विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज

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THE KEY

CHEMICAL KINETICS :

It is a branch of physical chemistry deals with the "Rate of Chemical Reactions" including the effect of temperature, pressure, concentration, etc., on the rates, and the mechanism by which the reaction takes place.

RATE OF CHEMICAL REACTION is defined as the change in concentration of a reactant (or a product) in a particular time interval. Average rate of reaction, Instantaneous rate of reaction.

Units of Reaction Rate are unit of concentration divided by the unit of time (mol $L^{-1}s^{-1}$ or mol $L^{-1}min^{-1}$ or so on).

FACTORS AFFECTING REACTION RATES :

(i) Concentration of reactants and

(ii) Reaction temperature

Besides these, presence of catalyst and surface area (if a reactant or a catalyst is a solid) exposure to radiation also affect the reaction rates.

EXPRESSIONS OR THE RATE :

For a general reaction : $aA + bB \longrightarrow cC + dD$,

The rate of disappearance of A = $-\dfrac{d[A]}{dt}$; Rate of disappearance of B = $-\dfrac{d[B]}{dt}$;

Rate of appearance of C = $\dfrac{d[C]}{dt}$ & Rate of appearance of D = $\dfrac{d[D]}{dt}$.

The positive sign shows that concentrations of C and D increases with time and the negative sign indicating that concentrations of A and B decrease with time.Thus the rate of general reaction.

$$\text{rate : } -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}.$$

RATE EQUATION AND RATE CONSTANT :

An expression which relates the rate of a reaction to the concentration of the reactants is called the ***Rate Equation*** **or** ***Rate Law***. Rate $\propto [A]^a \cdot [B]^b$ or Rate = $k\,[A]^a\,[B]^b$. The constant of proportionality, k is known as the ***Rate Constant*** (specific reaction rate) and may be defined as the rate at unit concentrations of the reactants. k depends on the temperature and is independent of the initial concentrations of the reactants. At a fixed temperature, k is constant characteristic of the reaction. Larger value of k indicates fast reaction and small k indicates slow reactions.

MOLECULARITY :

Molecularity of a reaction is defined as the numbers of particles (atoms, ions, groups or molecules) of reactants actually taking part in a single step chemical reaction.

Molecularity of a reaction is :

(i) Always a whole number (not zero) and never a fraction.

(ii) The value of molecularity of a simple or one step reaction does not exceed 3.

ORDER OF REACTION :

It is defined as the sum of the exponents (powers) of the molar concentrations of the reactants in the experimentally determined rate equations.

If rate of reaction $\alpha\, [A]^p\, [B]^q\, [C]^r$ or Rate of reaction = $k\,[A]^p\,[B]^q\,[C]^r$

order of reaction = p + q + r & the order w.r.t. A, B & C are p, q & r respectively.

For a "Reaction of nth order", the order of the reaction is n and the rate equation (or Rate law) is rate $\propto [A]^n = k\,[A]^n$.

The order of a reaction is obtained from the experimentally determined rate (and not from the stoichiometric equation) and may be zero, an integer or a fraction and never exceeds 3. In a multi-step complex reaction, the order of the reaction depends on the slowest step.

ZERO ORDER REACTION :

A reaction is said to be of zero order if the rate is independent of the concentration of the reactants.

A $\longrightarrow$ products ; Rate α k $[A]^\circ$ = k mol L^{-1} s^{-1}

EXAMPLES :

(i) $H_2(g) + Cl_2(g) \xrightarrow{hv} 2HCl(g)$

(ii) $N_2O(g) \xrightarrow[\text{Surface}]{\text{hot Pt.}} N_2(g) + \frac{1}{2} O_2(g)$

(iii) $2NH_3(g) \xrightarrow[\text{surface}]{\text{Mo or W}} N_2 + 3H_2$

(iv) $2HI(g) \xrightarrow[\text{surface}]{\text{Au}} H_2(g) + I_2(g)$

CHARACTERISTICS OF ZERO ORDER REACTION :

(1) Concentration of reactant decreases lineraly with time. $[A]_t = [A]_0 - kt$.

(2) Units of k are, mol l^{-1} time^{-1}.

(3) Time required for the completion of reaction $t = \frac{[A]_0}{k}$ & $t_{1/2} = \frac{0.5\,[A]_0}{k}$

FIRST ORDER REACTION :

A reaction is said to be of first order if its rate is proportinal to the concentration of one reactant only.

	A $\longrightarrow$	Products.
at time t = 0	a (or C_0)	0
at time t = t	a – x (or C_t)	x

Rate α [A] = k_1 [A] or $\frac{dx}{dt} = k_1(a-x)$ (1 st order differntial equation)

Integrated 1 st order rate equation is $k_1 = \frac{2.303}{t} \log \frac{a}{a-x}$.

Exponential form of 1 st order equation is $C_t = C_0 e^{-k_1 t}$

Characteristics Of First Order Reaction :

(1) Unit of rate constant is time^{-1}.

(2) Change in concentration unit will not change the numerical value of k_1.

(3) $t_{1/2} = \frac{0.693}{k_1}$ (Half-life); Average life = $\frac{1}{k}$;

(4) log (a – x) v/s t is a straight line with slope $-\frac{k_1}{2.303}$.

EXAMPLES :

(i) Radioactive disintegration is a first order reaction.

(ii) $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{Inversion}]{H^+ \text{ catalysed hydrolysis}} C_6H_{12}O_6 + C_6H_{12}O_6$.
(glucose) (fructose)

(iii) Mineral acid catalyzed hydrolysis of esters.

(iv) Decomposition of H_2O_2 in aqueous solution.

SECOND ORDER REACTION :

(i) When two molecules of the same reactant are involved or the concentrations of the both reactants are equal reactions 2A $\longrightarrow$ products or A + B $\longrightarrow$ products.

Differential rate equation $\frac{dx}{dt} = k_2(a-x)^2$

Integrated rate equation $k_2 = \frac{1}{t} \cdot \frac{x}{a(a-x)}$ or $k_2 t = \frac{1}{a-x} - \frac{1}{a}$.

(ii) When the initial concentrations of the two reactants are different;

$$\underset{a}{A} + \underset{b}{B} \longrightarrow \text{products}$$

differential rate equation $\frac{dx}{dt} = k_2 (a-x)(b-x)$.

Integrated rate equation $k_2 = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$

CHARACTERISTICS OF SECOND ORDER REACTION :

(i) Unit of rate constant L mol^{-1} $time^{-1}$.

(ii) Numerical value of k will depend upon unit of concentration.

(iii) $t_{1/2} \alpha\, a^{-1}$ (In general $t_{1/2} \alpha\, a^{(1-n)}$; n = order of reactions).

(iv) 2nd order reaction conforms to first order when one of the reactant in excess.

EXAMPLES :

(i) Saponification (hydrolysis of esters catalysed with alkali).

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

(ii) Hydrogenation of ethane $C_2H_4 + H_2 \xrightarrow{100°C} C_2H_6$.

(iii) $2\,O_3 \longrightarrow 3\,O_2$.

n

n^{th} ORDER REACTION.

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

$$k_n t = \frac{1}{n-1}\left\{\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}}\right\} \qquad [n \neq 1,\ n = \text{order}]$$

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

SIDE OR CONCURENT REACTION :

$$\begin{tikzcd} & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$

; $\quad ln \frac{[A]_0}{[A]_t} = (k_1 + k_2)\, t \quad ; \quad \frac{[B]}{[C]} = \frac{k_1}{k_2}$

CONSECUTIVE REACTION :

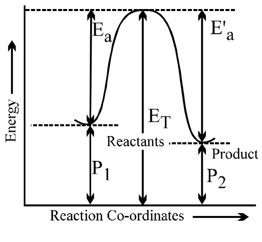
$$A \xrightarrow{k_1} B \xrightarrow{k_2} C\ ;\ t_{max} = \frac{1}{(k_1 - k_2)}\, ln\left(\frac{k_1}{k_2}\right); \quad [B]_{max} = [A]_0 \left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 - k_2}}$$

THRESHOLD ENERGY AND ACTIVATION ENERGY :

For a reaction to take place the reacting molecules must colloid together, but only those collisions, in which colliding molecules possess certain minimum energy is called threshold energy (E_T).

ACTIVATION ENERGY (E_a) :

The extra energy needed for the reactant molecules to be able to react chemically is known as Activation energy.



E_T = Threshold energy
E_a = Activation energy of forward reaction
E'_a = activation energy of backward reaction
P_1 = Potential energy of reactants
P_2 = Potential energy of products

INFLUENCE OF TEMPERATURE ON REACTION RATES :

TEMPERATURE COEFFICIENT :

The temperature coefficient of a chemical reaction is defined as the ratio of the reaction rates at two temperatures differing by 10°C. Its value usually lies between 2 & 3.

Temperature coefficient = $\dfrac{k_{t+10}}{k_t}$.

ARRHENIUS EQUATION :

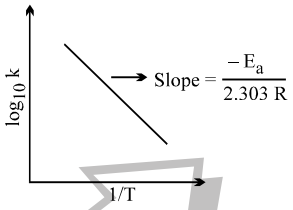
A quantitative relationship was proposed by Arrhenius $k = A.\ e^{-Ea/RT}$ Where,

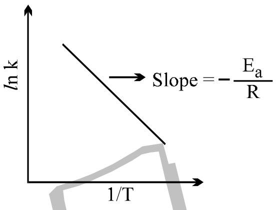
k = rate constant ; A = frequency factor (or pre – exponential factor);

R = gas constant ; T = Temperature (kelvin) ; E_a =Activation energy.

The Logarithmic expressions are $\log_{10}\dfrac{k_2}{k_1} = \dfrac{E_a}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$;Vant Hoff 's Isochore $\dfrac{d}{dt}\ln k = \dfrac{E_a}{RT^2}$

GRAPHICAL REPRESENTATIONS ARE :





METHODS OF DETERMINATION OF ORDER OF REACTIONS :

A few methods commonly used are given below :

1. **Hit & Trial Method** : It is method of using integrated rate equations, where the experimental values of a, x & t are put into these equations. One which gives a constant value of k for different sets of a, x & t correspond to the order of the reaction.

2. **Graphical Method** :

(i) A plot of log (a – x) versus 't' gives a straight lines for the First order reaction.

(ii) A plot of $(a - x)^{-(n-1)}$ versus 't' gives a straight line any reaction of the order n (except n = 1).

3. **Half Life Method** : The half life of different order of reactions is given by $a_n = \left(\dfrac{1}{2}\right)^n a_0$.

By experimental observation of the dependence of half life on initial concentration we can determine n, the order of reaction. $n = 1 + \dfrac{\log t_2 - \log t_1}{\log a_1 - \log a_2}$.

4. **Initial rate method.** Initial rate method is used to determine the order or reaction in cases where more than one reactant is used. It involves the determination of the order of different reactants separately. A series of experiments are performed in which concentration of one particular reactant is varied whereas conc. of other reactants are kept constant. In each experiment the initial rate is determined from the plot of conc. vs. time, e.g., if conc. of A is doubled, and initial rate of reaction is also doubled, order of reaction is l.

MECHANISM OF REACTIONS :

The path way which reactants are converted into the products is called the reaction mechanism. It should be clear that experimentally determined rate expression cannot be predicted from the stiochiometry of the reaction. For example for the reaction ;

$NO_2(g) + CO\ (g) \longrightarrow CO_2(g) + NO(g)$, the rate expression is ; rate = $-\dfrac{d}{dt}[NO_2] = k[NO_2]^2$, i.e. the expression has no dependence of CO (g) concentration.

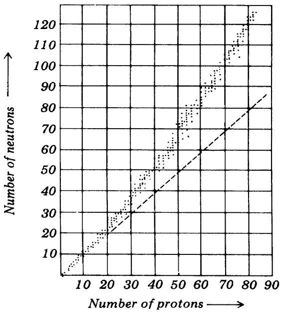
The reason is that the reaction occurs by a series of elementary steps.
The sequence of elementary processes leading to the overall stiochiometry is known as the "Mechanism of the reaction". A_n in a sequence of reactions leading to the formation of products from reactants, the slowest step is the rate determining step.
The mechanism proposed for the above reaction is a two step one.

$$NO_2 + NO_2 \longrightarrow NO + NO_3 \text{ (step 1 : slow)}$$
$$NO_3 + CO \longrightarrow CO_2 + NO_2 \text{ (step 2 : fast)}$$

The sum of the two gives the stiochiometry & the slow step decided the rate expression.

Nuclear Chemistry

Neutron / proton ratio and stability



- For atomic number < 20, most stable nuclei have n: p ratio nearly 1 : 1 (except H & Ar).
- For n/p ratio > 1.5, nucleus is unstable. Largest stable nucleus is ${}^{209}_{83}Bi$ for which n/p ratio is 1.52.
- For atomic number > 83, there are no stable nuclei.

Magic numbers and nuclear stability

Nuclei with 2, 8, 20, 28, 50, 82 or 126 protons or neutrons are unusually stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

- Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg. ${}^{4}_{2}He$, ${}^{16}_{8}O$, ${}^{40}_{20}Ca$ and ${}^{208}_{82}Pb$]. 165 such stable nuclei are known.
- There exist 55 known nuclei with even number of protons and odd number of neutrons, and 50 known stable nuclei with odd number of protons and even number of neutrons. On the other hand, the number of known stable nuclei having odd numbers of both neutrons and protons is only 4.

Expected emissions from unstable nucleus

1. ***n/p ratio above stability belt:*** electron (β^-) or neutron.
2. ***n/p ratio below stability belt:*** positron (β^+) or K capture.
3. ***Atomic number > 83,*** various particles, including α–particles.

Radioactive decay

- Radioactive decay is a first order process. Hence $-\dfrac{dN}{dt} = \lambda N$ or $N = N_0 e^{-\lambda t}$

  where N = number of radioactive nuclei at any time t ; N_0 = number of radioactive nuclei at t = 0 ; λ = decay constant.

- **Activity** activity (a) = $-\dfrac{dN}{dt} = \lambda N$

  S.I. units : disintegration per second (symbol s^{-1} or dps). This unit is also called *becquerel* (symbol Bq)
  Other units: Curie (Ci) $1Ci = 3.7 \times 10^{10}$dps.

- **Half life ($t_{1/2}$)** The time taken by half the nuclei (originally present) to decay. $t_{1/2} = 0.693/\lambda$

  Note : After *n* half–lives have passed, activity is reduced to $\dfrac{1}{2^n}$ of its initial value.

- **Average life (t_{av})** $t_{av} = 1/\lambda = 1.44\ t_{1/2}$

Isotopes : Nuclei with same atomic number but different atomic mass number.
Isobars : Nuclei with different atomic number but same atomic mass number.
Isotones : Nuclei with same number of neutrons but different number of protons.

THE ATLAS

Some basic concept

1.Rate of reaction.
2.Rate of reaction in terms of extent of reaction.
3.Average and instantaneous rate of reaction.
4.Dependence of rate of reaction on concentration, pressure, temperature and catalyst.
5.Rate law expression.
6.Order and molecularity of reaction.

CHEMICAL KINETICS

Experimental Aspects

1.Determination of order of reaction.
(a) Graphical Method.
(b) Initial rate method.
(c) Oswald's isolation method.
(d) Half life meyhod.
2. Differential and integerated expressions for
(a) Zero order
(b) First order
(c) nth order reaction
(d) $t_{1/2}$ and $t_{p/q}$ of a reaction.
(e) Rate constant expression in which conc. terms is replaced by other variables litre pressure, volume of reagent, obsorbance etc..
(f) Brancing Decay
(g) Conseqative or sequential Decay
(h) Mechanism of reaction
3. Radioactivity.

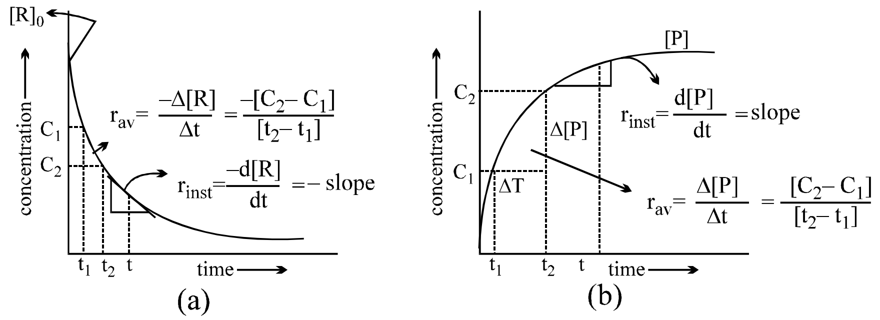
Theoretical Aspects

1.Collision theory of rate of reaction
2. Temperature depedence of rate of reaction
3. Transition state theory for rate of reaction
4. Mechanism of reaction and steady state approximation

GLOSSARY

IMPORTANT TERMS AND DEFINITIONS

1. **Rate of reaction.** It is defined as the change in concentration of reactant (or product) in a particular time interval. Its unit is mol $L^{-1}s^{-1}$. If time is in minutes, then units are mol L^{-1} min^{-1} and so on.
2. **Average rate.** The rate of reaction measured over a long time interval is called average rate of reaction. It is equal to $\Delta x/\Delta t$ as shown in fig.(a) and (b).



Instantaneous and average rate of reaction

3. **Instantaneous rate.** It is the rate of reaction when the average rate is taken over a very small interval of time. It is equal to dx / dt as shown in fig. (a) and (b).
4. **Rate law or rate equation.** It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.
5. **Rate constant.** When concentration of both reactants are unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.
6. **Molecularity.** Total number of molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number, It is never more than three. It cannot be zero.
7. **Order of a reaction.** The sum of the powers of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.
8. **Zero order reaction.** The rate of reaction does not change with the concentration of the reactants, i.e., $\text{rate} = k[A]^{\circ}$
9. **First order reaction.** The reaction in which the rate of reaction is directly proportional to the concentration of reacting substance. Rate constant of first order reaction is

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

where 'a' is initial concentration, (a–x) is the conc. of reactants after time 't'. The unit of 'k' is s^{-1} or min^{-1}. A plot between *l*n [A] vs. t is a straight line with slope equal to –k. [A] is concentration of reactants after time t.

10. **Half–life of a reaction.** The time taken for a reaction when half of the starting material has reacted is called half–life of a reaction. For first order reaction

$$t_{1/2} = \frac{0.693}{k}\text{, where k is rate constant.}$$

11. **Second order reaction**. The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2, e.g.,

$$\frac{dx}{dt} = k[A]^1[B]^1$$

12. **Third order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 3, e.g.,

$$\frac{dx}{dt} = k[A]^x[B]^y \text{ where } x + y = 3$$

13. **Specific rate constant (k).** It is defined as equal to rate of reaction when molar concentration of reactant is unity.
14. **Activation energy.** It is extra energy which must be possessed by reactant molecules so that collision between reactant molecules is effective and leads to formation of product molecules.
15. **Initial rate.** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called in initial rate of reaction.
16. **Arrhenius equation of reaction rate.** It gives the relation between rate of reaction and temperature.

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

where k = rate constant A = frequency factor, E_a = energy of activation
R = gas constant, T = temperature in kelvin.

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

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

17. **Photochemical reactions.** Those reactions which take place in the presence of light are called photochemical reactions. Photosynthesis is an example of photochemical reaction.
18. **Photosensitization.** The process in which a molecule that absorbs light transfers its extra energy to another molecule which may undergo a reaction. This process is called photosensitization.
19. **Chain reaction.** The sequence of reactions, where a reactive species produces more reactive species is called chain reaction. It involves free radicals.
20. **Elementary processes.** Some reactions occur by a series of elementary steps and such simple steps are called elementary processes.
21. **Mechanism of reaction.** The sequence of elementary processes leading to the overall stiochiometry of a chemical reaction is known as mechanism of a reaction.
22. **Slow reaction.** Those reactions which take place very slowly are called slow reactions, e.g., rusting of iron and reaction of oxalic acid with acidified $KMnO_4$ at room temperature are slow reactions.
23. **Life time.** The time in which 98% of the reaction is complete is called lifetime.
24. **Threshold energy.** The minimum energy that reacting species must possess in order to undergo effective collision to form product molecules is called threshold energy.
25. **Effective collision (f).** Those collisions which lead to the formation of product molecules are called effective collisions. Rate of reaction = f × z where 'z' is collision frequency and 'f' is fraction of collisions, which are effective.
26. **Collision frequency (z).** It is defined as total number of collisions per unit volume per unit time.
27. **Activated complex.** It is defined as unstable intermediate formed between reacting molecules which is highly unstable and readily changes into product.
28. **Thermodynamic stability.** A mixture of substances may not undergo reaction although thermodynamic predict the reaction to be spontaneous. Such substances are thermodynamically unstable at ordinary temperature but may not be kinetically unstable.
29. **Kinetic stability.** The reaction occurs only when the reactant crosses energy–barrier. Once it occurs, it becomes kinetically unstable because the reaction is spontaneous. The energy evolved helps the other reactants to cross energy–barrier. Thus, reactants should be thermodynamically as well as kinetically unstable so as to change into products at a particular temperature.

30. **Rate determining step.** The slowest step in the reaction mechanism is called rate determining step.

31. **Temperature coefficient.** It is the ratio of rate constant at temperature 308 K to the rate constant at temperature 298 K.

$$\text{Temperature coefficient} = \frac{\textit{Rate constant}\ \text{'k' at } 308\ \text{K}}{\textit{Rate constant}\ \text{'k' at } 298\ \text{K}}$$

It lies between 2 and 3.

32. **Pseudo first order reaction.** The reaction in which one reacted is in excess so order is one is called Pseudo first order reaction, e.g., acidic hydrolysis of ester.

$$CH_3COOC_2H_5 + H_2O\ (\text{excess}) \xrightleftharpoons{H^+} CH_3COOH + C_2H_5OH$$

33. **Einstein's law of photochemical equivalence.** Each atom or molecule is activated by 1 photon (quantum of light).

34. **Chain initiation step.** The step in which neutral molecule changes into free radicals by absorbing photons is called chain initiation step.

35. **Chain propagation step.** The step in which free radical reacts with neutral molecule to form a neutral molecule and a free radical is called chain propagation step.

36. **Chain termination step.** The step in which radicals combine to form neutral molecules.

37. **Fast reactions.** Those reactions which occur instantaneously and is complete in fraction of seconds are called fast reactions, e.g., $AgNO_3(aq) + HCl(aq) \longrightarrow AgCl \downarrow + HNO_3$, takes place in 10^{-12} seconds.

38. **Thermochemical reactions.** Those reactions initiated by heat energy are called thermochemical reactions. They can occur in dark. Temperature coefficient is generally high because rate of reaction increases with increase in temperature. ΔG is – ve for such reactions.

EXERCISE-I

RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

Q.1 In a catalytic experiment involving the Haber process, $N_2 + 3H_2 \longrightarrow 2NH_3$, the rate of reaction was measured as

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

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

Q.2 For the reaction $3BrO^- \rightarrow BrO_3^- + 2Br^-$ in an alkaline aquesous solution, the value of the second order (in BrO^-) rate constant at 80°C in the rate law for $-\frac{\Delta[BrO^-]}{\Delta t}$ was found to be $0.056 \text{L mol}^{-1}\text{s}^{-1}$.

What is the rate of constant when the rate law is written for (a) $\frac{\Delta[BrO_3^-]}{\Delta t}$, (b) $\frac{\Delta[Br^-]}{\Delta t}$?

Q.3 Dinitropentaoxide decomposes as follows :

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

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

$d[NO_2]/dt = k_2[N_2O_5]$

$d[O_2]/dt = k_3[N_2O_5]$

What is the relation between k_1, k_2 and k_3?

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

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

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

Q.5 For the elementary reaction $2A + B_2 \longrightarrow 2AB$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?

Q.6 Ammonia and oxygen reacts at higher temperatures as

$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

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

(i) rate of reaction.

(ii) rate of disappearance of ammonia

(iii) rate of formation of water

Q.7 In the following reaction $2H_2O_2 \longrightarrow 2H_2O + O_2$

rate of formation of O_2 is 3.6 M min^{-1}.

(a) What is rate of formation of H_2O?

(b) What is rate of disappearance of H_2O_2?

Q.8 The reaction $A(g) + 2B(g) \longrightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8$ atm, if $P_C = 0.2$ atm then calculate the ratio of rate of reaction relative to initial rate.

ZERO ORDER

Q.9 In the following reaction, rate constant is 1.2×10^{-2} M s^{-1} $A \longrightarrow B$. What is concentration of B after 10 and 20 min., if we start with 10 M of A.

Q.10 For the following data for the reaction $A \longrightarrow$ products. Calculate the value of k.

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

Q.11 The rate constant for a zero order reaction is 2×10^{-2} mol $L^{-1}sec^{-1}$, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.

Q.12 A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+, if the rate constant of disappearance of H^+ is 1×10^7 mole $litre^{-1}$ sec^{-1}. How long would it take for H^+ in drop to disappear?

Q.13 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given: order of reaction is zero)

FIRST ORDER

Q.14 A first order reaction is 75% completed in 72 min.. How long time will it take for
(i) 50% completion (ii) 87.5% completion

Q.15 A first order reaction is 20% complete in 10 min. calculate (i) the specific rate constant , (ii) the time taken for the reactions to go to 75% completion.

Q.16 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place in ten times that required for half of the reaction.

Q.17 A first order reaction has a rate constant is 1.5×10^{-3} sec^{-1}. How long will 5.0 g of this reactant take to reduce to 1.25 g.

Q.18 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?

Q.19 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0 % of the virus was found to be inactivated per minute . Evaluate k for inactivation process.

Q.20 If a reaction $A \longrightarrow$ Products, the concentrations of reactant A are C_0, aC_0, a^2C_0, a^3C_0, ... after time interval 0, t, 2t, 3t, ... where a is a constant. Given $0 < a < 1$. Show that the reaction is of first order. Also calculate the relation in k, a and t.

Q.21 The reaction $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is a first order gas reaction with $k = 2.2 \times 10^{-5}$ sec^{-1} at 320°C. What % of SO_2Cl_2 is decomposed on heating this gas for 90 min.

ORDER OF REACTION & RATE LAW

Q.22 At 800° C the rate of reaction

$$2\,NO + H_2 \longrightarrow N_2 + H_2O$$

Changes with the concentration of NO and H_2 are

	[NO] in M	$[H_2]$ in M	$-\frac{1}{2}\frac{d[NO]}{dt}$ in M sec^{-1}
(i)	1.5×10^{-4}	4×10^{-3}	4.4×10^{-4}
(ii)	1.5×10^{-4}	2×10^{-3}	2.2×10^{-4}
(iii)	3.0×10^{-4}	2×10^{-3}	8.8×10^{-4}

(a) What is the order of this reaction?
(b) What is the rate equation for the reaction?
(c) What is the rate when
$[H_2] = 1.5 \times 10^{-3}$ M and $[NO] = 1.1 \times 10^{-3}$M?

Q.23 The data below are for the reaction if NO and Cl_2 to form NOCl at 295 K

Concentration of Cl_2 [M]	Concentration of NO	Initial Rate (M s^{-1})
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order w.r.t NO and Cl_2 in the reaction.
(b) Write the rate expression
(c) Calculate the rate constant
(d) Determine the reaction rate when concentration of Cl_2 and NO are 0.2 M & 0.4 M respectively.

Q.24 The catalytic decomposition of N_2O by gold at 900°C and at an initial pressure of 200mm is 50% complete in 53 minutes and 73% complete in 100 minutes.
(i) What is the order of the reaction?
(ii) Calculate the velocity constant.
(iii) How much of N_2O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?

Q.25 The following data are for the reaction $A + B \rightarrow$ products:

Conc. A (M)	**Conc. 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	2.0×10^{-3}
0.5	0.5	1.0×10^{-2}

(i) What is the order with respect to A and B for the reaction?
(ii) Calculate the rate constant.
(iii) Determine the reaction rate when the concentrations of A and B are 0.2M and 0.35M, respectively.

Q.26 The pressure of a gas decomposing at the surface of a solid catalyst has been measured at different times and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	4×10^3	3.5×10^3	3×10^3	2.5×10^3

Determine the order of reaction, its rate constant.

Q.27 The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction?

Q.28 At 600°C, acetone (CH_3COCH_3) decomposes to ketene ($CH_2 = C = O$) and various hydrocarbons. Given the initial rate data in the table:
(a) What is the order?
(b) Write rate law
(c) Calculate rate constant
(d) Calculate the rate of decomposition when the acetone concentartion is 1.8×10^{-3} M

Experiment	Initial [CH_3COCH_3]	Rate M s^{-1}
1.	6.0×10^{-3} M	5.2×10^{-5}
2.	9.0×10^{-3} M	7.8×10^{-5}
3.	1.8×10^{-3} M	?

HALF LIFE

Q.29 The half life period of a first order reaction is 50 min. In what time will it go to 90% completion?

Q.30 A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 hrs., what percentage of the initial concentration would have changed into the product? What is the half life of this reaction?

Q.31 Show that in case of a first order reaction, the time required for 93.75% of the reaction to take place is four times that required for half of the reaction.

Q.32 The half time of the 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 deompose, calculate (i) time taken for NH_2NO_2 to decompose 99%, and (ii) volume of dry N_2O produced at this point, measured at STP.

Q.33 A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min. for B. If the concentartions of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?

Q.34 Two substances A ($t_{1/2}$= 5 mins) and B ($t_{1/2}$ = 15 mins) follow first order kinetics are taken in such a way that initially [A]= 4[B]. Calculate the time after which the concentration of both the substance will be equal.

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER INTEGRATED RATE LAW

Q.35 In this case we have

$A \longrightarrow B + C$

Time	t	∞
Total pressure of A + B+C	P_2	P_3

Find k.

Q.36 $A \longrightarrow B + C$

Time	t	∞
Total pressure of (B+C)	P_2	P_3

Find k.

Q.37 $A \longrightarrow B + C$

Time	0	t
Volume of reagent	V_1	V_2

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

Q.38 $A \longrightarrow 2B + 3C$

Time	t	∞
Volume of reagent	V_2	V_3

Reagent reacts with all A, B and C. Find k.

Q.39 $S \longrightarrow G + F$

Time	t	∞
Rotation of Glucose & Fructose	r_t	r_∞

Find k.

Q.40 At 27°C it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of reaction (in M sec^{-1}) and rate of reaction in terms of pressure.

Q.41 At 100°C the gaseous reaction $A \longrightarrow 2B + C$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half life period of the reaction?

Q.42 The reaction $AsH_3(g) \longrightarrow As(s) + \frac{3}{2} H_2(g)$ was followed at constant volume at 310°C by measuring the gas pressure at intervals Show from the following figures that reaction is of first order.

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

Q.43 The decomposition of N_2O_5 according to the equation $2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$ is a first order reaction. After 30 min. from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

Q.44 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

at 500°C is as follows:

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

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

Q.45 From the following data show that decomposition of H_2O_2 in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of $KMnO_4$)	22.8	13.3	8.25

Q.46 A definite volume of H_2O_2 under going spontaneous decomposition required 22.8 c.c. of standard permanganate solution for titration. After 10 and 20 minutes respectively the volumes of permanganate required were 13.8 and 8.25 c.c.

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

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

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

Q.47 The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	∞
Angle of rotation (degree)	+13.1	+ 11.6	+ 10.2	+9.0	+5.87	–3.8

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

Q.48 In the hydrolysis of propyl acetate in the presence of dilute hydrochloric acid in dilute aqueous solution the following data were recorded :

Time from start in minutes	60	350
Percentage of ester decomposed	18.17	69.12

Calculate the time in which half the ester was decomposed.

Q.49 Hydrogen peroxide solution was stored in a mild steel vessel. It was found, however, that the hydrogen peroxide decomposed on the walls of the vessel (a first order reaction). An experiment with 100 ml of a solution gave 10.31 ml oxygen (corrected to N.T.P.) after 5.1 days under similar storage conditions. Find how long the peroxide can be stored before the loss of 20.00 ml oxygen occurs (per 100 ml solution) if complete decomposition of the sample to H_2O_2 gave 46.34 ml oxygen.

Q.50 The reaction given below, rate constant for disappearance of A is $7.48 \times 10^{-3}\ \text{sec}^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec.

$$2A\,(g) \longrightarrow 4B(g) + C(g)$$

PARALLEL AND SEQUENTIAL REACTION

Q.51 For a reaction $x \begin{array}{l} \xrightarrow{k_1} y \\ \xrightarrow[k_2]{} z \end{array}$, calculate value of ratio, $\dfrac{[x]_t}{[y]+[z]}$ at any given instant t.

Q.52 $$\begin{tikzcd}[row sep=small] & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$ $k_1 = x\ hr^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\dfrac{[C]}{[A]}$ after one hour from the start of the reaction. Assuming only A was present in the beginning.

Q.53 A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as $$\begin{tikzcd}[row sep=small] & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$; $k_1 = 1.26 \times 10^{-4}\ sec^{-1}$ and $k_2 = 3.6 \times 10^{-5}\ sec^{-1}$. Calculate the % distribution of B & C.

Q.54 For a reaction $A \longrightarrow B \longrightarrow C$ $t_{1/2}$ for A & B are 4 and 2 minutes respectively. How much time would be required for the B to reach maximum concentration.

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

Q.55 In gaseous reactions important for understanding the upper atmosphere, H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ at 500 K and $E_a = 77\ kJ\ mol^{-1}$, then calculate E_a for the biolecular recombination of 2OH radicals to form H_2O & O at 500 K

Q.56 The energy of activation of a first order reaction is 104.5 kJ $mole^{-1}$ and pre – exponential factor (A) is $5 \times 10^{13}\ sec^{-1}$. At what temperature, will the reaction have a half life of 1 minute?

Q.57 The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from 27°C to 47°C. Find the activation energy for the reaction.

Q.58 The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/ mole and $3.46 \times 10^{-5}\ sec^{-1}$ respectively. Determine the temperature at which half life of the reaction is 2 hours.

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2\ (g)$$

Q.59 A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C. Calculate the
(a) rate constant for the reaction at 27°C & 47°C and
(b) energy of activatioin for the reaction.

Q.60 A catalyst lowers the activation energy for a certain reaction from 75 kJ to 25 kJ mol^{-1}. What will be the effect on the rate of reaction at 25°C, after things being equal.

Q.61 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate.

MECHANISM OF REACTION

Q.62 The reaction $2NO + Br_2 \longrightarrow 2NOBr$, is supposed to follow the following mechanism
(i) $NO + Br_2 \overset{\text{fast}}{\rightleftharpoons} NOBr_2$
(ii) $NOBr_2 + NO \xrightarrow{\text{slow}} 2NOBr$
Suggest the rate of law expression.

Q.63 For the reaction $2H_2 + 2NO \longrightarrow N_2 + 2H_2O$, the following mechanism has been suggested:
$2NO \rightleftharpoons N_2O_2$ equilibrium constant K_1 (fast)
$N_2O_2 + H_2 \xrightarrow{K_2} N_2O + H_2O$ (slow)
$N_2O + H_2 \xrightarrow{K_3} N_2 + H_2O$ (fast)
Establish the rate law for given reaction.

Q.64 Write a stoichiometric equation for the reaction whose mechanism is detailed below. Determine the value of the equilibrium constant for the first step. Write a rate law equation for the overall reaction in terms of its initial reactants.

$A_2 \rightleftharpoons 2A$ $k_1 = 10^{10}s^{-1}$ (forward)
$k_{-1} = 10^{10}M^{-1}s^{-1}$ (reverse)
$A + C \longrightarrow AC$ $k_2 = 10^{-4}M^{-1}s^{-1}$ (slow)

Q.65 Reaction between NO and O_2 to form NO_2 is $2NO + O_2 \longrightarrow 2NO_2$ follows the following mechanism

$NO + NO \underset{K-1}{\overset{K_1}{\rightleftharpoons}} N_2O_2$ (in rapid equilibrium)

$N_2O_2 + O_2 \xrightarrow{K_2} 2NO_2$ (slow)

Show that the rate of reaction is given by $\frac{1}{2}\left(\frac{d[NO_2]}{dt}\right) = K[NO]^2[O_2]$

Q.66 Deduce rate law expressions for the conversion of H_2 and I_2 to HI at 400°C corresponding to each of the following mechanisms:

(a) $H_2 + I_2 \longrightarrow 2HI$ (one step)

(b) I_2 1 2I
$2I + H_2 \longrightarrow 2HI$ (slow)

(c) I_2 1 2I
$I + H_2$ 1 IH_2
$IH_2 + I \longrightarrow 2HI$ (slow)

(d) Can the observed rate law expression rate = $k[H_2][I_2]$ distinguish among these mechanisms?

(e) If it is known that ultraviolet light causes the reaction of H_2 and I_2 to proceed at 200°C with the same rate law expression, which of these mechanisms becomes most improbable? Are any of these mechanisms proved?

RADIOACTIVITY

Q.67 Classify each of the following nuclides as "beta emitter", or "positron emitter":
$^{49}_{20}Ca$ $^{195}_{80}Hg$ $^{8}_{5}B$ $^{150}_{67}Ho$ $^{30}_{13}Al$ $^{94}_{36}Kr$. Note: $^{200}_{80}Hg$ and $^{165}_{67}Ho$ are stable

Q.68 Of the three isobars $^{114}_{48}Cd$ $^{114}_{49}In$ and $^{114}_{50}Sn$, which is likely to be radioactive? Explain your choice.

Q.69 Complete the following nuclear equations:

(a) $^{14}_{7}N + ^{4}_{2}He \rightarrow ^{17}_{8}O + ...$ (b) $^{9}_{4}Be + ^{4}_{2}He \rightarrow ^{12}_{6}C + ...$ (c) $^{9}_{4}Be\,(p, \alpha)........$

(d) $^{30}_{15}P \rightarrow ^{30}_{14}S + ...$ (e) $^{3}_{1}H \rightarrow ^{3}_{2}He + ...$ (f) $^{43}_{20}Ca(\alpha, ...) \rightarrow ^{46}_{21}Sc$

Q.70 What symbol is needed to complete the nuclear equation $^{63}_{29}Cu(p, ...)^{62}_{29}Cu$?

Q.71 Complete the following equations.

(a) $^{23}_{11}Na + ^{4}_{2}He \rightarrow ^{26}_{12}Mg + ?$ (b) $^{64}_{29}Cu \rightarrow \beta^{+} + ?$

(c) $^{106}Ag \rightarrow ^{106}Cd + ?$ (d) $^{10}_{5}B + ^{4}_{2}He \rightarrow ^{13}_{7}N + ?$

Q.72 How many α and β particle will be emitted when $^{a}_{c}X$ changes to $^{b}_{d}Y$?

Q.73 What is the α-activity in disintigration per minute 1 gm sample of ^{226}Ra. ($t_{1/2}$ = 1620 year)

Q.74 The half life of the nuclide Rn^{220} is 54.5 sec. What mass of radon is equivalent to 1 millicurie.

Q.75 The activity of the radioactive sample drops to $\left(\frac{1}{64}\right)^{th}$ of its original value in 2 hr find the decay constant (λ).

Q.76 $_{84}Po^{210}$ decays with α to $^{206}_{82}Pb$ with a half life of 138.4 days. If 1.0 gm of Po^{210} is placed in a closed tube, how much helium accumlate in 69.2 days at STP.

Q.77 The half life period of $_{53}I^{125}$ is 60 days. What % of radioactivity would be present after 240 days.

Q.78 At a certain instant a piece of radioactive material contains 10^{12} atoms. The half life of material is 30 days. Calculate the no. of disintegrations in one second.

Q.79 Calculate the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants. Given $t_{1/2}$ for $_1H^3$ = 12.3 years.

Q.80 A radioactive substance decays 20% in 10 min if at start there are 5×10^{20} atoms present, after what time will the number of atoms be reduced to 10^{18} atoms?

PROFICIENCY TEST

Q.1 ***Fill in the blanks with appropriate items :***

1. 1 Curie = _______ Bq.
2. $^{14}_{6}C$ decays by emission of _____________.
3. Emission of a β-particle by a nuclide results in the formation ______ of the element.
4. The number of α and β-particles emitted, when the following nuclear transformation takes place are _______ and ___________ respectively.

   $^{238}_{92}X \longrightarrow ^{206}_{82}Y$
5. The nuclides with same difference of number of neutrons and number of protons are called _____.
6. When $^{30}_{15}P$ emits a position, the daughter nuclide formed is _________.
7. A nuclide which lies above the zone of stability is likely to emit ___________.
8. $^{3}_{1}H$ and $^{4}_{2}He$ are _____________.
9. The half-life period of radioactive element if 87.5% of it disintegrates in 40 min is __________.
10. For collision to be effective the energy possessed by the colliding molecules should be equal to or greater than the ____________.
11. In the reaction, $H_2 + I_2 \longrightarrow 2HI$, the rate of disappearance of H_2 is _______ the rate of appearance of HI.
12. For an endothermic process, the minimum value of activation energy can be _______.
13. The rate of a reaction is ________ to the collision frequency.
14. The rate constant for the zero order reaction has the dimensions____________.
15. The reactions with molecularity more than three are _________.
16. A catalyst increases the rate of the reaction by__________ activation energy of reactants.
17. If activation energy of reaction is low, it proceeds at _______ rate.
18. In a multistep reaction, the ________ step is rate determining.
19. Rate constant of a reaction, generally __________ with increase in temperature.
20. The ratio $t_{7/8} / t_{1/2}$ for a first order reaction would be equal to _________.
21. For a zero order reaction, the rate of the reaction is equal to the ______ of the reaction.
22. The value of temperature coefficient is generally between _________.
23. For a certain reaction, $xM \longrightarrow yL$, the rate of reaction increases by 4 times when the concentration of M is doubled. The rate law is _________.
24. The rate equation $r = k [A][B]^{1/2}$ suggests that order of overall reaction is _______.
25. A plot of [A] vs t for a certain reaction $A \longrightarrow B$ with $r = k [A]^0$ will be a straight line with slope equal to ________.

26. $[E_{\text{activated complex}} - E_{\text{reactants}}]$ = ____________.

27. Among similar reactions, the endothermic reaction has _______ activation energy than exothermic reaction.

28. For a ______ order reaction the half-life ($t_{1/2}$) is independent of the initial conc. of the reactants.

29. For a first order reaction a graph of log [A] vs t has a slope equal to __________.

30. Average lifetime of a nuclei, T_{av} = __________________ $t_{1/2}$.

Q.2 ***True or False Statements :***

1. Order of a reaction can be written from the balanced chemical equation.
2. For a reaction having order equal to 3/2, the units for rate constant are $\sec^{-1}$.
3. In a complex reaction the rate of overall reaction is governed by the slowest step.
4. $t_{1/2}$ for a first order reaction is 6.93 s, the value of rate constant for the reaction would be $10 s^{-1}$.
5. The ratio $t_{1/2} / t_{7/8}$ for a first order reaction is equal to 1/3.
6. The rate of an exothermic reaction increases with the rise in temperature.
7. Molecularity of a reaction is always whole number.
8. The reactants which are thermodynamically unstable are always kinetically unstable also.
9. Order and molecularity of a single step reaction may or may not be same.
10. The activation energy of a catalysed reaction is more than the activation energy of the uncatalysed reaction.
11. For a zero order reaction $t_{3/4}$ is related to $t_{1/2}$ as $t_{3/4} = 1.5\ t_{1/2}$
12. A nuclide having one proton and one neutron is represented as ${}^{1}_{1}H$.
13. A radioactive element decays by emitting one α and two β-particles. The daughter element formed is an isotope of the parent element.
14. The daughter product formed by the emission of α-particle has mass number less by 4 units than the parent nuclide.
15. ${}^{27}_{13}Al$ is a stable isotope while ${}^{29}_{13}Al$ is expected to disintegrate by β-emission.
16. Half-life period of a radioactive substance can be changed by using some suitable catalyst.
17. Emission of a β-particle by a radioactive nuclide results in decrease in N / P ratio.
18. Positron has same mass as that of an electron.
19. ${}^{14}_{9}N$ and ${}^{16}_{8}O$ are isotones.
20. The S.I.unit of activity is Curie (Ci).

EXERCISE -II

Q.1 To investigate the decomposition of oxalic acid in concentrated H_2SO_4 at 50°C, a scientist prepared a 1/40 M solution of oxalic acid in 99.5 percent H_2SO_4, then removed aliquots at various reaction times t, and then determined the volumes υ of a potassium permanganate solution required to react with a 10 ml portion. The results are given below :

t, *min*	0	120	240	420	600	900	1440
υ,*mL*	11.45	9.63	8.11	6.22	4.79	2.97	1.44

Determine the reaction order with respect to oxalic acid and evaluate the specific rate constant.

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

Q.3 The approach to the following equilibrium was observed kinetically from both directions:
$PtCl_4^{2-} + H_2O \rightleftharpoons [Pt(H_2O)Cl_3^{-}] + Cl^-$ at 25°C, it was found that

$$-\frac{\Delta}{\Delta t}[PtCl_4^{2-}] = [3.9\times10^{-5}\ sec^{-1}][PtCl_4^{2-}] - [2.1\times10^{-3}\ L.mol^{-1}\ sec^{-1}]\times[Pt(H_2O)Cl_3]^-[Cl^-]$$

What is the value of equilibrium constant for the complexation of the fourth Cl^- by Pt(II)?

Q.4 The oxidation of certain metals is found to obey the equation $\tau^2 = \alpha t + \beta$ where τ is the thickness of the oxide film at time t, α and β are contants. What is the order of this reaction?

Q.5 The complex $[Co(NH_3)_5F]^{2+}$ reacts with water according to the equation.
$[Co(NH_3)_5F]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + F^-$
The rate of the reaction = rate const. x$[complex]^a$x$[H^+]^b$. The reaction is acid catalysed i.e. $[H^+]$ does not change during the reaction. Thus rate = $k'[Complex]^a$ where $k' = k[H^+]^b$, calculate 'a' and 'b' given the following data at 25^0C.

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

Q.6 The reaction $CH_3–CH_2–NO_2 + OH^- \longrightarrow CH_3–CH–NO_2 + H_2O$ obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M, What is the pseudo first order rate constant?

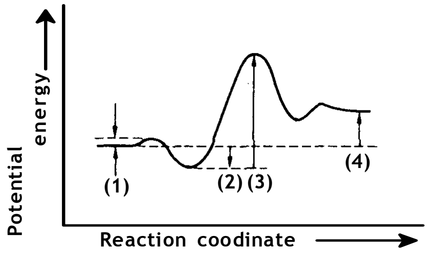
Q.7 A flask containing a solution a solution of N_2O_5 in CCl_4 was placed in a thermostat at 40°C. The N_2O_5 began to decompose by a first–order reaction, forming NO_2 and N_2O_4, which remained in the solution, and oxygen, which defined pressure. The measurements were started (t = 0) when 10.75ml gas had collected. At t = 2400 sec., 29.65ml was measured. After a very long time, (t = ∞)45.50ml was measured. Find the (a) rate constant, (b) half–life time for reaction at 40°C in CCl_4 solution. (c) What volume of gas should have collected after 4800 sec?

Q.8 At room temperature (20°C) orange juice gets spoilt in about 64 hours. In a referigerator at 3°C juice can be stored three times as long before it gets spoilt. Estimate (a) the activation energy of the reaction that causes the spoiling of juice. (b) How long should it take for juice to get spoilt at 40°C?

Q.9 A first order reaction, A → B, requires activation energy of 70 kJ mol^{-1}. When a 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintianed at 40°C? Assume that activation energy remains constant in this range of temperature.

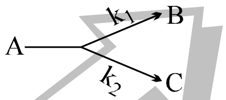
Q.10 Two reations (i) A → products (ii) B → products, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310K. The half life for this reaction at 310K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300K.

Q.11 Choose the correct set of identifications.



	(1)	(2)	(3)	(4)
(A)	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{overall}$ for $S \rightarrow P$	E_a for $EP \rightarrow E + P$
(B)	E_a for $E + S \rightarrow ES$	ΔE for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	$\Delta E_{overall}$ for $S \rightarrow P$
(C)	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{overall}$ for $S \rightarrow P$	ΔE for $EP \rightarrow E + P$
(D)	E_a for $E + S \rightarrow ES$	E_a for $ES \rightarrow EP$	E_a for $EP \rightarrow E + P$	$\Delta E_{overall}$ for $S \rightarrow P$
(E)	ΔE for $E + S \rightarrow ES$	$\Delta E_{overall}$ for $S \rightarrow P$	ΔE for $_1$ $EP \rightarrow E + P$	E_a for $EP \rightarrow E + P$

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



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

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

Q.13 Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as 20 volumes was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 6 hours, 10 mL of this solution was diluted to 100mL. 10mL of this diluted solution was titrated against 25mL of 0.025M $KMnO_4$ solution under acidic conditions. Calculate the rate constant for decomposition of H_2O_2.

Q.14 The reaction

$$\text{cis–Cr(en)}_2\text{(OH)}^+_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{trans–Cr(en)}_2\text{(OH)}^+_2$$

is first order in both directions. At 25°C the equilibrium constant is 0.16 and the rate constant k_1 is $3.3 \times 10^{-4} s^{-1}$. In an experiment starting with the pure *cis* form, how long would it take for half the equilibrium amount of the *trans* isomer to be formed ?

Q.15 A metal slowly forms an oxide film which completely protects the metal when the film thickness is 3.956 thousand ths of an inch. If the film thickness is 1.281 thou. in 6 weeks, how much longer will it be before it is 2.481 thou.? The rate of film formation follows first order kinetics.

Q.16 An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was – 20°. If optical rotation per mole of A, B & C are 60°, 40° & – 80°. Calculate half life and average life of the reaction.

Q.17 A bacterial preparation was inactivated in a chemical bath. The inactivation process was found to be first order in bacterial concentration having rate constant 1.7×10^{-2} sec^{-1}. Meanwhile the multiplication of bacteria (1bacterium $\rightarrow$ 2 bacteria) which also follows first order kinetics with rate constant 1.5×10^{-3} sec^{-1} also continued. Calculate the number of bacteria left after 2 minutes if the initial number of bacteria is 10^3.

Q.18 The formation in water of *d*–potassium chromo–oxalate from its *l*–form is reversible reaction which is first order in both directions, the racemate being the equilibrium product. A polarimeter experiment at 22°C showed that, after 506 sec, 12 mole % of the *l*–isomer was converted to the *d*–form. Find the rate constant for the forward and the reverse reactions.

Q.19 For a reversible first–order reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$

$k_1 = 10^{-2}\ s^{-1}$ and $[B]_{eq}/[A]_{eq} = 4$. If $[A]_0 = 0.01$ mole L^{-1} and $[B]_0 = 0$, what will be the concentration of B after 30 s ?

Q.20 For the reaction $\mathbf{A} \underset{\mathbf{k}_{-1}}{\overset{\mathbf{k}_1}{\rightleftharpoons}} \mathbf{P}$. Following data is produced:

Time / Hr.	0	1	2	3	4	∞
% A	100	72.5	56.8	45.6	39.5	30

Find k_1 , k_{-1} and K_{eq}.

Q.21 For the system $\underset{(g)}{A} \rightleftharpoons \underset{(g)}{B}$, ΔH for the forward reaction is –33 kJ/mol (Note : ΔH = ΔE in this case). Show that equilibrium constant $K = \frac{[B]}{[A]} = 5.572 \times 10^5$ at 300 K. If the activation energies E_f & E_b are in the ratio 20 : 31, calculate E_f and E_b at this temperature. Assume that the pre-exponential factor is the same for the forward and backward reactions.

Q.22 The conversion of A into B is an autocatalytic reaction $A \rightarrow B$ where B catalyzes the reaction. The rate equation is $-dx/dt = Kxy$ where x and y are concentrations of A and B at time t. Integrate this equation for initial concentrations x_0 and y_0 for A and B. Show that : $kt = \frac{2.303}{x_0 + y_0} \log \frac{x_0 y}{x y_0}$.

Q.23 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 $4.78 \times 10^{-3}\ min^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and composition of gas diffusing to be same.

Q.24(a) The reaction A proceeds in parallel channels $A \begin{array}{l} \nearrow B \\ \searrow C \end{array}$ Although the $A \rightarrow C$ branch is thermodynamically more favorable than the branch $A \rightarrow B$, the product B may dominate in quantity over C. Why may this be so?

(b) In the above problem, suppose the half life values for the two branches are 60minutes and 90 minutes, what is the overall half-life value?

Q.25 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E′ for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

$$E' = \frac{k_1E_1 + k_2E_2}{k_1 + k_2}$$

Q.26 For the mechanism $A + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} C \qquad C \xrightarrow{k_3} D$

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

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

Q.27 The reaction of formation of phosgene from CO and Cl_2 is $CO + Cl_2 \longrightarrow COCl_2$
The proposed mechanism is

(i) $Cl_2 \underset{K-1}{\overset{K_1}{\rightleftharpoons}} 2Cl$ (fast equilibrium) (ii) $Cl + CO \underset{K-2}{\overset{K_2}{\rightleftharpoons}} COCl$ (fast equilibrium)

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

Show that the above mechanism leads to the following rate law $\frac{d[COCl_2]}{dt} = K[CO][Cl_2]^{3/2}$.

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

Q.28 The following kinetic data have been obtained at 250 °C, for the reaction

$$CO\,(g) + Cl_2\,(g) \longrightarrow COCl_2(g)$$

SET – 1

Initial Pressure CO = 400 Pa

$Cl_2 = 800 \times 10^3$ Pa

Time(sec)	Pressure of $COCl_2$ (Pa)
0	0
2072	200
4140	300
10280	375
infinity	400

SET – 2

Initial Pressure CO = 1600×10^3 Pa

$Cl_2 = 400$ Pa

Time(sec)	Pressure of $COCl_2$ (Pa)
0	0
2070	300
4140	375
infinity	400

(i) Determine the order of reaction with respect to CO and Cl_2.

(ii) Calculate the rate constant, when pressure in pascal and time in seconds.

Q.29 The decomposition of a compound P, at temperature T according to the equation

$$2P_{(g)} \longrightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$$

is the first order reaction. After 30 minutres from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 mintute, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

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

Q.30 A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to$B^{(n-2)+}$ and $B^{(n+4)+}$ to$B^{(n-1)+}$. At *t=0*, the volume of the reagent consumed is 25 ml and at t = 10 min, the volume used up is 32 ml. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

Q.31 The catalytic decomposition of formic acid may take place in two ways :

(a) $HCOOH = H_2O + CO$ (b) $HCOOH = H_2 + CO_2$.

The rate constant and activation energy for reaction (a) are 2.79×10^{-3} min^{-1} at 236°C and 12.0 kcal mole^{-1} respectively and for reaction (b) are 1.52×10^{-4} min^{-1} at 237°C and 24.5 kcal mole^{-1} respectively. Find the temperature which will give a product made up of equimolar quantities of water vapour, carbon monoxide, hydrogen and carbon dioxide.

Q.32 The rate constant for the forward reaction A → Product is given by

$$\log k\,(\text{sec}^{-1}) = 14.34 - \frac{1.25\times10^4\,K}{T}$$

and the rate constant for the reverse reaction is 1.2×10^{-4} sec^{-1} at 50°C. Calculate the value of maximum rate constant possible for the backward reaction. Given : Enthalpy of the reaction = – 478 kJ/mol.

Q.33(a) The equilibrium between two isomers 'A' and 'B' can be represented as follow .

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

Where k_1 and k_2 are first order rate constants for forward and reverse reactions respectively. Starting with a non equilibrium mixture of conc. $[A]_0 = a$ and $[B]_0 = b$, it was found that 'x' mole of 'A' has reacted after time 't'. Give an expression for rate, $\frac{dx}{dt}$, and hence show that integerated rate expression

is $$\ln\left(\frac{P}{P-x}\right) = (k_1 + k_2)\,t \quad \text{where } P = \left(\frac{k_1a - k_2b}{k_1 + k_2}\right)$$

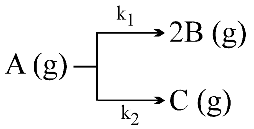
(b) After 69.3 minute $x = \frac{P}{2}$. Calculate k_1 and k_2 if equilibrium constant K = 4.

(Given : log2 = 0.3010)

Q.34 The gaseous reaction : $n_1A(g) \rightarrow n_2B(g)$ is first order with respect to A. It is studied at a constant pressure, with a_0 as the initial amount of A. Show that the volume of system at the concentration of A at time 't' are given by the expressions

$$V = V_0\left[\left(\frac{n_2}{n_1}\right) - \left(\frac{n_2}{n_1} - 1\right)\exp(-n_1kt)\right] \quad ; \quad [A]_t = [A]_0\left[\frac{\exp(-n_1kt)}{(n_2/n_1) - \{(n_2/n_1) - 1\}\exp(-n_1kt)}\right]$$

Q.35 For the following first order gaseous reaction



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

RADIOACTIVITY

Q.36 In a nature decay chain series starts with $_{90}Th^{232}$ and finally terminates at $_{82}Pb^{208}$. A thorium ore sample was found to contain 8×10^{-5} ml of helium at STP and 5×10^{-7} gm of Th^{232}. Find the age of ore sample assuming that source of He to be only due to decay of Th^{232}. Also assume complete retention of helium within the ore. (Half–life of $Th^{232} = 1.39 \times 10^{10}$Y)

Q.37 A 0.20 mL sample of a solution containing 1.0×10^{-7}Ci of $^{3}_{1}H$ is injected into the blood stream of a laboratory animal. After sfficient time for circulatory equilibrium to be established, 0.10 mL blood is found to have an activity of 20 dis/min. Calculate the blood volume of the animal.

Q.38 A sample of $^{131}_{53}I$, as iodine ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? ($t_{1/2}$ = 8 days.)

Q.39 Potassium having atomic mass=39.1u contains 93.10 atom % ^{39}K, having atomic mass 38.96371 u; 0.0118 atom % ^{40}K, which has mass of 40.0 u and is radioactive with $t_{1/2} = 1.3 \times 10^9$y and 6.88 atom % ^{41}K having a mass of 40.96184 u. Calculate the specific activity of naturally occurring potassium.

Q.40 A mixture of ^{239}Pu and ^{240}Pu has a specific activity of 6×10^9 dis/s/g. The half lives of the isotopes are 2.44×10^4 y and 6.08×10^3 y respectively. calculate the isotopic composition of this sample.

Q.41 $_{92}U^{238}$ by successive radioactive decays changes to $_{82}Pb^{206}$. A sample of uranium ore was analyzed and found to contain 1.0g of U^{238} and 0.1g of Pb^{206}. Assuming that all the Pb^{206} had accumulated due to decay of U^{238}, find out the age of the ore. (Half life of $U^{238} = 4.5 \times 10^9$ years).

Q.42 Fallout from nuclear explosions contains ^{131}I and ^{90}Sr. Calculate the time required for the activity of each of these isotopes to fall to 1.0 % of its initial value. Radioiodine and radiostrontium tend to concentrate in the thyroid and the bones, respectively, of mammals which ingest them. Which isotope is likely to produce the more serious long-term effects? Half-life of ^{131}I = 8 days, ^{90}Sr = 19.9 yrs.

Q.43 $_{84}Po^{218}$ ($t_{/12}$ = 3.05 min) decay to $_{82}Pb^{214}$ ($t_{1/2}$ = 2.68 min) by α-emission, while Pb^{214} is a β-emitter. In an experiment starting with 1 gm atom of Pure Po^{218}, how much time would be required for the number of nuclei of $_{82}Pb^{214}$ to reach maximum.

Q.44 A sample pitch blende is found to contain 50% Uranium and 2.425% Lead. Of this Lead only 93% was Pb^{206} isotope, if the disintegration contant is 1.52×10^{-10} yr^{-1}. How old could be the pitch blende deposit.

Q.45 A sample of Uraninite, a Uranium containing mineral was found on analysis to contain 0.214 gm of Pb^{206} for every gram of Uranium. Assuming that the lead all resulted from the radioactive disintegration of the Uranium since the geological formation of the Uraninite and all isotopes of Uranium other than ^{238}U can be neglected. Estimate the day when the mineral was formed in the Earth's crust. [$t_{1/2}$ of $^{238}U = 4.5 \times 10^9$ years]

EXERCISE -III

Q.1 The rate of a reaction is expressed in different ways as follows :

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

The reaction is:

(A) $4A + B \longrightarrow 2C + 3D$ (B) $B + 3D \longrightarrow 4A + 2C$

(C) $A + B \longrightarrow C + D$ (D) $B + D \longrightarrow A + C$

Q.2 Units of rate constant for first and zero order reactions in terms of molarity M unit are respectively

(A) $\sec^{-1}$, M $\sec^{-1}$ (B) $\sec^{-1}$, M (C) M $\sec^{-1}$, $\sec^{-1}$ (D) M, $\sec^{-1}$

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

(A) 1.50×10^{4} L mol^{-1} s^{-1} (B) 1.5×10^{11} L mol^{-1} s^{-1}

(C) 1.5×10^{10} L mol^{-1} s^{-1} (D) 1.5×10^{-11}

Q.4 Reaction $A + B \longrightarrow C + D$ follow's following rate law : rate $= k = [A]^{+\frac{1}{2}}[B]^{\frac{1}{2}}$. Starting with initial conc. of one mole of A and B each, what is the time taken for amount of A of become 0.25 mole. Given $k = 2.31 \times 10^{-3}\ \sec^{-1}$.

(A) 300 sec. (B) 600 sec. (C) 900 sec. (D) none of these

Q.5 Consider the following first order competing reactions:

$X \xrightarrow{k_1} A + B$ and $Y \xrightarrow{k_2} C + D$

if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their rate constants (k_2/k_1) is

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

Q.6 A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C. The energy of activation of the reaction is

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

Q.7 For the first order reaction $A \longrightarrow B + C$, carried out at 27 °C if 3.8×10^{-16} % of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is

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

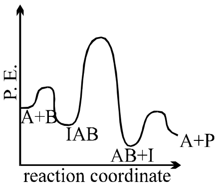
Q.8 The reactions of higher order are rare because

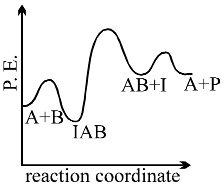
(A) many body collisions involve very high activation energy
(B) many body collisions have a very low probability
(C) many body collisions are not energetically favoured.
(D) many body collisions can take place only in the gaseous phase.

Q.9 The following mechanism has been proposed for the exothermic catalyzed complex reaction.

$$A + B \overset{\text{fast}}{\rightleftharpoons} IAB \xrightarrow{k_1} AB + I \xrightarrow{k_2} P + A$$

If k_1 is much smaller than k_2. The most suitable qualitative plot of potential energy (P.E.) versus reaction coordinate for the above reaction.

(A)


(B)


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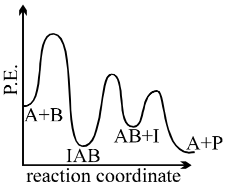

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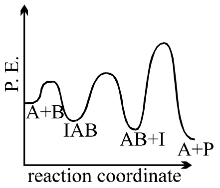


Question No. 10 to 11 (2 questions)

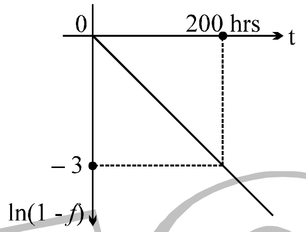
Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with respect to fraction of unoxidised metal **(1–*f*)** surface thickness relative to maximum thickness **(T)** of oxidised surface, when metal surface is exposed to air for considerable period of time

Rate law : $\frac{df}{dt} = k(1 - f)$**, where** $f = x/T$**,**

x = thickness of oxide film at time 't'

& T = thickness of oxide film at t = ∞

A graph of $\ln(1 - f)$ vs t is shown in the adjacent figure.



Q.10 The time taken for thickness to grow 50% of 'T' is

(A) 23.1 hrs (B) 46.2 hrs (C) 100 hrs (D) 92.4 hrs

Q.11 The exponential variation of 'f' with t(hrs) is given by

(A) $[1 - e^{-3t/200}]$ (B) $e^{-3t/200} - 1$ (C) $e^{-3t/200}$ (D) $e^{3t/200}$

Question No. 12 to 13 (2 questions)

For a hypothetical elementary reaction $A \begin{array}{l} \xrightarrow{k_1} 2B \\ \xrightarrow{k_2} 2C \end{array}$ where $\frac{k_1}{k_2} = \frac{1}{2}$

Initially only 2 moles of A are present.

Q.12 The total number of moles of A, B & C at the end of 50% reaction are

(A) 2 (B) 3 (C) 5 (D) None

Q.13 Number of moles of B are

(A) 2 (B) 1 (C) 0.666 (D) 0.333

Q.14 Two radioactive nuclides A and B have half lives of 50 min and 10 min respectively. A fresh sample contains the nuclides of B to be eight time that of A. How much time should elapse so that the number of nuclides of A becomes double of B

(A) 30 (B) 40 (C) 50 (D) None

Q.15 Give the correct order of initials **T** (true) or **F** (false) for following statements.

(i) On bombarding ${}_7N^{14}$ Nuclei with α-particle, the nuclei of the product formed after release of proton would be ${}_8O^{17}$.

(ii) ${}_{89}Ac^{228}$ and ${}_{90}Th^{229}$ belong respectively to Actinium and Neptunium series.

(iii) Nuclide and it's decay product after α-emission are called isodiaphers.

(iv) Half life of radium is 1580 years. Its average life will be 1097.22 years.

(A) TFTF (B) TTTF (C) FFTT (D) TFFF

EXERCISE-IV

OBJECTIVE PROBLEM

Q.1 For a first order reaction
(A) the degree of dissociation is equal to $(1 - e^{-kt})$
(B) a plot of reciprocal concentration of the reactent vs time gives a straight line.
(C) the time taken for completeion of 75% of reaction is thrice the $t_{1/2}$ of the reaction
(D) the pre-exponential factor in the Arrhenius equation has the dimensionof time, T^{-1}. **[JEE 1998]**

Q.2 The rate law for the reaction
$RCl + NaOH(aq) \longrightarrow ROH + NaCl$ is given by Rate = k[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) Decreased on increasing the temperature of reaction
(D) Unaffected by increasing the temperature of the reaction. **[JEE 1998]**

Q.3 Which of the following statement(s) is (are) correct
(A) A plot of log K_p versus 1/T is linear
(B) A plot of log [X] versus time is linear for a first order reaction, $X \longrightarrow P$
(C) A plot of log P versus 1/T is linear at constant volume.
(D) A plot of P versus 1/V is linear at constant temperature. **[JEE 1999]**

Q.4 The rate constnat for the reaction **[JEE SCR 2000]**

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is 3.0×10^{-5} sec^{-1}. if the rate is 2.4×10^{-5} mol litre^{-1} sec^{-1}, then the concentration of N_2O_5 (in mol litre^{-1}) is
(A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8

Q.5 If I is the intensity of absorbed light and C is the concentration of AB for the photochemical proces $AB + h\nu \longrightarrow AB^*$, the rate of formation of AB* is directly proportional to **[JEE SCR 2001]**
(A) C (B) I (C) I^2 (D) CI

Q.6 Consider the chemical reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$. The rate of this reaction can be expressed in term of time derivative of concentration of $N_2(g)$, $H_2(g)$ or NH_3 (g). Identify the correct relationshiop amongst the rate expressions. **[JEE SCR 2002]**
(A) Rate $= -d[N_2]/dt = -1/3\, d[H_2]/dt = 1/2 d[NH_3]/dt$
(B) Rate $= -d[N_2]/dt = -3\, d[H_2]/dt = 2d[NH_3]/dt$
(C) Rate $= d[N_2]/dt = 1/3\, d[H_2]/dt = 1/2 d[NH_3]/dt$
(D) Rate $= -d[N_2]/dt = -d[H_2]/dt = d[NH_3]/dt$

Q.7 In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in 2×10^4 sec. The rate constant of reaction in sec^{-1} is **[JEE SCR 2003]**
(A) 2×10^4 (B) 3.45×10^{-5} (C) 1.3486×10^{-4} (D) 2×10^{-4}

Q.8 The reaction, $X \longrightarrow$ Product follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M
(A) 1.73×10^{-4} M min^{-1} (B) 3.47×10^{-5} M min^{-1}
(C) 3.47×10^{-4} M min^{-1} (D) 1.73×10^{-5} M min^{-1} **[JEE SCR 2004]**

Q.9 Which of the following statement is incorrect about order of reaction? **[JEE 2005]**
(A) Order of reaction is determined experimentally
(B) It is the sum of power of concentration terms in the rate law expression
(C) It does not necessarily depend on stoichiometric coefficients
(D) Order of the reaction can not have fractional value.

RADIOACTIVITY

Q.10 Loss of a β – particle is equivalent to **[JEE 1998]**
(A) Increase of one proton only (B) Decrease of one neutron only
(C) Both (A) and (B) (D) None of these.

Q.11 Decrease in atomic number is observed during **[JEE 1998]**
(A) α – emission (B) β – emission (C) Positron emission (D) Electron capture.

Q.12 The number of neutrons accompanying the formation of ${}_{54}X^{139}$ and ${}_{38}Sr^{94}$ from the absorption of slow neutron by ${}_{92}U^{235}$ followed by nuclear fision is **[JEE 1999]**
(A) 0 (B) 2 (C) 1 (D) 3

Question No. 13 to 15 (3 questions)

Carbon 14 is used to determine the age of orgainc material. The procedure is based on the formation of ${}^{14}C$ by neutron capture in the upper atmosphere.

$$ {}_{7}N^{14} + {}_{0}n^{1} \longrightarrow {}_{6}C^{14} + {}_{1}H^{1} $$

${}^{14}C$ is absorbed by living organisms during photosynthesis. The ${}^{14}C$ content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ${}^{14}C$ in the dead being falls due to the decay which C^{14} undergoes.

$$ {}_{6}C^{14} \longrightarrow {}_{7}N^{14} + {}_{-1}e^{\circ} $$

The half life period of ${}^{14}C$ is 5770 years. The decay constant (λ) can be calculated by using the following formula $\lambda = \dfrac{0.693}{t_{1/2}}$

The comparison of the β^- activity of the dead matter with that of carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of ${}^{14}C$ to ${}^{12}C$ in living matter is $1 : 10^{12}$ **[JEE 2006]**

Q.13 Which of the following option is correct?
(A) In living organisms, circulation of ${}^{14}C$ from atmosphere is high so the carbon content is constant in organism
(B) Carbon dating can be used to find out the age of earth crust and rocks
(C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains constant in living organism
(D) Carbon dating cannot be used to determine concentration of ${}^{14}C$ in dead beings.

Q.14 What should be the age of fossil for meaningful determination of its age?
(A) 6 years (B) 6000 years
(C) 60000 years (D) it can be used to calculate any age

Q.15 A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be t_1 and t_2 at the places respectively, then

(A) The age of the fossil will increase at the place where explosion has taken place and $t_1 - t_2 = \dfrac{1}{\lambda} \ln \dfrac{C_1}{C_2}$

(B) The age of the fossil will decrease at the place where explosion has taken place and $t_1 - t_2 = \dfrac{1}{\lambda} \ln \dfrac{C_1}{C_2}$

(C) The age of fossil will be determined to be the same

(D) $\dfrac{t_1}{t_2} = \dfrac{C_1}{C_2}$

SUBJECTIVE PROBLEM

Q.1(a) In the Arrhenius equation $k = A\exp(-E/RT)$, A may be termed as the rate constant at __________. **[JEE 1997]**

(b) The rate constant for the first order decomposition of a certain reaction is discribed by the equation

$$\ln k\,(s^{-1}) = 14.34 - \frac{1.25\times10^4\,K}{T}$$

(i) What is the energy of activation for this reaction?

(ii) The rate constant at 500 K.

(iii) At what temperature will its half life period be 256 minutes? **[JEE 1997]**

(c) 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 the rate constant at 318 K and also the energy of activation. **[JEE 1997]**

(d) The rate constant for an isomerisation reaction $A \rightarrow B$ is $4.5 \times 10^{-3}\ min^{-1}$. If the initial concentration of A is 1 M. Calculate the rate of the reaction after 1 h. **[JEE 1999]**

Q.2 A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the 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 barrier by 20 kJmol^{-1}. **[JEE 2000]**

Q.3 The rate of a first order reaction is 0.04 mole litre^{-1} s^{-1} at 10 minutrs and 0.03 mol litre^{-1} s^{-1} at 20 minutes after initiation. Find the half life of the reaction. **[JEE 2001]**

Q.4 $2X(g) \longrightarrow 3Y(g) + 2Z(g)$

Time (in Min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

(a) Order of reaction (b) Rate constant

(c) Time taken for 75% completion of reaction (d) Total pressure when $P_X = 700$ mm. **[JEE 2005]**

RADIOACTIVITY

Q.5 ^{64}Cu (half-life = 12.8 hr) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay product and calculate partial half-lives for each of the decay processes. **[JEE'2002]**

Q.6 Fill in the blanks

(a) $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{137}_{52}A + ^{97}_{40}B +$ __________.

(b) $^{82}_{34}Se \longrightarrow 2\,^{0}_{-1}e +$ ______________. **[JEE 2005]**

ANSWER KEY

EXERCISE-I

RATE OF REACTION AND STOICHIOMETRIC COEFFICIENT

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

Q.2 (a) 0.019 mol L^{-1} s^{-1}, (b) 0.037 mol L^{-1} s^{-1}

Q.3 $2k_1 = k_2 = 4k_3$ Q.4 (i) $\frac{dx}{dt} = k[A][B]^2$, (ii) rate increases by 8 times

Q.5 rate increase by 27 times

Q.6 (i) $r = \frac{1}{4}\frac{d[NO]}{dt} = 9 \times 10^{-4}$ mol litre^{-1} sec^{-1}, (ii) 36×10^{-4} mol litre^{-1}sec^{-1}, (iii) 54×10^{-4} mol litre^{-1}sec^{-1}

Q.7 (i) 7.2 mol litre^{-1}min^{-1}, (ii) 7.2 mol litre^{-1} min^{-1} Q.8 1/6

ZERO ORDER

Q.9 (i) 7.2 M, (ii) Think Q.10 K = 0.01 M min^{-1}

Q.11 0.75 M Q.12 6×10^{-9} sec Q.13 1.2 hr

FIRST ORDER

Q.14 (i) 36 min., (ii) 108 min. Q.15 (i) 0.0223 min^{-1}, (ii) 62.17 min Q.17 924.362 sec

Q.18 expiry time = 41 months Q.19 $3.3 \times 10^{-4}s^{-1}$ Q.20 $k = \frac{2.303}{t}\log\frac{1}{a}$ Q.21 11.2%

ORDER OF REACTION & RATE LAW

Q.22 (a) Third order, (b) $r = k[NO]^2[H_2]$, (c) 8.85×10^{-3} M sec^{-1}.

Q.23 (a) order w.r.t NO = 2 and w.r.t Cl_2 = 1, (b) $r = K[NO]^2[Cl_2]$, (c) K = 8 $L^2mol^{-2}s^{-1}$, (d) rate = 0.256 mole $L^{-1}s^1$]

Q.24 (i) first order (ii) $k = 1.308 \times 10^{-2}$ min^{-1} (iii) 73%

Q.25 (i) rate=[A] [B] ; (ii) $k = 4 \times 10^{-2}M^{-1}s^{-1}$; (iii) rate = $2.8 \times 10^{-3}M \cdot s^{-1}$

Q.26 (i) Zero order, (ii) K = 5 Pa/s

Q.27 Zero order Q.28 (a) n =1, (b) $\frac{dx}{dt} = k[CH_3COCH_3]$, (c) 8.67×10^{-3} s^{-1}, (d) 1.56×10^{-5} M s^{-1}

HALF LIFE

Q.29 166.6 min Q.30 4.62×10^5 sec Q.32 (i) t = 13.96 hrs, (ii) 2.2176 litre

Q.33 54 min Q.34 15 min

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER INTEGRATED RATE LAW

Q.35 $k = \frac{1}{t}\ln\frac{P_3}{2(P_3 - P_2)}$ Q.36 $k = \frac{1}{t}\ln\frac{P_3}{(P_3 - P_2)}$

Q.37 $k = \frac{1}{t}\ln\frac{V_1}{(2V_1 - V_2)}$ Q.38 $k = \frac{1}{t}\ln\frac{4V_3}{5(V_3 - V_2)}$ Q.39 $k = \frac{1}{t}\ln\frac{r_\infty}{(r_\infty - r_t)}$

Q.40 8.12×10^{-6} Ms^{-1}, 0.012 atm min^{-1}

Q.41 (a) 90 mm, (b) 47 mm, (c) 6.49×10^{-2} per minutes, (d) 10.677 min.
Q.42 First order Q.43 $k_1 = 2.605 \times 10^{-3}\ min^{-1}$
Q.44 (i) $r = K[(CH_3)_2O]$, 0.000428 sec^{-1} Q.45 First order
Q.46 (a) first order, (b) 13.75 minutes, (c) 0.716
Q.47 966 min Q.48 206.9 min Q.49 11.45 days
Q.50 0.180 atm, 47.69 sec

PARALLEL AND SEQUENTIAL REACTION

Q.51 $\frac{1}{e^{(K_1+K_2)t}-1}$ Q.52 $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x}-1)$ Q.53 72.7, 22.3 Q.54 t = 4 min

TEMPERATURE DEPENDENCE OF RATE (ACTIVATION ENERGY)

Q.55 5 kJ mol^{-1} Q.56 349.1 k Q.57 55.33 kJ $mole^{-1}$ Q.58 306 k
Q.59 (a) $2.31 \times 10^{-12}\ min^{-1}$, $6.93 \times 10^{-2}\ min^{-1}$, (b) 43.85 kJ $mole^{-1}$
Q.60 rate of reaction increases 5.81×10^8 times
Q.61 10.757 k cal mol^{-1}

MECHANISM OF REACTION

Q.62 $r = K'\,[NO]^2[Br_2]$ Q.63 $r = K\,[NO]^2\,[H_2]$, where $K = k_2 \times K_1$
Q.64 $k_{eq} = 1$, rate $= k_2\,(C)\,(A_2)^{1/2}$ Q.66 (d) No, (e) mechanism (a) is incorrect

RADIOACTIVITY

Q.67 beta emitter : ^{49}Ca, ^{30}Al, 94 Kr, positron emitter : ^{195}Hg, ^{8}B, ^{150}Ho
Q.68 $^{114}_{49}In$, odd number of nucleons Q.69 (a) $^{1}_{1}H$, (b) $^{1}_{0}n$, (c) $^{6}_{3}Li$, (d) $^{0}_{+1}e$, (e) $^{0}_{-1}e$, (f) p (proton)
Q.70 d, deuteron Q.71 (a) $^{1}_{1}H$ (b) $^{64}_{28}Ni$ (c) $^{0}_{-1}\beta$ (d) $^{1}_{0}n$
Q.72 $\alpha = \frac{a-b}{4}$; $\beta = d + \frac{(a-b)}{2} - c$ Q.73 2.16×10^{12} events / min
Q.74 1.06×10^{-15} kg Q.75 $\lambda = 5.77 \times 10^{-4}\ sec^{-1}$ Q.76 32 ml
Q.77 6.25 % Q.78 2.674×10^5 dps Q.79 33.67 years Q.80 4.65 hour

PROFICIENCY TEST

Q.1
1. 3.7×10^{10} 2. β-rays 3. isobar 4. 8, 6
5. isodiaphers 6. $^{30}_{14}Si$ 7. β-particles 8. isotones
9. 10 min. 10. threshold energy 11. half 12. equal to ΔH
13. directly proportional 14. mol $L^{-1}s^{-1}$ 15. rare
16. lowering 17. faster 18. slowest 19. increases
20. 3 21. rate constant 22. 2 and 3 23. rate = $k[M]^2$
24. $1\frac{1}{2}$ 25. – k 26. Activation energy
27. higher 28. first 29. $-\frac{k}{2.303}$ 30. 1.44

Q.2
1. False 2. False 3. True 4. False
5. True 6. True 7. True 8. False
9. False 10. False 11. True 12. False
13. True 14. True 15. True 16. False
17. True 18. True 19. False 20. False

EXERCISE-II

Q.1 First order, k= 0.00144, 0.00144, 0.00145, 0.00145, 0.00150, 0.00140, average 0.00145min^{-1}

Q.2 (a) 6.25 ; (b) 14.3 ; (c) 0% Q.3 53.84 Q.4 $(d\tau/dt) = \alpha/2\tau$, –1 order

Q.5 a = b = 1 Q.6 $2 \times 10^{-2}\ \text{min}^{-1}$

Q.7 (a) $3.27 \cdot 10^{-4}\text{sec}^{-1}$; (b) 2120 sec; (c) 38.27 (measured : 55.00ml)

Q.8 (a) 43.46kJmol^{-1}, (b) 20.47 hour Q.9 % decomposition = 67.21%

Q.10 $k = 0.0327\ \text{min}^{-1}$ Q.11 B Q.12 0.537 Q.13 $k = 0.022\ \text{hr}^{-1}$

Q.14 4.83 mins Q.15 15.13 week Q.16 20 min, 28.66 min

Q.17 156 Q.18 $K_f = K_b = 0.00027\ \text{sec}^{-1}$ Q.19 0.0025 m

Q.20 $k=9.74\times10^{-5}\ \text{sec}^{-1}, k_{-1} = 4.18\times10^{-5}\text{sec}^{-1}$ Q.21 $E_f = 6 \times 10^4 J; E_b = 9.3 \times 10^4 J$

Q.23 0.26 : 1 Q.24 (b)$t_{1/2}$ = 36min

Q.26 (a) $\dfrac{d(D)}{dt} = \dfrac{k_1k_3(A)(B)}{k_2 + k_3}$; (b) $E_a = E_{a1} + E_{a3} - E_{a2}$. $A = \dfrac{A_1A_3}{A_2}$

Q.28 Set – I : $3.5 \times 10^{-4}S^{-1}$; Set – II : $6.7 \times 10^{-4}S^{-1}$

Q.29 P_t = 379.55 mm Hg, $t_{7/8}$ = 399.96 min Q.30 $0.0207\ \text{min}^{-1}$

Q.31 399^0C ; R = 1.987$\text{Kcal.mol}^{-1}\text{K}^{-1}$ Q.33 $k_2 = 2 \times 10^{-3}\ \text{sec}^{-1}, k_1 = 8 \times 10^{-3}\ \text{sec}^{-1}$

Q.35 0.805

RADIOACTIVITY

Q.36 $t = 4.89 \times 10^9$ years Q.37 V = 1.1 L Q.38 0.0958 mg

Q.39 Specific activity = 30.69 dis. $g^{-1}s^{-1}$ Q.40 ^{239}Pu = 45.1%, ^{240}Pu = 54.9%

Q.41 $t = 7.1 \times 10^8$ years Q.42 53.1 days, 132 yrs, ^{90}Sr is likely to be serious, the iodine will soon be gone

Q.43 4.125 min Q.44 3.3×10^8 years Q.45 1.4×10^9 yrs

EXERCISE-III

Q.1 B Q.2 A Q.3 D Q.4 B Q.5 D Q.6 B Q.7 C

Q.8 B Q.9 A Q.10 B Q.11 A Q.12 B Q.13 C Q.14 C

Q.15 A

EXERCISE-IV

OBJECTIVE PROBLEM

Q.1 A, D Q.2 B Q.3 A, B, D Q.4 D Q.5 B

Q.6 A Q.7 C Q.8 C Q.9 D

RADIOACTIVITY

Q.10 C Q.11 C, D Q.12 D Q.13 C Q.14 B

Q.15 A

SUBJECTIVE PROBLEM

Q.1 (a) infinte temperature ; (b) (i) 2.50×10^4 cal mol^{-1}, (ii) $2.35 \times 10^{-5}\ \text{sec}^{-1}$, (iii) 513 ;
(c) $K_{318} = 9.2 \times10^{-4}\ \text{sec}^{-1}$, E_a =18.33 K cal mol^{-1} ; (d) $A = 5.40\times10^{10}\ \text{sec}^{-1}, E_a=2.199\times10^4\ \text{Jmol}^{-1}$

Q.2 100 kJmol^{-1} Q.3 $t_{1/2}$ = 24.14 min Q.4 (a) 1, (b) $6.93 \times 10^{-3}\ \text{min}^{-1}$, (c) 200, (d) 950 mm

RADIOACTIVITY

Q.5 $^{64}_{30}$Zn , $^{64}_{28}$Ni , $(t_{1/2})_1$ = 33.68 hr, $(t_{1/2})_2$ = 67.36 hr, $(t_{1/2})_3$ = 29.76 hr Q.6 (a) $2\,^1_0n$, (b) $^{82}_{36}$Kr