccccc} A & \longrightarrow & 2B & + & C \\ 1 & & 0 & & 0 \\ 1-a & & \frac{2\times 2a}{3} & & \frac{1\times a}{3} \end{array}$$

$$\therefore \quad 1 - a + \frac{4a}{3} + \frac{a}{3} = 1.4 \qquad \therefore \ a = 0.6$$

$$\text{Also,} \quad K_{av} = \frac{2.303}{10}\log\frac{1}{0.4} = 0.092$$

$$K_{av} = K_1 + K_2$$

$$0.092 = 2K_2 + K_2$$

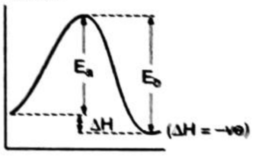
$$\therefore \quad K_2 = 0.03; \quad K_1 = 0.062$$

10.

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

$$K_f = Ae^{-E_a/RT}$$

$$K_b = Ae^{-E_b/RT}$$



$$\therefore \quad K_{eq.} = \frac{K_f}{K_b} = e^{(E_b - E_a)/RT} = e^{-\Delta H/RT}$$

$$(\because \Delta H = E_a - E_b)$$

11. $$2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\therefore \quad 2.303 \log_{10} \frac{4.5\times10^7}{1.5\times10^7} = \frac{E_a}{8.314}\left[\frac{373-323}{373\times323}\right]$$

$$\therefore \quad E_a = \mathbf{2.2\times10^4\ J\ mol^{-1}}$$

Now, $K = Ae^{-E_a/RT}$ $\quad\therefore\quad 4.5\times10^7 = Ae^{-\frac{2.2\times10^4}{8.314\times373}}$

$$\therefore \quad A = \mathbf{5.42\times10^{10}}$$

12. Given,

$K_2 = ?,\qquad T_2 = 458\text{ K},$

$K_1 = 5.5\times10^{-4},\qquad T_1 = 413\text{ K},$

$R = 1.987\text{ cal},\qquad E_a = 2.37\times10^4\text{ cal mol}^{-1}$

$$\because \quad 2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R}\frac{[T_2 - T_1]}{T_1 T_2}$$

$$2.303 \log_{10} \frac{K_2}{5.5\times10^{-4}} = \frac{2.37\times10^4}{1.987}\left[\frac{458-413}{458\times413}\right]$$

$$\therefore \quad K_2 = \mathbf{9.38\times10^{-3}\ sec^{-1}}$$

13. $$\because \quad \log_{10} K = \log_{10} A - \frac{E_a}{2.303RT}$$

or $\log_{10}$ vs. $\frac{1}{T}$ graph is linear with slope, $-\frac{E_a}{2.303R}$

$$\therefore \quad \text{Slope} = -\frac{E_a}{2.303\times R} = \frac{(3.0-2.0)}{(2\times10^{-3} - 5\times10^{-3})}$$

or $$\frac{E_a}{2.303\times2} = \frac{1}{3\times10^{-3}}$$

or $$E_a = \mathbf{1.54\times10^3\ cal = 15.4\ kcal}$$

14. Given,

$A = 1.11\times10^{11}\text{ sec}^{-1}\qquad E_a = 39.3\times10^3\text{ cal mol}^{-1},$

$R = 1.987\text{ cal},\qquad T = 573\text{ K}$

$$\because \quad K = Ae^{-E_a/RT}$$

$$\therefore \quad \ln K = \ln A - \frac{E_a}{RT}$$

or $$\log_{10} K = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\log_{10} K = \log_{10} 1.11\times10^{11} - \frac{39.3\times10^3}{2.303\times1.987\times573}$$

$$\therefore \quad K = \mathbf{1.14\times10^{-4}\ sec^{-1}}$$

Also, $$t_{1/2} = \frac{0.693}{1.14\times10^{-4}} = \mathbf{6078\ sec}$$

15. Given, $T_2 = 60 + 273 = 333\text{ K},\quad T_1 = 30 + 273 = 303\text{ K},$

$R = 1.987\times10^{-3}\text{ kcal}$

$\because \quad r = k[\text{Reactant}]^n$ (at a temperature T)

$\therefore \quad \frac{r_2}{r_1} = \frac{K_2}{K_1}$ (at temp. T_2 and T_1)

$\because \quad \frac{r_2}{r_1} = 5 \qquad \therefore \quad \frac{K_2}{K_1} = 5$

$$\because \quad 2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R}\frac{[T_2 - T_1]}{T_1 T_2}$$

$$\therefore \quad 2.303 \log_{10} 5 = \frac{E_a}{10^{-3}\times1.987}\left[\frac{333-303}{333\times303}\right]$$

$$\therefore \quad E_a = \mathbf{10.757\ kcal\ mol^{-1}}$$

16. $$r_1 = K_1[A]$$

and $$r_2 = K_2[B]$$

Since, $[A] = [B],\qquad r_1 = r_2$ when $K_1 = K_2$

Thus, $$10^{16} e^{\left(-\frac{3000}{T}\right)} = 10^{15} e^{\left(-\frac{2000}{T}\right)}$$

or $$16 - \frac{3000}{T\times2.303} = 15 - \frac{2000}{T\times2.303}$$

$$1 = \frac{1000}{T\times2.303}$$

or $$T = \frac{1000}{1\times2.303} = \mathbf{434.22\ K}$$

17. Rate constant at 300 K = k

$\therefore$ Rate constant at 310 K $= k + \left[k\times\frac{7}{100}\right] = 1.07k$

Thus, $$2.303 \log \frac{k_2}{k_1} = \frac{E_a^f}{R}\frac{[T_2 - T_1]}{T_2 T_1}$$

$$2.303 \log \frac{1.07k}{k} = \frac{E_a^f}{2}\left[\frac{310-300}{310\times300}\right]$$

$$\therefore \quad E_a^f = \mathbf{1258.68\ cal}$$

Now, equilibrium constant at 300 K = K'

Equilibrium constant at 310 K $= K' + \frac{3}{100}\times K' = 1.03K'$

Using $$2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$2.303 \log \frac{1.03K'}{K'} = \frac{\Delta H}{2}\left[\frac{310-300}{310\times300}\right]$$

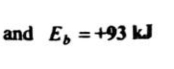
$$\therefore \quad \Delta H = 549.89\text{ cal}$$

Since, $$\Delta H = E_a^f - E_a^b$$

$$\therefore \quad 549.89 = 1258.68 - E_a^b$$

$$\therefore \quad E_a^b = \mathbf{708.79\ cal}$$

18. Given, $\Delta H = E_f - E_b = -33\text{ kJ}$



(a) $$K_f = Ae^{-E_f/RT}$$

$$K_b = Ae^{-E_b/RT}$$

$$\therefore \quad K_C = \frac{K_f}{K_b} = e^{[E_b - E_f]/RT}$$

$$= e^{\frac{33\times10^3}{8.314\times300}}$$

$$= \mathbf{5.572\times10^5}\text{ at 300 K}$$

(b) Given, $\frac{E_f}{E_b} = \frac{20}{31}$ and $E_f - E_b = -33\text{ kJ}$

$$\therefore \quad E_f - \frac{31}{20}E_f = -33\text{ kJ}$$

$$\therefore \quad E_f = \frac{33\times20}{11} = \mathbf{60\ kJ}\ \text{and}\ E_b = \mathbf{+93\ kJ}$$

19. $K = Ae^{-E_a/RT}$

For methyl nitrite $\quad K_1 = 10^{13}\ e^{[-152300/(8.314\times T)]}$

For ethyl nitrite $\quad K_2 = 10^{14}\ e^{[-157700/(8.314\times T)]}$

if $K_1 = K_2$, then

$$10^{13}\ e^{[-152300/(8.314\times T)]} = 10^{14}\ e^{[-157700/(8.314\times T)]}$$

$$10 = e^{(+157700-152300)/(8.314\times T)}$$

or $\quad 2.303\log_{10} = \dfrac{157700-152300}{8.314\times T} \quad \therefore\ T = \mathbf{282\ K}$

20. Given, $\dfrac{K_2}{K_1} = 1.75$

$T_1 = 25°\text{C} = 25+273 = 298\,\text{K}$,

$T_2 = 35°\ \text{C} = 35+273 = 308\,\text{K}$

(Since, temperature coefficient is ratio of rate constants at 35°C and 25°C respectively.)

$\because \quad 2.303\log_{10}\dfrac{K_2}{K_1} = \dfrac{E_a}{R}\dfrac{[T_2-T_1]}{T_1T_2}$

$\therefore \quad 2.303\log_{10} 1.75 = \dfrac{E_a}{1.987}\ \dfrac{[308-298]}{308\times 298}$

$\therefore \quad E_a = \dfrac{2.303\times 308\times 298\times 1.987}{10}\times \log 1.75\ \text{cal mol}^{-1}$

$E_a = \mathbf{10.27\ kcal\ mol^{-1}}$

21. Given, $\quad A \longrightarrow B$

and 20% solution of A decomposes 25% in 20 minute at 25°C

$\therefore \quad$ Initial amount $a = 20$

$\therefore \quad$ Amount left $(a-x) = 20\times\dfrac{75}{100} = 15$

$\therefore \quad K_{25} = \dfrac{2.303}{20}\log_{10}\dfrac{20}{15} \quad (\because\ t = 20\,\text{minute})$

$= 0.0144\ \text{minute}^{-1}$

Now, $\quad 2.303\log_{10}\dfrac{K_{40}}{K_{25}} = \dfrac{E_a}{R}\dfrac{[T_2-T_1]}{T_1T_2}$

$\therefore \quad 2.303\log_{10}\dfrac{K_{40}}{K_{25}} = \dfrac{70\times 10^3}{8.314}\left[\dfrac{313-298}{313\times 298}\right]$

$\dfrac{K_{40}}{K_{25}} = 3.872$

$\therefore \quad K_{40} = 0.05575\ \text{min}^{-1}$

$(\because\ K_{25} = 0.0144)$

Now suppose amount m is left in 30% solution in 20 minute at 40°C.

$$K_{40} = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$0.05575 = \frac{2.303}{20}\log_{10}\frac{30}{m}$$

$\therefore \quad m = 9.838$

$\therefore \quad$ % decomposition $= \dfrac{(a-m)}{a}\times 100$

$= \dfrac{30-9.838}{30}\times 100 = \mathbf{67.21\%}$

22. Given, $\dfrac{K_{293}}{K_{276}} = 3;\ T_2 = 293\,\text{K}$ and $T_1 = 276\,\text{K}$

(a) $\quad 2.303\log_{10}\dfrac{K_2}{K_1} = \dfrac{E_a}{R}\dfrac{[T_2-T_1]}{T_1T_2} \qquad (R = 2\,\text{cal})$

$\therefore \quad 2.303\log_{10} 3 = \dfrac{E_a}{2}\dfrac{[293-276]}{293\times 276}$

$\therefore \quad E_a = 10453.95\,\text{cal} = \mathbf{10.454\ kcal}$

(b) Also, $\quad 2.303\log_{10}\dfrac{K_3}{K_2} = \dfrac{E_a}{R}\dfrac{[T_3-T_2]}{T_3T_2}$

This time, $E_a = 10.454\,\text{kcal};\ T_3 = 313\,\text{K}$ and $T_2 = 293\,\text{K}$

$\therefore \quad 2.303\log_{10}\dfrac{K_3}{K_2} = \dfrac{10.454\times 10^3}{2}\dfrac{[313-293]}{313\times 293}$

$\therefore \quad \dfrac{K_3}{K_2} = 3.12$

Now, $\quad \dfrac{K_3}{K_2} = \dfrac{t_2}{t_3} \quad \because\ K \propto \dfrac{1}{\text{time}}$

Also if milk is not soured up to 64 hr at 20°C, it will not sour up to 192 hr at 3°C. Similarly we can have

$$t_3 = t_2\times\frac{K_2}{K_3} = 64\times\frac{1}{3.12} = \mathbf{20.5\ hr}$$

23. Given, $\quad t = \dfrac{2.303}{K_{298}}\log_{10}\dfrac{100}{90} = \dfrac{2.303}{K_{308}}\log_{10}\dfrac{100}{75}$

$\therefore \quad \dfrac{K_{308}}{K_{298}} = 2.73$

Also, $\quad 2.303\log_{10}\dfrac{K_{308}}{K_{298}} = \dfrac{E_a}{R}\dfrac{[T_2-T_1]}{T_1T_2}$

$\therefore \quad 2.303\log_{10} 2.73 = \dfrac{E_a}{8.314}\times\dfrac{10}{298\times 308}$

$\therefore \quad E_a = 76.6227\ \text{kJ mol}^{-1} = \mathbf{18.33\ kcal\ mol^{-1}}$

Now, $\quad K = Ae^{-E_a/RT}$

$K_{318} = 3.56\times 10^9\times e^{-76622.7/(8.314\times 318)}$

$= 3.56\times 10^9\times 2.59\times 10^{-13}$

$= \mathbf{9.22\ \times 10^{-4}\ sec^{-1}}$

24. Given,

$T_2 = 273+35 = 308\ \text{K},\quad T_1 = 273+25 = 298\,\text{K}$

$E_a = 35\times 10^3\,\text{cal mol}^{-1},\qquad R = 1.987\ \text{cal}$

$\because \quad 2.303\log_{10}\dfrac{K_2}{K_1} = \dfrac{E_a}{R}\dfrac{[T_2-T_1]}{T_1T_2}$

$\therefore \quad 2.303\log_{10}\dfrac{K_2}{K_1} = \dfrac{35\times 10^3}{1.987}\dfrac{[308-298]}{308\times 298}$

$\therefore \quad \dfrac{K_2}{K_1} = 6.812$ or $K_2 = 6.812\times K_1$

$\therefore$ The factor by which the rate constant changes is **6.812.**

$\because \quad$ Rate $= K[\ \ ]$

$\therefore$ The factor by which rate changes is also **6.812.**

25. For I order reaction, $K = \dfrac{0.693}{t_{1/2}}$

(a) $\therefore$ At 27°C $\ K_1 = \dfrac{0.693}{30} = 2.31\times 10^{-2}\ \text{minute}^{-1}$

At 47°C $\ K_2 = \dfrac{0.693}{10} = 6.93\times 10^{-2}\ \text{minute}^{-1}$

(b) Now, $\quad 2.303\log_{10}\dfrac{K_2}{K_1} = \dfrac{E_a}{R}\dfrac{[T_2-T_1]}{T_1T_2}$

$$\therefore\ 2.303\log_{10}\frac{6.93\times10^{-2}}{2.31\times10^{-2}}=\frac{E_a}{8.314}\times\frac{[320-300]}{320\times300}$$

$\therefore$ $E_a = 43850\ \text{J mol}^{-1}$ or $E_a = \mathbf{43.85\ kJ\ mol^{-1}}$

(c) For a reaction $E_{aF.R.} - E_{aB.R.} = \Delta H$

$\therefore$ $43.85 - E_{aB.R.} = -50.0$

or $E_{aB.R.} = 43.85 + 50.0 = \mathbf{93.85\ kJ\ mol^{-1}}$

26. $K_1 = 0.693/360\ \text{min}^{-1}$ at 653 K and

$E_a = 200\times10^3$ J, $K_2 = ?$ at 723 K, $R = 8.314$ J

$\therefore$ From $2.303\log_{10}(K_2/K_1) = (E_a/R)[(T_2-T_1)/(T_1T_2)]$

$$K_2 = 0.068\ \text{min}^{-1}$$

Now, $t=\dfrac{2.303}{0.068}\log_{10}\dfrac{100}{25}=\mathbf{20.39\ minute}$

27. $\because$ $K = Ae^{-E_a/RT}$

Case I. $K_1 = Ae^{-100/RT}$

Case II. $K_2 = Ae^{-25/RT}$

$$\therefore\ \frac{K_1}{K_2}=\frac{e^{-100/RT}}{e^{-25/RT}}=e^{-75/RT}$$

or $\log_e\dfrac{K_2}{K_1}=\log e^{75/RT}$ (ΔH in kJ)

$\log_e\dfrac{K_2}{K_1}=\dfrac{75}{RT}=\dfrac{75\times10^3}{8.314\times293}$ (ΔH in J)

$$\frac{K_2}{K_1}=2.35\times10^{13}$$

Since, $r = K[\ ]^n$ $\because$ n and [ ] are same for Case I and II.

$$\therefore\ \frac{r_2}{r_1}=\frac{K_2}{K_1}=\mathbf{2.35\times10^{13}}$$

28. Let E_a and E'_a be the energy of activation in presence and absence of catalyst for hydrogenation reaction, then

$$K = Ae^{-E_a/RT}$$

In presence of catalyst: $K_1 = Ae^{-E_a/(R\times500)}$

In absence of catalyst : $K_2 = Ae^{-E'_a/(R\times400)}$

Given, the two rates are same, *i.e.*, $r_1 = r_2$; $\therefore$ $K_1 = K_2$

Therefore, $e^{-E_a/(R\times500)} = e^{-E'_a/(R\times400)}$

or $$\frac{E_a}{R\times500}=\frac{E'_a}{R\times400}$$

or $\dfrac{E_a}{500}=\dfrac{E_a-20}{400}$ $\because$ $E_a - E'_a = 20$

$\therefore$ $E_a = \mathbf{100\ kJ\ mol^{-1}}$

29. **(a) Given,** $\ln K = 14.34 - \dfrac{1.25\times10^4}{T}$

Also we have $\ln K = \ln A - \dfrac{E_a}{RT}$

Therefore, comparing these two

$$\frac{E_a}{R}=1.25\times10^4$$

$\therefore$ $E_a = 1.25\times10^4\times R\ \text{cal mol}^{-1}$

$= 1.25\times10^4\times1.987\ \text{cal mol}^{-1}$

$E_a = \mathbf{24.83\ kcal\ mol^{-1}}$

(b) $\ln K = 14.34 - \dfrac{1.25\times10^4}{500}$ (since $T = 500$ K)

$\therefore$ $K = \mathbf{2.35\times10^{-5}\ sec^{-1}}$

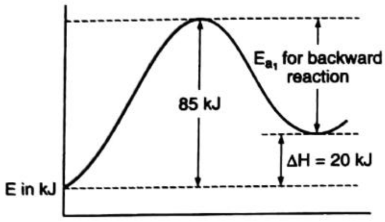
(c) $K = \dfrac{0.693}{256\times60}$

$\therefore$ $\ln\dfrac{0.693}{256\times60} = 14.34 - \dfrac{1.25\times10^4}{T}$

or $-10.00 = 14.34 - \dfrac{1.25\times10^4}{T}$

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

30.



ΔH of forward reaction = 20 kJ mol^{-1}

Energy of activation for forward reaction

$(E_a) = 85\ \text{kJ mol}^{-1}$

$\therefore$ Energy of activation for backward reaction

$= E_a - \Delta H$

$= 85 - 20 = \mathbf{65\ kJ\ mol^{-1}}$

31. (I) $A \longrightarrow$ Products

(II) $B \longrightarrow$ Products

$\because$ $t_{1/2}$ for (I) at 310 K = 30 minute

$\therefore$ K_{I} at $310 = \dfrac{0.693}{30} = 0.0231\ \text{min}^{-1}$ ...(1)

$\because$ Rate = K[ ]

and both reactions are of I order

Also given, $\dfrac{K_{\text{I}}\text{ at }310}{K_{\text{I}}\text{ at }300} = 2$ ...(2)

Also given, $\dfrac{K_{\text{II}}\text{ at }310}{K_{\text{I}}\text{ at }310} = 2$ ...(3)

Also we have, $\dfrac{E_{a_{\text{II}}}}{E_{a_{\text{I}}}} = \dfrac{1}{2}$ ...(4)

For I : $2.303\log_{10}\dfrac{K_{\text{I}}\text{ at }310}{K_{\text{I}}\text{ at }300}=\dfrac{E_{a_{\text{I}}}}{R}\left[\dfrac{310-300}{310\times300}\right]$ ...(5)

For II : $2.303\log_{10}\dfrac{K_{\text{II}}\text{ at }310}{K_{\text{II}}\text{ at }300}=\dfrac{E_{a_{\text{II}}}}{R}\left[\dfrac{310-300}{310\times300}\right]$ ...(6)

Dividing Eq. (5) by (6),

$\therefore$ $\dfrac{\log_{10}\dfrac{K_{\text{I}}\text{ at }310}{K_{\text{I}}\text{ at }300}}{\log_{10}\dfrac{K_{\text{II}}\text{ at }310}{K_{\text{II}}\text{ at }300}}=\dfrac{E_{a_{\text{I}}}}{E_{a_{\text{II}}}}=2$ By Eq. (4) ...(7)

or $\log_{10}\dfrac{K_{\text{I}}\text{ at }310}{K_{\text{I}}\text{ at }300}=2\log_{10}\left[\dfrac{K_{\text{II}}\text{ at }310}{K_{\text{II}}\text{ at }300}\right]$

or $$\frac{K_I \text{ at } 310}{K_I \text{ at } 300} = \left[\frac{K_{II} \text{ at } 310}{K_{II} \text{ at } 300}\right]^2 \qquad \ldots(8)$$

By Eqs. (2) and (8),

or $$\left[\frac{K_{II} \text{ at } 310}{K_{II} \text{ at } 300}\right]^2 = 2$$

or $$K_{II} \text{ at } 310\,\text{K} = \sqrt{2} K_{II} \text{ at } 300\,\text{K} \qquad \ldots(9)$$

By Eqs. (3) and (9),

$$2 \times K_I \text{ at } 310\,\text{K} = \sqrt{2}\,(K_{II} \text{ at } 300\,\text{K}) \qquad \ldots(10)$$

$$K_{II} \text{ at } 300\,\text{K} = \frac{2 \times K_I \text{ at } 310}{\sqrt{2}}$$

By Eqs. (1) and (10),

$$K_{II} \text{ at } 300\,\text{K} = \sqrt{2} \times 0.0231$$

$$K_{II} \text{ at } 300\,\text{K} = 3.27 \times 10^{-2} \text{ min}^{-1}$$

$$= \mathbf{0.0327\ min^{-1}}$$

32. Given,

$K = ?$ $\qquad A = 4 \times 10^{13} \text{ sec}^{-1}$

$E_a = 98.6 \times 10^3 \text{ J mol}^{-1}$ $\qquad t_{1/2} = 10 \times 60 \text{ sec}$

$\because \quad K = Ae^{-E_a/RT} \qquad \therefore K = 4 \times 10^{13} e^{-(98.6 \times 10^3)/8.314 \times T}$

Now for I order reaction, $K = \frac{0.693}{t_{1/2}} = \frac{0.693}{600} \text{ sec}^{-1}$

$$\therefore \quad \frac{0.693}{600} = 4 \times 10^{13} e^{-(98.6 \times 10^3)/8.314 \times T}$$

or $$\log_e \frac{0.693}{600} = \log_e 4 \times 10^{13} - \frac{98.6 \times 10^3}{8.314 \times T}$$

or $$\log_{10} \frac{0.693}{600} = \log_{10} 4 \times 10^{13} - \frac{98.6 \times 10^3}{8.314 \times 2.303 \times T}$$

$$\therefore \quad T = \mathbf{311.35\ K}$$

33. In parallel path reactions, rate constant are additive. Thus,

$$K_{AV} = K_1 + K_2 + \ldots + K_n$$

$$K_{AV} = K + 2K + \ldots + nK = \frac{n}{2}(n+1)K$$

$$\because \quad K = Ae^{-E_a/RT}$$

$$\therefore K_{AV} = A_1 e^{-E/RT} + 2A_2 \times e^{-2E/RT} + \ldots + nA_n \times e^{-nE/RT} \qquad \ldots(\text{i})$$

$$A_{AV} \times e^{-E_{av}/RT} = A_1 e^{-E/RT} + 2A_2 \times e^{-2E/RT} + \ldots + nA_n \times e^{-nE/RT} \ldots(\text{ii})$$

On differentiating Eq. (ii)

$$A_{AV} \cdot \frac{E_{av}}{RT^2} \cdot e^{-E_{av}/RT} = A_1 \frac{E}{RT^2} \cdot e^{-E/RT} + 2A_2 \frac{2E}{RT^2} \times e^{-2E/RT} + \ldots + nA_n \times \frac{nE}{RT^2} \times e^{-nE/RT}$$

$$A_{AV} + E_{av} \cdot e^{-E_{av}/RT} = E \times A_1 \times e^{-E/RT} + 2E \times 2A_2 \times e^{-2E/RT} + \ldots + nE \times nA_n \times Ee^{-nE/RT}$$

$$E_{AV} \times K_{AV} = K \times E + 2K \times 2E + \ldots + nK \times nE = K \times E[1^2 + 2^2 + \ldots n^2]$$

$$E_{AV} \times \frac{n}{2}(n+1)K = K \times E\left[\frac{2n^3 + 3n^2 + n}{6}\right] = K \times E \times \left[\frac{n(2n+1) \times (n+1)}{6}\right]$$

$$\therefore \quad E_{AV} = \frac{E}{3} \times [2n+1]$$

34. For I order reaction $r_1 = K\,[C]^1$

$$\therefore \quad \frac{R_1}{R_2} = K_1 / K_2 = \text{temperature coefficient}$$

Let temperature coefficient be a $\frac{R_{35}}{R_{25}} = \frac{K_{35}}{K_{25}} = a$

$$\frac{R_{45}}{R_{35}} = \frac{K_{45}}{K_{35}} = a \qquad \therefore \quad \frac{R_{45}}{R_{25}} = a \times a = a^2$$

Similarly, $\frac{R_{75}}{R_{25}} = a^5$

For I reaction $(R_{75})_I = 2^5 \times (R_{25})_I$

For II reaction $(R_{75})_{II} = 3^5 \times (R_{25})_{II}$

$$\therefore \quad \frac{(R_{75})_{II}}{(R_{75})_I} = \frac{3^5}{2^5} = 7.9537 \qquad [\because (R_{25})_I = (R_{25})_{II}]$$

35. (a) Rate of decomposition of NH_3.

(b) Rate of formation of N_2 and rate of formation of H_2.

(c) $$-\frac{1}{2}\frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3}\frac{d[H_2]}{dt} = K[NH_3]^0$$

$$\therefore \quad \frac{d[N_2]}{dt} = K = 2.5 \times 10^{-4}\,\text{Ms}^{-1}$$

$$\frac{d[H_2]}{dt} = 3K = 3 \times 2.5 \times 10^{-4} = \mathbf{7.5 \times 10^{-4}\ Ms^{-1}}$$

(d) $$-\frac{d[NH_3]}{dt} = \frac{K_1[NH_3]}{1 + K_2[NH_3]}$$

if $[NH_3]$ is very very low $[1 + K_2[NH_3] \simeq 1]$

or $$-\frac{d[NH_3]}{dt} = K_1[NH_3], \text{ i.e., Ist order reaction}$$

if $[NH_3]$ is very very high

$$-\frac{d[NH_3]}{dt} = \frac{K_1}{\frac{1}{[NH_3]} + K_2} = \frac{K_1}{K_2} = K'\left[\frac{1}{[NH_3]} + K_2 \simeq K_2\right]$$

i.e., **zero order.**

36. For the given change

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

On substituting values as given,

$$K_1[N_2O_5] = \frac{1}{2}K_2[N_2O_5] = 2K_3[N_2O_5]$$

or $$\mathbf{2K_1 = K_2 = 4K_3}$$

37. Unit of rate = mol litre^{-1} time^{-1}

Unit of rate constant = time^{-1}

The overall order for reactions is 1.

Thus, $\quad$ rate = K [Reactant]^1

or $$K = \frac{\text{rate}}{[\text{Reactant}]^1} = \frac{\text{mol litre}^{-1}\text{ time}^{-1}}{\text{mol litre}^{-1}} = \mathbf{time^{-1}}$$

38. Rate law with order equal to molecularity (necessarily integer) are elementary process. For the given reaction $\text{O.R.} = 1 + 3/2 = 5/2$. Since, molecularity can never be fractional and thus, for given reaction O.R. is not equal to molecularity.

Thus, given reaction is **not elementary process.**

39. Order of reaction $= 1+1+2=4$

Apparent molecularity $= 5+1+6=\mathbf{12}$

40. Rate of reaction $= \frac{1}{2} \times$ rate of disappearance of A

$$= \frac{1}{2}\left(-\frac{\Delta[A]}{\Delta t}\right) = \frac{1}{2}\left[\frac{0.5-0.4}{10}\right] = \mathbf{0.005\ mol\ L^{-1}\ minute^{-1}}$$

41. Loss in concentration of A in Ist hour $= \frac{0.6-0.5}{1} = 0.1$

Gain in concentration of B in Ist hour $= \frac{0.2-0}{1} = 0.2$

(i) $\because$ 0.1 mole of A changes to 0.2 mole of B in a given time and thus,

$$n = 2$$

(ii) Equilibrium constant, $K = \frac{[B]^n}{[A]} = \frac{[0.6]^2}{0.3}$

$$= 1.2 \text{ mol litre}^{-1}$$

($\because$ Equilibrium is attained after 5 hr, where $[B] = 0.6$ and $[A] = 0.3$)

(iii) Initial rate of conversion of A = changés in conc. of A during Ist hour

$$= \frac{0.1}{1} = \mathbf{0.1\ mol\ litre^{-1}\ hour^{-1}}$$

42. (i) The unit of rate constant suggest the second order for reaction. Thus,

Rate of reaction $= K\,[O_3][O]$

or $\quad 0.15 = 1.5 \times 10^7 \left[\frac{0.76}{0.0821 \times 298 \times 760}\right][O]$

$$\left(\because \frac{n}{V} \text{ for } O_3 = \frac{P}{RT} = \frac{0.76}{0.0821 \times 298 \times 760}\right)$$

$\therefore \quad [O] = 2.45 \times 10^{-4}$ or $\frac{n}{V}$ for $O = \mathbf{2.45 \times 10^{-4}}$

$\therefore \quad \frac{P}{RT}$ for $O = 2.45 \times 10^{-4}$

or $\quad P_O = 2.45 \times 10^{-4} \times 0.0821 \times 298$

$= 5.99 \times 10^{-3}$ atm

$= 5.99 \times 10^{-3} \times 760$ mm $= 4.5$ mm

(ii) Also, rate of reaction

$$= \frac{1}{2}\frac{d[O_2]}{dt} = \frac{1}{2} \text{ rate of formation of } O_2$$

$\therefore$ Rate of formation of $O_2 = 2 \times 0.15 = \mathbf{0.30\ mol\ L^{-1}\,t^{-1}}$

43. Rate of reaction $= -\frac{d[CO_2]}{dt} = -\frac{d[OH^-]}{dt} = \frac{d[HCO_3]}{dt}$

Also the unit of K suggest it to be II order. Thus, rate of reaction

$= K\,[CO_2][OH^-] = 4 \times 10^{-3} \times 10^{-6} \times 10^{-1}$

$= \mathbf{4 \times 10^{-10}\ mol\ L^{-1}\ sec^{-1}}$

44. Rate $= K$ [Reactant]^n $\qquad$ if [Reactant] $= a$; rate $= r_1$

$r_1 = K[a]^n$ $\qquad$ if [Reactant] $= 4a$; rate $= 2r_1$

$2r_1 = K[4a]^n$

$\therefore \frac{1}{2} = \left[\frac{1}{4}\right]^n \qquad \therefore n = \mathbf{\frac{1}{2}}$

45. $(r_0)_1 = K[A_0]_1^a \qquad$ (a is order of reaction)

$(r_0)_2 = K[A_0]_2^a$

$\therefore \quad \frac{(r_0)_1}{(r_0)_2} = \left\{\frac{[A_0]_1}{[A_0]_2}\right\}^a$

or $\quad a = \frac{\log (r_0)_1 - \log (r_0)_2}{\log [A_0]_1 - \log [A_0]_2}$

$= \frac{\log[2.40 \times 10^{-4}] - \log[0.60 \times 10^{-4}]}{\log[2 \times 10^{-3}] - \log[1 \times 10^{-3}]}$

$= \frac{-3.62 + 4.22}{-2.70 + 3} = 2$

$\therefore \quad r = K[A]^2$

Also, $\quad K = \frac{r}{[A]^2} = \frac{2.40 \times 10^{-4}}{[2 \times 10^{-3}]^2} = \mathbf{60\ mol^{-1}\ L\ sec^{-1}}$

46. (a) $\quad$ Rate $= K[A]^1[B]^2[C]^0$

(b) Let initial conc. of A, B and C be a, b, c mol litre^{-1}

Then, $\quad$ rate $r_1 = K\,a^1 b^2 c^0 \qquad$ ...(1)

Now if conc. of A, B and C are doubled, *i.e.*, $2a, 2b$ and $2c$ respectively, then,

$r_2 = K(2a)^1(2b)^2(2c)^0 \qquad$ ...(2)

By Eqs. (1) and (2), $\frac{r_1}{r_2} = \frac{1}{8} \quad \therefore r_2 = \mathbf{8r_1}$

47. (a) $\quad$ Rate $= K[A]^2[B]^1[C]^0$

(b) $\quad$ Unit of rate = mol litre^{-1} time^{-1}

Unit of rate constant $= \mathbf{L^2\ mol^{-2}\ time^{-1}}$

(c) Let initial conc. of A, B and C be a, b, c respectively.

$\therefore \quad r_1 = K(a)^2(b)^1(c)^0 \qquad$ ...(1)

Now, $\quad [A] = 2a; \quad [B] = 3b$

$\therefore \quad r_2 = K(2a)^2(3b)^1(c)^0 \qquad$ ...(2)

By Eqs. (1) and (2), $\frac{r_1}{r_2} = \frac{1}{12} \quad \therefore r_2 = \mathbf{12\,r_1}$

48. Consider a reaction $A \longrightarrow$ Product

$\therefore \quad r_1 = K[A]^1 \quad$ for I order $\qquad$ ...(1)

$\therefore \quad r_2 = K[A]^2 \quad$ for II order $\qquad$ ...(2)

$\therefore \quad r_3 = K[A]^3 \quad$ for III order $\qquad$ ...(3)

$\because K$ is same in all.

If $[A] = 1$ $\qquad \mathbf{r_1 = r_2 = r_3}$

If $[A] < 1$ $\qquad \mathbf{r_1 > r_2 > r_3}$

If $[A] > 1$ $\qquad \mathbf{r_3 > r_2 > r_1}$

49. $\quad$ Rate $= K[A][B]^{2/3}$

$\therefore \quad$ O.R. $= 1 + \frac{2}{3} = \frac{5}{3} = \mathbf{1.67}$

Unit of rate $\left(\frac{dx}{dt}\right)$ is **mol L^{-1} time^{-1}**

Unit of rate constant : rate constant

$$(K)=\frac{dx/dt}{[\text{Reactant}]^{5/3}}=\frac{\text{mol litre}^{-1}t^{-1}}{\left(\frac{\text{mol}}{\text{litre}}\right)^{5/3}}$$

$$=\mathbf{mol^{-2/3}L^{+2/3}time^{-1}}$$

50. For, $2NO+O_2\longrightarrow 2NO_2$

$$\text{Rate}=K\,[NO]^2[O_2]$$

Let a mole of NO and b mole of O_2 be taken to start a reaction at any time in a vessel of V litre

$$\therefore\quad r_1=K\left[\frac{a}{V}\right]^2\left[\frac{b}{V}\right]\qquad\ldots(1)$$

if volume of vessel is reduced to $V/4$, then for same mole of NO and O_2

$$r_2=K\left[\frac{a}{V/4}\right]^2\left[\frac{b}{V/4}\right]$$

$$=64K\left[\frac{a}{V}\right]^2\left[\frac{b}{V}\right]\qquad\ldots(2)$$

By Eqs. (1) and (2),

$$\therefore\quad \frac{r_2}{r_1}=\mathbf{64}\qquad\text{or}\qquad \mathbf{r_2\ \text{is 64 times of}\ r_1.}$$

51. $\text{Rate}=K[\text{Reactant}]^n$

For Case I : Let a mole of reactant in vessel of V litre

$$\therefore\quad r_1=K\left[\frac{a}{V}\right]^n\qquad\ldots(1)$$

For Case II : The volume is doubled, rate becomes half

$$\therefore\quad \frac{r_1}{2}=K\left[\frac{a}{2V}\right]^n\qquad\ldots(2)$$

$\therefore$ By Eqs. (1) and (2),

or $\quad 2=(2)^n\quad\therefore\ n=1$

Note : The above fact is not valid for solution phase reactions.

52. $$\frac{dx}{dt}=K\left[\frac{a-x}{1+bx}\right]$$

On integrating

or $$\int dx\frac{(1+bx)}{(a-x)}=K\int dt$$

$$\int\frac{dx[1-b(a-x)+ab]}{(a-x)}=K\int dt$$

or $$\int dx\frac{(1+ab)}{(a-x)}-\int dx\cdot b=K\,dt$$

or $\quad -(1+ab)\log(a-x)-bx=Kt+C$

at $t=0, x=0$

$\therefore\quad C=-(1+ab)\log a$

or $\quad -(1+ab)\log(a-x)-bx=Kt-(1+ab)\log a$

or $$Kt=(1+ab)\log\left[\frac{a}{(a-x)}\right]-bx$$

at $\quad t=t_{1/2}, x=\frac{a}{2}$

$$\therefore\quad Kt_{1/2}=(1+ab)\log\left[\frac{a}{a-a/2}\right]-\frac{ba}{2}$$

$$=(1+ab)\log 2-\frac{ab}{2}=\log 2+ab\log 2-ab\times 0.5$$

$$t_{1/2}=\frac{\log 2+ab(\log 2-0.5)}{K}$$

53. $\text{Rate}=K\times[A]$

$$0.04=K[A]_{10}\quad\text{and}\quad 0.03=K[A]_{20}$$

$$\frac{[A]_{10}}{[A]_{20}}=\frac{0.04}{0.03}=\frac{4}{3}$$

Also, $$t=\frac{2.303}{K}\log\frac{[A]_{10}}{[A]_{20}}\qquad\text{when } t=10\,\text{min.}$$

$$10=\frac{2.303}{K}\log\frac{4}{3}\quad\therefore\ K=\frac{2.303}{10}\log\frac{4}{3}=0.0288\ \text{min}^{-1}$$

$$t_{1/2}=\frac{0.693}{K}=\frac{0.693}{0.0288}=\mathbf{24.06\ min}$$

54. $\text{Rate}=K\,[\text{ester}]^1[H_3O^+]^0$

(a) $\quad r_1=K[\text{ester}]^1[H_3O^+]^0$

Let, initial conc. of ester $=a$, initial conc. of $H_3O^+=b$

$\therefore\quad r_1=K[a]^1[b]^0$

If conc. of ester is doubled, *i.e.*, $[\text{ester}]=2a$, then

$$r_2=K[2\times a]^1[b]^0$$

$$\therefore\quad \frac{r_1}{r_2}=\frac{1}{2}\qquad\text{or}\quad r_2=\mathbf{2r_1}$$

(b) $\quad r_1=K[a]^1[b]^0$

If conc. of H_3O^+ is doubled, *i.e.*, $[H_3^+O]=2b$

$$r_3=[a]^1[2b]^0$$

$$\therefore\quad \frac{r_1}{r_3}=1\qquad\text{or}\quad r_1=r_3$$

55. We have,

$$-\frac{1}{2}\frac{d[A]}{dt}=-\frac{d[B]}{dt}=\frac{1}{2}\frac{d[C]}{dt}=\frac{1}{3}\frac{d[D]}{dt}=\text{rate of reaction}$$

$$\because\quad \frac{d[C]}{dt}=1.0\ \text{mol litre}^{-1}\text{sec}^{-1}$$

$$\therefore\quad -\frac{d[A]}{dt}=\frac{d[C]}{dt}=\mathbf{1.0\ mol\ L^{-1}\,sec^{-1}}$$

$$-\frac{d[B]}{dt}=\frac{1}{2}\frac{d[C]}{dt}=\frac{1}{2}=\mathbf{0.5\ mol\ L^{-1}\,sec^{-1}}$$

$$\frac{d[D]}{dt}=\frac{3}{2}\frac{d[C]}{dt}=\frac{3}{2}\times 1=\mathbf{1.5\ mol\ L^{-1}\,sec^{-1}}$$

Also, $\because\quad \text{Rate}=\frac{1}{2}\frac{d[C]}{dt}$

$$\therefore\quad \text{Rate}=\frac{1}{2}\times 1=\mathbf{0.5\ mol\ L^{-1}\,sec^{-1}}$$

56. $\text{Rate}=K[A]^m[B]^n$

For Case I : $\quad 0.05=K[0.1]^m[0.2]^n\qquad\ldots(1)$

For Case II : $\quad 0.10=K[0.2]^m[0.2]^n\qquad\ldots(2)$

For Case III : $\quad 0.05=K[0.1]^m[0.1]^n\qquad\ldots(3)$

By Eqs. (1) and (2), $\frac{1}{2}=\left(\frac{1}{2}\right)^m\quad\therefore\ m=1$

By Eqs. (1) and (3), $1 = \left(\frac{1}{2}\right)^n \quad \therefore \quad n = 0$

Thus, $\quad \text{Rate} = K[A]^1[B]^0 \quad \therefore \text{O.R.} = 1+0 = 1$

Now $\quad 0.05 = K[0.1]^1\,[0.2]^0$

$\therefore \quad K = \frac{0.05}{0.1} = 0.5\,\text{sec}^{-1}$

For I order reaction, $t_{1/2} = \frac{0.693}{K} = \frac{0.693}{0.5} = 1.386\ \text{sec}^{-1}$

57. Let $\quad \text{Rate} = K[A]^m[B]^n$

(a) $\quad r_1 = 1\times10^{-4} = K[0.1]^m[0.1]^n \quad \ldots(1)$

$r_2 = 9\times10^{-4} = K[0.1]^m[0.3]^n \quad \ldots(2)$

$r_3 = 2.7\times10^{-3} = K[0.3]^m[0.3]^n \quad \ldots(3)$

By Eqs. (1) and (2), $\frac{r_1}{r_2} = \frac{1\times10^{-4}}{9\times10^{-4}} = \left(\frac{1}{3}\right)^n \Rightarrow n = 2$

By Eqs. (2) and (3), $\frac{r_2}{r_3} = \frac{9\times10^{-4}}{27\times10^{-4}} = \left(\frac{1}{3}\right)^m \Rightarrow m = 1$

$\therefore \quad \text{Rate} = K[A]^1[B]^2$

(b) Also, by Eq. (1), $1\times10^{-4} = K[0.1]^1[0.1]^2$

$K = \mathbf{10^{-1} = 0.1\ L^2\,mol^{-2}\,min^{-1}}$

58. Rate of reaction $= -\frac{1}{2}\frac{dP_{NO}}{dt} = -\frac{dP_{H_2}}{dt}$

For P_{H_2} constant :

$$-\frac{1}{2}\frac{dP_{NO}}{dt} = 1.5 = K(359)^m(P_{H_2})^n$$

$$-\frac{1}{2}\frac{dP_{NO}}{dt} = 0.25 = K(152)^m(P_{H_2})^n$$

$\therefore \quad \frac{1.5}{0.25} = \left(\frac{359}{152}\right)^m \quad \therefore \ m = 2$

For P_{NO} constant :

$$-\frac{dP_{H_2}}{dt} = 1.60 = (P_{NO})^m(289)^n$$

$$-\frac{dP_{H_2}}{dt} = 0.79 = (P_{NO})^m(147)^n$$

$\therefore \quad \frac{1.60}{0.79} = \left(\frac{289}{147}\right)^n \quad \therefore \ n = 1$

$\therefore \quad \text{Rate} = K[P_{NO}]^2[P_{H_2}]^1$

$\therefore$ Order of Reaction $= 2+1 = 3$

59. For the reaction $2NO + Cl_2 \longrightarrow 2NOCl$

$\text{Rate} = K[Cl_2]^m[NO]^n \quad \ldots(1)$

where, m and n are order of reaction with respect to Cl_2 and NO respectively.

From the given data :

$1\times10^{-3} = K[0.05]^m[0.05]^n \quad \ldots(2)$

$3\times10^{-3} = K[0.15]^m[0.05]^n \quad \ldots(3)$

$9\times10^{-3} = K[0.05]^m[0.15]^n \quad \ldots(4)$

By Eqs. (2) and (3), $m = 1$

By Eqs. (2) and (4), $n = 2$

(a) $\therefore$ Order w.r.t. NO **is 2** and with respect to Cl_2 **is 1.**

(b) Also rate expression $r = \mathbf{K[Cl_2]^1[NO]^2}$

(c) And rate constt, $K = \frac{r}{[Cl_2]^1[NO]^2} = \frac{1\times10^{-3}}{[0.05]^1[0.05]^2}$

$= \mathbf{8\ L^2\ mol^{-2}sec^{-1}}$

(d) Further, $\quad r = K[Cl_2]^1[NO]^2$

$= 8[0.2]^1[0.4]^2 = \mathbf{0.256\ mol\ L^{-1}sec^{-1}}$

60. (a) $\mathbf{Rate = K[A]^2[B]^0}$

(b) $\mathbf{K = 4\times10^{-2}\ L\ mol^{-1}sec^{-1}}$

(c) $\mathbf{Rate = 16\times10^{-4}\ mol\ L^{-1}sec^{-1}}$

61. $\text{Rate} = K[HgCl_2]^m[K_2C_2O_4]^n$

$\therefore \quad \frac{0.0032}{60} = K[0.0418]^m[0.404]^n \quad \ldots(1)$

$\frac{0.0068}{65} = K[0.0836]^m[0.404]^n \quad \ldots(2)$

$\frac{0.0031}{120} = K[0.0836]^m[0.202]^n \quad \ldots(3)$

Solving Eqs. (1), (2) and (3), we get

$m = 1$

$n = 2$

$\therefore \quad \text{O.R.} = m+n = 1+2 = 3$

62. $\because \quad \text{Rate} = K[A]^m[B_2]^n$

$\therefore$ Rate of disappearance of $B_2 = K[A]^m[B_2]^n$

$r_1 = 1.8\times10^{-3} = K[0.015]^m[0.15]^n \quad \ldots(1)$

$r_2 = 1.08\times10^{-2} = K[0.09]^m[0.15]^n \quad \ldots(2)$

$r_3 = 5.4\times10^{-3} = K[0.015]^m[0.45]^n \quad \ldots(3)$

By Eqs. (1) and (2), $\frac{1.8\times10^{-3}}{1.08\times10^{-2}} = \left[\frac{0.015}{0.09}\right]^m \ \therefore m = 1$

By Eqs. (1) and (3), $\frac{1.8\times10^{-3}}{5.4\times10^{-3}} = \left[\frac{0.15}{0.45}\right]^n \ \therefore n = 1$

$\therefore$ Rate of disappearance of $B_2 = K[0.015]^1[0.15]^1$

$\therefore \mathbf{O.R. = 2}$

Also $\quad 1.8\times10^{-3} = K[0.015]^1[0.15]^1$

$K = \mathbf{0.8\ litre\ mol^{-1}\ time^{-1}}$

Now $\quad \frac{1}{2}\frac{d[AB]}{dt} = -\frac{d[B_2]}{dt}$

$\therefore \quad \frac{d[AB]}{dt} = 2\times\left(-\frac{d[B_2]}{dt}\right)$

$= 2\times K[A]^1[B_2]^1$

$= 2\times0.8\times(0.02)^1(0.04)^1$

$= \mathbf{1.28\times10^{-3}}$

63. Let rate expression be,

$r = K[NO]^m[H_2]^n \quad \ldots(1)$

Case I : $\quad [NO]\times10^{-4} = 1.5 \quad \therefore [NO] = 1.5\times10^4$

$[H_2]\times10^{-3} = 4.0 \quad \therefore [H_2] = 4.0\times10^3$

$-\frac{1}{2}\frac{d[NO]}{dt}\times10^{-4} = 4.4 \quad \therefore -\frac{1}{2}\frac{d[NO]}{dt} = 4.4\times10^4$

$\therefore$ By Eqs. (1), $4.4\times10^4 = K[1.5\times10^4]^m[4.0\times10^3]^n \ \ldots(2)$

Similarly for case II and III, we can write

Case II : $2.2\times10^4 = K[1.5\times10^4]^m[2.0\times10^3]^n$ ...(3)

Case III : $0.24\times10^4 = K[0.5\times10^4]^m[2.0\times10^3]^n$ ...(4)

By Eqs. (2) and (3), $2=(2)^n$ $\therefore n=1$

By Eqs. (3) and (4), $9.16=(3)^m$ $\therefore m=2$

$\therefore$ O.R. with respect to NO is **2** and with respect to H_2 = **1**

For rate constt. use Eq. (2) with $m=2$ and $n=1$

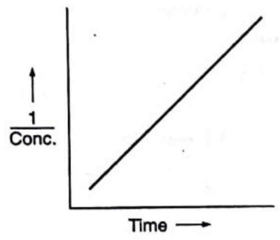
$$4.4\times10^4 = K[1.5\times10^4]^2[4.0\times10^3]^1$$

$$\therefore \quad K = \mathbf{4.88\times10^{-8}\ mol^{-2}L^2min^{-1}}$$

64. From the graph it is evident that concentration of 40 reduces to 20 in 5 minute, 20 reduces to 10 in 5 minute and 10 reduces to 5 in again 5 minute, which shows that half life period is independent of concentration, a characteristic of a first order reaction. In a first order reaction the concentration of the reactant **can never be theoretically zero.**

65. The reaction is of second order, because for II order,

$$K = \frac{1}{t}\cdot\frac{x}{a(a-x)}$$



or $$t = \frac{1}{K}\cdot\frac{x}{a(a-x)}$$

or time (t) vs. $\frac{1}{\text{conc.}}$ graph is linear.

66. Since, K has unit min^{-1} and thus, given reaction is of I order

Now Rate $= K[\ ]^1$

$$\text{Rate} = 10^{-3}\times[0.2]^1 = \mathbf{2\times10^{-4}\ mol\ dm^{-3}min^{-1}}$$

Also $$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$\therefore \quad 10^{-3} = \frac{2.303}{200}\log_{10}\frac{100}{(100-x)}$$

$$\therefore \quad x = \mathbf{18.12\%}$$

67. $A \longrightarrow B$ $K = 4.5\times10^{-3}\ min^{-1}$

$[A]_0 = 1M$

For I order reaction, $K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$

at $t = 60$ min, $(a-x) = ?$

$$4.5\times10^{-3} = \frac{2.303}{60}\log_{10}\frac{1}{(a-x)}$$

$$\therefore \quad (a-x) = 0.7634$$

Thus, rate after 60 minute $= K(a-x)$

$$= 4.5\times10^{-3}\times0.7634 = \mathbf{3.4354\times10^{-3}}$$

68. (a) Initial rate $= K[\ ]^1 = 1\times10^{-2}[1] = 1\times10^{-2}$

$\therefore$ Rate $= \mathbf{1\times10^{-2}\ mol\ L^{-1}sec^{-1}}$

(b) Now $$K = \frac{2.303}{t}\log_{10}\frac{a}{(a-x)}$$

$$10^{-2} = \frac{2.303}{1\times60}\log_{10}\frac{1}{(1-x)}$$

($\because t = 1$ minute $= 60$ sec)

$\therefore \quad (1-x) = 0.549$

$\therefore$ Rate after 1 minute $= K[\ ]$ after 1 minute $= K[0.549]$

$= 10^{-2}[0.549]$

Rate after 1 minute $= \mathbf{5.49\times10^{-3}\ mol\ L^{-1}sec^{-1}}$

69. $t_{99\%} = \frac{2.303}{K}\log_{10}\frac{100}{100-99}$ ...(1) ($\because a=100; x=99$)

$t_{90\%} = \frac{2.303}{K}\log_{10}\frac{100}{100-90}$ ...(2) ($\because a=100; x=90$)

$\therefore$ By Eqs. (1) and (2), $\frac{t_{99\%}}{t_{90\%}} = \frac{\log_{10}100}{\log_{10}10} = 2$

$$\therefore \quad t_{99\%} = \mathbf{2\times t_{90\%}}$$

70. $A \longrightarrow$ Products

$\therefore \quad -\frac{dC_A}{dt} = KC_A^n$ ($\because$ order is n)

On integrating $\frac{-(C_A)^{1-n}}{1-n} = Kt + \text{constant}$ ...(1)

at $t=0, C_A = C_0$ $\therefore$ constant $= -\frac{C_0^{1-n}}{1-n}$ ...(2)

$\therefore$ By Eqs. (1) and (2), $-\frac{C_A^{1-n}}{1-n} = Kt - \frac{C_0^{1-n}}{1-n}$

or $Kt = \frac{1}{(n-1)}[C_A^{1-n} - C_0^{1-n}]$ ...(3)

if $C_A = \frac{C_0}{2}$ at $t = t_{1/2}$ then by Eq. (3)

$$Kt_{1/2} = \frac{1}{(n-1)}\left[\left(\frac{C_0}{2}\right)^{1-n} - (C_0)^{1-n}\right]$$

$= \frac{1(C_0)^{1-n}}{(n-1)}\times[2^{n-1}-1]$ ...(4)

Similarly, if $C = \frac{C_0}{4}$ at $t = t_{3/4}$, then by Eq. (3)

$Kt_{3/4} = \frac{C_0^{1-n}}{(n-1)}[4^{n-1}-1]$ ...(5)

By Eqs. (4) and (5), $\frac{t_{1/2}}{t_{3/4}} = \mathbf{\frac{2^{n-1}-1}{4^{n-1}-1}}$

Thus the ratio depends only on 'n'.

71. For zero order reaction : $t = \frac{x}{K}$ or $K = \frac{x}{t}$

If $t = t_{20\%} = 20$ minute, $x = 20$

Then $K = \frac{20}{20} = \mathbf{1\ mol\ L^{-1}time^{-1}}$

If $t = t_{40\%} = 40$ minute, $x = 40$

Then, $K = \frac{40}{40} = 1\ \text{mol L}^{-1}\ \text{time}^{-1}$

Thus, reaction is of **zero order.**

72. $$-\frac{dC}{dt} = \frac{K_1 C}{1+K_2 C} = \frac{K_1}{\frac{1}{C}+K_2}$$

(a) If C is very very high $1/C$ is smallest and thus negligible.

$$\therefore \quad -\frac{dC}{dt} = \frac{K_1}{K_2} = \text{constant}$$

Thus order of reaction is **zero.**

(b) If C is very very low. $1+K_2C = K'$

$$\therefore \quad -\frac{dC}{dt} = \frac{K_1 C}{K'} = K'' \cdot C$$

Thus order of reaction is **unity.**

73. $$\frac{-dC}{dt} = \frac{\alpha C}{1+\beta C}$$

or $\frac{-dC(1+\beta C)}{C} = \alpha \cdot dt$ or $\frac{-dC}{C} - dC \cdot \beta = \alpha \cdot dt$

$-\ln C - \beta C = \alpha t + \text{constant}$ ...(1)

at $t = 0, C = C_0$

$\therefore\ -\ln C_0 - \beta C_0 = \alpha 0 + \text{constant}$

or $\text{constant} = -\ln C_0 - \beta C_0$

$\therefore$ By (1) $-\ln C - \beta C = \alpha t - \ln C_0 - \beta C_0$

or $\ln \frac{C_0}{C} + \beta(C_0 - C) = \alpha \cdot t$ ...(2)

if $t = t_{1/2},\ C = \frac{C_0}{2}$

$\therefore$ By Eq. (2) $\ln \frac{C_0}{C_0/2} + \beta\left[C_0 - \frac{C_0}{2}\right] = \alpha t_{1/2}$

or $t_{1/2} = \frac{1}{\alpha} \ln 2 + \frac{\beta \cdot C_0}{2\alpha}$ ...(3)

74. $$2A \longrightarrow 3B + C$$

Initial pressure	P°	0	0
Pressure at $t = t$	$P^\circ - 2a$	$3a$	a
Pressure at $t = 2t$	$P^\circ - 2x$	$3x$	x

Given, $P^\circ - 2a + 3a + a = P$

$\therefore\ P^\circ + 2a = P$ ...(1)

Now for I order reaction at time t

$K = \frac{2.303}{t} \log \frac{P^\circ}{P^\circ - 2a} = \frac{2.303}{t} \log \frac{P^\circ}{2P^\circ - P}$ ...(2)

Let total pressure at $t = 2t$ be A, then $P^\circ - 2x + 3x + x = A$

or $P^\circ + 2x = A$

$K = \frac{2.303}{2t} \log \frac{P^\circ}{P^\circ - 2x} = \frac{2.303}{2t} \log \frac{P^\circ}{2P^\circ - A}$ ...(3)

$K = \frac{2.303}{t} \log \left[\frac{P^\circ}{2P^\circ - A}\right]^{1/2}$ ...(4)

By Eqs. (2) and (4) $\left[\frac{P^\circ}{2P^\circ - P}\right]^2 = \left[\frac{P^\circ}{2P^\circ - A}\right]$

$$[2P^\circ - A] \cdot P^\circ = [2P^\circ - P]^2$$

$$\therefore \quad P^\circ \cdot A = 2(P^\circ)^2 - (2P^\circ - P)^2$$

$$\therefore \quad A = 2P^\circ - \frac{(2P^\circ - P)^2}{P^\circ}$$

75. For I order reaction : $K = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

If $t = t$, $a = C_0$ and $(a-x) = aC_0$

$$K = \frac{2.303}{t} \log_{10} \frac{C_0}{aC_0} = \frac{2.303}{t} \log_{10} \frac{1}{a}$$

If $t = 2t$, $a = C_0$ and $(a-x) = a^2C_0$

$$K = \frac{2.303}{2t} \log_{10} \frac{C_0}{a^2C_0} = \frac{2.303}{t} \log_{10} \frac{1}{a}$$

If $t = 3t$, $K = \frac{2.303}{3t} \log_{10} \frac{C_0}{a^3C_0} = \frac{2.303}{t} \log_{10} \frac{1}{a}$

K comes constant and thus, it is **I order reaction.**

Also, $K = \frac{2.303}{t} \log_{10} \frac{1}{a}$

76. Given, $a = 1\,\text{mole}$, $x = 3/4\,\text{mole}$, $t = 1\,\text{hr}$

(a) **For I order :** $K = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$

$$K = \frac{2.303}{1} \log_{10} \frac{1}{1-\frac{3}{4}} = \frac{2.303}{1} \log_{10} 4$$

$$K = \mathbf{1.386\ hr^{-1}}$$

(b) **For II order :**

$$K = \frac{1}{t \times a} \cdot \frac{x}{(a-x)} = \frac{1}{1\times 1} \cdot \frac{3}{4\left(1-\frac{3}{4}\right)} = 3$$

$$K = \mathbf{3\ L\ mol^{-1}\,hr^{-1}}$$

77. $\because \quad t = \frac{2.303}{K} \log_{10} \frac{a}{(a-x)}$

If $t = \frac{t}{2}$, $x = \frac{a}{2}$; $\therefore\ t_{1/2} = \frac{2.303}{K} \log_{10} \frac{a}{a - \frac{a}{2}}$ ...(1)

If $t = t_{99\%}$, $x = \frac{99a}{100}$; $t_{99\%} = \frac{2.303}{K} \log_{10} \frac{a}{a - \frac{99a}{100}}$ ...(2)

By Eqs. (1) and (2),

$$t_{99\%} = \frac{\log_{10} 100}{\log_{10} 2} \times t_{1/2} = \frac{2}{0.3010} \times 2.1 = \mathbf{13.95\ hour}$$

Also, mole of N_2O formed $= \frac{99}{100} \times$ mole of NH_2NO_2 taken

$$= \frac{99}{100} \times \frac{6.2}{62} = 0.099$$

$\therefore$ Volume of N_2O formed at STP $= 0.099 \times 22.4 = \mathbf{2.217\ L}$

78. $t = 10,\ (a-x) = 13.8$

$t = 20,\ (a-x) = 8.25$

$t = 0,\ a$

$\because \quad K = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

$\therefore \quad K = \frac{2.303}{10} \log_{10} \frac{a}{13.8}$ ...(1)

$K = \frac{2.303}{20} \log_{10} \frac{a}{8.25}$ ...(2)

By solving Eqs. (1) and (2),

$$K = \mathbf{5.1 \times 10^{-2}\ minute^{-1}}$$

$$a = \mathbf{23.09}$$

79. $\because \quad K = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$ $\quad \ldots(1)$

Case I : $a \propto 200\,\text{mm}, \quad x \propto 200 \times \frac{50}{100}$ or $x \propto 100\,\text{mm}$

$$t_{1/2} = 53\,\text{minute}$$

$$\therefore \quad K_1 = \frac{2.303}{53} \log_{10} \frac{200}{200-100} = 1.307 \times 10^{-2}\,\text{minute}^{-1}$$

Case II : $a \propto 200\,\text{mm}, \quad x \propto 200 \times \frac{73}{100}$

or $\quad x \propto 146\,\text{mm}$

$$t_{73\%} = 100\,\text{minute}$$

$$\therefore \quad K_2 = \frac{2.303}{100} \log_{10} \frac{200}{200-146} = 1.309 \times 10^{-2}\,\text{minute}^{-1}$$

(a) The Eq. (1) gives same value of K and thus, reaction obeys **I order.**

(b) $K = \frac{K_1 + K_2}{2} = \frac{(1.307 + 1.309) \times 10^{-2}}{2}$

$$= \mathbf{1.308 \times 10^{-2}\,minute^{-1}}$$

(c) $t_{1/n} \propto (a)^0$ for first order reaction and thus, reaction will proceed to 73% completion in 100 minute if initial pressure is **600 mm.**

80. $$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

	$2N_2O_5$	$4NO_2$	O_2
Mole at $t = 0$	a	0	0
$t = 30$	$(a-x)$	$2x$	$x/2$
$t = \infty$	0	$2a$	$a/2$

$\because$ No. of mole $\propto$ pressure developed

$\therefore \quad a \propto P_0 \quad$ at $\quad t = 0$

$a + \frac{3x}{2} \propto 284.5 \quad$ at $\quad t = 30\,\text{minute}$

$\frac{5a}{2} \propto 584.5 \quad$ at $\quad t = \infty$

Thus, $a \propto \frac{2 \times 584.5}{5}$ or $x \propto 233.8$ at $\quad t = 0$

$x \propto 33.8 \quad$ at $\quad t = 30$ minute

$a - x \propto 200.0$

$$\because \quad K = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

$$\therefore \quad K = \frac{2.303}{30} \log_{10} \frac{233.8}{200} = \mathbf{5.206 \times 10^{-3}\,minute^{-1}}$$

81. Reaction mixture after a long time or on heating is supposed to show completion.

	$A \longrightarrow$	B	$+\ 2C$	
at $t = 0$	a	0	0	Mole before dissociation
at $t = t$	$(a-x)$	x	$2x$	Mole after dissociation
at $t = \infty$	0	a	$2a$	Mole after complete dissociation

Let a mole of A are present and x mole of A dissociate in time t.

Also, Total mole at any time $\propto$ pressure at that time

$\therefore \quad a + 2x \propto 264 \quad$ at $\quad t = 14\,\text{minute} \quad \ldots(1)$

$\therefore \quad 3a \propto 450 \quad$ at $\quad t = \infty \quad \ldots(2)$

and $\quad a \propto P^\circ \quad$ at $\quad t = 0 \quad \ldots(3)$

Let P° is initial pressure

(a) By Eqs. (2) and (3),

$$\therefore \quad \mathbf{P^\circ = 150\,mm}$$

(b) $\quad K = \frac{2.303}{14} \log_{10} \frac{150}{150-57}$

$\because$ By Eqs. (1) and (2), $x \propto 57$

$$= \mathbf{3.415 \times 10^{-2}\,minute^{-1}}$$

(c) $\quad t_{1/2} = \frac{0.693}{K} = \frac{0.693}{3.415 \times 10^{-2}} = \mathbf{20.29\,minute}$

82. $$AsH_3(g) \longrightarrow As(s) + \frac{3}{2}H_2(g)$$

	$AsH_3(g)$	$As(s)$	$\frac{3}{2}H_2(g)$
Mole at $t = 0$	a	0	0
Mole at $t = t$	$a - x$	x	$\frac{3x}{2}$

$\because \quad$ Mole $\propto$ Pressure $\quad$ (at constant V and T)

Now $\quad a \propto 0.9654 \quad$ at $\quad t = 0$ hr

$a - x + \frac{3x}{2} \propto 1.06 \quad$ at $\quad t = 5.5$ hr

$\therefore \quad x \propto 0.1892 \quad$ at $\quad t = 5.5$ hr

As being solid and hence, its mole should not be counted for pressure.

$$\because \quad K = \frac{2.303}{t} \log_{10} \frac{a}{(a-x)}$$

$$\therefore \quad K_1 = \frac{2.303}{5.5} \log_{10} \frac{0.9654}{0.9654 - 0.1892}$$

$$= \mathbf{3.96 \times 10^{-2}\,hr^{-1}}$$

Similarly, $\quad a \propto 0.9654$

$a - x + \frac{3x}{2} \propto 1.076 \quad$ at $t = 6.5$ hr

$\therefore \quad x \propto 0.2212$

$$\therefore \quad K_2 = \frac{2.303}{6.5} \log_{10} \frac{0.9654}{0.9654 - 0.2212}$$

$$= \mathbf{4.00 \times 10^{-2}\,hr^{-1}}$$

Similarly, $\quad a \propto 0.9654$

$a - x + \frac{3x}{2} \propto 1.1 \quad$ at $t = 8$ hr

$\therefore \quad x \propto 0.2692 \quad$ at $t = 8$ hr

$$\therefore \quad K_3 = \frac{2.303}{8} \log_{10} \frac{0.9654}{0.9654 - 0.2692}$$

$$= \mathbf{4.08 \times 10^{-2}\,hr^{-1}}$$

$$\therefore \quad K = \frac{K_1 + K_2 + K_3}{3} = \frac{(3.96 + 4.00 + 4.08) \times 10^{-2}}{3}$$

$$= \mathbf{4.01 \times 10^{-2}\,hr^{-1}}$$

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

For I $\therefore \quad 425 \propto (350)^{1-n} \quad \ldots(1)$

For II $\therefore \quad 275 \propto (540)^{1-n} \quad \ldots(2)$

For III $\therefore \quad 941 \propto (158)^{1-n} \quad \ldots(3)$

By Eqs. (1) and (2), $\frac{425}{275} = \left(\frac{350}{540}\right)^{1-n}$

Taking log, $\quad \log \frac{425}{275} = (1-n) \log \frac{350}{540} \quad \therefore \ \mathbf{n = 2}$

84. At pH = 5, the half life is 500 for all concentrations of sugar, *i.e.*, $t_{1/2} \propto [\text{sugar}]^0$. Thus, the reaction is I order with respect to sugar.

Now $\quad \text{rate} = K[\text{sugar}]^1 [H^+]^m$

Also for $[H^+]$ $\quad t_{1/2} \propto [H^+]^{1-m} \quad \therefore \; 500 \propto [10^{-5}]^{1-m}$

$$50 \propto [10^{-6}]^{1-m} \quad \therefore \; 10 = (10)^{1-m}$$

or $\quad 1 - m = 1 \quad \therefore \; m = 0$

Therefore, **rate** $= \boldsymbol{K\,[\text{sugar}]^1\,[H^+]^0}$.

85. (a) Rate of reaction $= \dfrac{\text{Change in pressure}}{\text{Time in min}} = \dfrac{2-1.2}{50}$

$$= \frac{0.8}{50} = \mathbf{1.6 \times 10^{-2}\ atm\ min^{-1}}$$

(b) $\because$ Change in molarity may be derived by

$$PV = nRT; \quad \frac{n}{V} = \frac{P}{RT}$$

$$\frac{n}{V} = \frac{0.8}{0.0821 \times 298} = 0.0327$$

Rate of reaction $= \dfrac{\text{Change in molarity}}{\text{Time in second}} = \dfrac{0.0327}{50 \times 60}$

$$= \mathbf{1.09 \times 10^{-5}\ mol\ L^{-1}\ sec^{-1}}$$

86. $\because$ $$K = \frac{2.303}{t}\log_{10}\frac{a}{a-x} \qquad \ldots(1)$$

Case I: $K = \dfrac{2.303}{15}\log_{10}\dfrac{100}{100-17} = 1.24 \times 10^{-2}$ $\left(\begin{array}{l}\text{if } a = 100 \\ x = 17 \text{ at } t = 15\end{array}\right)$

Case II: $K = \dfrac{2.303}{30}\log_{10}\dfrac{100}{100-32} = 1.28 \times 10^{-2}$ $\quad (x = 32 \text{ at } t = 30)$

Case III: $K = \dfrac{2.303}{45}\log_{10}\dfrac{100}{100-44.5} = 1.31 \times 10^{-2}$ $\quad (x = 44.5 \text{ at } t = 45)$

Thus, all the values of K are same and hence equation (1) is valid, *i.e.*, **reaction obeys I order kinetics.**

87. $$C_4H_8 \xrightarrow{\Delta} 2C_2H_4$$

Mole at $t = 0$	a	0
Mole at $t = t$	$(a-x)$	$2x$

Case (a) When $\dfrac{2x}{a-x} = 1$, then $x = \dfrac{a}{3}$

$\because$ $$t = \frac{2.303}{K}\log_{10}\frac{a}{a-x}$$

$$= \frac{2.303}{2.48 \times 10^{-4}}\log_{10}\frac{a}{a-\frac{a}{3}} = 1635.2\,\text{second}$$

$$= \mathbf{27.25\ minute}$$

Case (b) When $\dfrac{2x}{a-x} = 100$, then $x = \dfrac{100}{102}a$

$$t = \frac{2.303}{2.48 \times 10^{-4}}\log_{10}\frac{a}{a-\frac{100a}{102}} = 15856.9\text{ sec}$$

$$= \mathbf{264.2\ minute}$$

88. Since, rate constant $= 1.0 \times 10^7$ mol litre^{-1}sec^{-1}

$\therefore$ Zero order reaction.

For zero order: $t = \dfrac{x}{K} = \dfrac{\text{concentration used}}{\text{rate constant}} \qquad \ldots(1)$

$\because$ 0.05 mL has 3×10^{-6} mole of H^+

$\therefore$ 1000 mL has $\dfrac{3 \times 10^{-6} \times 10^3}{0.05} = 0.6 \times 10^{-1}$ mol/litre of H^+

$\therefore$ By Eq. (1), $\quad t = \dfrac{0.6 \times 10^{-1}}{1 \times 10^7} = \mathbf{6 \times 10^{-9}\ second}$

89. $$Cl_2O_7 \longrightarrow Cl_2 + \frac{7}{2}O_2$$

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

(a) Since, pressure of Cl_2O_7 is given and therefore,

$$a \propto 0.062$$

$$(a-x) \propto 0.044$$

$\because$ $\quad K = \dfrac{2.303}{t}\log_{10}\dfrac{a}{a-x} \quad \therefore K = \dfrac{2.303}{55}\log_{10}\dfrac{0.062}{0.044}$

$$K = \mathbf{6.23 \times 10^{-3}\ sec^{-1}}$$

(b) Let at $t = 100$ sec, $(a-x) \propto P$

$\therefore$ $\quad 6.23 \times 10^{-3} = \dfrac{2.303}{100}\log_{10}\dfrac{0.062}{P} \quad \therefore P = \mathbf{0.033\ atm}$

90. Consider I order reaction :

$$Kt = 2.303\log_{10}\frac{a}{(a-x)}$$

or $\quad Kt = 2.303\log_{10}a - 2.303\log_{10}(a-x) \qquad \ldots(1)$

In terms of pressure Eq. (1) may be written as,

$\because$ $$a \propto P_0$$

$$(a-x) \propto P$$

$$Kt = 2.303\log_{10}P_0 - 2.303\log_{10}P$$

or $\quad \log_{10}P = -\dfrac{K}{2.303}t + \log_{10}P_0$

Thus, log P *vs.* time graph is linear with intercept equal to log P_0 and slope equal to $-\dfrac{K}{2.303}$. Since, linear results are given and thus, decomposition may be said **to be of I order.**

91. $$NH_4NO_2(s) \longrightarrow N_2(g) + 2H_2O(l)$$

Mole at $t = 0$	a	0	0
Mole at $t = t$	$(a-x)$	x	$2x$

The volume of N_2 formed at any time is proportional to the amount of NH_4NO_2 decomposed in that time.

	At $t = \infty$	$V_{N_2} = 33.05$ mL	$\therefore\ a \propto 33.05$
I	At $t = 10$	$V_{N_2} = 6.25$ mL	$\therefore\ x \propto 6.25$
II	At $t = 15$	$V_{N_2} = 9.0$ mL	$\therefore\ x \propto 9.0$
III	At $t = 20$	$V_{N_2} = 11.40$ mL	$\therefore\ x \propto 11.40$
IV	At $t = 25$	$V_{N_2} = 13.65$ mL	$\therefore\ x \propto 13.65$

Now use, $\quad K = \dfrac{2.303}{t}\log_{10}\dfrac{a}{a-x}$

Case I $\quad K = \dfrac{2.303}{10}\log_{10}\dfrac{33.05}{33.05-6.25}$

$$K = \mathbf{2.0 \times 10^{-2}\ min^{-1}}$$

Similarly, calculate K for each case. The values of K come almost constant and thus, showing that reaction is I order. For K, take average of all values of K.

92. The volume of $KMnO_4$ used at any time is proportional to conc. of H_2O_2 at that time.

	At $t = 0$	$V = 25$	$\therefore\ a \propto 25$
I	At $t = 10$	$V = 16$	$\therefore\ (a-x) \propto 16$
II	At $t = 20$	$V = 10.5$	$\therefore\ (a-x) \propto 10.5$
III	At $t = 30$	$V = 7.09$	$\therefore\ (a-x) \propto 7.09$

Now use, $K = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$

For I $\quad K_1 = \frac{2.303}{10}\log_{10}\frac{25}{16} = \mathbf{4.46\times10^{-2}\ minute^{-1}}$

For II $\quad K_2 = \frac{2.303}{20}\log_{10}\frac{25}{10.5} = \mathbf{4.34\times10^{-2}\ minute^{-1}}$

For III $\quad K_3 = \frac{2.303}{30}\log_{10}\frac{25}{7.09} = \mathbf{4.20\times10^{-2}\ minute^{-1}}$

The values of K come almost constant and thus, confirming I order reaction. For velocity constant, take average of all values of K.

93. Volume of O_2 at any time $\propto$ Mole of H_2O_2 decomposed

$\therefore \quad a \propto 35.75$

At $t = 10, x \propto 6.30$

$\therefore \quad K = \frac{2.303}{10}\log_{10}\frac{35.75}{35.75-6.30} = 1.94\times10^{-2}$

At $t = 15, x \propto 8.95$

$K = \frac{2.303}{15}\log_{10}\frac{35.75}{35.75-8.95} = 1.92\times10^{-2}$

At $t = 20, x \propto 11.40$

$K = \frac{2.303}{20}\log_{10}\frac{35.75}{35.75-11.40} = 1.92\times10^{-2}$

At $t = 25, x \propto 13.50$

$K = \frac{2.303}{25}\log_{10}\frac{35.75}{35.75-13.50} = 1.90\times10^{-2}$

Since, K values are constant using I order equation and thus, reaction **obeys I order kinetics.**

$K = \mathbf{1.92\times10^{-2}\ minute^{-1}}$

94. $\because$ Volume of alkali used $\propto$ Mole of acid at that time

$\therefore$ At $t = 0$, *i.e.*, $\quad V_0 \propto$ Mole of HCl

$\therefore$ At $t = t$, *i.e.*, $\quad V_t \propto$ Mole of HCl + Mole of CH_3COOH formed at $t = t$

At $t = \infty$, *i.e.*, $\quad V_\infty \propto$ Mole of HCl + Total mole of CH_3COOH formed

$\therefore \quad a \propto V_\infty - V_0 \quad$ *i.e.*, total ester

$(a-x) \propto V_\infty - V_t \quad$ *i.e.*, left ester at $t = t$

At $t = 75$,

$K_1 = \frac{2.303}{75}\log_{10}\frac{42.03-19.24}{42.03-24.20} = 3.27\times10^{-3}\ \text{min}^{-1}$

At $t = 119$,

$K_2 = \frac{2.303}{119}\log_{10}\frac{42.03-19.24}{42.03-26.60} = 3.28\times10^{-3}\ \text{min}^{-1}$

At $t = 259$,

$K_3 = \frac{2.303}{259}\log_{10}\frac{42.03-19.24}{42.03-32.23} = 3.26\times10^{-3}\ \text{min}^{-1}$

Since, K values are constant and thus, reaction **obeys I order kinetics.**

Also, $\quad K = \frac{K_1+K_2+K_3}{3} = \mathbf{3.27\times10^{-3}\ min^{-1}}$

95. At $t = 0$, Rotation $r_0 \propto$ Mole of sugar + rotation due to external factor

At $t = t$, Rotation $r_t \propto$ Left sugar + rotation due to external factors

At $t = \infty$, Rotation $r_\infty \propto$ External factors

$\therefore \quad a =$ Mole of sugar $\propto r_0 - r_\infty \quad$ at $t = 0$

$(a-x) =$ Left mole of sugar $\propto r_t - r_\infty \quad$ at $t = t$

$\therefore \quad K_1 = \frac{2.303}{30}\log_{10}\frac{46.75+18.75}{41+18.75} = 3.06\times10^{-3}\ \text{min}^{-1}$

$K_2 = \frac{2.303}{90}\log_{10}\frac{46.75+18.75}{30.75+18.75} = 3.11\times10^{-3}\ \text{min}^{-1}$

$K_3 = \frac{2.303}{230}\log_{10}\frac{46.75+18.75}{12.75+18.75} = 3.18\times10^{-3}\ \text{min}^{-1}$

Since, K values are constant and thus, **reaction obeys I order kinetics.**

Also, $\quad K = \mathbf{3.12\times10^{-3}\ min^{-1}}$

96. $\quad CH_3\cdot O\cdot CH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$

	$CH_3\cdot O\cdot CH_3(g)$	$CH_4(g)$	$H_2(g)$	$CO(g)$
Initial P	0.40 atm			
Final P at 12 min.	$(0.40-P)$	P	P	P

For ideal gas behaviour, Mole $\propto$ Pressure (at constant V and T)

$\therefore \quad a \propto 0.40; \quad (a-x) \propto (0.40-P)$

$\therefore \quad K = \frac{2.303}{t}\log_{10}\frac{a}{a-x}$

$\frac{0.693}{14.5} = \frac{2.303}{12}\log_{10}\frac{0.40}{(0.40-P)} \quad \therefore\ P = 0.175$ atm

$\therefore$ Pressure of ether decomposed $= 0.175$

Now, $\quad$ Total pressure $= 0.40 - P + P + P + P$

$= 0.40 + 2P = 0.40 + 2\times0.175$

$= \mathbf{0.75\ atm}$

97. $\quad A + OH^- \longrightarrow$ Products

	A	OH^-
$t = 0$	0.002	0.3
$t = 30$	$\left[0.002-\frac{0.002\times1}{100}\right]$	$\left[0.3-\frac{0.002\times1}{100}\right]$

Using $\quad K = \frac{2.303}{t(a-b)}\log_{10}\frac{b(a-x)}{a(b-x)}$

$$K = \frac{2.303}{30\times(0.002-0.3)}\log_{10}\frac{0.3\times\left[0.002-\frac{0.002\times1}{100}\right]}{0.002\left[0.3-\frac{0.002\times1}{100}\right]}$$

$K = \mathbf{1.12\times10^{-3}\ L\ mol^{-1}\,sec^{-1}}$

98. $\quad \text{Rate} = K[A][B]^2$

$\therefore \quad 10^{-2} = K[1][1]^2$ or $K = 10^{-2}\ \text{litre}^2\text{mol}^{-2}\text{sec}^{-1}$

Now, $\text{rate}_{II} = 10^{-2}\times0.5\times(0.5)^2$

or New rate $= \mathbf{1.2\times10^{-3}\ mol/L\text{-}sec}$

99. **For A:** $\quad \text{rate} = K_A[A]^1 \quad$ ...(1)

and $\quad (t_{1/2})_A = \frac{0.693}{K_A} \quad$ ...(2)

For B: $\quad \text{rate} = K_B[B]^2 \quad$ ...(3)

and $\quad (t_{1/2})_B = \frac{1}{a\cdot K_B} \quad$ ...(4)

where a is initial concentration

(a) Initial rate of A, $r_A = K_A \times a$

Initial rate of B, $r_B = K_B \times a^2$

$\therefore \quad \frac{r_A}{r_B} = \frac{K_A}{K_B}\times\frac{1}{a} \quad$ ...(5)

From Eqs. (2) and (4) if $(t_{1/2})_A = (t_{1/2})_B$,

then $$\frac{0.693}{K_A} = \frac{1}{K_B \cdot a}$$

or $$\frac{K_A}{K_B} = 0.693 \times a \qquad \ldots(6)$$

$\therefore$ From Eqs. (5) and (6)

$$\frac{r_A}{r_B} = \frac{0.693a}{a} = \mathbf{0.693}$$

(b) After lapse of I half-life the new rates are r'_A and r'_B

$$r'_A = K_A \times \frac{a}{2}$$

$$r'_B = K_B \times \left(\frac{a}{2}\right)^2$$

$$\therefore \qquad \frac{r'_A}{r'_B} = \frac{K_A}{K_B} \times \frac{2}{a} \qquad \ldots(7)$$

$$\frac{r'_A}{r'_B} = 0.693 \times a \times \frac{2}{a} = \mathbf{1.386}$$

[From Eqs. (6) and (7)]

100.

$$\begin{array}{llcccc} & CH_3OCH_3(g) & \longrightarrow & CH_4(g) + & CO(g) + & H_2(g) \\ \text{Pressure at } t = 0 & 0.4 & & 0 & 0 & 0 \\ \text{Pressure at } t = 4.5\,\text{hr} & 0.4 - a & & a & a & a \\ & = A & & & & \end{array}$$

$$K = \frac{2.303}{t} \log \frac{0.4}{A}$$

$$4.78 \times 10^{-3} = \frac{2.303}{4.5 \times 60} \log \frac{0.4}{A} \quad \therefore \; A = 0.110$$

$$\therefore \qquad 0.4 - a = 0.110 \qquad \text{or} \qquad a = 0.29$$

Now molecular weight of mixture

$$= \frac{0.11 \times 46 + 0.29 \times 16 + 0.29 \times 28 + 0.29 \times 2}{0.98}$$

$$= 18.78$$

$$\therefore \qquad \frac{r_0}{r_m} = \sqrt{\frac{18.78}{46}} \times \frac{0.4}{0.98} = \mathbf{0.261} \quad (P_0 = 0.4\,;\, P_m = 0.98)$$

101.

$$\begin{array}{lccccc} & 4PH_3(g) + & \text{Inert gas} \longrightarrow & P_4(g) + & 6H_2(g) + & \text{Inert gas} \\ t = 0 & P & P' & 0 & 0 & \\ t = t & (P - A) & P' & \frac{A}{4} & \frac{6A}{4} & P' \\ t = \infty & 0 & P' & \frac{P}{4} & \frac{6P}{4} & P' \end{array}$$

$$\begin{array}{lll} t = 0 & P = 262.40 & = P_{PH_3} + P_{I(g)} \\ t = 60 & P = 272.90 & = P_{PH_3(\text{Left})} + P_{P_4(g)} + P_{H_2(g)} + P_{I(g)} \\ t = 120 & P = 275.51 & = P_{PH_3(\text{Left})} + P_{P_4(g)} + P_{H_2(g)} + P_{I(g)} \\ t = \infty & P = 276.40 & = P_{P_4(g)} + P_{H_2(g)} + P_{I(g)} \end{array}$$

$$\therefore \qquad \frac{P}{4} + \frac{6P}{4} + P' = 276.40$$

$$\therefore \qquad 7P + 4P' = (276.40) \times 4 \qquad \ldots(1)$$

Also, at $t = 0$, $P + P' = 262.40$ ...(2)

$$\therefore \qquad P = 18.66 \text{ mm}$$

$$P' = 243.74 \text{ mm}$$

At $t = 60$, Pressure $= 272.90 = (P - A) + P' + \frac{A}{4} + \frac{6A}{4}$

$$272.90 = 18.66 - A + 243.74 + \frac{7A}{4}$$

$$\therefore \; A = 14.0 \text{ mm} \quad \therefore \; K = \frac{2.303}{t} \log \frac{[P_{PH_3}]_0}{[P_{PH_3}]_{60}}$$

$$= \frac{2.303}{60} \log \frac{18.66}{(18.66 - 14)}$$

$$= \mathbf{2.31 \times 10^{-2}\ sec^{-1}}$$

At $t = 120$, Pressure $= 275.51 = P - A' + P' + \frac{A'}{4} + \frac{6A'}{4}$

$$275.51 = 18.66 - A' + 243.74 + \frac{7A'}{4}$$

$$\therefore \qquad A' = 17.48 \text{ mm}$$

$$\therefore \qquad K = \frac{2.303}{120} \log \frac{18.66}{(18.66 - 17.48)} = \mathbf{2.30 \times 10^{-2}\ sec^{-1}}$$

$\therefore$ Reaction is of first order.

102. After 6 hour

Meq. of H_2O_2 in 10 mL diluted solution

$$= 25 \times 0.025 \times 5 = 3.125$$

Meq. of H_2O_2 in 10 mL conc. solution

$$= 3.125 \times 10 = 31.25$$

Meq. of H_2O_2 in 10 mL of 20 volume H_2O_2 present initially

$$= \frac{68 \times 20 \times 10}{22400 \times 17} \times 1000 = 35.71$$

[$\because$ 22400 mL O_2 = 68 g H_2O_2

$$\therefore \qquad 20 \text{ mL } O_2 = \frac{68 \times 20}{22400} \text{ g } H_2O_2 \text{ in 1 mL}$$

$$= \frac{68 \times 20 \times 10}{22400} \text{ g } H_2O_2 \text{ in 10 mL]}$$

$$\therefore \qquad K = \frac{2.303}{6} \log \frac{35.71}{31.25} = \mathbf{0.022\ hr^{-1}}$$

103.

$$\begin{array}{lccl} & B^{n+} \longrightarrow & B^{(n+4)+} & \\ \text{Millimole at } t = 0 & a & 0 & 2e + B^{n+} \longrightarrow B^{(n+2)+} \\ t = t & (a - x) & x & 5e + B^{(n+4)+} \longrightarrow B^{(n-1)+} \end{array}$$

Let normality be N for reducing agent.

Thus, at $t = 0$ $\quad a \times 2 = N \times 25 \;\therefore\; a = \frac{25}{2} N$

$$\text{at } t = t \; \underset{\text{For } B^{n+}}{(a - x) \times 2} + \underset{\text{for } B^{(n+4)+}}{x \cdot 5} = N \times 32$$

$$\therefore \qquad 3x = 7N \quad \text{or} \quad x = \frac{7}{3} N$$

Now, $$K = \frac{2.303}{10} \log \frac{25/2N}{\left(\frac{25}{2} - \frac{7}{3}\right) N} = \frac{2.303}{10} \log \frac{25 \times 6}{2 \times 61}$$

$$K = \mathbf{2.07 \times 10^{-2}\ min^{-1}}$$

104. Let rate $= K\,[CH_3COF]^a\,[H_2O]^b$

Case I: $[H_2O] >> [CH_3COF]$

Case II: $[H_2O] << [CH_3COF]$

According to Ostwald isolation method, we can assume $[H_2O]$ in excess in case I and $[CH_3COF]$ in excess in case II.

Case I: Using I order for CH_3COF (by hit and trial)

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

$$K_1 = \frac{2.303}{10} \log \frac{0.01}{0.00857} = 0.0154$$

$$K_2 = \frac{2.303}{20}\log\frac{0.01}{0.00735} = 0.0154$$

Thus, $K_{av.} = 0.0154$

Thus order with respect to $[CH_3COF]$ is one or $a = 1$

Case II : Using I order for H_2O

$$K_1' = \frac{2.303}{10}\log\frac{0.02}{0.0176} = 0.0128$$

$$K_2' = \frac{2.303}{20}\log\frac{0.02}{0.0156} = 0.0124$$

$$K_3' = \frac{2.303}{40}\log\frac{0.02}{0.0122} = 0.0124$$

$$K'_{av.} = 0.0125\ \text{min}^{-1}$$

Thus order with respect to $[H_2O]$ is one or $b = 1$

Now, $\text{rate} = K_T[CH_3COF]^1[H_2O]^1$

Also, $\text{rate} = K_1[CH_3COF]$

$$\therefore \quad K_T = \frac{K_1}{[H_2O]} = \frac{0.0154}{1.0} = \mathbf{1.54\times10^{-2}\ min^{-1}}$$

105. **For I :** $K = \frac{1}{t}\frac{x}{a(a-x)}$ (II order equation)

Given, $a = 0.1M$, $x = \frac{0.1\times30}{100} = 0.03$, $t = 60\,\text{min}$

$$\therefore \quad K_1 = \frac{1}{60\times0.1}\times\frac{0.03}{(0.1-0.03)} = 0.07\ \text{min}^{-1}$$

Also, for I : $K_1 = Ae^{-E_a/RT}$

For II : $K_2 = Ae^{-E_a'/RT}$

$$\therefore \quad \frac{K_1}{K_2} = e^{(E_a'-E_a)/RT} = e^{-10.46/RT} = e^{-10.46/8.314\times10^{-3}\times373}$$

$$\text{or} \quad K_2 = \frac{K_1}{e^{-10.46/8.314\times10^{-3}\times373}} = \frac{0.07}{0.034} = \mathbf{2.10\ min^{-1}}$$

Now, for II: $K_2 = \frac{1}{t}\frac{x}{a(a-x)}$; $a = 0.05$;

$$x = \frac{0.05\times70}{100} = 0.035$$

$$\therefore \quad t = \frac{1}{2.10\times0.05}\times\frac{0.035}{\left(0.05-\frac{0.05\times70}{100}\right)}$$

$$= \mathbf{22.22\ min}$$

106. By Step (ii) $\frac{-d[I^-]}{dt} = K_3[I^-][HOCl]$ ...(a)

By step (i) $\frac{K_1}{K_2} = \frac{[HOCl][OH^-]}{[OCl^-][H_2O]}$ ...(b)

By step (iii) $\frac{K_1'}{K_2'} = \frac{[H_2O][OI^-]}{[OH^-][HOI]}$ ...(c)

By Eqs. (b) and (a)

$$\frac{-d[I^-]}{dt} = K_3[I^-].\frac{K_1}{K_2}\frac{[OCl^-][H_2O]}{[OH^-]}$$

$$= K_3\cdot\frac{K_1}{K_2}\frac{[OCl^-][I^-]}{[OH^-]}$$

[Since $[H_2O]$ is constant]

$$\therefore \quad \frac{-d[I^-]}{dt} = K\frac{[OCl^-][I^-]}{[OH^-]}$$

107. By step (iii) $\frac{d[COCl_2]}{dt} = K_3[COCl][Cl_2]$ ...(a)

By step (i) $\frac{K_1}{K_2} = \frac{[Cl]^2}{[Cl_2]}$ ...(b)

By step (ii) $\frac{K_1'}{K_2'} = \frac{[COCl]}{[CO][Cl]}$ ...(c)

Thus from Eqs. (b) and (c)

$$[COCl] = \frac{K_1'}{K_2'}\cdot[CO]\times\sqrt{\frac{K_1}{K_2}\cdot[Cl_2]} \quad \text{...(d)}$$

From Eqs. (a) and (d)

$$\frac{d[COCl_2]}{dt} = K_3\frac{K_1'}{K_2'}\left(\frac{K_1}{K_2}\right)^{1/2}[CO][Cl_2]^{1/2}\cdot[Cl_2]$$

$$\boldsymbol{\frac{d[COCl_2]}{dt} = K\cdot[CO][Cl_2]^{3/2}}$$

108. The rate of formation of urea is given by Eq. (iii)

$$\frac{d[\text{urea}]}{dt} = K[NH_3][HNCO] \quad \text{...(a)}$$

By step (ii) we have : $\frac{[NH_3][HNCO]}{[NH_4NCO]} = K_{C_1}$ ...(b)

By step (i) we have : $\frac{[NH_4NCO]}{[NH_4CNO]} = K_{C_2}$ ...(c)

$\therefore$ By Eqs. (b) and (c)

$$[NH_3][HNCO] = K_{C_1}\cdot K_{C_2}[NH_4CNO] \quad \text{...(d)}$$

$\therefore$ By Eqs. (a) and (d)

$$\frac{d[\text{urea}]}{dt} = K\cdot K_{C_1}\cdot K_{C_2}[NH_4CNO]$$

$$\boldsymbol{\frac{d[\text{urea}]}{dt} = K'[NH_4CNO]}$$

109.

$$A \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B$$

	A	B
$t = 0$	2 mol litre^{-1}	0
At eq.	$(2-X)$ mol litre^{-1}	X

$K_1 = 2\times10^{-3}\ \text{mol L}^{-1}\text{sec}^{-1}$ (zero order)

$K_2 = 3\times10^{-3}\ \text{sec}^{-1}$ (Ist order)

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

At equilibrium $\frac{dx}{dt} = 0 \quad \therefore \ 0 = K_1 - K_2[X]_{eq.}$

$$\therefore \quad [X]_{eq.} = \frac{K_1}{K_2} = \frac{2\times10^{-3}}{3\times10^{-3}} = 0.66\ \text{mol litre}^{-1} = K_c$$

	$A \rightleftharpoons$	B
Initial eq.	1.34	0.66
Moles added at eq.	1.34	$0.66 + 0.5 = 1.16$

Addition of B will bring backward reaction

at time t	$(1.34 + X)$	$(1.16 - X)$

$$\because \quad [B] = \frac{3}{4}[A]_{Ieq.} = \frac{3}{4}\times1.34 = 1.005$$

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

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

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

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

at $\quad t = 0, \quad X = 0$

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

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

110.

$$\begin{array}{ccc} A_0 & \longrightarrow & B \\ 0.01 & & 0 \\ 0.01 - x_{eq.} & & x_{eq.} \end{array}$$

$$\frac{[B]_{eq.}}{[A]_{eq.}} = \frac{10^{-2}}{K_b} = 4 = \frac{[x]_{eq.}}{0.01 - [x]_{eq.}}$$

$\therefore \quad K_b = 0.25 \times 10^{-2}$

and $\quad x_{eq.} = \frac{0.04}{5} = 0.008$

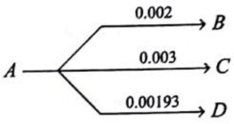
$$t = \frac{2.303}{(K_f + K_b)} \log \frac{[x]_{eq.}}{[x]_{eq.} - x}$$

$$30 = \frac{2.303}{1.25 \times 10^{-2}} \log \frac{0.008}{(0.008 - x)}$$

$\therefore \quad \frac{0.008}{0.008 - x} = 1.455$

$\therefore \quad x = \mathbf{2.50 \times 10^{-3}}$

111.



What is pressure of B after 100 sec.

$$K_{av} = 0.002 + 0.003 + 0.00193$$
$$= 0.00693$$

Mole of (A) Left $Kt = 2.303 \log \frac{8}{[A]} = 0.00693 \times 100$

$$= 2.303 \log \frac{8}{[A]}$$

$$\log \frac{8}{[A]} = \frac{0.00693 \times 100}{2.303} = 0.3010$$

$$\frac{8}{[A]} = 2$$

$\therefore$ mole of (A) left $= 4$

$[A]$ decomposed $= 8 - 4 = 4$ mole

mole of B formed $= \frac{0.002}{0.00693} \times 4 \times 1 = \mathbf{1.154}$

112. $MnO_4^- + [Fe(H_2O)_2(C_2O_4)_2]^{2-} + 8H^+ \longrightarrow$

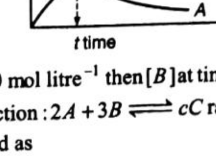
$$Mn^{2+} + Fe^{3+} + 4CO_2 + 6H_2O$$

$\because \quad -\frac{d[MnO_4^-]}{dt} = -\frac{1}{8}\frac{d[H^+]}{dt}$

$\therefore \quad \frac{r_{H^+}}{r_{MnO_4^-}} = 8$

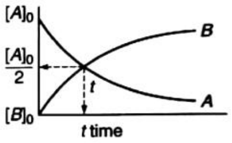
• SINGLE INTEGER ANSWER PROBLEMS •

1. The decomposition of equal mole of two reactants P and Q obey I order kinetics with half life 54 and 18 minute respectively. If both are allowed to run for 54 minute. The ratio of mole of P and Q left after decomposition will be.
2. A reaction obeys II order kinetics. If the half life period of the reaction is equal to its average life, then the value of reactant concentration at $t = 0$ is ……
3. A straight line with negative slope was found in graph of $\log_e K$ *vs.* $\frac{1}{T}$ with an angle of 45° with y-axis. The energy of activation is …… cal.
4. A straight line was obtained on plotting $\log_{10}\frac{dx}{dt}$ *vs.* $\log_{10}(a-x)^n$ with an intercept on $\log\left(\frac{dx}{dt}\right)$ axis equal to 0.6021. The rate constant for the reaction is …… $\text{litre}^{n-1}\text{mole}^{1-n}t^{-1}$.
5. Energy of activation for a reversible reaction is 6 kcal (E_a forward) and heat of reaction is –3 kcal. The energy of activation for backward reaction in kcal is ……
6. A reaction occurs in 'n' parallel paths. For each path having energy of activation as $E, 2E, 3E, \ldots nE$ and rate constant $K, 2K, 3K, \ldots nK$ respectively. If $E_{AV} = 3E$, then n is ……
7. If $\frac{d[\text{NH}_3]}{dt} = 34\ \text{g hr}^{-1}$ for the reaction
$$\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$$
then $\frac{d[\text{H}_2]}{dt}$ is ………g hr^{-1}.
8. The half-life period of a reaction, becomes 16 times when reactant concentration is halved. The order of reaction is ……
9. The half lives of two parallel path reaction $A \begin{cases} \to B \\ \to C \end{cases}$ are 4 hrs and 12 hrs respectively. The average half-life for the decay of A is ……
10. The unit of rate constant for a reaction is $\text{litre}^2\text{mol}^{-2}t^{-1}$. The order of reaction is ……
11. For the I order reaction $3A \longrightarrow 2B$, the concentration of A and B at the intersection is given in figure.



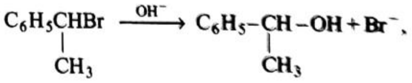
if $[A]_0 = 20\ \text{mol litre}^{-1}$ then $[B]$ at time t is equal to ……

12. For the reaction : $2A + 3B \rightleftharpoons cC$ rate of formation of C is expressed as
$$\frac{d[C]}{dt} = -\frac{3[dA]}{dt}$$
The value of c is :
13. The order of reaction for $\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ if it is carried over water is :
14. The decomposition of NH_3 on solid surface, *e.g.*, Pt shows the order of reaction equal to :
15. The time required to complete 99.9% decay is …… times of the time required to complete 90% decay.
16. The rate of decomposition of a substance increases 2.25 times of concentration of reactant is increased by 1.5 times at same T. The order of reaction is :
17. For an elementary reaction $A \longrightarrow B$ shown in the figure.



The sum of slopes for curve A and B at the intersection point is:

18. In the above curve if rate constant for A is 0.34660, then t is:
19. The half life period for a reaction is 50 minute. If initial concentration is halved, the half life period is reduced to 25 minute. The order of reaction is :
20. For the reaction involving single reactant $C_o\sqrt{t_{1/2}}$ is found to be constant, where C_o is initial concentration and $t_{1/2}$ is half life. The order of reaction is ……
21. Energy of activation for free radical combination is ……
22. For the reaction



$$\underset{\displaystyle\text{CH}_3}{\text{C}_6\text{H}_5\text{CHBr}} \xrightarrow{\text{OH}^-} \text{C}_6\text{H}_5-\underset{\displaystyle\text{CH}_3}{\text{CH}}-\text{OH} + \text{Br}^-,$$

rate law was found as :
$$\text{Rate} = 4.8\times10^{-5}[\text{Br}^-][\text{OH}^-] + 2.4\times10^{-6}[\text{Br}^-]$$
If the concentration of OH^- is 0.001 M, the % by which S_{N^2} path is followed is ……

23. A certain substance A is mixed with an equal amount of B. At the end of 1 hr, A is 70% reacted. How much % of A will be left unreacted at the end of 2.5 hr, if the reaction with respect to A is of I order ?
24. The rate of reaction depends on concentration as $-\frac{dC_A}{dt} = \frac{K_1C_A}{1+K_2C_A}$. If C_A being very high, then order of reaction is ……

25. A chemical reaction occurs in three paths having rate constants K_1, K_2 and K_3 respectively. If E_{a_1}, E_{a_2} and E_{a_3} are 5, 4, 8 kJ respectively and overall rate constant $K = \frac{K_1 K_3}{K_2}$. Assuming $A_{av} = \frac{A_1 A_3}{A_2}$ the overall energy of activation in kJ is ......

26. $t_{99.6\%} = t_{1/2} \times a$; the value of a is ......

27. Half-life of a reactant was found to be 9 hours, when 1.0 M reactant was allowed to carry out reaction. If 0.5 M reactant was taken then half-life was found 45 hours. The order of reaction is ......

28. For a consecutive I order reaction of both the steps $A \xrightarrow{K_1} B \xrightarrow{K_2} C$. If 20 M of A are taken and $K_2 = 2K_1$, the maximum concentration of B will be ...... M

29. Two first order reaction involving reactants A and B have the same frequency factor and activation energy of A is 10.46 kJ more than B. If A dissociates 30% in 60 minute at 100°C, the time taken in minute to dissociate 70% at the same temperature.

30. The rate of gaseous reaction expressed by $r = K[A][B]$. If pressure of gas A and B are doubled at the same conditions, the rate of reaction will be increased by ...... times.

31. 10 mole of a radioactive element undergoes decay follow I order to give three products B, C and D with rate constant 0.002, 0.003 and 0.00193 sec^{-1} respectively. How much mole are decayed in 100 sec.

32. For a given reaction $A \longrightarrow B$, temperature coefficient is constant. If $\frac{K_{55°C}}{K_{25°C}} = 8$ what is the value of $\frac{K_{65°C}}{K_{35°C}}$ in nearest possible integer. K is rate constant.

33. The rate of decomposition of HI is given by; rate $= K[HI]^2$. The rate constant K is 1×10^{-6} litre $mol^{-1} sec^{-1}$ at 600 K. Find out the number of moles of HI $\times 10^{-10}$ decomposed in first second when HI sample is taken in 1 litre container at 1 atm pressure.

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

$[R]$ (molar)	1.0	0.75	0.40	0.10
t (min.)	0.0	0.05	0.12	0.18

The order of reaction is: **(IIT 2010)**

35. An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively. What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? (take $\log_{10} 2 = 0.3$) **(IIT 2012)**

ANSWERS

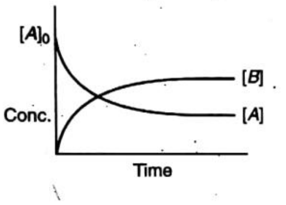
1. Four **2.** One **3.** Two **4.** Four **5.** Nine **6.** Four **7.** Six **8.** Five **9.** Three **10.** Three **11.** Eight **12.** Six
13. Zero **14.** Zero **15.** Three **16.** Two **17.** Zero **18.** Two **19.** Zero **20.** Three **21.** Zero **22.** Two **23.** Five **24.** Zero
25. Nine **26.** Eight **27.** Zero **28.** Five **29.** Seven **30.** Four **31.** Five **32.** Eight **33.** Four **34.** Zero **35.** Nine

OBJECTIVE PROBLEMS (One Answer Correct)

1. The rate of combination of free radicals :
   (a) increases with increase in temperature
   (b) decreases with increase in temperature
   (c) dependent of temperature
   (d) altogether different for different reactions and independent of temperature

2. A consecutive reaction $P \xrightarrow{K_1} Q \xrightarrow{K_2} R$ leads to :
   (a) maxima in $[P]$ if $K_1 > K_2$
   (b) maxima in $[Q]$ if $K_1 > K_2$
   (c) maxima in $[Q]$ if $K_1 < K_2$
   (d) maxima in $[P]$ if $K_1 < K_2$

3. At the intersection point of two curves $nA \longrightarrow mB$, the concentration of B can be given by assume I order :



(a) $\frac{m}{m+n}[A]_0$ (b) $\frac{m}{n}[A_0]$
(c) $\frac{m}{m-n}[A_0]$ (d) $\frac{n}{m+n}[A_0]$

4. Select the incorrect statement :
   (a) Half-life period of all reactions decreases with increase in temperature.
   (b) Half life period of I order reaction is always constant.
   (c) Higher is rate constant of a reaction, lesser will be its energy of activation.
   (d) Rate of reaction whether exothermic or endothermic usually increases with temperature.

5. The rate constants of three reactions involving reactant A only obeying I, II, III order respectively is same. Which of the following is true ?
   (a) $r_3 > r_2 > r_1$ if $[A] > 1$ (b) $r_1 > r_2 > r_3$ if $[A] < 1$
   (c) $r_1 = r_2 = r_3$ if $[A] = 1$ (d) All of these

6. $\log_e K$ vs. $1/T$ plots shows a straight line having slope of 120° and intercepts on the Y-axis of 2, then :
   (a) $E_a = 8.0$ cal, $A = 100$
   (b) $E_a = 8.0$ cal, $A = 2$
   (c) $E_a = 3.46$ cal, $A = 7.38$
   (d) $E_a = 3.46$ cal, $A = 100$

7. The temperature coefficients of two reactions are 2 and 3 respectively. Which would be correct for these reactions?
   (a) $E_{a_1} < E_{a_2}$ (b) $E_{a_1} > E_{a_2}$
   (c) $E_{a_1} = E_{a_2}$ (d) Nothing can be said

8. A reaction occurs in three rate determining steps having rate constants K_1, K_2 and K_3 respectively and arrehenius factor A_1, A_2, A_3 respectively. The overall rate constant $K = \frac{K_1K_2}{K_3}$. If energy of activations for each step is E_{a_1}, E_{a_2} and E_{a_3} respectively, then overall energy of actiavtion is :
   (a) $E_{a_1} + E_{a_2} + E_{a_3}$
   (b) $\frac{E_{a_1} \times E_{a_2}}{E_{a_3}}$
   (c) $E_{a_1} + E_{a_2} - E_{a_3}$
   (d) $K_3\left[\frac{E_{a_1}}{K_2} + \frac{E_{a_2}}{K_1} + \frac{K_3E_{a_3}}{K_1K_2}\right]$

9. For a I order reaction $-\frac{d[A]}{dt} = K[A]_0$. The reaction is carried out by taking 100 mol litre^{-1} of A, then concentration of A decayed after time $\frac{1}{K}$ is :
   (a) 53.21 mol litre^{-1} (b) 36.79 mol litre^{-1}
   (c) 61.21 mol litre^{-1} (d) 26.79 mol litre^{-1}

10. For two I order reactions : $A \longrightarrow B$; $K_1 = 10^{15} e^{-\frac{2\times10^3}{T}}$
    $C \longrightarrow D$; $K_2 = 10^{14} e^{-\frac{10^3}{T}}$
    The temperature at which both have same rate if $[A] = [C]$ is made initially :
    (a) 707.2°C (b) 434.2°C
    (c) 727°C (d) 707.2 K

11. H_2O and oxygen atoms react in upper atmospheric level bimolecularily to form two OH radicals having heat of reaction 72 kJ at 400 K and energy of activation being 77 kJ mol^{-1}. E_a for bimolecular combination of two OH radicals to form H_2O and O-atom is :
    (a) – 5 kJ (b) + 5 kJ
    (c) – 10 kJ (d) + 10 kJ

12. The rate of appearance of NO_2 (in atm m^{-1}) following the reaction, $N_2O_4 \longrightarrow 2NO_2$ when initial pressure of N_2O_4 is reduced from 0.50 atm to 0.25 atm in 5 minutes is :
    (a) 0.1 (b) 0.2
    (c) 0.25 (d) 0.3

13. At 3 km altitude, water boils at 90°C and 300 seconds are taken to cook a '3 minute egg'. The temperature coefficient for the process of cooking is :
    (a) 2.66 (b) 1.66
    (c) 3.66 (d) 0.6

14. The rate constant, the energy of activation and the Arrhenius parameter of a chemical reactions at 25°C are 3.0×10^{-4} sec^{-1}, 104.4 kJ mol^{-1} and 6.0×10^{14} sec^{-1} respectively. The value of rate constant as $T \longrightarrow \infty$ is :
    (a) 2.0×10^{18} sec^{-1} (b) 6.0×10^{14} sec^{-1}
    (c) infinity (d) 3.6×10^{30} sec^{-1}

15. Select the incorrect statement :

(a) Rate of exothermic reactions increases with increase in temperature.

(b) Alkaline hydrolysis of ester is irreversible reaction.

(c) For $N_2 + 3H_2 \rightleftharpoons 2NH_3$; if rate of formation of NH_3 is 0.001 kg hr, than rate of consumption of H_2 is 0.0015 kg/hr.

(d) In Arrhenius equation :

$$K = Ae^{-Ea/RT};\ \text{if } T \to \infty\ K = A$$

16. A consecutive reaction : $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ shows a :

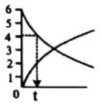
(a) Maxima in the concentration of A

(b) Maximum in the concentration of B

(c) Maxima in the concentration of C

(d) None of the above

17. For the unimolecular reaction $A \to B$, the figure given below shows that at the time t curves represents :



Thus t is :

(a) $t_{1/3}$ (b) $t_{1/2}$

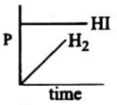
(c) $t_{2/3}$ (d) $t_{1/4}$

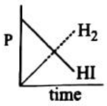
18. If c is the concentration of n mole of gas at pressure P and temperature T, then for the ideal gas reaction, the rate of reaction can be given by:

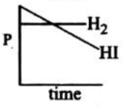
(a) $-\dfrac{d[A]}{dt}$ (b) $-\dfrac{1}{RT}\dfrac{dP}{dt}$

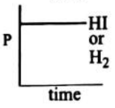
(c) $-\dfrac{1}{v}\dfrac{dn}{dt}$ (d) either of these

19. Decomposition of HI on gold surface is zero order reaction. Which of the following graph correctly represents this reaction?

(a) 

(b) 

(c) 

(d) 

20. The reaction $A \to B + C$ has rate constant $1 \times 10^{-3}\ Ms^{-1}$. If one starts the reaction with one mole of A than $t_{1/2}$ and completion of reaction time would be:

(a) 1000 s, 500 s (b) 500 s, 1000 s

(c) 750 s, 400 s (d) 400 s, 800 s

21. The half of a gaseous compound ($A_{(g)} \to B_{(s)}$) initially at 2 atm is 200 sec. If the initial pressure is taken as 1 atm, the half life reduces to 100 sec. The order of reaction is:

(a) 0 (b) 1

(c) 2 (d) 3

22. Which one is incorrect statement?

(a) Always $E_a > \Delta H$ for an endothermic reaction.

(b) $E_b < \Delta H$ for an endothermic reaction.

(c) $E_a \gtrless \Delta H$ for an exothermic reaction.

(d) Always $E_a < \Delta H$ for an exothermic reaction.

23. For a I order reaction which one is not correct?

(a) The concentration of product increases linearly with time

(b) The concentration of product increases exponentially with time

(c) The degree of dissociation 'α' is given by $1 - e^{-kt}$

(d) The reaction never goes for completion

24. Select the incorrect statement:

(a) A spontaneous reaction is not necessarily a fast reaction.

(b) Larger the activation energy, greater is the effect on rate constant with rise in temperature.

(c) The reactivity of bromine is more in liquid state than in vapour state.

(d) Reactions with low energy of activation are fast.

25. For the process $2O_3 \to 3O_2$, mechanism is:

$$O_3 \overset{\text{fast}}{\rightleftharpoons} O_2 + O \quad ; \quad O + O_3 \xrightarrow{\text{slow}} 2O_2$$

The rate law is:

(a) $r = k[O_3]^2$ (b) $r = k[O_3]^2 \cdot [O_2]^{-1}$

(c) $r = k[O_3] \cdot [O_2]$ (d) $r = k[O_3]^2 \cdot [O_2]^{-3}$

26. The rate constant of a reaction depends on :

(a) temperature

(b) initial concentration of the reactants

(c) time of reaction

(d) extent of reaction

27. The specific rate constant of a first order reaction depends on the:

(a) concentration of the reactant

(b) concentration of the product

(c) time required to complete half of the reaction

(d) none of these

28. For an endothermic reaction ΔH represents enthalpy of the reaction, the minimum value of the energy of activation will be:

(a) less than ΔH (b) zero

(c) more than ΔH (d) equal to ΔH

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

(a) $2.0 \times 10^{18}\ s^{-1}$ (b) $6.0 \times 10^{14}\ s^{-1}$

(c) infinity (d) $3.6 \times 10^{30}\ s^{-1}$

30. The variation of rate constant K for a given reaction with temperature is given by the expression :

$$\ln K_T = \ln K_0 + \left(\frac{\ln 3}{10}\right)T$$

The value of temperature coefficient is :

(a) 2 (b) 3

(c) 4 (d) 5

31. Reaction $2A + B \xrightarrow{K} C + D$, shows first order with respect to A and second order with respect to B. The reaction was allowed with molarity a_0 M of A and $2a_0$ M of B at $t = 0$. If after time $t = 30$ minute the molarity of C was $\frac{a_0}{4}$, the rate of reaction after 30 minutes can be written as :

(a) $r = \frac{7K\,a_0^3}{16}$ (b) $r = \frac{27K\,a_0^3}{32}$

(c) $r = \frac{247K\,a_0^3}{64}$ (d) $r = \frac{49K\,a_0^3}{32}$

32. The rate expression for a reaction is $-\frac{dc}{dt} = \frac{\alpha c}{1 + \beta c}$ (α and $\beta > 0$). The half life of the reaction can be given by :

(a) $\frac{1}{\alpha}\ln 2 + \beta c_0$ (b) $\frac{1}{\alpha}\ln 2 + \frac{\beta c_0}{2\alpha}$

(c) $\ln 2 + \frac{\beta c_0}{2}$ (d) $\ln 2 + \frac{\beta c_0}{2\alpha}$

33. Rate constant for nth order reaction is given by :

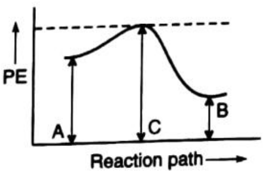
$$K \cdot t = \frac{1}{(n-1)}[C_A^{1-n} - C_0^{1-n}]$$

Thus, for a reaction of nth order, the ratio of $\frac{t_{1/2}}{t_{3/4}}$ is :

(a) 2^n (b) 2^{n-1}

(c) 2^{1-n} (d) $\frac{2^{n-1} - 1}{4^{n-1} - 1}$

34. With respect to the figure given below which of the following statements is correct?



(a) E_a for the forward reaction is $C - B$

(b) E_a for the forward reaction is $B - A$

(c) $E_{a\,(\text{forward})} < E_{a\,(\text{backward})}$

(d) E_a (for reverse reaction) $= C - A$

35. A consecutive reaction : $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ shows a :

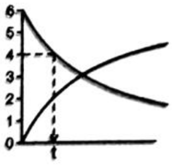
(a) maxima in the concentration of A

(b) maximum in the concentration of B

(c) maxima in the concentration of C

(d) none of the above

36. For the unimolecular reaction $A \longrightarrow B$, the figure given below shows that at the time t curves represents :



Thus t is given by :

(a) $t_{1/3}$ (b) $t_{1/2}$

(c) $t_{2/3}$ (d) $t_{1/4}$

37. The rate of a certain reaction depends on concentration according to the equation :

$$-\frac{dC}{dt} = \frac{K_1 C}{1 + K_2 C}$$

The order of reaction, where (i) concentration is very very high, (ii) very very low will be respectively :

(a) zero, 1 (b) 1, zero

(c) 1, 2 (d) 1, 1

38. The reaction : $CO + Cl_2 \longrightarrow COCl_2$ has the following mechanism.

(i) $Cl_2 \underset{K_2}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast)

(ii) $Cl + CO \underset{K_2'}{\overset{K_1'}{\rightleftharpoons}} COCl$ (fast)

(iii) $COCl + Cl_2 \xrightarrow{K_3} COCl_2 + Cl$ (slow)

The rate expression will be :

(a) $r = K[CO][Cl_2]$ (b) $r = K[CO][Cl_2]^{3/2}$

(c) $r = K[CO]^2[Cl_2]$ (d) $r = [CO]^{3/2}[Cl_2]$

39. What will be the order of reaction given below ?

$$NH_4CNO \longrightarrow NH_2CONH_2$$

If the reaction is completed in three steps as :

(i) $NH_4CNO \rightleftharpoons NH_4NCO$ (fast equilibrium)

(ii) $NH_4NCO \rightleftharpoons NH_3 + H{-}N{=}C{=}O$ (fast equilibrium)

(iii) $NH_3 + H{-}N{=}C{=}O \longrightarrow NH_2CONH_2$ (slow)

(a) 2 (b) 3

(c) 1 (d) zero

40. The temperature coefficient of a reaction is 2. By what factor, the rate of reaction will increases when temperature is raised by 30°C :

(a) 21 (b) 6

(c) 8 (d) 16

41. Select the wrong statement :

(a) Rate of chain reaction involving nascent atoms and free radicals as intermediate depends on shape of the vessel

(b) Energy of activation is definitely +ve for unimolecular reactions
(c) Reaction having rate independent of concentration, never goes to completion
(d) Stoichiometry of reaction does not indicates its order

42. The *trans* → *cis* isomerisation of 1,2-dichloroethylene proceeds with an activation energy of 55.5 kcal mol^{-1}. The heat of reaction at constant pressure for above transformation is 1.0 k cal mol^{-1}. The activation energy for *cis* → *trans* transformation of 1,2-dichloroethylene is :
(a) 56.5
(b) 54.5
(c) 55.5
(d) none of these

43. The energy of activation for a reaction is 25 kJ mol^{-1}. To what temperature should it be raised from 300 K in order that the reaction rate increases 10 times.
(a) 389.5 K
(b) 489.5 K
(c) 289.5 K
(d) none of these

44. For the reaction $RX + OH^- \longrightarrow ROH + X^-$ at 50°C the rate expression is given as :

$$\text{rate} = 4.7 \times 10^{-5}[RX][OH^-] + 0.24 \times 10^{-5}[RX]$$

what percentage of RX reacts by the S_N2 mechanism when $[OH^-] = 0.001\ M$
(a) 0.192
(b) 0.0192
(c) 19.2
(d) 1.92

45. For a given reaction $A \longrightarrow$ Product, the graph plotted between $\log t_{1/2}$ *vs.* $\log [A]$ leads to an angle of 315°. The order of reaction is :
(a) 0
(b) 1
(c) 2
(d) 3

46. Find out ratio of two rates $\frac{r_1}{r_2}$ shown for the elementary reaction :

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

	P_A	P_B
r_1 for case I	6 atm	8 atm
r_2 for case II	6 atm	2 atm

(a) 8
(b) 16
(c) 32
(d) 64

47. Reactants A and B shows I order decomposition individually. If $[A_0] = 8[B_0]$ and $t_{1/2}$ for A and B are 10 and 20 minutes respectively then if both starts decomposing at the same time, after how much minute the concentration of both A and B will be same :
(a) 20
(b) 40
(c) 60
(d) 80

48. Mechanism of a hypothetical reaction $X_2 + Y_2 \longrightarrow 2XY$ is given below :
(i) $X_2 \longrightarrow X + X$ (fast)
(ii) $X + Y_2 \rightleftharpoons XY + Y$ (slow)
(iii) $X + Y \longrightarrow XY$ (fast)
The overall order of the reaction will be :
(a) 1
(b) 2
(c) 0
(d) 1.5

49. A first order reaction has a specific reaction rate of $10^{-2} \sec^{-1}$. How much time will it take for 20 g of the reaction to reduce to 5g?
(a) 238.6 sec
(b) 138.6 sec
(c) 346.5 sec
(d) 693.0 sec

SOLUTIONS (One Answer Correct)

1. (d) $r = K[\ ]^n$ and $K = Ae^{-E_a/RT}$. $E_a = 0$ for free radical combination. K is constant with T.

2. (b) $[R]$ can be maximum only if its decay is slower than P, *i.e.*, $K_2 < K_1$.

3. (a)

$$[A]_{\text{left}} = [B]_{\text{formed}} = \frac{m}{n}[A]_{\text{decayed}},$$

$$[A_0]e^{-\lambda t} = \frac{m}{n}[1 - e^{-\lambda t}][A_0]$$

$$\therefore \quad ne^{-\lambda t} = m - me^{-\lambda t} \text{ or } e^{-\lambda t} = \frac{m}{m+n}$$

$$\therefore \quad [B]_{\text{formed}} = \frac{m}{n}\left[1 - \frac{m}{m+n}\right][A_0]$$

$$= \frac{m}{n}\left[\frac{m+n-m}{m+n}\right][A_0]$$

$$= \frac{m}{m+n}[A_0]$$

4. (c) $K = Ae^{-E_a/RT}$. K depends upon E_a, T and nature of reaction; but always increases with T. Thus rate always increases with T.

5. (d) $r_1 = K[A]^1$; $r_2 = K[A]^2$; $r_3 = K[A]^3$

6. (c) $\ln K = \ln A - \frac{E_a}{RT}$

Intercept $= \ln A = 2$;

Also $-\frac{E_a}{R} = \tan\theta (\tan 120 = -1.73)$

$2.303 \log [A] = 2$

$\log [A] = \frac{2}{2.303}$ $\therefore E_a = 1.73 \times 2\text{cal} = 3.46 \text{ cal}$

$[A] = 7.38$

7. (a) Temperature coefficients are :

I. $\frac{K_1}{K_2} = \frac{E_{a_1}}{2.303R}\frac{[T_2 - T_1]}{T_1T_2} = 2$

II. $\frac{K_1'}{K_2'} = \frac{E_{a_2}}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] = 3$

if $\frac{K_1}{K_2} < \frac{K_1'}{K_2'}$ then $E_{a_2} > E_{a_1}$

8. (c)

$$K = \frac{K_1K_2}{K_3} = \frac{A_1e^{-E_{a_1}/RT} \cdot A_2e^{-Ea_2/RT}}{A_3 \cdot e^{-E_{a_3}/RT}}$$

$$= \frac{A_1A_2}{A_3} \cdot e^{-\left[\frac{E_{a_1}}{RT} + \frac{E_{a_2}}{RT} - \frac{E_{a_3}}{RT}\right]}$$

$$K_{AV} = A_{AV} \cdot e^{-\frac{E_a}{RT}}$$

$$\because \quad E_a = E_{a_1} + E_{a_2} - E_{a_3}$$

9. (c) $[A] = [A]_0 e^{-Kt} = [100]e^{-K/K} = \frac{[100]}{e} = \frac{100}{2.718}$

$= 36.79 \text{ mole litre}^{-1}$

$\therefore \quad [A]_{\text{decayed}} = 61.21$

10. (a) $r_1 = K_1[A]$ $\because r_1 = r_2$ $\log_{10} K_1 = 15 - \frac{2000}{2.303T}$

$r_2 = K_2[C]$ $\therefore K_1 = K_2$ $\log K_2 = 14 - \frac{1000}{2.303T}$

or $15 - \frac{2000}{T \times 2.303} = 14 - \frac{1000}{T \times 2.303}$

$\therefore \quad T = \frac{1000}{2.303} = 434.22 \text{ K}$

11. (b) $H_2O + O \overset{E_a = 77\text{ kJ}}{\rightleftharpoons} 2OH$; $\Delta H = 72 \text{ kJ}$

$2OH \longrightarrow H_2O + O$; $\Delta H = -72 \text{ kJ}$

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

$E_{a(f)} - 77 = -72$

$E_{a(f)} = +5 \text{ kJ}$

12. (a) $r = -\frac{d[N_2O_4]}{dt} = -\frac{[0.50 - 0.25]}{5} = \frac{0.25}{5}$

$= 0.05 \text{ atm min}^{-1}$

$\therefore \quad \frac{d[NO_2]}{dt} = 2 \times -\frac{d[N_2O_4]}{dt} = 2 \times 0.05$

$= 0.1 \text{ atm min}^{-1}$

13. (b) Temperature coefficient

$$= \frac{K_{373}}{K_{363}} = \frac{(t)_{363}}{(t)_{373}} = \frac{300}{180} = 1.66 \qquad \left(K \propto \frac{1}{t}\right)$$

14. (b) $K = Ae^{-E_a/RT}$ if $T \longrightarrow \infty$, $e^{-E_a/RT} = 1$, or $K = A$

15. (c) $-\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$

$$\therefore \quad -\frac{d[H_2]}{dt} = \frac{3}{2} \times \frac{0.001}{17 \times 10^{-3}} \text{ mol/hr}$$

$$= \frac{3}{2} \times \frac{0.001}{17 \times 10^3} \times 2 \text{ g/hr}$$

$$= 3 \times \frac{0.001 \times 10^3}{17 \times 10^3} \text{ kg/hr}$$

$$= 1.76 \times 10^{-4} \text{ kg/hr}$$

16. (b) Maximum in the concentration of B.

17. (a) Two mole of A are decayed out of six in time t.

18. (d) The rate of reaction $= -\frac{dc}{dt} = -\frac{1}{V}\frac{dn}{dt} = -\frac{1}{RT}\frac{dP}{dt}$.

19. (b) For zero order reaction: $P_{HI} = P_{HI}^0 - Kt$. Also P_{H_2} continuously increases.

20. (b) This is zero order reaction from the values of K (Ms^{-1})

$\therefore \quad t_{1/2} = \frac{(A_0)}{2K} = \frac{1}{2 \times 10^{-3}} = 500 \text{ sec}$

and $t_{1/2} = \frac{[A_0]}{K} = \frac{1}{10^{-3}} = 1000 \text{ sec}$

21. (a) $t_{1/2} \propto (P)^{1-n}$

$200 \propto (2)^{1-n}$

$100 \propto (1)^{1-n}$

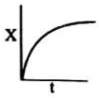
$\therefore\quad 2 = 2^{1-n}$

$\therefore\quad 1 = 1-n \qquad \therefore\quad n = 0$

22. (d) $E_a - E_b = \Delta H$

In exothermic reaction $E_a \gtrless \Delta H$ depending upon the nature of reaction.

23. (a) $X = a(1-e^{-Kt})$



24. (c) Vapour state of Br_2 is more reactive as it possesses higher energy level and more collision frequency.

25. (b) $r = K[O_3][O]$

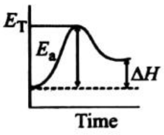
Also $K_c = \dfrac{[O_2][O]}{[O_3]} \qquad \because\ [O] = \dfrac{K_c[O_3]}{[O_2]}$

$\therefore\quad r = K[O_3]^2 \cdot [O_2]^{-1}$

26. (a) $K = Ae^{-E_a/RT}$

27. (d) $K = \dfrac{0.693}{t_{1/2}}$

28. (c)



$E_a > \Delta H$ but for exothermic reactions $E_a >$ or $< \Delta H$

29. (b) $K = Ae^{-E_a/RT}$ at $T \to \infty$, $K = A$

30. (b)

$$\ln K_{T_1} = \ln K_0 + \left[\frac{\ln 3}{10}\right] T_1$$

$$\ln K_{T_2} = \ln K_0 + \left[\frac{\ln 3}{10}\right] T_2$$

$\therefore\quad \ln K_2 - \ln K_1 = \left[\dfrac{\ln 3}{10}\right](T_2 - T_1)$

or $\quad \ln \dfrac{K_2}{K_1} = \left[\dfrac{\ln 3}{10}\right] \times (T_2 - T_1)$

if $T_2 - T_1 = 10^\circ C$, then temperature coefficient $= \dfrac{K_2}{K_1}$

or $\quad \ln \dfrac{K_2}{K_1} = \left[\dfrac{\ln 3}{10}\right] \times 10$

or $\quad \dfrac{K_2}{K_1} = 3$

31. (d)

	$2A$	$+$	B	$\longrightarrow$	C	$+$	D
$t = 0$	a_0		$2a_0$		0		0
$t = 30$	$\left(a_0 - \frac{a_0}{2}\right)$		$\left(2a_0 - \frac{a_0}{4}\right)$		$\frac{a_0}{4}$		$\frac{a_0}{4}$

After $t = 30 \qquad$ rate $= K[A][B]^2$

$\therefore\qquad$ rate $= K\left[a_0 - \dfrac{a_0}{2}\right]^1 \left[2a_0 - \dfrac{a_0}{4}\right]^2$

$$= K\frac{a_0}{2} \times \frac{49a_0^2}{16} = \frac{49Ka_0^3}{32}$$

32. (b)

$$-\frac{dc}{dt} = \frac{\alpha c}{1+\beta c}$$

$$\frac{-dc(1+\beta c)}{c} = \alpha \cdot dt$$

$$-\frac{dc}{c} - dc\cdot\beta = \alpha \cdot dt$$

on integration $\qquad -\ln c - c\beta = \alpha t + \text{constant}$

at $t = 0, c = c_0$

$\therefore\qquad -\ln c_0 - c_0\beta = \text{constant}$

Therefore $\qquad -\ln c - c\beta = \alpha t - \ln c_0 - c_0\beta$

$$\ln\frac{c_0}{c} + \beta(c_0 - c) = \alpha t$$

at $t = t_{1/2}$; $c = \dfrac{c_0}{2}$

$\therefore\qquad \ln\dfrac{c_0}{\frac{c_0}{2}} + \beta\left(c_0 - \dfrac{c_0}{2}\right) = \alpha t_{1/2}$

or $\qquad \ln 2 + \dfrac{c_0\beta}{2} = \alpha t_{1/2}$

$$t_{1/2} = \frac{1}{\alpha}\left[\ln 2 + \frac{c_0\beta}{2}\right]$$

33. (d) $\qquad A \longrightarrow \text{Product}$

$\therefore\qquad -\dfrac{dC_A}{dt} = KC_A^n \qquad (\because$ order is $n)$

On integrating $\dfrac{-(C_A)^{1-n}}{1-n} = Kt + \text{constant} \qquad \ldots(1)$

at $t = 0, C_A = C_0 \quad \therefore\ \text{constant} = -\dfrac{C_0^{1-n}}{1-n} \qquad \ldots(2)$

$\therefore$ By Eqs. (1) and (2), $\quad -\dfrac{C_A^{1-n}}{1-n} = Kt - \dfrac{C_0^{1-n}}{1-n}$

or $\qquad Kt = \dfrac{1}{(n-1)}[C_A^{1-n} - C_0^{1-n}] \qquad \ldots(3)$

if $C_A = \dfrac{C_0}{2}$ at $t = t_{1/2}$ then by Eq. (3)

$$Kt_{1/2} = \frac{1}{(n-1)}\left[\left(\frac{C_0}{2}\right)^{1-n} - (C_0)^{1-n}\right]$$

$$= \frac{(C_0)^{1-n}}{(n-1)} \times [2^{n-1} - 1] \qquad \ldots(4)$$

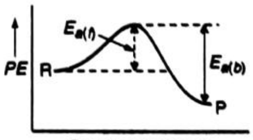
Similarly, if $C = \dfrac{C_0}{4}$ at $t = t_{3/4}$, then by Eq. (3)

$$Kt_{3/4} = \frac{C_0^{1-n}}{(n-1)}[4^{n-1} - 1] \qquad \ldots(5)$$

By Eqs. (4) and (5),

$$\frac{t_{1/2}}{t_{3/4}} = \frac{2^{n-1} - 1}{4^{n-1} - 1}$$

34. (c)



$E_{a(b)} > E_{a(f)}$

35. (b) Maximum in the concentration of B.

36. (a) Two moles of A are decayed out of six in time t.

37. (a) $$-\frac{dC}{dt}=\frac{K_1C}{1+K_2C}=\frac{K_1}{\frac{1}{C}+K_2}$$

(i) If C is very very high $1/C$ is smallest and thus negligible.

$$\therefore \quad -\frac{dC}{dt}=\frac{K_1}{K_2}=\text{constant}$$

Thus order of reaction is **zero.**

(ii) If C is very very low. $1+K_2C=K'$

$$\therefore \quad -\frac{dC}{dt}=\frac{K_1C}{K'}=K''\cdot C$$

Thus, order of reaction is **unity.**

38. (b) By step (iii) $\frac{d[\text{COCl}_2]}{dt}=K_3[\text{COCl}][\text{Cl}_2]$ ... (a)

By step (i) $\frac{K_1}{K_2}=\frac{[\text{Cl}]^2}{[\text{Cl}_2]}$ ... (b)

By step (ii) $\frac{K_1'}{K_2'}=\frac{[\text{COCl}]}{[\text{CO}]\,[\text{Cl}]}$ ... (c)

Thus from Eqs. (b) and (c)

$$[\text{COCl}]=\frac{K_1'}{K_2'}\cdot[\text{CO}]\times\sqrt{\frac{K_1}{K_2}\cdot[\text{Cl}_2]} \quad \ldots (d)$$

From Eqs. (a) and (d)

$$\frac{d[\text{COCl}_2]}{dt}=K_3\frac{K_1'}{K_2'}\left(\frac{K_1}{K_2}\right)^{1/2}[\text{CO}][\text{Cl}_2]^{1/2}[\text{Cl}_2]$$

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

39. (c) The rate of formation of urea is given by Eq. (iii)

$$\frac{d[\text{urea}]}{dt}=K[\text{NH}_3][\text{HNCO}] \quad \ldots (a)$$

By step (ii) we have: $\frac{[\text{NH}_3][\text{HNCO}]}{[\text{NH}_4\text{NCO}]}=K_{C_1}$ ... (b)

By step (i) we have: $\frac{[\text{NH}_4\text{NCO}]}{[\text{NH}_4\text{CNO}]}=K_{C_2}$ ... (c)

$\therefore$ By Eqs. (b) and (c)

$$[\text{NH}_3][\text{HNCO}]=K_{C_1}\cdot K_{C_2}[\text{NH}_4\text{CNO}] \quad \ldots (d)$$

$\therefore$ By Eqs. (a) and (d)

$$\frac{d[\text{urea}]}{dt}=K\cdot K_{C_1}\cdot K_{C_2}[\text{NH}_4\text{CNO}]$$

$$\frac{d[\text{urea}]}{dt}=K'[\text{NH}_4\text{CNO}]$$

40. (c) $$\frac{K_{T+10}}{K_T}=2 \;;\; \frac{K_{T+20}}{K_{T+10}}=2 \;;\; \frac{K_{T+30}}{K_{T+20}}=2$$

On multiplying $\frac{K_{T+30}}{K_T}=2\times2\times2=8$

41. (c) Zero order reaction takes place at constant rate and goes for completion.

42. (b) $$\Delta H=E_{a_f}-E_{a_b}$$

$$\therefore \quad E_{a_b}=E_{a_f}-\Delta H=55.5-1.0=54.5$$

43. (a) $$\frac{K_T}{K_{300}}=10$$

$$2.303\log\frac{K_T}{K_{300}}=\frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$2.303\log 10=\frac{25\times10^3}{8.314}\left[\frac{T_2-300}{T_2\times300}\right]$$

$$T_2=389.5\text{ K}$$

44. (d) The rate expression involves S_{N^1} and S_{N^2} steps as

$$RX+\text{OH}^-\longrightarrow R^++X^-\xrightarrow{\text{OH}^-}\text{ROH}+X^-$$

$$RX+\text{OH}^-\longrightarrow \text{HO}{-}{-}{-}{-}R{-}{-}{-}{-}X^-\longrightarrow \text{HO}R+X^-$$

$$\text{rate}=\underset{S_{N^2}}{4.7\times10^{-5}\,[RX]\,[\text{OH}^-]}+\underset{S_{N^1}}{0.24\times10^{-5}\,[RX]}$$

$$\%\,S_{N^2}=\left[\frac{r_{S_{N^2}}}{r_{S_{N^1}}+r_{S_{N^2}}}\right]\times100$$

$$=\left[\frac{4.7\times10^{-5}[RX][\text{OH}^-]}{0.24\times10^{-5}[RX]+4.7\times10^{-5}[RX][\text{OH}^-]}\right]\times100$$

$$=\left[\frac{4.7\times10^{-5}[\text{OH}^-]}{0.24\times10^{-5}+4.7\times10^{-5}[\text{OH}^-]}\right]\times100$$

$$=\left[\frac{4.7\times10^{-5}\times0.001}{0.24\times10^{-5}+(4.7\times10^{-5}\times0.001)}\right]\times100$$

$$=1.92$$

45. (c) $$t_{1/2}\propto[A]^{1-n}=K[A]^{1-n}$$

$$\log t_{1/2}=\log K+(1-n)\log[A]$$

$$1-n=\tan 315=-1$$

$$\therefore \quad n=2$$

46. (b) For case I: $r_1=K(P_A)(P_B)^2$

$$=K\times6\times8^2=384\text{ K}$$

For case II: $r_2=K\times6\times(2)^2=24\text{ K}$

$$\therefore \quad \frac{r_1}{r_2}=\frac{384\text{ K}}{24\text{ K}}=16$$

47. (c) $$\frac{N_{0A}}{N_A}=e^{K_A\cdot t}$$

$$\frac{N_{0B}}{N_B}=e^{K_B\cdot t}$$

Given $N_{0B}=\frac{N_{0A}}{8}$ and after time t, $N_A=N_B$

$$\therefore \quad \frac{\frac{N_{0A}}{N_A}}{\frac{N_{0B}}{N_B}}=e^{(K_A-K_B)t}$$

$$\frac{\frac{N_{0A}}{N}}{\frac{N_{0A}/8}{N}}=e^{(K_A-K_B)t}$$

or $$\ln 8=[K_A-K_B]\,t=\left[\frac{0.693}{10}-\frac{0.693}{20}\right]t$$

or $$2.08=\frac{0.693}{20}\times t$$

$$t=\frac{2.08\times20}{0.693}=60\text{ minutes}$$

48. (b) **Solution 1:** (a)

Rate determining step is not applicable when slow reaction is reversible and thus steady state approximation concept should be used.

According to steady state approximation concentration of intermediate remains constant most of the time so rate of reaction with respect to intermediate is taken to be zero.

$$X_2 \xrightarrow{k_1} 2X$$

$$X + Y_2 \xrightarrow{k_2} XY + Y$$

$$Y + XY \xrightarrow{k_3} X + Y_2$$

$$X + Y \xrightarrow{k_4} XY$$

At steady state approximation, rate of formation of intermediate = rate of disappearance of intermediate or rate of reaction for intermediate = 0

$$r = \frac{d[X]}{dt}$$

$$= 2k_1[X_2] - k_2[X][Y_2] + k_3[XY][Y] + k_4[X][Y]$$

$$= 0 \qquad \ldots\text{(i)}$$

$$r = \frac{d[Y]}{dt}$$

$$= k_2[X][Y_2] - k_3[Y][XY] - k_4[X][Y]$$

$$= 0 \qquad \ldots\text{(ii)}$$

$$k_2[X][Y_2] = k_3[Y][XY] + k_4[X][Y] \qquad \ldots\text{(iii)}$$

on substituting the value of equation (iii) into equation (i) :

$$r = 2k_1[X_2]^1$$

So order of reaction is 1.

Solution 2 (d)

On the basis of rate determining step.

(i) $X_2 \longrightarrow X + X$ (fast)
(ii) $X + Y_2 \longrightarrow XY$ (slow)
(iii) $X + Y \longrightarrow XY$ (fast)

Note that $X + Y_2 \rightleftharpoons XY$ cannot be slow as it involves equilibrium. So mechanics of this reaction may be taken as

(i) $X_2 \rightleftharpoons X + X$ (fast)
(ii) $X + Y_2 \longrightarrow XY$ (slow)
(iii) $X + Y \longrightarrow XY$ (fast)

So step (ii) is rate determining step

$$r = k[X][Y_2] \qquad \ldots\text{(i)}$$

X can be replaced by fast equilibrium given in step (i)

$$K = \frac{[X]^2}{[X_2]}$$

$$[X]^2 = k[X_2]$$

$$[X] = [k[X_2]]^{1/2} \qquad \ldots\text{(ii)}$$

If value of equation (ii) is placed in equation (i) then

$$r = k[Y_2][k[X_2]]^{1/2}$$

So order of reaction is 1.5.

49. (b) $K = 10^{-2} = \frac{0.693}{t/2}$

So, $\frac{t}{2} = \frac{0.693}{10^{-2}} = 69.3$ sec

For the reduction of 20 g of reactant into 5 g two half lives will be used.

So, time required = 2 × 69.3 = 138.6 sec

• PREVIOUS YEARS PROBLEMS •

1. The rate constant for the reaction;
$2N_2O_5 \longrightarrow 4NO_2 + O_2$ is $3.0 \times 10^{-5} sec^{-1}$. If the rate is $2.40 \times 10^{-5}\ M\ sec^{-1}$, then the concentration of N_2O_5 (in M) is: **(IIT 2000)**
(a) 1.4 (b) 1.2
(c) 0.04 (d) 0.8

2. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process $AB + h\nu \longrightarrow AB^x$, the rate of formation of AB^x is directly proportional to: **(IIT 2001)**
(a) C (b) I
(c) I^2 (d) $C \cdot I$

3. Consider the chemical reaction;
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$. The rate of this reaction can be expressed in terms of $N_{2(g)}$, $H_{2(g)}$ and $NH_{3(g)}$ as: **(IIT 2002)**

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

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

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

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

4. In a first order reaction, the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant in sec^{-1} is: **(IIT 2003)**
(a) 2×10^4 (b) 3.45×10^{-5}
(c) 1.386×10^{-4} (d) 2×10^{-4}

5. 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 rate of reaction when concentration of X is 0.01 M is: **(IIT 2004)**
(a) 1.73×10^{-4} M/min (b) 3.47×10^{-5} M/min
(c) 3.47×10^{-4} M/min (d) 1.73×10^{-5} M/min

6. Which one of the following statement for order of reaction is not correct? **(IIT 2005)**
(a) Order can be determined experimentally.
(b) Order of reaction is equal to sum of the powers of concentration terms in differential rate law.
(c) It is not affected with stoichiometric coefficient of the reactants.
(d) Order cannot be fractional.

7. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)^+]; K_1 = 6.8 \times 10^{-3}$
$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+; K_2 = 1.6 \times 10^{-3}$
then the formation constant of $[Ag(NH_3)_2]^+$ is: **(IIT 2006)**
(a) 6.8×10^{-6} (b) 1.08×10^{-5}
(c) 1.08×10^{-6} (d) 6.8×10^{-5}

8. Consider a reaction $aG + bH \longrightarrow$ Products. When concentration of both the reactants G and H is doubled, the rate increases 8 times. However, when concentration of G is doubled, keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is: **(IIT 2007)**
(a) 0 (b) 1
(c) 2 (d) 3

9. Under the same reaction conditions, the initial concentration of 1.386 mol dm^{-3} of a substance becomes half in 40 seconds and 20 seconds through I order and zero order kinetics. Ratio $\left(\dfrac{K_1}{K_0}\right)$ of the rate constants for I order (K_1) and zero order (K_0) of the reaction is: **(IIT 2008)**
(a) 0.5 mol^{-1}dm^{-3} (b) 1.0 mol dm^{-3}
(c) 1.5 mol dm^{-3} (d) 2.0 mol^{-1}dm^3

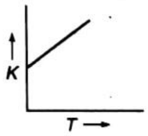
10. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (K) was found to follow the equation:

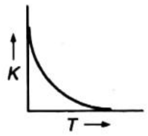
$$\log K = -\frac{2000}{T} + 6.0$$

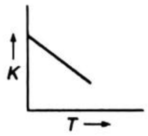
The pre-exponential factor A and the activation energy E, respectively are: **(IIT 2009)**
(a) $1.0 \times 10^6 s^{-1}$ and 9.2 kJ mol^{-1}
(b) 6.0 s^{-1} and 16.66 kJ mol^{-1}
(c) $1.0 \times 10^6 s^{-1}$ and 16.66 kJ mol^{-1}
(d) $1.0 \times 10^6 s^{-1}$ and 38.3 kJ mol^{-1}

11. Plots of variation of the rate constant 'K' with temperature (T) are given below. The plot that follows Arrhenius equation is: **(IIT 2010)**

(a)


(b)


(c)


(d)


12. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be :

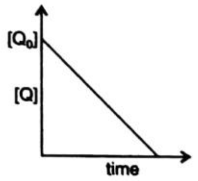
($R = 8.314\ JK^{-1}\ mol^{-1}$ and $\log_{10}2 = 0.301$)

[JEE (Main) 2013]

(a) 58.5 $kJ\ mol^{-1}$ (b) 60.5 $kJ\ mol^{-1}$
(c) 53.6 $kJ\ mol^{-1}$ (d) 48.6 $kJ\ mol^{-1}$

13. In the reaction,

$$P + Q \longrightarrow R + S$$



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

[JEE (Advanced-I) 2013]

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

14. For the elementary reaction $M \to N$, the rate of disappearance of M increases by a factor of 8 upon doubling the concentration of M. The order of the reaction with respect to M is :

[JEE (Advanced-II) 2014]

(a) 4 (b) 3
(c) 2 (d) 1

15. For the non-stoichiometre reaction $2A + B \longrightarrow C + D$, the following kinetic data were obtained in three separate experiments, all at 298 K.

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

The rate law for the formation of C is :

[JEE (Main) 2014]

(a) $\frac{d[C]}{dt} = k[A][B]$ (b) $\frac{d[C]}{dt} = k[A]^2[B]$
(c) $\frac{d[C]}{dt} = k[A][B]^2$ (d) $\frac{d[C]}{dt} = k[A]$

16. Higher order (> 3) reactions are rare due to :

[JEE (Main) 2015]

(a) low probability of simultaneous collision of all the reacting species
(b) increase in entropy and activation energy as more molecules are involved
(c) shifting of equilibrium towards reactants due to elastic collisions
(d) loss of active species on collision

17. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be : **[JEE (Main) 2016]**

(a) $6.93 \times 10^{-4}\ mol\ min^{-1}$ (b) 2.66 $L\ min^{-1}$ at STP
(c) $1.34 \times 10^{-2}\ mol\ min^{-1}$ (d) $6.93 \times 10^{-2}\ mol\ min^{-1}$

18. Two reactions R_1 and R_2 have identical pre-exponential factors. Activation energy of R_1 exceeds that of R_2 by 10 $kJ\ mol^{-1}$. If k_1 and k_2 are rate constants for reactions R_1 and R_2 respectively at 300 K, then $\ln(k_2/k_1)$ is equal to : ($R = 8.314\ J\ mol^{-1}\ K^{-1}$) **[JEE (Main) 2017]**

(a) 8 (b) 12
(c) 6 (d) 4

SOLUTIONS (Previous Year Problems)

1. (d) $r = K[N_2O_5]$ I order as unit of $K = sec^{-1}$

$$2.40 \times 10^{-5} = 3.0 \times 10^{-5}[N_2O_5]$$

$$\therefore \quad [N_2O_5] = \frac{2.40}{3.0} = 0.8M$$

2. (d) In photo initiated primary process rate of reaction is directly proportional to intensity of light used. In case of pure solids rate ∝ I (Lamberts law). In case of solution rate $\propto I \cdot C$ (Bear's law).

3. (a) Follow text.

4. (c) $K = \frac{2.303}{t} \log \frac{C_0}{C}$

$$= \frac{2.303}{2 \times 10^4} \log \frac{800}{50} = 1.386 \times 10^{-4} sec^{-1}$$

5. (c) $K = \frac{2.303}{40} \log \frac{0.1}{0.025} = 0.0347$

$$\text{Rate} = K \times [X] = 0.0347 \times 0.01 = 3.47 \times 10^{-4}\ M\ min^{-1}$$

6. (d) Order can be fractional.

7. (b) Formation constant of $[Ag(NH_3)_2]^+$

$$Ag^+ + 2NH_3 \rightarrow [Ag(NH_3)_2]^+ = K$$

$$\therefore \ K = K_1 \times K_2$$

$$= 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 1.08 \times 10^{-5}$$

8. (d)

$$r = K[G]^a\,[H]^b \qquad \ldots\text{(i)}$$

$$8r = K[2G]^a\,[2H]^b \qquad \ldots\text{(ii)}$$

$$2r = K[2G]^a\,[H]^b \qquad \ldots\text{(iii)}$$

By Eqs. (ii) and (iii)

$$\therefore \quad 4 = 2^b$$

$$\therefore \quad b = 2$$

By Eqs. (i) and (ii) $8 = 2^{a+b} = 2^{a+2}$

$$\therefore \quad a = 1$$

$\therefore$ O.R. $= a + b = 1 + 2 = 3$

9. (a) For I order : $K_1 = \dfrac{0.693}{t_{1/2}} = \dfrac{0.693}{40}$

For zero order : $K_0 = \dfrac{a}{2t_{1/2}} = \dfrac{1.386}{2\times 20}$

$$\therefore \quad \frac{K_1}{K_0} = \frac{0.693}{1.386} = 0.5$$

10. (d)

$$\log_e K = -\frac{E_a}{RT} + \log_e A$$

or

$$\log_{10} K = -\frac{E_a}{RT\times 2.303} + \log_{10} A$$

$$\therefore \quad \log_{10} A = 6, \quad A = 10^6$$

Also $\dfrac{E_a}{R\times 2.303} = 2000$

$$\therefore \quad E_a = 2.303\times 8.314\times 2000\,\text{J}$$

$$= 38294.28\,\text{J} = 38.3\,\text{kJ}$$

11. (a) Since, $K = Ae^{-E_a/RT}$ and thus, K increases exponentially with rise in temperature.

12. (c) $\because \dfrac{r_2}{r_1} = \dfrac{k_2}{k_1} = 2$

Now $2.303 \log_{10} \dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$$2.303 \log_{10} 2 = \frac{E_a}{8.314}\times\left[\frac{310-300}{310\times 300}\right]$$

$$\therefore \quad E_a = \frac{2.303\times 0.301\times 8.314\times 310\times 300}{10} = 53598.6\,\text{J}$$

$$= 53.6\,\text{kJ mol}^{-1}$$

13. (d) $P + Q \longrightarrow R + S$

Given : $T_{75\%} = 2\times T_{50\%}$ (for P)

Since $t_{1/2}$ is independent of concentration and thus it is first order for P.

From graph it is clear that reaction is of zero order with respect to Q

$$[Q]_t = [Q]_0 - Kt$$

so overall order will be $= 1 + 0 = 1$

14. (b) Consider, rate $(r) = K[M]^n$ where n is order of reaction

$$\frac{r_1}{r_2} = \frac{1}{8} = \frac{[M]^n}{[2M]^n} \Rightarrow n = 3$$

15. (d) Let rate expression be $r = K[A]^m[B]^n$

$$\therefore \quad 1.2\times 10^{-3} = K(0.1)^m(0.1)^n \qquad \ldots\text{(i)}$$

$$1.2\times 10^{-3} = K(0.1)^m(0.2)^n \qquad \ldots\text{(ii)}$$

$$2.4\times 10^{-3} = K(0.2)^m(0.1)^n \qquad \ldots\text{(iii)}$$

By (i) and (ii) $n = 0$

By (i) and (iii) $m = 1$

$$\therefore \quad \frac{dc}{dt} = K[A]^1$$

16. (a) It is the reason for given fact.

17. (a) In 50 minutes, concentration of H_2O_2 becomes $\dfrac{1}{4}$ of initial *i.e.*, two half lives are used.

or $\quad 2\times t_{1/2} = 50$ minutes

or $\quad t_{1/2} = 25$ minutes

$$\therefore \quad K = \frac{0.693}{25} \text{ per minute}$$

$$r_{H_2O_2} = K\times[H_2O_2]$$

$$r_{H_2O_2} = \frac{0.693}{25}\times 0.05$$

$$= 1.386\times 10^{-3}\ \text{mol litre}^{-1}\ \text{minute}^{-1}$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

$$r_{O_2} = \frac{1}{2}\times r_{H_2O_2} = \frac{1}{2}\times 1.386\times 10^{-3}$$

$$r_{O_2} = 0.693\times 10^{-3}$$

$$r_{O_2} = 6.93\times 10^{-4}\ \text{mol litre}^{-1}\ \text{minute}^{-1}$$

Note : The framing of question is not correct. The units for concentration of H_2O_2 is given as mol/litre whereas O_2 is reported in mol/minute. It has not been given that volume of solution is 1 litre.

18. (d) $k_1 = Ae^{-E_{a_1}/RT}$; $k_2 = Ae^{-E_{a_2}/RT}$

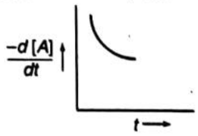
$$\frac{k_2}{k_1} = e^{\frac{1}{RT}(E_{a_1} - E_{a_2})}$$

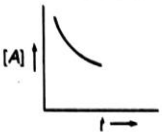
$$\ln\frac{k_2}{k_1} = \frac{E_{a_1} - E_{a_2}}{RT} = \frac{10\times 10^3}{8.314\times 300} \approx 4$$

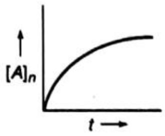
OBJECTIVE PROBLEMS (More Than One Answer Correct)

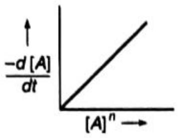
1. Which of the following statements are correct?
   (a) Zero order reactions are complex reactions.
   (b) A reaction having I order may be either elementary reaction or complex reaction.
   (c) A reaction having II order reaction must have molecularity = 2.
   (d) A reaction with molecularity = 2 must be a II order reaction.

2. Which of the following plots are correctly made for the reaction $nA \rightleftharpoons (A)_n$, if it obeys I order reaction?

(a) 

(b) 

(c) 

(d) 

3. Select the correct statements :
   (a) Order of a reaction may be changed with change in the experimental conditions.
   (b) Rate of reaction either exothermic or endothermic both decrease with decrease in temperature.
   (c) A reaction mixture thermodynamically stable should be kinetically unstable.
   (d) A negative catalyst increases the energy of activation.

4. For a gaseous reaction : $A_{(g)} \longrightarrow B_{(g)}$, the rate expression may be given as :
   (a) $-\frac{d[A]}{dt} = K[A]^n$
   (b) $-\frac{1}{V}\frac{dn_A}{dt} = K[A]^n$
   (c) $-\frac{1}{RT}\cdot\frac{dP_A}{dt} = K[A]^n$
   (d) $-\frac{dP}{dt} = K(P_A)^n$

5. For which of the conditions K = Arrhenius factor?
   (a) $E_a = 0$
   (b) Free radical combinations
   (c) $T = \infty$
   (d) $T = 0$

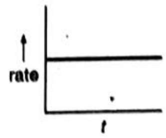
6. Which of the following relations are correct if ΔH represents only magnitude?
   (a) Exothermic reactions : $E_{a_{(f)}} + \Delta H = E_{a_{(b)}}$
   (b) Endothermic reactions : $E_{a_{(f)}} = E_{a_{(b)}} + \Delta H$
   (c) Exothermic reactions : $\Delta H > E_a$
   (d) Endothermic reactions : $\Delta H < E_a$

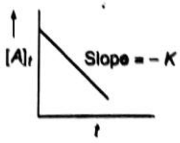
7. Which of the following graphs represent zero order if

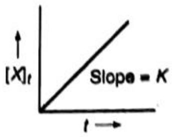
$$A \longrightarrow P$$

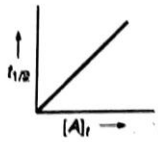
$t = 0\ [A]_0$

$t = t\ [A]_t \qquad [X]_t \quad ?$

(a) 

(b) 

(c) 

(d) 

8. Which one is correct according to collision theory of rate of reaction?
   (a) Threshold energy level is a characteristic of reaction
   (b) Energy of activation decreases with rise in temperature
   (c) The energy of adsorbed activated complex is lower than simple activated complex
   (d) The energy of activated complex (both activated or adsorbed) is higher than reactant or product

9. The rate expression for the reaction :

$$NH_4CNO \rightleftharpoons NH_2CONH_2$$

can be derived from the mechanism :

(i) $NH_4CNO \underset{K_2}{\overset{K_1}{\rightleftharpoons}} NH_4NCO$ (Fast)

(ii) $NH_4NCO \xrightarrow{K_3} NH_3 + HNCO$ (Fast)

(iii) $NH_3 + HNCO \xrightarrow{K_4} NH_2CONH_2$ (Slow)

Which of the following statements are correct about rate expression?
   (a) $\frac{d_{[\text{urea}]}}{dt} = \frac{K_1K_3}{K_2}[NH_4NCO]$
   (b) $\frac{d_{[\text{urea}]}}{dt} = \frac{K_1K_3}{K_2K_4}[NH_4NCO]$
   (c) $\frac{d_{[\text{urea}]}}{dt} = K[NH_4NCO]$
   (d) $\frac{d_{[\text{urea}]}}{dt} = \frac{K_1 \times K_2}{K_3 \times K_4}[NH_4NCO]$

10. The rate of formation for $C_6H_6 + 3H_2 \underset{K_b}{\overset{K_f}{\rightleftharpoons}} C_6H_{12}$ for the forward reaction is first order with respect to C_6H_6 and H_2 each. Which are correct?
   (a) $K_c = \frac{K_f}{K_b}$
   (b) $K_c = \frac{[C_6H_{12}]}{[C_6H_6][H_2]^3}$
   (c) $r_f = K_f[C_6H_6][H_2]$
   (d) $r_b = K_b[C_6H_{12}][H_2]^{-2}$

11. The rate law for the reaction:

$$RCl + NaOH(aq) \rightarrow ROH + NaCl$$

is given by, Rate= $k_1[RCl]$. The rate of the reaction will be :

(a) doubled on doubling the concentration of sodium hydroxide

(b) halved on reducing the concentration of alkyl halide to one half

(c) increased on increasing the temperature of the reaction

(d) unaffected by increases the temperature of the reaction.

12. For a I order reaction

(a) The degree of dissociation is equal to $(1-e^{-kt})$

(b) A plot of reciprocal of reactants, concentration *vs* time gives a straight line

(c) The time taken for completion of 75% reaction in thrice to that of $t_{1/2}$ of the reaction

(d) The pre exponential factor in the Arrhenius equation has the dimension of time T^{-1}.

13. The rate constant of a reaction becomes equal to A, then which are not correct?

(a) $-\frac{E_a}{RT}=0$ (b) $E_A=-RT$

(c) $T=0$ (d) $T=\infty$

14. Two first order exothermic reactions : $A \xrightarrow{K_1} B$ and $P \xrightarrow{K_2} Q$ at T K have their rate constants such that $K_1 > K_2$. If temperature is increased to T_2K($T_2 > T$), the rate constant K_1 changes to K_3 and K_2 to K_4. Select the correct statements.

(a) $K_1 < K_3$ (b) $K_2 < K_4$

(c) $K_3 > K_4$ (d) $K_4 > K_3$

15. For the first order reaction,

$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ **[IIT 2011]**

(a) the concentration of the reactant decreases exponentially with time

(b) the half-life of the reaction decreases with increasing temperature

(c) the half-life of the reaction depends on the initial concentration of the reactant

(d) the reaction proceeds to 99.6% completion in eight half-life duration

16. According to the Arrhenius equation:

[JEE (Advanced) I 2016]

(a) A high activation energy usually implies a fast reaction

(b) Rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy

(c) Higher the magnitude of activation energy, stronger is the temperature dependence of the rate constant

(d) The pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy

17. For 'invert sugar', the correct statement(s) is (are):

(Given : specific rotations of (+)-sucrose, (+)-maltose, L-(–)-glucose and L-(+)-fructose in aqueous solution are + 66°, + 140°, – 52° and + 92°, respectively)

[JEE (Advanced) II 2016]

(a) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose

(b) 'invert sugar' is an equimolar mixture of D-(+)-glucose and D-(–)-fructose

(c) specific rotation of 'invert sugar' is –20°

(d) on reaction with Br_2 water, 'invert sugar' forms saccharic acid as one of the products

18. In a bimolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is (are) :

[JEE (Advanced) II 2017]

(a) The value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(b) The activation energy of the reaction is unaffected by the value of the steric factor

(c) Since P = 4.5, the reaction will not proceed unless an effective catalyst is used

(d) Experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation

SOLUTIONS (More Than One Answer Correct)

1. (a,b) Only elementary bimolecular reaction have order reaction = 2

2. (a,b,c,d) $-\frac{d[A]}{dt} = K[A]^n$

3. (a,b) Kinetic stability and thermodynamic stability has no relation. Also the function of negative catalyst to slow down the speed of reaction is not at all related with energy of activation.

4. (a,b,c,d) Rate of reaction

$$= \frac{d[A]}{dt} = K[A]^n \text{ or } -\frac{dP_A}{dt} = K(P_A)^n$$

$$= -\frac{1}{V}\frac{dn_A}{dt} = K[A]^n \qquad \because [A] = \frac{n_A}{V}$$

$$= -\frac{1}{RT}\frac{dP_A}{dt} = K[A]^n \qquad \because [A] = \frac{P_A}{RT}$$

5. (a,b,c) $K = Ae^{-E_a/RT}$; $E_a = 0$ for free radical combinations.

6. (a,b,d) For any reaction : $\Delta H = E_{a_{(f)}} - E_{a_{(b)}}$

   Also, for exothermic reaction $\Delta H \gtrless E_a$

7. (a,b,c,d) $t_{1/2} \propto (a)^{1-n}$; $[A]_t - Kt$ and $X = Kt$ are integrated form of zero order.

8. (a,b,c,d) For basic concept follow **concepts of physical chemistry by Dr. P. Bahadur; Prakash Publications Muzaffarnagar**. Adsorption is always exothermic.

9. (a,c) $\frac{d}{dt}[NH_2CONH_2] = K_4[NH_3][HNCO]$ from (iii)

   Applying steady state approximation to HNCO or NH_3

$$\frac{d[HNCO]}{dt} = 0 = K_3[NH_4NCO] - K_4[NH_3][HNCO]$$

$$\therefore \qquad \frac{K_3}{K_4} = \frac{[NH_3][HNCO]}{[NH_3CNO]}$$

$$\frac{d[\text{urea}]}{dt} = K_4 \times [NH_3][HNCO] = K_4 \times \frac{K_3}{K_4}[NH_4NCO]$$

   Also, $[NH_4NCO] = \frac{K_1}{K_2} \times [NH_4CNO]$

$$\therefore \qquad \frac{d[\text{urea}]}{dt} = K_3 \times \frac{K_1}{K_2}[NH_4CNO]$$

$$= K[NH_4CNO]$$

10. (a,b,c,d) $K_c = \frac{K_f}{K_b} = \frac{[C_6H_{12}]}{[C_6H_6][H_2]^3} = \frac{[C_6H_{12}]}{[C_6H_6][H_2][H_2]^2}$

$$r_f = K_f \times [C_6H_6][H_2]$$

$$r_b = K_b \times \text{Unknown}$$

   at eq. $r_f = r_b$

$$\therefore \qquad K_f[C_6H_6][H_2] = K_b \times \text{Unknown}$$

$$\therefore \qquad \text{Unknown} = \frac{K_f}{K_b} \times [C_6H_6][H_2]$$

$$r_b = K_b \times \text{Unknown}$$

$$r_b = K_b \times \frac{K_f}{K_b} \times [C_6H_6][H_2]$$

$$= K_f \times [C_6H_6][H_2]$$

$$= K_b \times [C_6H_{12}][H_2]^{-2}$$

11. (b, c) The reaction shows I order. Also rate of reaction increases with temperature.

12. (a, d) $N = N_0 \cdot e^{-\lambda t}$

$$\propto = \frac{N_0 - N}{N_0} = \frac{N_0[1 - e^{-\lambda t}]}{N_0} = 1 - e^{-\lambda t}$$

   Also $A = Ke^{-E_a/RT}$

13. (b, c) $K = Ae^{-E_a/RT}$ if $-\frac{Ea}{RT} = 0$.

   Also if $T = \infty$, then E_a approaches zero therefore $K = Ae^0 = A$

14. (a, b, c) Rate constant of a reaction whether exothermic or endothermic increases with temperature.

15. (a, b, d) For the first order reaction
    (i) $N = N_0e^{-kt}$; thus concentration of reactant decreases exponentially with time.
    (ii) $t_{1/2} \propto [N_0]^0$ at constant temperature and thus half life is independent of initial concentration of reactant.
    (iii) Also $t_{1/2} = \frac{0.693}{k}$

    The rate of reaction and rate constant increase with temperature and thus $t_{1/2}$ decreases with temperature.

    (iv) $t_{99.6\%} = \frac{2.303}{k}\log\frac{100}{0.4} = \frac{2.303}{k}\log 250$

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

$$\therefore \; t_{99.6} = t_{1/2} \times \frac{2.303}{0.693}\log 250 = t_{1/2} \times 3.323 \times 2.40$$

$$= 8 \times t_{1/2}$$

16. (b, c, d) $K = Ae^{-E_a/RT}$

    (Higher is E_a, lesser is rate constant, lesser is rate of reaction)

$$\frac{dK}{dT} = A\frac{E_a}{RT^2}$$

$$\frac{dK}{dT} \propto E_a$$

    A is frequency factor *i.e.*, no. of collisions per unit time per unit volume.

17. (b, c) Sucrose ($C_{12}H_{22}O_{11}$) undergoes hydrolysis to form glucose and fructose and the process is known as inversion of sugar.

$$\text{Sucrose} \xrightarrow{\text{Hydrolysis}} D(+)\text{-glucose} + D(-)\text{ fructose}$$

$$[\alpha] = +52^\circ \qquad [\alpha] = -92^\circ$$

$$[\alpha]_{\text{mix}} = 0.5 \times (+52^\circ) + 0.5 \times (-92^\circ) = -20^\circ$$

$[\alpha]$ for L-(–)-glucose = -52°

$\therefore$ $[\alpha]$ for D(+)-glucose = $+52^\circ$

Similarly for fructose $[\alpha] = -92^\circ$

Glucose with Br_2 water a weak oxidant will give gluconic acid. Strong oxidant will lead for saccharic acid.

18. (b, d)

Although Arrhenius factor or pre exponential factor (A) was theoretically proposed by Arrhenius in his equation : $K = Ae^{-Ea/RT}$. He could not consider the specific orientation of molecules at the time of collision which usually predominate in bimolecular reaction. If specific orientation of bimolecular reaction is taken in account, then Arrhenius equation can be modified by putting a term 'p' known as stearic factor as :

Arrhenius equation :

$$k = A_{\text{Arr.}} \times e^{-Ea/RT}$$

If p is stearic factor.

$$k = p \cdot A_{\text{Arr.}} \times e^{-Ea/RT}$$

Collision theory :

$$p \cdot A_{\text{Arr.}} = Z$$

where Z is experimentally determined frequency factor.

$$\frac{Z_{\text{actual}}}{A_{\text{Arr.}}} = p$$

Since p is usually less than unity the $Z_{\text{actual}} < A_{\text{Arr}}$. But here $p = 4.5$.

Thus, $Z_{\text{actual}} > A_{\text{Arr.}}$

it means that reaction occures more quickly than particles collide.

COMPREHENSION BASED PROBLEMS

Comprehension 1 : From the following data form the reaction between A and B,

$[A] \times 10^4$ mol litre^{-1}	$[B] \times 10^5$ mol litre^{-1}	Initial rate mol litre^{-1}sec^{-1}	
		$r \times 10^4$ 300 K	$r \times 10^3$ 320 K
2.5	3.0	5.0	2.0
5.0	6.0	4.0	—
1:0	6.0	1.6	—

[1] The order of reaction with respect to A and with respect to B, respectively are :

(a) 2, 1 (b) 1, 2

(c) 2, 2 (d) 2, 3

[2] The rate constant at 300 K:

(a) 2.66×10^{-8} (b) 1.33×10^{-8}

(c) 2.66×10^{8} (d) 1.33×10^{8}

[3] The energy of activation:

(a) 55.3 kJ (b) 65.44 kJ

(c) 44.5 kJ (d) 75.44 kJ

[4] The pre-exponential factor:

(a) 1.140×10^{8} (b) 1.140×10^{10}

(c) 1.140×10^{18} (d) 1.140×10^{-18}

Comprehension 2: For the reaction $A \longrightarrow B$, the rate law expression is $-\frac{d[A]}{dt} = K[A]^{1/2}$. If initial concentration of A is A_0.

[1] Integrated form of the rate expression:

(a) $Kt = 2[A_0^{1/2} - A^{1/2}]$ (b) $Kt = 2[A_0^{-1/2} - A^{-1/2}]$

(c) $Kt = 1/2[A_0^{1/2} - A^{1/2}]$ (d) $Kt = 1/2[A^{-1/2} - A^{-1/2}]$

[2] Slope and intercept of the plots of $\log \sqrt{A}$ *vs.* t are respectively:

(a) $-\frac{K}{2}, A_0^{-1/2}$ (b) $-\frac{K}{2}, A_0^{1/2}$

(c) $2K, A_0^{1/2}$ (d) $-K, 2A_0$

[3] The half-life of the reaction is given by:

(a) $\frac{\sqrt{2}(\sqrt{2}-1)}{K} \cdot A_0$ (b) $\frac{\sqrt{2}(\sqrt{2}-1)A_0^{1/2}}{K}$

(c) $\frac{2 \cdot A_0}{K}$ (d) $\frac{(\sqrt{2}-1)A_0^{1/2}}{2K}$

SOLUTIONS

Comprehension 1

Let rate expression be $r = K[A]^m[B]^n$

[1] (a) $\therefore \quad 5.0\times10^{-4} = K[2.5\times10^{-4}]^m[3.0\times10^{-5}]^n \qquad \ldots(1)$

$4.0\times10^{-3} = K[5.0\times10^{-4}]^m[6.0\times10^{-5}]^n \qquad \ldots(2)$

$1.6\times10^{-2} = K[1.0\times10^{-3}]^m[6.0\times10^{-5}]^n \qquad \ldots(3)$

By Eqs. (2) and (3), $m = 2 \qquad \ldots(4)$

By Eqs. (1) and (4), $n = 1$

$\therefore$ Rate $= K[A]^2[B]^1$

or order with respect to A and B are **2 and 1** respectively.

[2] (c) By Eq. (1),

$$5.0\times10^{-4} = K[2.5\times10^{-4}]^2[3\times10^{-5}]^1$$

$$\therefore \quad \mathbf{K = 2.66\times10^{8}\ L^2\ mol^{-2}\ sec^{-1}} \quad (\text{at } 300\ \text{K})$$

[3] (a) $\because \quad 2.303\log_{10}\dfrac{K_2}{K_1} = \dfrac{E_a}{R}\dfrac{[T_2 - T_1]}{T_1T_2}$

$$\left[\because \frac{r_2}{r_1} = \frac{K_2}{K_1}\right]$$

$$\because \quad 2.303\log_{10}\frac{2.0\times10^{-3}}{5.0\times10^{-4}} = \frac{E_a}{8.314}\left[\frac{320-300}{300\times320}\right]$$

$$\because \quad E_a = \mathbf{55.33\ kJ}$$

[4] (c) Also, $2.303\log_{10} K = 2.303\log_{10} A - \dfrac{E_a}{RT}$

$$2.303\log_{10} 2.66\times10^{8} = 2.303\log_{10} A - \frac{55.33\times10^{3}}{8.314\times300}$$

$$\therefore \quad A = \mathbf{1.140\times10^{18}}$$

Comprehension 2

[1] (a) $-\dfrac{d[A]}{dt} = K[A]^{1/2}$ or $-\dfrac{dA}{[A]^{1/2}} = Kdt$

On integrating $\quad -\int [A]^{-1/2}dA = K\int dt$

$$-2A^{1/2} = Kt + C \qquad \ldots(1)$$

at $t = 0$; $A = A_0 \ \therefore\ C = -2A_0^{1/2} \qquad \ldots(2)$

By Eqs. (2) and (1), $-2A^{1/2} = Kt - 2A_0^{1/2}$

or $\quad Kt = 2[A_0^{1/2} - A^{1/2}] \qquad \ldots(3)$

[2] (b) Plot of $A^{1/2}$ *vs.* t will be **linear** because Eq. (3) yields,

$$2A^{1/2} = -Kt + 2A_0^{1/2}$$

or $\quad A^{1/2} = -\dfrac{K}{2}t + A_0^{1/2}$ (similar to $y = mx + C$)

[3] (b) If $t = t_{1/2}$, $A = A_0/2$

$\therefore$ By Eq. (3),

$$Kt_{1/2} = 2\left[A_0^{1/2} - \left(\frac{A_0}{2}\right)^{1/2}\right] = 2A_0^{1/2}\left[1 - \frac{1}{\sqrt{2}}\right]$$

$$Kt_{1/2} = \frac{2[\sqrt{2}-1]}{\sqrt{2}}\cdot A_0^{1/2} = \sqrt{2}(\sqrt{2}-1)A_0^{1/2}$$

$$\therefore \quad t_{1/2} = \frac{\sqrt{2}(\sqrt{2}-1)}{K}A_0^{1/2}$$

STATEMENT EXPLANATION PROBLEMS

In each sub question given below a statement **(S)** and explanation **(E)** is given. Choose the correct answers from the codes (a), (b), (c) and (d) given for each question:

(a) S is correct but E is wrong
(b) S is wrong but E is correct
(c) Both S and E are correct and E is correct explanation of S
(d) Both S and E are correct but E is not correct explanation of S

1. The molecularity of first step is 1 and of second step is 2.

S : For the reaction given below, the molecularity of first step is 1 and of second step is 2.

$$2O_3(g) \longrightarrow 3O_2(g)$$

Step 1 $\quad O_3(g) \rightleftharpoons O_2(g) + O(g)$

Step 2 $\quad O_3(g) + O \xrightarrow{\text{slow}} 2O_2(g)$

E : O(*g*) is an intermediate and rate of reaction is $K[O_3]^2[O_2]^{-1}$ and order of reaction is 1.

2. S : Observed rate constant of the given reaction given below decreases with temperature.

$$\mathrm{NO} + \mathrm{NO} \underset{K_b}{\overset{K_f}{\rightleftharpoons}} N_2O_2$$

$$N_2O_2 + O_2 \xrightarrow[\text{slow}]{K} 2NO_2$$

$$\overline{2NO + O_2 \longrightarrow 2NO_2}$$

E : K_c of the reaction being exothermic and decrease in K_c overweigh increase in K with increase in temperature.

3. S : The plots of $\log t_{1/2}$ *vs.* $\log[A]_0$ gives a straight line with slope $(1-n)$.

E : $t_{1/2} \propto [A]_0^{1-n}$

4. S : Larger is the activation energy, lesser is the effect of a given temperature rise on rate constant 'K'.

E : $K = Ae^{-E_a/RT}$

5. S : For a free radical combination, $K = A$.

E : E_a is zero for free radical combination.

6. S : Every collision of reactant molecule is not successful.

E : Every collision of reactant molecule with proper orientation is successful one.

7. S : A plot of $\log \frac{dX}{dt}$ *vs.* $\log(a-x)$ leads to value of K as antilog (intercept) and slope equal to order of reaction.

E : $\frac{dX}{dt} = K(a-x)^n$

8. S : For a IInd order reaction $A + B \rightarrow$ Product, the rate can be given as : $K[A]^2$ or $K\ [A][B]$ or $K\ [B]^2$.

E : Either $[A]$ or $[B]$ may or may not influence the rate of reaction.

9. S : The acid hydrolysis of ester takes place more rapidly in D_2O than H_2O.

E : D_3O^+ is stronger acid than H_3O^+ or H_2D^+O.

10. S : Emission of light as a result of exposure of P to air in night is called phosphorescence.

E : Phosphorus burns in O_2 to give P_2O_5 and conversion of chemical energy into light energy producing cold light and the phenomenon is called chemi-luminescence.

11. S : Activation energy always increases the potential energy of reaction system.

E : The minimum kinetic energy that a molecule must possess in order to react on collision is called its activation energy.

12. S : The rate of reaction whether exothermic or endothermic, increases with temperature.

E : The rate of reaction = $K\,[\text{reactant}]^n$ and K increases with temperature.

13. S : A catalyst always lower the energy of activation.

E : The catalyst-reactant interaction forms activated adsorbed complex and adsorption is always exothermic.

14. S : A catalyst does not affect the heat of reaction.

E : It increases the rate of reaction.

15. S : The elementary reaction is single step reaction and does not possess mechanism.

E : An elementary reaction has order of reaction and molecularity same.

16. S : Temperature coefficient is the ratio of two rate constants preferally at 35°C and 25°C.

E : It can also be given as $e^{-\frac{E_a}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]}$

17. S : The rate expression of $2NO_2 + F_2 \longrightarrow 2NO_2F$ is $r = K[NO_2][F_2]$.

E : The reaction has the mechanism

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

$$NO_2 + F \xrightarrow{\text{fast}} NO_2F$$

18. S : For the reaction $2O_3 \longrightarrow 3O_2$, the rate = $K[O_3]^2[O_2]^{-1}$.

E : The reaction has –ve order for O_2

19. S : Threshold energy of a reaction is dependent of temperature.

E : The energy of activation decreases with increase in temperature.

20. S : The emission of light during burning of *P* in O_2 is called chemi-luminescence.

E : The chemical energy is converted into light energy.

21. S : Photosynthesis in plants involves reaction of CO_2 and H_2O in presence of light and chlorophyll.

E : It is chlorophyll which absorbs light and passes this energy to reactant molecules.

22. S : Order of reaction can never be fractional for an elementary reaction.

E : An elementary reaction takes place by one step mechanism.

23. S : Every collision between molecules leads to a chemical reaction.

E : Only those molecules react during collisions which acquire threshold energy level.

24. S : For each ten degree rise of temperature the specific rate constant is nearly doubled.

E : Energy-wise distribution of molecules in a gas is an exponential function of temperature.

25. S : The instantaneous rate of reaction can be studied in chemical kinetics.

E : Ionic reactions occur instantaneously.

26. S : All catalytic reactions show zero order for catalyst used.

E : The rate of reaction does not depend on concentration of catalyst.

ANSWERS (Statement Explanation Problems)

1. (c) $K_c = \dfrac{[O_2][O]}{[O_3]}$

$$\text{rate} = K\,[O_3][O] = \frac{K_c[O_3]\times[O_3]}{[O_2]} = \frac{K^1[O_3]^2}{[O_2]}$$

2. (c)
$$\text{Rate} = K\,[N_2O_2][O_2]$$
and
$$K_c = \frac{[N_2O_2]}{[NO]^2}$$
$\therefore$
$$\text{rate} = K\cdot K_c[NO]^2[O_2] = K_{\text{obs}}\,[NO]^2[O_2]$$

3. (c) $\log\, t_{1/2} = \log\left[\dfrac{2^{n-1}-1}{K\,(n-1)}\right] + (1-n)\,\log[A]_0$

4. (b) Higher activation energy, greater is the effect of given temperature rise on rate constant '*K*'.

5. (c) $K = Ae^{-E_a/RT}$, if $E_a = 0$ then $K = A$

6. (a) A successful collision leads to a chemical reaction when the reactant molecules collide with proper orientation and attain threshold energy level.

7. (c) $\log\dfrac{dX}{dt} = \log K + n\log(a-x)$

8. (c) In each case order is IInd.

9. (c) Explanation is correct reason for statement.

10. (b) The phenomenon is called chemi-luminiscence.

11. (d) Both are facts.

12. (c) Explanation is correct reason for statement.

13. (c) Explanation is correct reason for statement.

14. (d) Both statement and explanation are correct.

15. (c) Explanation is correct reason for statement.

16. (d) Both statement and explanation are correct.

17. (c) Explanation is correct reason for statement.

18. (d) Both statement and explanation are correct.

19. (d) Both statement and explanation are correct.

20. (c) Chemiluminesence refers for emission of light as a result of chemical change.

21. (c) Chlorophyll acts as photosensitizer. Neither CO_2 nor H_2O absorbs light.

22. (c) An elementary reaction is one step reaction and in such reactions order of reaction and molecularity are same. Note that molecularity can never be fractional.

23. (b) Explanation is correct and suggests that statement is wrong.

24. (c) Explanation is correct reason for statement.

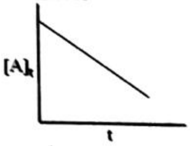
25. (b) Ionic reactions are not studied in kinetics as their $t_{1/2}$ is 10^{-2} sec.

26. (c) Explanation is correct reason for statement.

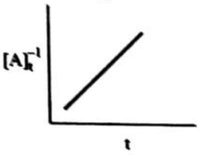
MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

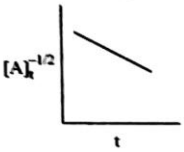
1\. **List A** **List B**

(a) 

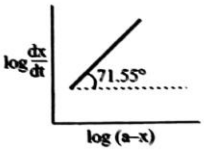
(i) O.R. = 1/2

(b) 

(ii) O.R. = zero

(c) 

(iii) O.R. = 2

(d) 

(iv) O.R. = 3

2\.

	List A		List B
(a)	Elementary reactions	1.	No energy of activation
(b)	Complex reactions	2.	Low energy of activation
(c)	Free radical combinations	3.	High energy of activation
(d)	Slow reactions	4.	Several elementary steps
(e)	Fast reactions	5.	Single step

3\.

	List I		List II
A.	Flash photolysis	p.	Intensity of light
B.	Rate of photochemical reaction	q.	Fast reactions
C.	Chemiluminescence	r.	$4P + 5O_2 \longrightarrow 2P_2O_5$
D.	Phosphorescence	s.	ZnS

Type II : Only One Match From Each List

4\.

List A	List B	List C
A. Rate of reaction	1. $-\frac{\Delta[A]}{\Delta t} = -\frac{d[A]}{dt}$	a. $\Delta H = +\text{ve or} - \text{ve}$
B. Rate constant of a reaction	2. $V_t = V_0$	b. $\Delta H = -\text{ve}$
C. Equilibrium constant	3. $V_t \neq V_0$	c. $t \to 0$
D. $V_t = \frac{V_0 \cdot T}{273}$	4. Increases	d. $\Delta t \to 0$
E. $V_t = V_0 + \frac{V_0 \cdot t}{273}$	5. Decreases	e. $T \to 0$

5\.

	Linear plots	Slope	Order
(A)	$\ln\left(\frac{dx}{dt}\right)$ vs $\ln[A]_t$	1. $-k$	a. Two
(B)	$[A]_t$ vs time	2. $\frac{-E_a}{R}$	b. Zero
(C)	$\frac{1}{[A]_t}$ vs time	3. $1-n$	c. One
(D)	$\log_e k$ vs T	4. Zero	d. n
(E)	$\log[A]_t$ vs time	5. k	e. Any order
(F)	$\log t_{1/2}$ vs $\log[A]_0$	6. n	f. 1– slope

ANSWERS

1\. a – ii; b – iii; c – i; d – iv
2\. a – 5; b – 4; c – 1; d – 3; e – 2
3\. A – q ; B – p; C – r; D – s
4\. A – 1 – d; B – 4 – a; C – 5 – b; D – 3 – e; E – 2 – c
5\. A – 6 – d; B – 1 – b; C – 5 – a; D – 2 – e; E – 1 – c; F – 3 – f