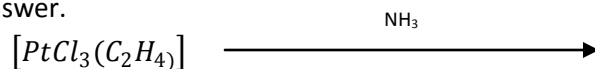


PAPER I

MODULE I

- What is lattice energy? How does it vary with the charge and distance of the ions?
 - Calculate the lattice energy of AgCl using Born-Meyer equation, given $r=3.07\text{\AA}$, $A=1.748$ and $\rho=0.345\text{\AA}$.
- Write down the Lewis structure for CNO and OCN ions and comment on each.
 - The C-Cl distance in CH_3Cl and CF_3Cl are 1.78\AA and 1.75\AA respectively. Explain.
 - Predict the shapes of the following with the VSEPR theory – i) XeF_4 ii) ClF_3 iii) SF_4 iv) PCl_4 .
 - Show with the help of molecular orbital picture that O_2 molecule is paramagnetic.
 - The dipole moment of CO_2 is zero though the C-O bonds are polar. – Explain.
- Draw the LCAO-MO diagrams for O_2 and hence predict the bond orders of O_2 , O_2^- , O_2^+ .
- Using the following data in KJmol^{-1} , calculate ΔH_{MF} and ΔH_{MF_2} and explain why MF is not a stable entity. Dissociation energy = 158; Electron affinity = -335; First ionization potential = 590, second ionization potential = 1142; sublimation energy = 201, lattice energy of MF = -795, lattice energy of MF_2 = -2665.
- HF forms stronger H-bonds than H_2O . Still ΔH_{vap} of HF is lower than that of H_2O – explain.
 - The iodine atom in IF_5 is actually slightly below the plane of the base of the tetragonal pyramid. Explain.
 - H_2O has a higher boiling point compared to H_2S , contrary to expectations – explain.
 - Using VSEPR theory predict the shapes of PCl_3F_2 .
 - Why boron is paramagnetic while carbon is diamagnetic?
 - State the Werner Coordination theory.
- Define Lattice energy of an ionic crystal. How does it vary with the charge and distance of ions? Write down the Born-Landé equation and explain the terms involved in it.
 - Predict the bond angle of NH_3 and PH_3 molecules using VSEPR theory. Explain with proper reason which one is more basic?
 - i) NaHF_2 is found but NaHCl_2 does not exist – explain.
ii) The dipole moment of water is 6.17×10^{-30} Cm. The H-O-H angle is 104° and the O-H distance is 96pm. Calculate the percent of ionic character of the O-H bond.
 - Explain –
 - H_2 exists, but He_2 does not exist.
 - Water contracts in volume on heating from 0°C to 4°C .
 - i) HF forms stronger H-bonds than H_2O , still ΔH_{vap} of HF is lower than that of H_2O – explain.
ii) Calculate the bond order of
- Using VSEPR theory predict the shapes of PCl_5 & O_8F_4 . Indicate the state of hybridization of the central atom in each case.
 - What is the difference between 'equivalent' and 'non-equivalent' hybrid orbitals? Explain with examples.
 - Explain why
 - NF_3 is pyramidal but BF_3 is planar.
 - BeCl_2 is linear.

- d) Explain why
- Oxygen molecule is paramagnetic?
 - The dipole moment of CO_2 is zero though the C-O bonds are polar.
- e) Give the structure and IUPAC name of the stereospecific product of the following reaction. Explain your answer.



8. a) Give the structure and IUPAC name of the stereospecific product of the following reaction. Explain your answer. $[\text{PtCl}_3(\text{C}_2\text{H}_4)]^- \xrightarrow{\text{NH}_3}$

b) Draw the MO diagram of CO and hence state the π -acidic ligand character of it.

c) How would you identify the cis- and trans isomers of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ by chemical methods?

9. a) Give a brief account on Schottky and Frenkel defects.

b) State Bent's rule. Discuss the bond angles $\angle\text{H-C-H}$ and $\angle\text{F-C-F}$ in CH_2F_2 in the light of Bent's rule.

c) What is ambidentate ligand?

10. Carbon monoxide and nitrogen are isoelectronic but the former is quite reactive while the later is not. Explain.

11. The dipole moment of NH_3 is greater than that of NF_3 – comment. Give the geometry of PCl_5 .

12. State with reasons the expected change in the bond order and bond distance in the following ionisable process : $\text{NO} \longrightarrow \text{NO}^+ + \text{e}^-$

13. On the basis of VSEPR theory, write the possible structures of ClF_3 and predict the most favoured structure showing your arguments.

14. Write down a Born-Haber cycle to find the heat of formation $\text{NaCl}_2(\Delta H_1)$, where 1st and 2nd ionization enthalpy of Na is 494 & 4563 KJ/mol. The electron affinity of Chlorine is 347 KJ/mol. Sublimation enthalpy of Na = 109KJ/mol. The dissociation enthalpy of $\text{Cl}_2(\text{g})=242$ KJ/mol. The lattice energy of formation is 2154 KJ/mol. Hence comment on the result.

15. Construct the M_2O diagram of NO and hence calculate the bond order of NO^+ .

16. What is the difference between ambidentate & polydentate ligand. Explain with examples.

17. How would you identify Cis and Trans isomers of $[\text{CO}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ by chemical methods.

18. The dipole moment of HCl is 1.03D. The distance between H and Cl atom is 1.29\AA . Calculate % ionic character of HCl molecule.

19. Transition metal ions often form coloured complexes. Give reasons for the same using suitable example.

i) H_2O has a higher boiling point compared to H_2S contrary to expectations- explain.

ii) HCl forms normal salt (NaCl) only, but HF can form an acid salt (KHF_2). – explain.

20. i) What is polydentate ligands? Give example.

ii) Compare the thermal stability of MgCO_3 and CaCO_3 .

iii) Write IUPAC nomenclature of the following compounds (a) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$

(b) $[\text{CoCl}(\text{NH}_3)_5]^{2+}$

iv) Calculate Limiting radius ration for cubic lattice structure.

v) The melting point of KCl is 776°C and that of AgCl is 455°C - Explain.

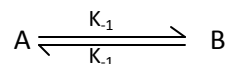
21. Calculate the total energy of an electron having mass m and radius r. give the significance of negative sign in energy of an electron.

22. Give the de Broglie hypothesis and from de Broglie equation derive the Bohr's equation.
23. How would you chemically distinguish between $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ & $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$.
24. Construct a Born Haber cycle for M^+X^- crystal (say NaCl). What is the importance of such cycle?
25. Hydrogen can be placed in the alkali-metal group or in the halogen group of the periodic table of elements". Justify the statements.
26. i) To which of the following atoms or ions Bohr's theory can be applied? H^+ , He, He^+ , Li^+ , Li^{2+} , Be^+ , Be^{2+} .
- ii) From the Bohr's energy expression for H-atom obtain Rydberg equation and hence calculate the shortest and the longest wave length limits of Lyman series in the spectrum of hydrogen atom. (Given $R_H = 109677\text{cm}^{-1}$)
- iii) Find out the ground state term symbols for carbon and nitrogen atom.
27. i) Given the first Bohr radius of H-atom = 0.529Å . calculate the first Bohr radius of He^+ ion.
- ii) The ground state electronic configuration of nitrogen $1S^2, 2S^2, 2P^3$ which is
- | | | | | | | | | | |
|----|----|---|---|---------|----|----|---|---|-------------------------------|
| 1l | ↑ | ↑ | ↑ | but not | 1l | ↑ | ↑ | ↓ | . Explain with proper reason. |
| 2S | 2P | | | | 2S | 2P | | | |
- iii) Discuss the origin and the significance of magnetic quantum number. What will be the values of l and m_l for P_z and d_z orbitals?
28. In H-atom, show that
- i) $|E_p| = 2E_k$ and
- ii) $\lambda = 2\pi a_0/n$
- where E_p = P.E. of the electron, E_k = K.E. of electron, λ = de Broglie wave length of electron, a_0 = radius of the ground state of H atom and n is the quantum number of the orbit.
29. Write down the electronic configuration of Zn^{2+} & Cr^{2+} .
30. Write down the Heisenberg's Uncertainty principle.
31. Calculate the radius of 1st Bohr's orbit.
32. a) What are the bond orders of N_2 and N_2^+ .
- b) Find out the ground state term symbols for boron ($z=5$)
- c) Give the significance of magnetic Q.N.
- d) Show that the Planck's constant and the angular momentum have the same dimension.
- e) In the ground state H-atom, the total energy of the electron is -13.6eV . Determine its kinetic energy and potential energy.
- f) Find out the ground state term symbols for $\text{Na}[z=11]$.
- g) Write down the electronic configuration of Zn^{2+} , Cr^+ , Cu^+ , Fe^{2+} .
- h) State the Hund's rule of maximum multiplicity.
- i) Write down the relation between kinetic energy of a moving particle and the wavelength associated with its value.
- j) Standard states chosen for the reactants and products.
- k) The stoichiometric representation of the reaction. Justify your answer.
33. How does solubility of a gas in case of a liquid depend on temperature?

34. One end of a capillary tube 10 cm in length is connected to water supply which has a pressure of 1.8 atm & the other end to a vessel open to air. At 25°C, the tube delivers 1.2 lit/min. Calculate diameter of the capillary if viscosity coefficient η for water at 25°C be 0.01 poise.
35. How viscosity coefficient varies with temperature in case of liquid & gas respectively?
36. i) How does surface tension of a liquid vary with temperature.
 ii) An excess pressure of 364 Pa is required to produce a hemispherical bubble at the end of a capillary tube of 0.3 mm diameter immersed in acetone. Calculate γ .
 iii) State Stokes' law.
 a) Find the change in surface energy when two identical Hg droplets of radius 2 mm merged isothermally to form one drop. Surface tension of Hg is 490 dyne cm^{-1} at that temperature.
37. The solubility product of Mg(OH)_2 is 1.4×10^{-11} at 25°C. What is the solubility of Mg(OH)_2 in gm/lit?
38. How viscosity coefficient varies with temperature in case of liquid & gas respectively?
39. Derive the expression for viscosity coefficient of gas, clearly mentioning the assumption.
40. In the absolute method of determination of viscosity coefficient (η) by Poiseuille formula. What should be the error in radius if error in η is to be kept within 4%.
41. Comment on the temperature dependence of viscosity coefficient of Liquid.
42. For the reaction –
 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) = 2\text{HI}(\text{g})$
 $K_c = 50.0$ at 448°C and $K_c = 66.9$ at 350°C. Find ΔE^0 and ΔH^0 of the reaction.
43. a) Consider the following reversible reaction $\text{A} \xrightleftharpoons[k_2]{k_1} \text{B}$ where both forward and backward reactions are of first order. Obtain an integrated rate expression that relates k_1 and k_2 with the equilibrium concentration x_e of B.
 b) (i) Explain what is the order of reaction $\text{A} \rightarrow \text{P}$, when slope of $\log(t_{1/2})$ vs, $\log[A]$ is -1.
 (ii) Concentration of reactant decreases linearly with time.
 c) At 27°C and at a pressure of 1 atm, only 0.25 fraction of the total surface is covered by molecular N_2 . What is the standard free energy change for the adsorption process at 27°C?
44. a) 'A unimolecular gaseous reaction shows second order kinetics at low pressure' – explain using Lindemann mechanism.
 b) Consider the following two competing irreversible first order reactions : $\text{A} \xrightarrow{k_1} \text{B}$ and $\text{A} \xrightarrow{k_2} \text{C}$, show that i) $[A] = [A]_0 e^{-(k_1 + k_2)t}$ ii) For the set of initial concentration $[B]_0 = [C]_0 = 0$ and $k_1/k_2 = 2$, plot $[A]$, $[B]$, $[C]$ as a function of time on the same graph.
 c) A certain reaction is 20% complete in 15 minutes at 25°C but for the same extent of reaction, it takes only 5 minutes at 35°C. What is the activation energy of the reaction?
 d) Derive the relation between equivalent conductance and specific conductance.
 e) For the consecutive reaction $\text{A} \xrightarrow{k_1} \text{B} \xrightarrow{k_2} \text{C}$, plot C vs. t on the same graph paper.
 f) Give an example of autocatalytic reaction.
 g) Plot rate vs. time for zero order and 1st order reaction.

- h) A suitable linear plot involving rate constant (k) at different temperature gives E_{act} and frequency factor A. Give the plot.
- i) Consider two reactions I and II, the frequency factor of I is 100 times that of II, the activation energy of I is 4.6 Kcal higher than that of II. Show that, the rate constants for the reactions have very nearly the same value at 227°C.
- j) At 25°C, the specific rate constant for the hydrolysis of ethyl acetate by NaOH is 6.46 lit mol⁻¹ min⁻¹. Starting with concentrations of base and ester of 0.02 moles lit⁻¹, what proportion of ester will be hydrolysed in 10 min?
- k) Derive Langmuir adsorption isotherm clearly mentioning the assumptions.
- l) Consider the following reaction
 $2NO + O_2 \longrightarrow 2NO_2$ takes place in two steps
- i) $2NO \xrightleftharpoons[K_{-1}]{K_1} N_2O_2$ ii) $N_2O_2 + O_2 \xrightarrow{K_2} 2NO_2$ (slow). Derive the rate law for the process.
- m) How does equivalent conductance vary with concentration in case of both strong and weak electrolyte?
- n) State Kohlrausch's law of independent migration of ion. Using this law, how will you get equivalent conductance of weak electrolyte at infinite dilution – explain with an example.
- o) How does specific conductance of KCl solutions vary with concentrations? Why?
- p) State Kohlrausch's law of independent migration of ions. Equivalent conductances at infinite dilution of HCl, NaCl and CH₃COONa are 426.2, 126.5 and 91 ohm⁻¹cm₂ geqv⁻¹ respectively. The specific conductance of 0.1(M) CH₃COOH solution at 25°C.
- q) Is 5.24x10⁻⁴ ohm⁻¹cm⁻¹. Calculate the degree of dissociation of 0.1(M)CH₃COOH solution.
45. a) In a particular experiment on KCl, the apparatus consisted of a tube of diameter 4.176mm & it contained an aqueous solution of KCl at a concentration of 0.021 mole/lit. A steady current of 1.82 mA was passed & the cationic boundary advanced 3.18 mm in 100 sec. Find the transport number of K⁺ & Cl⁻.
- b) What do you mean by degree of dissociation in terms of equivalent conductance?
46. The rate constant of the ionic reaction $S_2O_8^{2-} + I^- \longrightarrow$ product in aqueous medium increases in presence of KCl at a certain temperature – explain briefly.
47. Show that for nth order reaction the ratio of time taken to complete 3/4th of reaction and 1/2 of the reaction depends only on n.
48. How ionic mobility is related to ion conductance?
49. How will you get the value of E_{act} from log k vs. 1/T plot.
50. The specific conductance of pure water at 25°C is 5.55 x 10⁻⁸ ohm⁻¹cm⁻¹. $\lambda_{H^+}^0 = 350$ ohm⁻¹ cm²mole⁻¹ and $\lambda_{OH^-}^0 = 200$ ohm⁻¹ cm²mole⁻¹. Determine $\lambda_{H_2O}^0$ and K_w (ionic product of water) at 25°C.
51. Find order of reaction in the following cases
- i) $t_{1/2} \times a = \text{constant}$ (a being the initial conc, of reactant)
- ii) On doubling the concentration of reactant, rate of the reaction is doubled.

52. Show that for a first order reaction, the time required for 99.9% completion of reaction is almost 10 times for 50% completion.
53. Draw an energy profile diagram for catalysed vs. uncatalysed reaction on the same graph paper & explain the nature of graph.
54. What do you mean by primary kinetic salt effect?
55. a) Consider the following reversible reaction

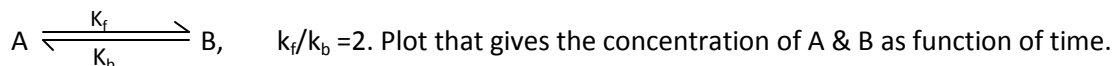


Derive that $(k_1+k_{-1})t = \ln \frac{x_e}{x_e-x}$

Where x_e is equilibrium concentration of the reactant.

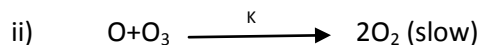
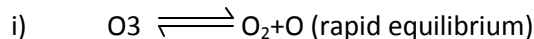
- b) At 378.5°C, the half life period for the first order thermal decomposition of ethylene oxide is 363 min and the energy of activation of reaction is 52,000 cal/mole. From these data, estimate the time required for ethylene oxide to be 75%, decomposed at 450°C.
- c) Explain how rate constant can be determined from $\log \frac{C_0}{C}$ vs t graph for 1st order reaction?
56. What do you mean by transport number of cation and anion? What is the relation between them?
57. a) The gas phase reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$ has $k = 2.05 \times 10^{13} \exp(-24.65 \text{ kcal mol}^{-1}/RT) \text{ sec}^{-1}$,
 i) give the values of A & E_a , ii) Find k at 0°C, iii) find $t_{1/2}$ at 0°C

b) Consider the following reversible reaction, first order in both directions



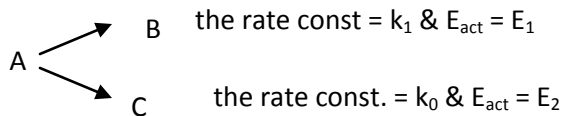
58. A zero order reaction must be a multistep one – Explain.
59. How does half life ($t_{1/2}$) depends on initial concentration of reactant in case of i) zero-order reaction ii) first order reaction.
60. Rate of reaction becomes doubled when concentration of A is doubled & the rate becomes 4 times when conc. Of B is doubled. Find out order of the reaction.
61. Justify – a catalyst cannot change the thermodynamic equilibrium of a process.

a) The decomposition of O_3 is given by



Show that the rate of reaction = $\frac{k \cdot k_1 [O_3]^2}{[O_2]}$ where k_1 is equilibrium constant for first step.

b) Consider a simultaneous reaction



If E be the total activation energy, prove that $E = \frac{E_1 k_1 + E_2 k_2}{k_1 + k_2}$

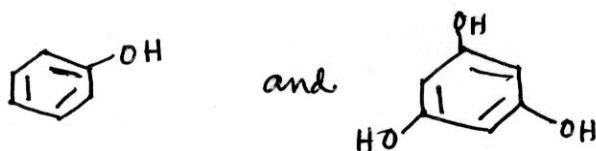
62. At 10°C the ionic product of water is 0.314×10^{-14} and at 34°C it is 2.16×10^{-14} . Calculate the heat of formation of H_2O from H^{\oplus} and OH^{\ominus} ions.
63. An aqueous solution at 25°C is 0.01 molar in propionic acid and 0.02 molar in sodium-propionate. Find i) hydrogen ion concentration and ii) degree of dissociation [$k_a = 1.34 \times 10^{-5}$]
64. A solution composed of 0.05 molar benzoic acid & 0.1 molar sodium benzoate gives a pH of 4.50 at 25°C . Find the dissociation constant of the acid.

PAPER I
MODULE II

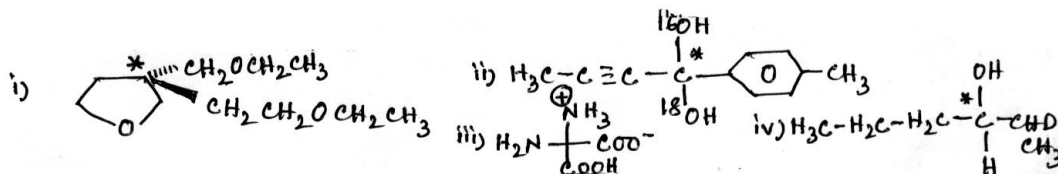
1. What is topomerisation?
2. Draw all possible conformations of cis and trans 1,3-dimethylelohexane.
3. What are the elements of symmetry in triphenylene?
4. What do you mean by atropisomerism?
5. What do you mean by 'Butane-gauche' interaction?
6. "The kinetic order of a solvolysis reaction can not be used as a criterion of its mechanism" – Comment on the statement.
7. $\text{CH}_3\text{CH}_2\text{Cl}$ hydrolyses slowly in the aq. Medium but the reaction is rapid in the presence of catalytic amount of KI – Explain why it is so.
8. ROH reacts with NaBr in the presence of H_2SO_4 to give RBr. Why is H_2SO_4 required?
9. Justify the following facts:
 - i) Triphenylmethyl cation is so stable that some of its salts can be stored for months.
 - ii) A solution of triphenyl acetic acid in concentrated H_2SO_4 affords MeOCPh_3 when poured into methanol.
10. a) The following fulvalenes are significantly polar – explain



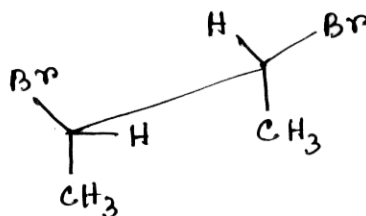
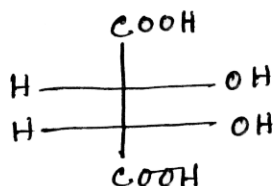
- b) Draw the orbital diagram of the following compound $\text{HC} \equiv \text{C} - \text{CH} = \text{N}^+ - \text{Me}$ (syn)
- c) Compare the aromatic character of pyrrole, thiophene and furan.
- d) Which one is expected to have higher 'enol' content and why?



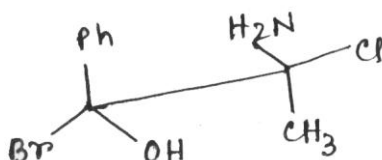
11. a) Calculate $[\alpha]_D^{25}$ of 1(M) solution of 2-Chloropentane in a 10 cm cell when the observed rotation is $+3.64^\circ$
- b) Find out the absolute configuration of the asterisked chiral centres of each of the following compounds. Give explanation in each case :



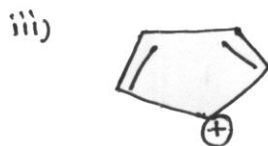
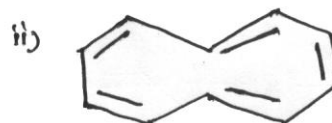
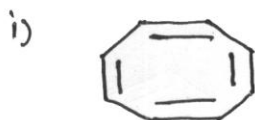
- c) What is meant by racemisation? Active 2-Benzoyl propanoic acid undergoes racemisation, when treated with $NaOEt$ in ethanol – give an explanation.
12. a) Stilbene has two diastereoisomers, one having homotopic and other enantiotopic faces. Write down the structures of diastereoisomers and identify the enantiotopic faces.
- b) Write down the following interconversions –
- i) Fisher to Sawhorse & vice versa



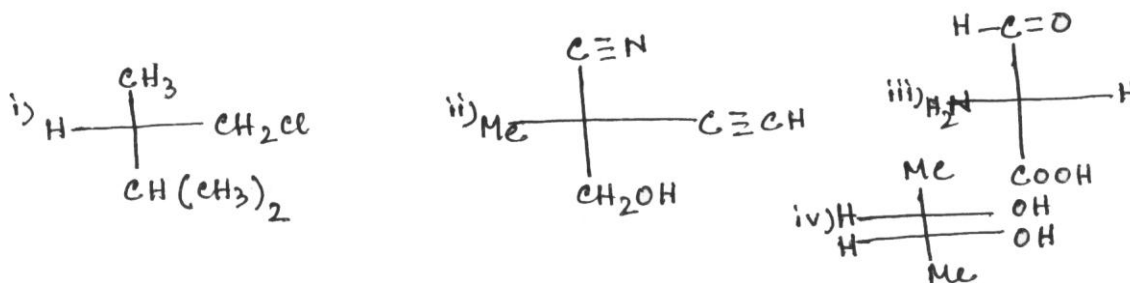
- ii) Sawhorse to Newman to Fischer



- c) Compare the boiling points of salicyl-aldehyde and p-hydroxybenzaldehyde. Give reasons.
- d) Draw the structure of the stable conformations of trans-1,3-diteriaru butyl cyclohexane with reason.
- e) Draw potential energy diagram of butane as a function of a dihedral angle ϕ about C_2-C_3 .
13. The observed order of basicity of methylamines in water is $(CH_3)_2NH > H_3C-NH_2 > (CH_3)_3N$, whereas that in gas phase is $(CH_3)_3N > (CH_3)_2NH > H_3CNH_2$. Explain these observations.
14. Explain why maleic acid, ($pK_{a1} = 1.92$; $pK_{a2} = 6.04$) is stronger for first ionization but weaker for the second than the isomeric fumaric acid ($pK_{a1}=3.03$; $pK_{a2}=4.44$).
15. Which of the following compounds are aromatic, anti-aromatic or non-aromatic? Justify.



16. Identify each of the following as R or S.



17. a) Draw all the stereoisomers of 3-Chloro-2-pentanol; $\text{CH}_3\text{CH}(\text{OH})\text{CHClCH}_2\text{CH}_3$

b) Give the stereochemical relationship of the stereoisomers.

c) Which one is expected to have higher enol content and why?



d) Compare the boiling points of salicylaldehyde and p-hydroxy benzaldehyde. Give reasons.

e) Compare the basicity of MeNH_2 and Me_3N in water and chlorobenzene.

18. a) Draw erythro-3-bromo-2-butanol in Newman, Sawhorse and Flying wedge formula.

b) Draw potential energy diagram of 1-propanol as a function of dihedral angle (ϕ) about $\text{C}_1\text{-C}_2$ bond.

c) Cis-1,2 Dibromocyclohexane represents a chiral molecule but it can not be resolved. Comment on it.

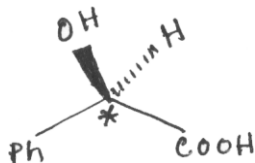
19. Comment on the 1st and 2nd acidity of maleic acid and fumaric acid.

20. a) Write the structure of D-glyceraldehyde and L-Alanine in Fisher projection formula.

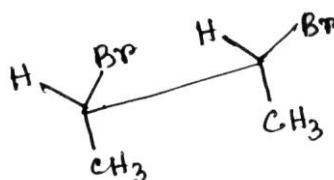
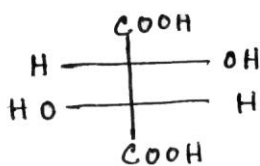
b) What is optical purity? What is resolution? Schematically represent how can you separate (+) and (-) acid form their mixture.

c) Write down the structure of anti-ethylmethylketoxime and anti benzaldoxime.

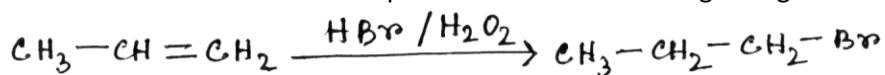
d) Find out the absolute configuration of the asterisked chiral centers of each of the following compounds:



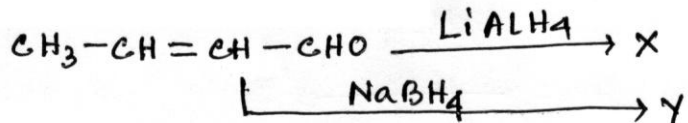
21. a) Write down the following inter conversions-Fisher to Sawhorse and vice versa.



- b) Write down the mechanistic steps involved in the following change



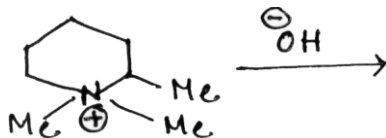
- c) Why dry HCl is used in formation of acetal – explain.
d) Give the products of the following reactions



22. a) Arrange the following compounds in increasing order of enol contents of them.



- b) Explain – Alkaline hydrolysis of RCH_2Cl to RCH_2OH is slow, but the reaction is rapid if catalytic amount of KI are added to the reaction mixture
c) Identify the major product of this reaction. Explain the mechanism.

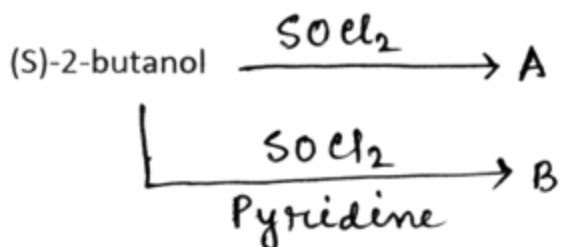


- d) Explain the mechanism of conversion of benzene to nitrobenzene with a proper energy profile diagram.

23. a) Give the mechanism of sulphonation of benzene and how can you establish the mechanism using isotope.

- b) $\text{CH}_3\text{COCH}_2\text{Cl}$ is an effective substrate for $\text{S}_{\text{N}}2$ reaction – explain.

c)

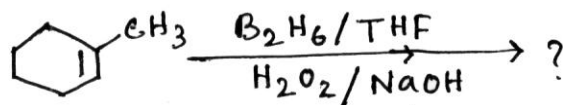


identify A and B. Explain the mechanisms and stereochemistry of the reactions.

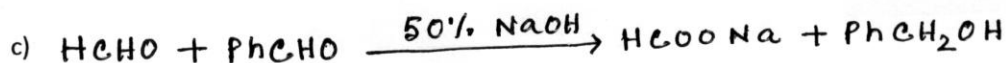
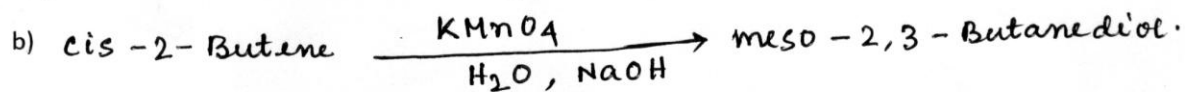
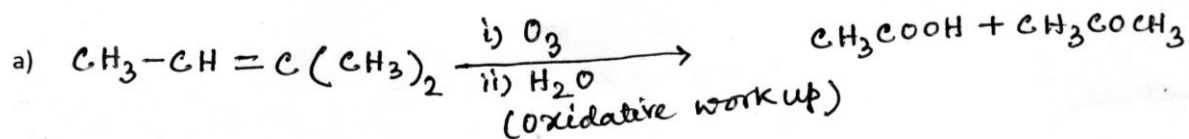
- d) The energy barrier between the two chair conformations of cyclohexane is 44 KJ/mol. Draw the energy diagram along with ring inversion for the above.

24. a) When butanamide is treated with bromine in aqueous NaOH solution, N,N dipropylurea is recovered along with n-propylamine – explain.

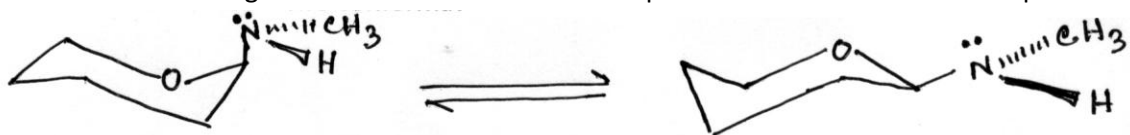
25. predict the product & suggest a mechanism for the following reaction :



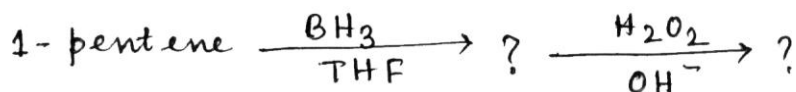
26. Write down the mechanism of the following transformations.



27. Between the following two conformations find out the preferred conformation with explanation

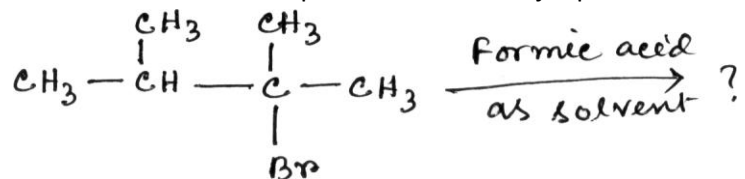


28. a) Predict the principal organic product of the following reaction



Give the mechanism of the reactions.

b) Give the mechanistic steps and mark the major product for the following reaction :



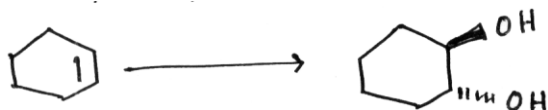
29. a) *Cis*-butenedioic acid (Maleic acid) is a much stronger acid than *trans*-butenedioic acid (Fumaric acid) – Explain.

b) The pK_a values of MeNH_2 , Me_2NH , Me_3N are 10.64, 10.77 and 9.80 respectively – Explain.

c) Give equations for the tautomerism in which each of the following compounds is the more stable tautomer.



30. How would you carry out the following transformation:



31. Predict the products of the following reactions. Give stereochemistry when it is appropriate.

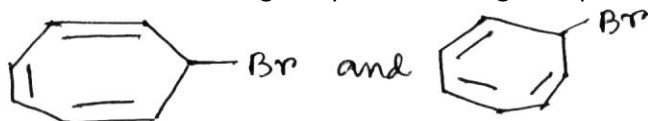


32. a) Compound (I) is readily soluble in aqueous NaOH and gives a red colour with FeCl_3 solution while compound (II) does neither. Justify the observation.



33. a) Draw the orbital picture of $\text{CH}_3\text{COCH}=\text{CH}_2$. Write state of hybridization of each carbon atom.

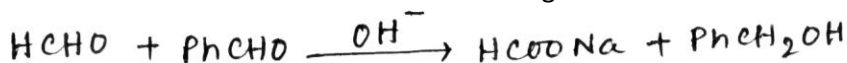
b) Which of the following compounds has higher dipole moment and why?



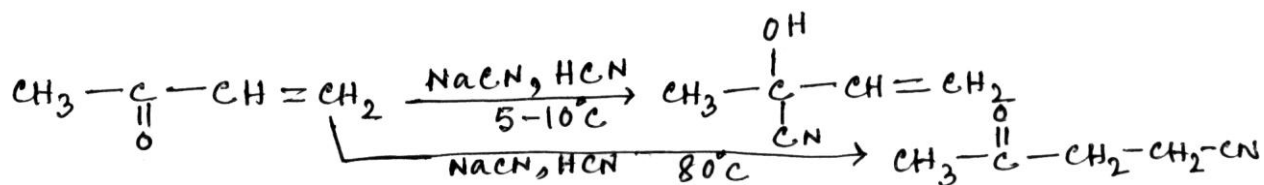
c) What product do you expect when $\text{Me}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ (1 mol) is treated with mepba (1 mol)?

d) Explain the role of Li^+ in LiAlH_4 reduction of carbonyl compound.

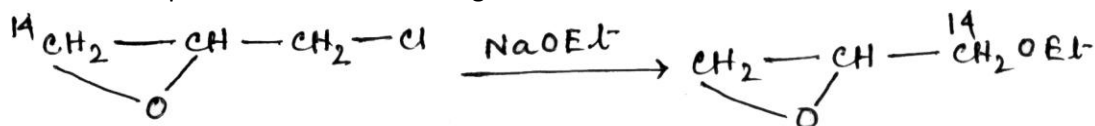
e) Give the suitable mechanism for the following reaction



34. a) Explain the following observations



b) Provide an explanation for the following transformation



35. a) Arrange the following carboxylic acids in increasing order of acid strength. Explain with proper reason – benzoic acid, salicylic acid, phydroxy benzoic acid, 2,6-dihydroxy benzoic acid.

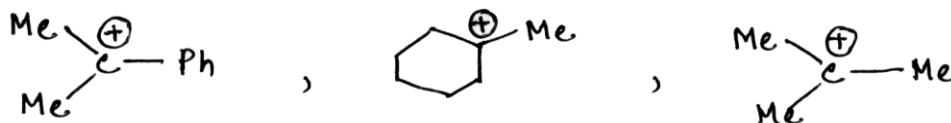
b) How would you explain the formation of but-2-ene as the major product in the reaction of 2-bromobutane with NaOEt/EtOH .

c) Draw the energy profile diagram for the sulphonation of naphthalene with concentrated sulphuric acid. With the help of this diagram comment on the structure of the major product under each of the following conditions –

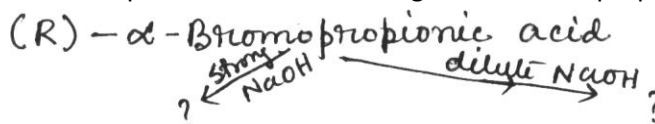
i) The reaction is performed at 160°C

ii) The reaction is performed at 80°C

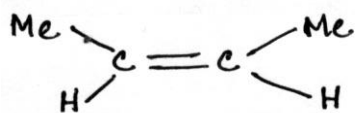
36. a) Compare the dipole moments of furan and pyrrole.
 b) Is pyridine more basic than pyrrole – Explain.
 c) Draw the energy profile diagram of a S_N1 reaction. Comment on the stereochemistry of the process if one starts with a chiral compound. Illustrate your answer with one example.
37. a) i) Comment on relative stability of the following carbocation.



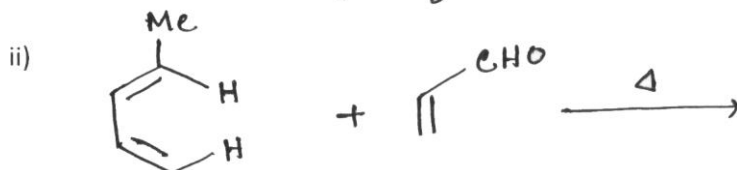
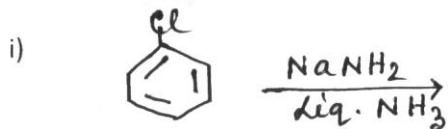
- ii) Compare the strength of the basis methylamine, dimethyl amine and trimethyl amine in aqueous medium.
- b) $(CH_3)_3C-Cl$ under acetolysis at faster rate than $(CD_3)_3C-Cl$ in presence of $NaOAc-ACOH$. Explain the nature of kinetic isotopic effect and mechanism involved in the above reaction.
- c) Write the products in the following reaction with proper explanation



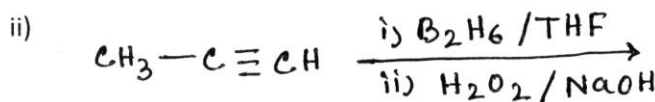
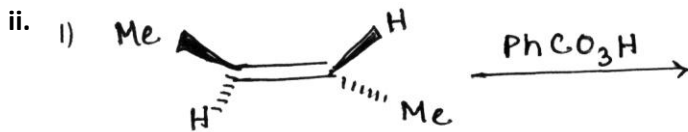
38. a) “Addition of singlet carbene to a dofin is stereospecific whereas addition of triplet carbene is non stereospecific” – Explain.
 b) What do you mean by “nonclassical carbocations”? in what respect they differ from “classical carbocations”? Give two examples of “nonclassical carbocations”.
39. a) What are singlet & triplet carbenes? Draw their orbital diagrams. While singlet carbenes in addition to double bonds with retention of stereochemical identity of almene, the addition of triplet carbenes lead to a loss of stereochemical identity. Explain mechanistically with reference to addition to



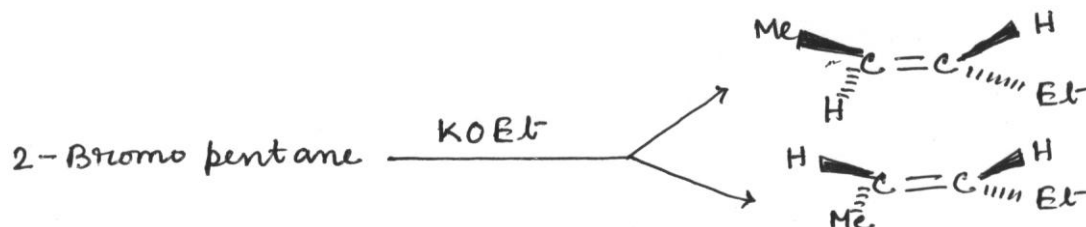
- b) Predict the products of the following reactions and suggest possible mechanism.



- c) Acetals are stable in alkali not in acid – explain.
40. a) $LiAlH_4$ is more powerful reducing agent than $NaBH_4$. – Why?
- i. Cyclopentadiene gives Diels-Alder reaction at faster rate than 1,3-butadiene – Explain.



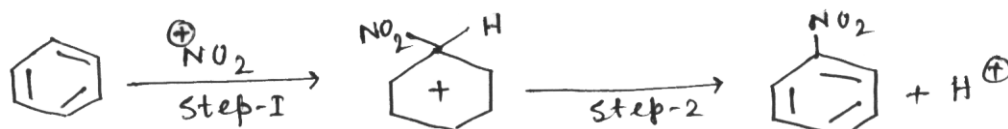
- iii) Give an example of mixed aldol condensation reaction with mechanism.
- iii. What do you mean by primary and secondary kinetic isotope effect? Explain with one example in each case.
- iv. Account for the yields of the following reactions



- v. Write down the names and the structure of the elimination products for the following elimination reactions

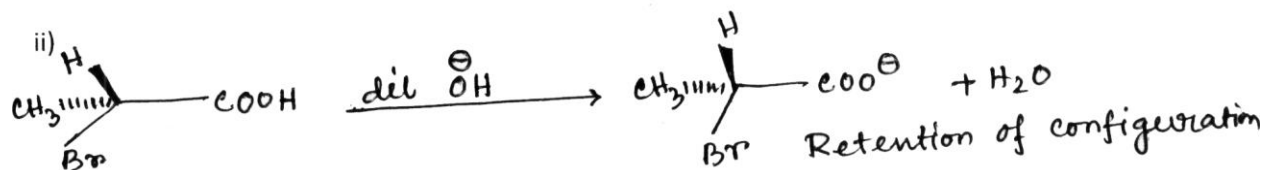


- vi. i) Acetamide is feebly basic, though the N atom possesses a lone-pair of electrons – explain.
 ii) Cyclopentane-1,2-dione exists almost 100% in the enol form – Explain.
41. a) i) Which one is more stable? Acetic acid or acetate in aqueous solution Benzene or cyclohexene.
 ii) Why does CH_3COOH behave as an acid in aqueous medium?
- b) i) Write down the difference between π -complex and σ -complex.
 ii) Aniline is less basic than methylamine in basic medium – Explain.
- c) i) The mechanism for nitration of benzene involves two steps as given below

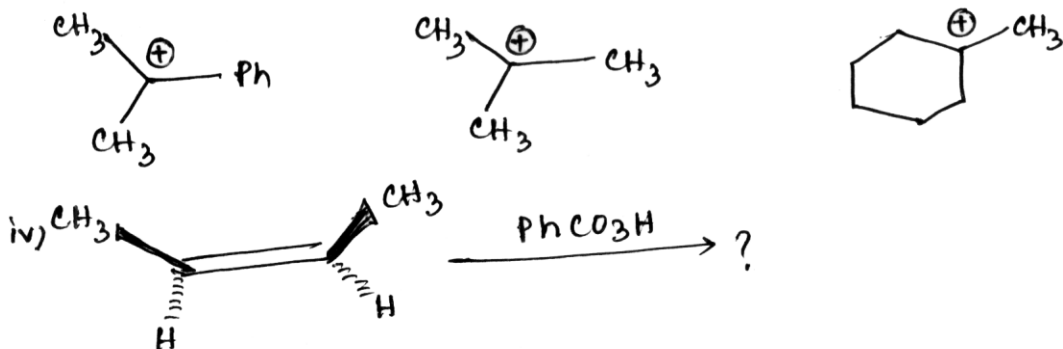


in the reaction $K_H/K_D=1.0$, which one is the R.D. step?

- ii) Explain the stereochemistry for the reaction



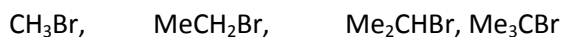
iii) Comment on the relative stability of the following carbocations.



d) Compare the reactivity of pyrrole, furan and thiophene towards electrophilic substitution reactions.

42. a) What is Keto-enol tautomerism?

b) Compare the rate of S_N1 reaction with base (OH^-) for the following halides:



vii. What is $E1CB$ reaction – explain.

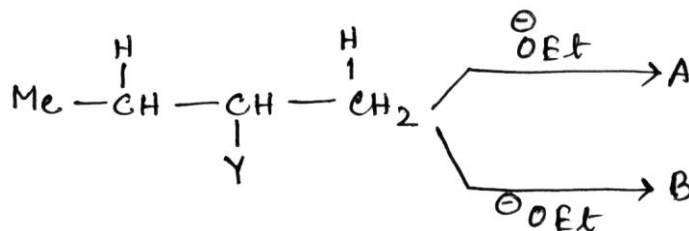
viii. What is tautomerism? Give an example of ring-chain tautomerism.

43. Why peroxide effect is not applicable for addition of HCl and HI with alkene, but it is applicable for HBr addition – explain.

44. Among the two compounds,

$MeCH_2 - CHMeBr$ & $MeCH_2 - CMe_2Br$, which has higher yield in $E1$ reaction – explain.

45. State the Hofmann & Saytzev rule for $E2$ elimination reaction. What will be Hofmann (A) & Saytzev (B) product for the following compound.



PAPER III
MODULE V

1. Efficiency of a Carnot cycle lies between 0 and 1 – explain
2. Show that for an open system $(\delta u / \delta n_i)_{S,V,n_j} = (\delta H / \delta n_i)_{S,P,n_j}$
3. Calculate ΔS for the process $\text{H}_2\text{O} (1, -10^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -10^\circ\text{C})$. Specific heat of water and ice over the temp range is 1.0 and 0.5 Cal/K/gm respectively and latent heat of fusion of ice is 80 Cal/gm.
4. The slope of adiabat is steeper than isothermal. – Justify.
5. State the following properties as intensive or extensive.
 - i) Chemical Potential ii) Enthalpy iii) Pressure iv) Surface tension
6. Derive the relation between the enthalpy of a reaction at constant volume & enthalpy of a reaction at constant pressure.
7. Calculate the enthalpy change at 1500K for the reaction $2\text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) = 2\text{H}_2\text{O} (\text{g})$ from the following data.
 $\Delta H_{300\text{K}} = 115.0 \text{ Kcal}$ and the values of $C_p(\text{cal/deg/mole})$ are for $\text{H}_2 (\text{g}) = 6.95 - 0.0002T$, $\text{O}_2 (\text{g}) = 6.10 + 0.0032T$ and $\text{H}_2\text{O} (\text{g}) = 7.19 + 0.0024T$
8. Prove that $C_p - C_v = \alpha^2 TV / \beta$
9. Derive Gibbs – Helmholtz equation.
10. Show that $(\delta u / \delta v)_T = 0$ for ideal gas & $(\delta u / \delta v)_T = a / v^2$ for real gas, ($\eta = 1 \text{ mol}$)
11. Deduce the relationship : $\mu = -1/C_p (\delta H / \delta p)_T$ for Joule Thomson expansion.
12. Heat of neutralization of HCN and NaOH is -2900 cal, Heat of reaction -13,800 cal. Calculate the heat of ionization of one mole of HCN.
13. Chemical potential is defined as $\mu_i = (\delta G / \delta n_i)_{T,p,n_j}$ i # j show that $(\delta \mu_i / \delta T)_{p,n_j} = -\bar{S}_i$
14. Draw T-S diagram for an ideal gas which undergoes cannot cycle & calculate the work obtained from the cycle & efficiency of the system.
15. One mole of an ideal gas expands from 10 lit to 50 lit at 27°C in the following two ways –
 - i. Isothermally reversibly
 - ii. Against a constant pressure of 1 atm.
 Show by calculation in which case, more heat will be absorbed during expansion.
16. Show that $C_p - C_v = nR$ for n mole of an ideal gas.
17. Prove that $(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V$
18. Derive Nernst distribution law.
19. How does distribution coefficient depend on temperature?
20. Show that $\frac{\partial (\frac{\Delta G}{T})}{\partial (\frac{1}{T})} = \Delta H$
21. a) State Hess's law of constant heat summation.
 b) ΔH of formation of $\text{H}_2\text{O}(1)$ is -68 k cal at 25°C . Calculate ΔH at 100°C , assuming the molar heat capacities of $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(1)$ to be 7.0, 7.0 and 18.0 cal k^{-1} respectively.

c) Using Maxwell's relationship, prove that

$$\left(\frac{\partial S}{\partial P}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_S$$

d) Show that $\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\Delta H/T^2$

22. a) The resistance of 0.01(N) KCl solution of specific conductance $0.00141 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C , when placed in a conductivity cell was found to be 71 ohms at the same temperature. The same cell when filled with pure water, offered a resistance of 1.82×10^6 ohms. The ionic mobilities at infinite dilution of H^+ & OH^- ions are 363×10^{-5} and $205 \times 10^{-5} \text{ cm}^2 \text{ volt}^{-1} \text{ s}^{-1}$ respectively. Calculate (i) cell constant (ii) Transport no. of H^+ & OH^- (iii) The ionic product of water at 25°C (iv) The pH of water.

b) In case of weak electrolyte, how the equivalent conductance varies with dilution?

23. a) Prove the equivalence of Clausius statement and Kelvin-Planck's statement of the second Law of thermodynamics.

24. Justify or criticize that dG is always negative for any spontaneous process.

25. Multistep work of expansion is reversible in nature – explain graphically.

26. Calculate the entropy of mixing of 2 moles of N_2 and 3 moles of H_2 behaving as ideal gases.

27. Derive Clapeyron equation and integrate it to obtain the following relationship for solid \rightleftharpoons Liquid transformation.

$$\Delta P = \frac{\Delta H_{fns}}{\Delta V_{fns}} \cdot \frac{\Delta T}{T_m} \quad \text{where } \Delta T \text{ is the increase in melting point corresponding to the increase in pressure, } \Delta P.$$

28. Define chemical potential. Is it an extensive or intensive property?

29. Plot $\ln K_p$ vs $1/T$ for i) exothermic reaction ii) endothermic reaction

30. a) i) Show graphically that the reversible work of compression is minimum. ii) Justify for an irreversible process, ΔS (system +surrounding) is positive.

b) Show that $\mu_{J,T} = \frac{V}{C_p}(T\alpha - 1)$. Where α is temperature coefficient of volume expansion.

31. a) Find out the relation between C_p and C_v for an ideal gas.

b) The molar heat capacity at constant volume of $\text{O}_2(\text{g})$ is given by

$$C_v = \alpha + \beta T + \gamma T^2 \quad \text{where } \alpha = 17.23 \text{ J K}^{-1} \text{ mol}^{-1}, \beta = 13.61 \times 10^{-3} \text{ J K}^{-2} \text{ mol}^{-1}, \gamma = 42.55 \times 10^{-7} \text{ J K}^{-3} \text{ mol}^{-1}. \text{ What is the change in molar internal energy when } \text{O}_2 \text{ is heated from } 298 \text{ to } 500 \text{ K?}$$

c) What is Joule-Thomson co-efficient? Explain the value of it for a gas obeying this, given gas equation $P(V-b)=RT$.

d) What do you mean by "heat of formation" of any compound?

e) From the Maxwell relationship, prove that $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

32. a) Prove that for an ideal gas $\left(\frac{\partial H}{\partial V}\right)_T = 0 = \left(\frac{\partial H}{\partial P}\right)_T$

b) Joule-Thompson expansion is an isenthalpic process – explain.

c) Form 1st law of thermodynamics, show that E is a state function.

d) Free expansion of a real gas occurring in an adiabatic enclosure is isothermal – justify the statement.

33. State Stoke's law.

34. Write the relation between enthalpy change of a reaction with change of temperature from T_1 to T_2 . ($T_2 > T_1$).
35. a) From Clausius inequality, show that $dS \geq dQ/T$
 b) For adiabatic reversible expansion of an ideal gas from $P_1, V_1 \rightarrow P_2, V_2$ show that $P_1 V_1^\gamma = P_2 V_2^\gamma$,
 $\gamma =$ heat capacity of the gas.
36. Show that for spontaneity of a process, $dH_{p,s} \leq 0$
37. 0.1 mole of a mono-atomic perfect gas with C_v independent of temperature is made to undergo a reversible cyclic process consisting of the following steps:
 State 1 (1 lit, 1 atm \rightarrow State 2 (1 lit, 3 atm)
 State 2 \rightarrow State 3 (2 lit, 3 atm)
 State 3 \rightarrow State 4 (2 lit, 1 atm)
 State 4 \rightarrow State 1
 Calculate q , W , δU for each step and for the complete cycle. Comment on thermodynamic nature of these functions on the basis of evaluated values.
38. Derive thermodynamic equation of state $(\frac{\partial H}{\partial P})_T = V - T(\frac{\partial V}{\partial T})_P$
39. Calculate heat of formation of Sucrose ($C_{12}H_{22}O_{11}$). Heat of combustion of sucrose, C and H are 1348.90, 44.05 and 68.32 Kcal/mol respectively.
40. Show that Vant Hoff isobar for liquid equilibrium vapour reduces to Clausius Clapeyron equation.
41. What do you mean by heat of neutralization?
42. Show that $C_p - C_v = T(\frac{\partial P}{\partial T})_v (\frac{\partial V}{\partial T})_P$ and hence prove that $C_p - C_v$ for water at 4°C the temperature at which the density of water is maximum.
43. The decomposition of Ammonium Carbonate takes place according to $\text{NH}_2\text{COONH}_4 (\text{s}) = 2\text{NH}_3 (\text{g}) + \text{CO}_2 (\text{g})$. Show that if all $\text{NH}_3 (\text{g})$ and $\text{CO}_2 (\text{g})$ results from decomposition of Ammonium Carbamate $K_p = \frac{4}{27}P^3$, where P is the total pressure at equilibrium.
44. For the equation $\text{H}_2\text{O} (\text{g}) = \text{H}_2 (\text{g}) + \frac{1}{2} \text{O}_2 (\text{g})$
 $\Delta H^0 = 242\text{KJ/mol}$ at 290 K. Find out ΔH^0 310 K. Given, $C_p(\text{H}_2\text{O}, \text{g}) = 310$ K. Given, $C_p(\text{H}_2\text{O}, \text{g}) = 35.5$, $C_p(\text{H}_2, \text{g}) = 28.8$ & $C_p(\text{O}_2, \text{g}) = 29.1$. All unites of J/mol/K
45. Show that $(\frac{\partial S}{\partial V})_p = (\frac{\partial P}{\partial T})_s$
46. For a certain reaction $\Delta G = 13580 + (16.1)T \log_{10} T - 72.59T$. Find ΔS and ΔH of the reaction at 27°C .
47. Find the conditions of equilibrium and spontaneity of a process in terms of Gibbs free energy using Clausius Inequality.
48. ΔH^0 and ΔG^0 for the reaction $\text{Br}_2 (\text{g}) \rightleftharpoons 2\text{Br} (\text{g})$ is -320 cal and -1440 cal respectively at 25°C . Calculate the value of K_p at 500°C .
49. Classify each of the following properties are intensive or extensive (i) viscosity coefficient (ii) Gibbs free energy (iii) Volume (iv) Pressure.
50. Prove that $(\frac{\partial P}{\partial T})_v = \frac{\alpha}{\beta}$
51. For which of the following system, energy is conserved in every process?

- i. A closed system ii. An open system iii. An isolated system iv. A system enclosed in adiabatic walls.
52. a) Show that for a Van-der Waals gas, $(\frac{\partial C_v}{\partial V})_T = 0$
 b) Gibbs' energy of a pure substance always decreases with increase of temperature at constant pressure – justify.
 c) Classify the following systems as open, closed or isolated
 i) Thermoflask
 ii) Human Body
 iii) Clinical thermometer
 iv) A solution being boiled under reflux.
 d) One often writes $dE = C_v dT$. Explain whether the statement is always true.
 e) An ideal gas undergoes compression under the condition $TV^{\gamma-1} = \text{constant}$ [$\gamma = C_p/C_v$]
53. Prove that $(\frac{\partial V}{\partial S})_T = (\frac{\partial T}{\partial P})_S$
54. Plot μ vs T for solid, liquid & vapour state on the same graph paper.
55. Prove that $(\frac{\partial H}{\partial P})_T = V(1 - \alpha T)$
56. Show that Clausius-Clapeyron equation can be derived from Vant-Hoff equation.
57. The latent heat of fusion of ice at 0°C being 1440Cal/mole and heat capacity of ice per mole being 8.7 Cal/mole . Calculate latent heat of fusion at -20°C .
58. The enthalpy of vapourisation of water is 40.69 KJ/mol , the molar volume of liquid water is $0.019 \times 10^{-2}\text{ m}^3/\text{mol}$ and molar volume of steam is $30.199 \times 10^{-3}\text{ m}^3/\text{mol}$, all at 100°C and 1 atm . Calculate the rate of change in boiling point of water at 100°C with atmospheric pressure.
59. Draw and explain phase diagram of H_2O .
60. Derive the relation between K_p and K_c .
61. Prove that $C_p - C_v = -T((\frac{\partial P}{\partial V})_T(\frac{\partial V}{\partial T})_P)^2$. Hence prove that $C_p \geq C_v$ always.
62. At 2000K , the free energy change (in Cal) for the reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ is given by $\Delta G^0 = 22,000 - 2.5T$. Calculate K_p at this temperature.
63. Prove that $C_p - C_v = [V - (\frac{\partial H}{\partial P})_T](\frac{\partial P}{\partial T})_V$
64. Derive Vant Hoff equation using Vant Hoff reaction isotherm.
65. For the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$. calculate K_p and K_c at 300K and 1 atm from the following standard free energy of formation at 300K .
 $\Delta G_T^0(\text{N}_2\text{O}_4) = 24.4\text{ KCal/mol}$ $\Delta G_T^0(\text{NO}_2) = 12.3\text{ Kcal/mol}$
 At what pressure would N_2O_4 be 50% dissociated at 300K ?
66. i) Show that $(\frac{\partial H}{\partial P})_T = -C_{p\mu j, T}$
 ii) Draw and explain T-S diagram for an ideal gas which undergoes the Carnot's Cycle. What does the enclosed area signify?
 iii) 0.5 mol of an ideal mono atomic gas initially at 5 atm pressure and 0°C is allowed to expand against a constant external pressure of 0.5 atm . Conditions are such that the final volume is 10 times the initial volume, the final gas pressure equals to the external pressure. Calculate W , q , ΔE , ΔH for the process.

- iv) $\int_t^2 dq_{rev}$ is an inexact differential but $\int_t^2 dq_{rev}/T$ is an exact differential – explain.
- v) Calculate ΔA for vapourisation of 0.1 mole H_2O at 1 atm pressure and $100^\circ C$ temperature [Given volume of H_2O (l) at $100^\circ C$ is 18.8 ml mol^{-1} and that of H_2O (g) is 30.6 ml mol^{-1}].
- vi) For an irreversible adiabatic process, show that $dS > 0$ always.
67. a) The partition coefficient of iodine between CS_2 & water is 62.5. When iodine is distributed between CS_2 & KI solution (containing 6.40 gm/lit) the iodine concentration in CS_2 layer is 0.190 mole/lit & the total iodine in aqueous layer is 0.030 mole/lit. Find out the equilibrium constant for the reaction $KI + I_2 \rightleftharpoons KI_3$.
- b) Draw phase diagram of CO_2 & explain the nature of curve.
68. a) The heat of neutralization of HCN by NaOH is 2900 cal. The heat of ionization of one mole of HCN is 13800 cal. Calculate the heat of reaction for the process $H^+ + OH^- = H_2O$.
69. Derive thermodynamically Vant Hoff's Reaction isotherm.
70. For the reaction at $25^\circ C$, $PCl_5 (g) = PCl_3 (g) + Cl_2 (g)$, $\Delta H = 22 \text{ Kcal/mole}$. Calculate K_p at $25^\circ C$ & at $600^\circ C$, assuming ΔH to be independent of temperature. Give standard free energy of formation ΔG_T^0 (in Kcal/mole) at $25^\circ C$, $Cl_2 (g) = 0.00$, $PCl_3 = -68.42$, $PCl_5 (g) = 77.6$
71. Show that $(\frac{\partial E}{\partial V})_T = a/V^2$ for the gas obeying the equation $(P + a/V^2)(V - b) = RT$
72. a) State Hardy-Schulze rule.
- b) Derive the expression of elevation of boiling point, clearly mentioning the assumptions.
- c) Calculate the osmotic pressure at $25^\circ C$ of a solution containing 1 gm glucose & 1 gm sucrose per lit. If the solution is a single 2 gm substance & osmotic pressure is same, what will be its mol. wt.?
- d) What are the differences between lyophobic sol and lyophilic sol criteria for acceptable wave function.
- e) Show that in a binary mixture, if one constituent follows Raoult's law, then the other constituent will also follow Raoult's law.
- f) Find out osmotic pressure of a 0.001 (M) aq. K_2SO_4 solution at $27^\circ C$
- g) Boiling point of acetone is $56.5^\circ C$ and its latent heat of vaporization is 6920 cal/mol. Hence, calculate the molal boiling point elevation constant of acetone.
- h) A solution of HCl in water contains 18.25 gm HCl per 100 gm solution and its density is 1.10 gm/cc. calculate the molarity and mol fraction of HCl.
- i) Write a brief note on electrophoresis and end osmosis.
- j) What do you mean by critical micellar concentration (CMC)? How equivalent conductance varies with micelle formation?
- k) What do you mean by first overtone? What will be the expression of energy for first overtone?
- l) Intensity of 'Stokes' line is higher than anti-Stokes' line – justify. Derive the expression for 'depression in freezing point' when a non volatile, non electrolyte solute is added to a pure solvent.
- m) The presence of non volatile, non electrolyte solute always lower the vapor pressure of pure solvent – explain.
- n) State and explain Raoult's law of lowering of vapour pressure.

- o) What is Gold Number?
- p) Explain briefly the term 'Tyndall Effect'?
- q) A Solution containing 5 gm of an organic solute per 25 gm of CCl_4 boils at 815°C and at 1 atm pressure. If normal boiling point of CCl_4 is 76.80°C , and $K_b = 5$. Calculate the molecular weight of the solute.
73. a) What do you mean by Vant Hoff factor (i) How this is related to osmotic pressure of a solution.
b) What are the criteria for a solution to be ideal?
c) At 100°C the vapour pressure of a solution of 6.5 gm of a solute in 100 gm of water is 732 mm. What is the boiling point of the solution.
d) What do you mean by Hot Bands?
74. a) What do you mean by pre-dissociation – Explain with a suitable diagram.
b) In the far IR Spectrum of HBr is a series of lines having a separation of 16.94 cm^{-1} . Calculate the moment of inertia and the intermolecular distance.
c) Between fluorescence & phosphorescence, which one is more favourable process and why?
d) H_2 molecule is Raman active – explain how?
e) Find the reduced mass for the molecule AB [atomic wt. A =12, B = 14 on $^{12}\text{C} =12.00$ scale]. The force constant and bond length are 1630 Nm^{-1} & 117 pm respectively. Calculate rotational constant (in cm^{-1}) & harmonic frequency of vibration.
f) In the pure rotational spectrum of CO [$J = 0 \rightarrow 1$], $\bar{\nu} = 3.84235\text{ cm}^{-1}$. Calculate the inter nuclear distance of the molecule, $\mu_{\text{CO}} = 11.38365 \times 10^{-27}\text{ kg}$.
g) Give reason to find out whether the symmetric vibration of CO_2 is IR or Raman active.
h) What do you mean by zero-point energy?
i) For HCl fundamental and first overtone are shown at 2886 cm^{-1} and 5668 cm^{-1} . Calculate the bond force constant for HCl.
j) What do you mean by fluorescence and phosphorescence?
k) A heteronuclear diatomic molecule of reduced mass 1.63×10^{-24} absorbs at 2880 cm^{-1} . Calculate force constant assuming harmonic oscillator model.
l) The fundamental and first overtone transition of NO molecule are entered at 1876 cm^{-1} and 3729 cm^{-1} respectively. Evaluate a) equilibrium vibrational frequency, b) zero point energy.
m) What do you mean by stokes and antistokes line in Raman spectra?
n) Discuss all the possible photophysical processes tht could take place when a molecule is excited to the lowest vibrational level of its first excited singlet state. State the distinctive features of the radiative processes in this case.
o) The first line in rotational spectrum of CO is 3.84235 cm^{-1} . Calculate the bond length of CO. Given $C=12.000$, $O = 16.000$. Absolute mass of H-atom = $1.67 \times 10^{-27}\text{ kg}$.
p) Which modes of CO_2 are IR active & which are Raman active?
q) Explain the process 'fluorescence' in brief .
r) How anharmonicity is reflected in the vibrational spectrum of a diatomic molecule? Explain using curves.
s) Describe how radioisotopes can be used to detect the presence of brain tumor?
t) What is nuclear binding energy? Calculate the binding energy per nucleon of C^{12} (given the mass in a m u $\text{C}^{12} \rightarrow 11.99671$; $n \rightarrow 1.00867$; $p \rightarrow 1.00728$)

- u) Define radioactive equilibrium. Derive the relation between half life with decay constant.
- v) What is the relation between half life time and average life time of a radioactive element?
- w) What is the mechanism of action of radiation therapy?
- x) A radioactive element takes infinite time to decay completely – Explain.
- y) What is the biological effect of radiation?
75. a) The half life of a radioelement is 231 minutes. How long will it take for $\frac{9}{10}$ th fraction of a sample of this element to decay?
- b) Nuclear fission products of U^{235} are always β -active. Explain.
- c) What do you mean by mass defect? Write down the relation between mass defect and nuclear binding energy. Calculate mass defect; nuclear binding energy per nucleus and packing fraction of $^{12}C_6$ from the following data
- $c=12.0000$ a.m.u.
 $n=1.00893$ a.m.u.
 $p= 1.00758$ a.m.u.
 $e=0.00055$ a.m.u.
 1 a.m.u. 931.5 Mev
- What will be the fate of a radio element $\sum X^A$ after emission of (i) an α -particle (ii) a β -particle?
76. a) Identify A & B in the following mechanism
- i) $^{23}_{11}\text{Na} + ^1_1\text{P} \rightarrow ^{23}_{12}\text{Mg} + A$
- ii) $^7_3\text{Li} + B \rightarrow 2^4_2\text{He}$
- b) Write Fajan & Soddy's displacement law regarding radioactive elements.
- c) What do you mean by Spallation? How does it differ from fission ?
- d) In the nuclear reaction represented by $^{14}_7\text{N} (\alpha, \beta) ^{17}_8\text{O}$, indicate the target, recoil nucleus as well as projectile and ejectile.

PAPER II
MODULE III

- What is isoelectric point? Draw the titration curve of glutamic acid ($pI = 3.22$). Write all the structures of the compound in each step.
 - Isoelectric point of glycine is 5.97 whereas that of lysine is 9.8 – Explain.
- A peptide was broken into smaller peptides by CNBr and into two different peptides by trypsin. Their sequences were as follows:
CNBr-1, gly-thr-lys-ala-glu
CNBr-2, Ser-met
Tryp 1, Ser-met-gly-thr-lys
Tryp 2, ala-glu
Determine the sequences of the parent peptide.
- What are the advantages associated with SPPS? Illustrate your answer in the light of the synthesis of alanyl-glycine.
- What happens when alanine is treated with ninhydrin.
- Draw the zwitterionic form of arginine.
- Why do amino acids show Zwitterionic structures? Indicate the Zwitterionic structures for the following amino acids at their isoelectric points :
 - Alanine
 - Aspartic acid
 - Glutamic acid
- draw the Zwitterionic structure of any one acidic and one basic amino acid.
- Write the principle of formal titration.
- What are essential and non-essential amino acid? Give example.
- What happens when an amino acid is made to react with AC_2O /Pyridine?
- Write down the reactions of an α -amino acid with nitrous acid.
- How is HPLC used in the separation of biomolecules? What are its advantages over classical chromatographic methods?
 - Name three biologically important peptides.
- Amino acid sequence affects alpha-helix stability – justify.
 - What do you mean by coil or loop conformation? Where is it found?
 - What is denaturation of proteins? Mention the conditions under which denaturation occurs.
 - A protein conformation is stabilized by weak interaction – Explain.
 - Peptide bond is essentially planar – Justify.
 - Draw the structure of the tripeptide YGF (1-letter symbol).
- Peptides show a high degree of resonance stabilization – Explain.
- What is SPPS? How can the N-terminus of the polypeptide chain be protected?
- Show necessary steps for synthesis of polypeptide by SPPS with proper example(s).
- How can you identify the N-terminus of a polypeptide? (Choose any one method for identification)
- C-N in peptide bond is longer than the normal C-N single bond – justify.
- Write short note on tertiary structure of protein.
- Differentiate between globular proteins and fibrous proteins.

21. a) What is an aldose and a ketose? Give example.
- b) What do you mean by epimer? How will you convert glucose to galactose?
- c) What do you mean by invert sugar?
- d) Convert the following
 - Threose to Xylose
 - D-Glucose → D-Arabinose
- e) Write briefly on the structure, occurrence and biological importance of any two disaccharides.
- f) Define “anomeric effect” with an example.
- g) Write down the Haworth representations of fructose in pyranose and furanose forms.
- h) What is glycosidic bond?
- i) What do you mean by “inversion of cane sugar?”
- j) What is mutarotation of D-glucose?
- k) What is epimerization?
- l) What is the difference between starch, glycogen and cellulose?
22. How would you convert D-glucose to D-fructose?
23. What are maltose and sucrose? Give reasons why maltose is a reducing sugar whereas sucrose is not.
24. Glucose, mannose and fructose. Give identical osazone—explain.
25. Distinguish between proteoglycan and glycoproteins.
26. Are d-mannose and D-galactose epimers? Give reasons.
27. Write the name of different phospholipids. Draw any 1 structure.
28. What is the physiological importance of phospholipids?
29. What is saponification value? How is it determined experimentally?
30. What is glycolipid? How many glycolipids are there? Write the structure of any one glycolipid.
31. What is lysolecithin? Write its structure.
32. What is sphingomyelin. Write the structure of sphingomyelin. Write the structure of structural backbone of sphingolipids.
33. Name and give the composition of the glycosaminoglycan which serves as lubricant and shock absorber in joints.
34. Write down the structure of plasmalogen.
35. Discuss the biological significance of fats.
36. What are lipoproteins? Which one is known as the good cholesterol and why?
37. What do you mean by
 - i) Reichert Meissel number
 - ii) Iodine number
38. What are ribose & 2-deoxyribose? What are the positions through which two sugar units in DNA and RNA are joined by phosphate ester group.
39. Why are RNA molecules less stable in alkali?
40. What is heparin? What is its main function?
41. a) Which experiment proves that DNA is the genetic material? Explain how did they conclude?

- b) What are the main chemical differences between DNA and RNA.
- c) Fetal Hb has a low BPG affinity – explain.
- d) What are porphyrins? Write down the structure of metalloporphyrin.
- e) What are the characteristics of Z-DNA(zee).
- f) Why are the major and minor grooves of unequal size?
- g) What are lecithins and cephalins? Explain with the aid of suitable example.
- h) What is the melting temperature (T_m) of DNA? which base is responsible for higher T_m in DNA and why?
- i) Draw the porphyrin unit.
- j) Which of the following compounds is different from others? i) GMP ii) deoxy guanosin monophosphate iii) guanylic acid and iv) guanosine-5-phosphate.
- k) The backbone of nucleic acid is constructed by which of the following
 i) Peptide bond ii) phosphodiester bond iii) H-bond or iv) glycosidic bond?
- l) Bruret test is answered by compounds having at least (i) one (ii) two (iii) three or (iv) four peptide linkages.
- m) What is porphyria? How are they caused?
- n) State the functions of ferrochelatase and ALA synthase.
- o) Write down the structure of
- Uroporphyrinogen III
 - Coproporphyrinogen I
- p) An anaemic individual, whose blood has only half the normal Hb content, may appear to be in good health. Yet, a normal individual is incapacitated by exposure to sufficient Co to occupy half his heme sites (Co binds to Hb with 200 times greater affinity than does O₂) – explain.
- q) Give the structure of galactocerebroside.
- r) What are lipoproteins?
- s) What is isoprene unit? How is it related to the nomenclature of various terpenes?

PAPER III
MODULE VI

1. "All the enzymes are protein in nature" – Comment on this statement.
2. What do you mean by holoenzyme and apoenzyme?
3. Define prosthetic group and give one example.
4. Name the major classes of enzymes and give examples of each class.
5. Give the example of metal ion.
6. Define coenzyme with example.
7. Name one enzyme which is non protein in nature. What is its action?
8. Define active site of enzyme.
9. Why are cofactors required for some enzymatic reactions?
10. If only a few of the amino acid residues of an enzyme are involved in its catalytic activity, why are most enzymes composed of a much larger number of amino acids?
11. Justify the statement. Many vitamins are coenzyme precursors.
12. What are the different ways by which metal can participate in enzyme catalysis? Explain briefly.
13. Identify the following :
 - a) Enzymatically inactive protein resulting from the removal of a holoenzyme's cofactor.
 - b) Cofactors which are permanently associated with the protein.
14. In order to complete the catalytic cycle, the coenzyme must return to its original state' – why? Give one example.
15. On what basis are enzymes classified? Give examples of each class of enzymes.
16. Explain oxidoreductase enzyme with an example.
17. Give an example of transferase type of enzyme.
18. Explain PALPO with example.
19. Differentiate between synthase and synthetase enzyme with example.
20. How do you determine the rate constant of an enzyme catalysed reaction from transition state theory?
21. What is rate limiting step?
22. What roles do proximity and orientation play in enzymatic catalysis?
23. What is free energy of activation? Explain with graphical representation. Which rate of the enzymatic reaction can be determined.
24. a) Explain transition state theory from which rate of the enzymatic reaction can be determined.
b) The native three dimensional conformation of the enzyme molecule required for its catalytic activity – explain.
25. i) Explain geometric specificity with an example.
ii) Write short notes on Lock and Key hypothesis.
iii) How does proximity affect for enzyme-substrate binding – explain with suitable example.
iv) 'Multistep reactions have rate determining step' – justify the statement.
v) Define binding energy.
vi) The enzyme fumarase catalyses the fumarate. Predict the action of fumarase on maleate, the cis-isomer of fumarate – Explain.
vii) State one biochemical reaction in which riboflavin derivative plays as coenzyme.

- viii) Thiamin plays an important role in carbohydrate and amino acid metabolism –
Comment.
26. i) Derive Michaelis-Menten equation. Mention the significance of K_M .
ii) distinguish between sequential model and symmetry model with example.
iii) Define feed back inhibition with example.
27. a) Compare competitive and uncompetitive inhibition with example.
b) What is PALPO? How does enzyme catalyzed reaction depend on it?
c) Determine the fraction of V_{max} that would be found in each case when $[S]=1/2 K_M, 2K_M$ and $10K_M$.
28. a) Explain double reciprocal plot.
b) How does the enzymatic reaction depend on the substrate concentration?
c) Give short note on acid base catalysis.
d) An enzyme was assayed at an initial substrate concentration of 2×10^{-5} M. in 6 minutes half of the substrate had been used. The K_M for the substrate is 5×10^{-3} M. Calculate (a) V_{max} and (b) concentration of product produced in 15 minutes.
e) How does covalent modification regulate enzyme activity? Illustrate with example.
29. i) Why do allosteric enzymes show sigmoidal kinetics? Explain with example.
ii) Distinguish between sequential and ping pong reaction with example.
iii) Explain irreversible inhibition with an example.
iv) What is an isoenzyme? Give example.
v) Write the catalytic mechanism of trypsin.
vi) Mention the significance of V_{max} .
vii) Write the units of K_M and v .
viii) What is enzyme activity? Write its unit.
ix) What is zymogen. Give example.
30. a) What are the differences between noncompetitive and uncompetitive inhibition?
b) 'Enzyme catalysed reaction is regulated by covalent modification' – explain.
c) (i) If the half-time of a first order reaction is 0.3 sec. What is its rate constant K ?
(ii) How long will it take for 95 percent of the reactant to disappear?
d) What are the features of competitive inhibition? Give example.
e) Give one example to show how proteolytic cleavage regulated by the modulators?
f) How is the activity of aspartate transcarbamoylase enzyme regulated by the modulators?
g) Show that the enzyme catalysed reaction depends on pH.
31. What is enzyme inhibition?
32. What is allosteric enzyme? Give example.
33. How does phosphorylation-dephosphorylation regulate the enzymatic activity?
34. What is cooperativity of enzyme?
35. Distinguish with example between k-enzymes and M-enzymes.
36. a) Define enzyme activity unit. What is the difference between enzyme activity and specific activity?
b) What is katal?
c) Write the significance of specific activity.

- d) 'Ethanol is used for treating methanol poisoning' – Explain why?
37. Briefly describe the unique characteristics of the enzyme Ribonuclease.
38. What is induced fit hypothesis?
39. a) What is Michaelis Menten constant ? Write its significance.
 b) "Non competitive inhibition can be overcome by increasing the substrate concentration" – why?
 c) What is the steady state approximation for studying the kinetic behavior of an enzyme catalysed reaction?
40. How does NAD/NADP act as a role in enzyme catalysed reaction?
41. An enzyme has a K_M of 4.7×10^{-5} M. if the V_{max} of the preparation is $22 \mu\text{moles/lit/min}$.
 i) What velocity would be observed in the presence of 2×10^{-4} M substrate and 5×10^{-4} M of a competitive inhibitor, where k_i is 3×10^{-4} M.
 ii) What is the degree of inhibition in this case.
42. An enzyme was assayed at an initial substrate conc of 2×10^{-5} M. in 6 min, half of the substrate had been used. The K_M for the sub. is 5×10^{-3} M. Calculate i) k , ii) V_{max} and iii) the conc. of product produced in 15 min.
43. Differentiate between isosteric enzyme and allosteric enzyme.
44. How does temperature affect the rate of the enzymatic reaction?
45. Write one reaction where TPP acts as a coenzyme.
46. An enzyme was assayed at an initial sub. conc. Of 10^{-5} M. the K_m for the substrate is 2×10^{-3} M. At the end of 1 min., 2% of the substrate had been converted to product. (a) what percent of the substrate will be converted to product at the end of 3 min? What will be the product and substrate concentration after 3 min?
47. 'Multistep reactions have rate determining steps' – justify.
48. Glucose-6-phosphate was hydrolysed enzymatically (at pH 7 and 25°C) to glucose and inorganic phosphate. The concentration of glucose-6-phosphate was 0.1M at the start. At equilibrium, only 0.05% of the original glucose-6-phosphate remained. Calculate (a) K'_{eq} for the hydrolysis of glucose-6-P. (b) $\Delta G'$ for the hydrolysis reaction.
49. Define turnover no. and write its unit.
50. a) Write the principle of affinity chromatography.
 b) What is Svedberg unit?
 c) What is meant by salting in?
51. Write down the principle of the following biochemical techniques:
 a) Molecular exclusion chromatography.
 b) Ion exchange chromatography
 c) Salting in and salting out
52. What is pI?
53. Four amino acids (Leucine, Lysine, Alanine and Phenylalanine) are to be separated by paper chromatography. Draw the separation pattern and explain the reason.
54. What is dialysis?
55. What is SDS-PAGE?

56. Sedimentation coefficient increases with molecular weight in ultracentrifugation technique – explain.
57. Briefly describe how electrophoresis is used in the separation of biomolecules.
58. State the basic principle of gas-liquid chromatography.
59. Write the usefulness of affinity chromatography?
60. What is R_f ?
61. What is isoelectric precipitation?
62. Mention some applications of ultracentrifugation.
63. What are the factors that affect the mobility and sharpness of separation of bands in electrophoresis?
64. Explain in brief how adsorption chromatography helps to separate enzyme protein?
65. Briefly describe solvent fractionation.
66. What is ultrafiltration technique?
67. Describe briefly the used of proteases in food industry.
68. Write the enzymes involved in the production of glucose from starch.
69. Write down the steps involved in the production of glucose from cellulose industrially.
70. Mention the usefulness of proteases in detergent and leather industry.
71. How do you state the enhancement of the rate of a chemical reaction?
72. What is FAD?
73. What is the significance of k_{cat} ?
74. How will chymotrypsin be activated from its zymogen?
75. Why Lineweaver Burk Plot is more applicable in enzymatic reaction?
76. Sketch the following curves for an enzyme obeying Michaelis-Menten kinetics:
 - I) v Vs [coenzyme]
 - II) v Vs time for $S \gg K_M$
 - III) Product concentration vs time for $S \gg K_M$
 - IV) $1/v$ Vs $1/[S]$ for an enzyme that shows 'substrate inhibition' at high substrate concentration.

PAPER IV
MODULE VII

1. a) Arrange the following (higher to lower) according to the size of the molecule.
Mitochondria, Paramecium, Bacterium, Chloroplast, Myoglobin, Ribosome
- b) Calculate the approximate volumes of human liver cell (in cubic micrometer) which is roughly spherical in shape and has a diameter of about 20 μm .
- c) Write the marker enzymes of ER and peroxysome.
- d) If a mitochondrion were 2 μm s in length, how many angstroms would it be?
2. a) Briefly describe the structure of mitochondria.
- b) Calculate the approximate volume of *E. coli* cell which is cylindrical in shape, with a diameter of about 1 μm and length of about 2 μm .
- c) How do you identify golgi apparatus in an eukaryotic cell?
- d) Write the functions of mitochondria.
- e) Write a short note on chloroplast.
3. a) Write the differences between animal cell and plant cell.
- b) Arrange the following in descending order
Paramecium, DNA, ribosome, chloroplast, mitochondria.
- c) Nucleus is called 'the brain of the cell' – explain.
- d) What is lysosome?
- e) Draw and label eukaryotic cell.
4. Write the functions of chloroplast.
5. What is ribosome?
6. i) Did mitochondria and chloroplast evolve from ancient bacteria? Justify your comment.
- ii) Endoplasmic reticulum (ER) is absent in prokaryotes but present in eukaryotes. What advantages do eukaryotes get due to ER?
- iii) Write the functions of lysosome and ribosome.
7. a) Discuss the function of different parts of a nucleus.
- b) Write the structure and function of golgi apparatus.
- c) What is cytoskeletal element?
- d) What is polysome?
8. a) In mature RBC nucleus inactive then how do they survive?
- b) Write the marker enzyme of lysosome and mitochondria.
- c) Which type of cells would be expected to have more mitochondria; heart or liver cells? justify.
- d) Write one difference between smooth and rough endoplasmic reticulum on the basis of structure and function each.
- e) Briefly state the functions of endoplasmic reticulum.
- f) Chloroplast is absent in animal cell but present in plant cell. What advantages do plant cells get due to chloroplast?
- g) Compare between prokaryotic cell and eukaryotic cell.
- h) Write short notes on cytoskeletal elements.

- i) Define peroxisome.
- 9. a) Write the structural characteristics of ribosomes in both prokaryotic and eukaryotic cell.
- b) How do you prove that the golgi complex is connected with the process of cell secretion?
- c) What are lamins?
- d) Write the functions of peroxisome.
- e) Write the function of RER.
- 10. a) Membrane lipids are in constant motion – justify.
- c) What are the basic components of biomembranes? Biological membranes are ‘asymmetric’ – justify.
- 11. i) What drives the movement of lipid molecules and proteins within the bilayer? How can such movement be measured?
- ii) Three systems of cytoskeletal filaments exist in most eukaryotic cells. compare them in terms of composition, structure and function.
- 12. What is ‘liposome’? write its utility.
- 13. Write briefly how biomolecules take part to form cell organelles.
- 14. Describe the fluid mosaic model of biological membrane.
- 15. What do you mean by ‘ribotyping’?
- 16. Distinguish between continuous and synchronous cultures?
- 17. Write the difference between complex media and synthetic media.
- 18. What do you mean by
 - a) Lyophilization
 - b) Pasteurization
- 19. Write the mode of action of pericillin.
- 20. What is probiotic therapy?
- 21. What is the significance of antibiotics in Kirby-3 over method.
- 22. What is the basic principle of an autoclave.
- 23. What are the different phases of growth (in bacteria).
- 24. Show the growth curve of bacteria.
- 25. What is the significance of spore-forming bacteria. Give one example.
- 26. Give an example for each of the following :
 - a) Gram positive bacteria
 - b) Gram negative bacteria
- 27. a) What do you mean by the following terms:
 - i) Defined media
 - ii) Semi defined media.
- 28. Why are amino acids, purines and pyrimidines of ten growth factors, whereas glucose is usually not?
- 29. a) List some of the most important uses of nitrogen, phosphorus and sulphur that microorganisms obtain from their surrounding?
- b) Why amylase is active at pancreatic juice but inactive in stomach?
- c) Why bicarbonate buffer is most important in extracellular fluids?
- d) Define glomerular filtration rate.

30. a) What do you mean by digestion? What are the different organs involved in the digestive system? Describe the role of different enzymes that are involved in digestion.
- b) What are the roles of bile in digestive process?
- c) How does carbohydrate from the diet absorb in our body?
31. a) Describe briefly the functions of juxta glomerular apparatus.
- b) What are the anterior pituitary hormones?
32. a) Renal tubular re-absorption is highly selective – explain.
- b) How is glucose transported through the renal tubular membrane?
33. How do protein digest in the human body?
34. Mention the main functions of kidney.
35. What do you mean by acidosis and alkalosis?
36. Water plays an important role in electrolyte metabolism – comment.
37. What is PER?
38. Describe nitrogen balance and biological value. In which context these parameters are important?
39. a) What is BMR?
- b) What are the factors affecting BMR?
40. Describe briefly the factors controlling nitrogen balance.
41. Write notes on Respiratory Quotient(RQ).
42. NPU is a better nutritional index than BV – justify.
43. Why is arsenic a toxic to human?
44. Hg^{2+} (mercuric ion) is more toxic than Hg_2^{2+} (mercurous ion) – comment.
45. What are organophosphorus compounds? Name two organophosphorus pesticides and write its toxic effects.
46. Why is lead a toxic to human?
47. Mention the toxic effects of mercury.
48. What are the food sources for potassium and calcium? (Name two in each case).
49. Explain why lack of iodine in the diet causes goiter?
50. Discuss the role of fluorine and manganese in nutrition.
51. What is the nutritional requirement of sodium?
52. Discuss the role of phosphorus in nutrition.
53. “Excessive intake of fluoride is harmful to the body” – justify.
54. Write notes on nutritional requirement of Zn.
55. Briefly describe biological functions of calcium.
56. Explain why a large excess of iron is generally not used therapeutically over long periods.
57. List the dietary requirement of potassium and molybdenum.
58. What are the significance of chlorine in nutrition?
59. Name the thyroid hormones, their chemical structure and major functions.

PAPER V
MODULE IX

1. Write down the rates of pyruvate after the formation of it, in glycolysis. What do you mean by Cori cycle? Schematically represent the Cori cycle.
2. a) Why must the NADH produced in glycolysis be oxidized to NAD^+ and thus be recycled?
b) What are the overall chemical changes that occur during one complete turn of citric acid cycle?
c) Glyoxylate and citric acid cycle have several reactions in common, but what two enzymes are unique to glyoxylate cycle?
d) Can the glycolytic pathway operate in the reverse direction?
3. How can glucose be formed from the non-carbohydrate sources? Describe may one pathway of formation of glucose from non-carbohydrate sources with schematic diagram. Describe the role of hexokinase and pyruvate kinase in regulation of glycolysis?
4. What is galactosemia? What is its cause?
5. a) What are oxidative phosphorylation and substrate level phosphorylation?
b) Name one inhibitor of electron transport chain complex I and one of complex II.
c) Phosphoenol pyruvate has high phosphate group transfer potential – why?
d) What is the significance of pentose phosphate pathway?
e) What is photo respiration?
f) What are anaplerotic reactions of TCA cycle?
g) What is an uncoupler? Give an example.
6. a) Fructose-2, 6-bisphosphate is one of the important regulators of glycogenesis and glycolysis – show the hormonal regulation of glycogenesis through the regulation of concentration of Fructose-2, 6-bisphosphate.
b) Describe the conversion of pyruvate to PEP mentioning all the enzymes, coenzymes/cofactors. How this step is egulated?
c) Briefly describe the regulation of TCA cycle. write down the two reversible steps in glycolysis.
7. a) Compare and contrast cyclic and non-cyclic photophosphorylation. Differentiate between oxidative and substrate level phosphorylation.
b) What is the light reaction? State the reaction catalyzed by the enzyme RnBP carboxylase with its coenzymes/ cofactors, if any.
c) Briefly describe the regulation of glycolysis.
8. What is the significance of P/O ratio?
9. Give the reactions by which NAD^+ is replenished under anaerobic condition.
10. What is glyconeogenesis? Write the rate controlling steps of this pathway.
11. Glucose-6-P is at the cross roads of carbohydrate metabolism – Briefly show that different fates of Glucose-6-P depending on glucose demand.
12. Which carbon atom of the products of aldolase reaction would be radioactive if glucose labelled with ^{14}C at C_1 is metabolized by glycolytic pathway?
13. Inhibition of complex II of ETC does not completely block the pathway – justify.

14. Write down the structure of CAMP and state one of its function in carbohydrate metabolism.
15. What is substrate level phosphorylation? Give a reaction from glycolysis where substrate level phosphorylation occurs.
16. Describe the pathway by which galactose is converted into a glycolytic intermediate.
17. Pyruvate dehydrogenase and another TCA cycle enzyme have many similarities – justify with the name of the TCA cycle enzyme.
18. What is the dark reaction?
19. Name the carrier of fatty acid transport across mitochondria and give the reaction.
20. a) How much energy, in the form of ATP, is obtained from β -oxidation of 1 mole of palmitoylco A?
 b) what are ketone bodies? Mention their role in metabolism.
 c) What are essential fatty acids and what is their significance?
21. a) Fatty acids are activated in cytosol for oxidation but are oxidized in the mitochondria – describe how activated fatty acids are transported to mitochondria. How does this process regulates the fatty acid metabolism?
 b) Write down the different steps involved in β -oxidation of an unsaturated fatty acid.
 c) Calculate the energy yield of palmitic acid during β -oxidation.
22. a) Write down the steps involved in β -oxidation of an unsaturated fatty acid.
 b) Identify the lipid synthesis pathway that would be affected by abnormally low level of CTP. Describe one such synthesis pathway of lipid metabolism involving CTP.
 c) Write down the committed step in cholesterol biosynthesis with enzyme, coenzyme/cofactor, if any. What is atherosclerosis?
23. Inborn errors of metabolism are associated with deficiency or absence of an enzyme – justify the statement with any one of the examples from $\alpha\alpha$ metabolism.
24. What are sulfonamides? How do they work?
25. Write a note on oxidative domination. Give one condition related to the disorder of this metabolic process.
26. What is the significance of folic acid in metabolism?
27. One of the symptoms of Kwashiorkor in children is the de-pigmentation of the skin and hair – Explain the biochemical basis of this symptom with necessary reaction.
28. Write down the overall urea cycle reaction showing the sources of N and C atoms of urea.
29. What do you mean by transamination of amino acids? Give example.
30. Give the chemical reaction involved in activation of fatty acid.
31. Give an example of biological donor of methyl groups.
32. What is albinism?
33. a) What do you mean by essential and non essential amino acids? Give examples.
 i) What are branched chain amino acids? Give examples.
 ii) What do you mean by oxidative deamination of glutamate?
 iii) What do you mean by porphyrias? State one porphyria with its causative enzyme.
 iv) What do you mean by glucogenic and ketogenic amino acids?
 v) What are phycobiliproteins? Give examples.

- vi) Which is the rate limiting step in heme synthesis? Which porphyria is associated with the deficiency of the enzyme catalyzing the rate limiting step?
34. What is Lesch-Nyhan Syndrome? What is its cause?
 35. Why does a deficiency of adenosine deaminase result in SCID?
 36. Briefly describe the salvage pathway showing its cause.
 37. How are deoxyribonucleotides synthesized from corresponding ribonucleotides synthesized from corresponding ribonucleotides? Briefly describe the enzymatic reaction.
 38. FdUMP and methotrexate, when taken together are less effective chemotherapeutic agents than when either drug is taken alone – justify the statement giving reactions.
 39. Regulation of pyrimidine nucleotide biosynthesis in bacteria and in animals are different – State true or false with proper explanation.
 40. a) Illustrate the reaction catalysed by thymidylate synthase with its coenzymes/cofactors. What are sulfa-drugs? State their target of action.
b) Describe the reaction catalysed by ATCase. Explain its significance. What is SCID? How is it related to purine metabolism?
 41. a) Justify the following statement:
Phenyl ketonuria is a congenital disease.
b) Write down the cause(s) of gout? How can it be treated?
c) How are stercobilin and urobilin formed from bilirubin?
 42. What do you mean by inborn errors of amino acid metabolism?
 43. Why are phenylketonurics warned against eating products containing artificial sweetener aspartame?
 44. What are the two forms of carbamoyl phosphate synthetase(CPS)?
 45. Describe the first step of pyrimidine biosynthesis with enzyme, coenzyme(if any).
 46. Write down an active form of folic acid. Give one example of its use.
 47. What pathway produces ribose? Give one use in the biological system.
 48. Outline any one synthetic route of guanine.
 49. What are bile pigments? State their function and structural features.
 50. Outline the best method to synthesize any one pyrimidine?
 51. Show a convenient method for synthesis of :
i) Purine
ii) Pyrimidine
 52. Draw the porphyrin unit.
 53. Write short notes on Alkaptonuria.
 54. What is SIDS? What is its cause?
 55. What are the precursors of urea produced by urea cycle?
 56. What is cardiolipin? What is its clinical significance?
 57. Write down the pathway of phenylalanine break down.
 58. What are the precursors of heme biosynthesis?
 59. Write down the first step of heme biosynthesis mentioning its enzyme and coenzyme/cofactor, if any. Name one disorder related to heme biosynthesis with its cause.

PAPER V

MODULE X

1. a) Write the different phases of cell division. Which phase of cell cycle takes more time?
b) Which enzyme is involved in the cell cycle event? Mention the catalytic and regulatory subunits of that enzyme.
c) What is ATPase? Write briefly the mechanism of action of any one ATPase.
d) What is signal transduction?
e) What are the checkpoints for regulating a cell cycle event?
2. a) Mention the name of cyclin-CDK complexes that take part in a cell cycle event? Write the functions of each complex.
b) What are the cell surface receptors that are involved in signal transduction? Give at least one example for each of those receptors.
c) What is APC? How does it act?
d) Name one anion transporter and glucose transporter.
e) Mention the duration of different phases of cell cycle.
3. a) What is contact inhibition?
b) Mention major chronological events of cell cycle.
c) Which non-channel is essential for passage of electrical signal from motor neuron to muscle fibre?
d) What are red cell membrane proteins?
e) What are the different types of receptors found in living system?
4. What do you mean by symport and antiport? Explain with an example for each.
5. What is active transport? How does it differ from passive transport? Explain with at least one example for each.
6. What is the role of $\text{Na}^+\text{-K}^+$ ATPase in active transport?
7. What is G_0 (quiescent phase) of cell cycle?
8. What is the significance of meiosis?
9. What is meant by cell line?
10. At what stage of the cell division the centromere divides?
11. a) Explain how the Na^+/K^+ -ATPase operates. Describe the consequences of inhibition of the Na^+/K^+ -ATPase.
b) What are G-proteins? How are they involved in signal transduction?
12. a) Defective glucose and water transport in two forms of diabetes—justify.
b) Distinguish anaphase of mitosis from anaphase I of meiosis.
c) Mention the localization and importance of spectrin.
13. a) Distinguish between :
 - i. Voltage gated channel and Ligand gated channel.
 - ii. Simple and facilitated diffusion.
b) What are the different types of ATPases in primary active transport?
14. What are the advantages of cell culture?

15. What is 'Homologous chromosomes'?
16. Explain the term "critical micelle concentration"?
17. There are different components of a cell membrane. the following are the agents which are required for isolation of these components for analysis:-
 - i. High ionic strength salt solution (1 M NaCl)
 - ii. Organic solvents
 Mention which membrane components are separated by them.
18. What are the functions of "GAP" and "GEF" in signal transduction?
19. What are second messengers? Explain with examples.
20. Explain the regulation of Cdk1 in the animal cell cycle.
21. What do you mean by gated channels?
22. Briefly describe the function of transmembrane receptor protein.
23. Define resting membrane potential.
24. Differentiate between serum and plasma.
25. Describe briefly the pathways of blood clotting.
26. Comment on the Rh blood group.
27. Lactate dehydrogenase is an important enzyme in therapeutic application – justify.
28. What are the clinical significance of the following enzymes?
 - i) SGOT
 - ii) SGPT
29. What is CPK? How many isoenzymes are identified? Justify the statement that CPK is useful in clinical diagnosis?
30. What precaution would you adopt during collection of blood for estimation of Ca^{2+} and why?
31. Highlight the functional tests for liver disease with their reference range.
32. Name one disorder related to heme biosynthesis?
33. Write note on glycogen storage disease.
34. What do you mean by obstructive and neonatal jaundice?
35. What is myocardial infarction?
36. Lipoproteins play a crucial role in many diseases like atherosclerosis – justify.
37. Thalassaemia occurs due to abnormal globin chain synthesis – explain.
38. Briefly explain how glucose homeostasis is maintained in our body.
39. What is Type II Diabetes Mellitus?
40. How can you distinguish between obstructive jaundice and infective jaundice with the help of blood biochemical parameters?
41. a) Name one abnormal hemoglobin citing its structural and functional abnormality.
b) What are important serum lipoproteins? Give brief clinical significance of each.
42. Name two genetic disorders related to glycogen metabolism.
43. Why NaF is used in vial used for collecting blood for estimation of glucose?
44. What is normal range of bilirubin and creatinine?
45. Name the blood groups. What is the significance?
46. Name the disease in which serum lipase is elevated. Give normal range.
47. Briefly describe different factors affecting blood sugar level.
48. What is positive after potential?

49. How are the sensitivity of hormone receptors regulated?
50. What is the main difference between carrier and channel proteins?
51. Explain the G-protein mediated signaling pathway.
52. How do insulin regulate glucose metabolism?
53. How does a hormone act at the target cell?

PAPER VI
MODULE XI

1. a) Explain the difference between macrophage and monocyte.
 - b) What are the two primary roles of thymus?
 - c) What are meant by the terms “agglutinin” and “precipitin”?
 - d) Explain the difference between the terms ‘antigen presenting cells’ and ‘target cells’.
 - e) Briefly describe the classical pathway of complement activation. How is it different from lectin pathway?
2. a) Where are the hypervariable regions located on an antibody molecule and what are their functions?
 - b) Give a schematic diagram of IgE and label its parts and domains.
 - c) What do you mean by immunogen and how is it different from antigen?
 - d) Draw a diagram illustrating the general structure, including domains of a class I MHC molecule.
 - e) What is the difference between polyclonal and monoclonal antibody?
 - f) Give one example each of primary and secondary lymphoid organs in humans. What do you mean by innate immunity?
3. a) What do you mean by adjuvant?
 - b) Explain why the second child of a Rh-positive father and a Rh-negative mother is at a risk of a haemolytic disease.
 - c) What is haptin? Give example.
 - d) What is the difference between allotype and idiootype?
 - e) Distinguish between attenuated and inactivated vaccines.
 - f) What is cytokine? Give example.
 - g) Give an example of professional and non-professional antigen presenting cells.
4. a) Is it possible to perform Ouchterlony Assay using a Fab fragment as the antibody? Explain.
 - b) Briefly describe the classical pathway of complement activation.
 - c) Explain briefly whether the following statements are true or false:
 - i. Processed exogenous antigens are presented by MHC-I molecules, or Dendritic cells express MHC-II constitutively, whereas in B-cell they need to be activated.
 - ii. Babies can acquire IgE-mediated allergies by passive transfer of maternal antibody.
 - iii. Antihistamines are effective for the treatment of type III hypersensitivity.
 - iv. A mouse immunized with IgG1 will produce Ab that reacts with all subclasses of IgG in human.
 - d) Explain briefly whether the following statements are true or false:
 - i. Precipitation tests are generally more sensitive than agglutination tests.
 - ii. A papain digest of anti-SRBC Ab can agglutinate sheep RBCs.
 - e) Draw a schematic diagram of a secretory IgA.
5. a) According to the clonal selection theory, all the Ig molecule on a single B cell have the same antigenic specificity. Explain why the presence of both IgM and IgD on the same B cell does not violate the unispecificity implied by clonal selection.
 - b) What type of enzyme is represented by CIs and what are the substrates for this enzyme?

- c) Draw a diagram illustrating the general structure including domains of a class II MHC molecule.
 - d) How do NK cells destroy their targets?
 - e) Explain the difference between antibody – affinity and antibody avidity. Which of these properties of an Ab better reflects its ability to contribute to the humoral immune response to the invading bacteria.
6. Draw a diagram of class II MHC molecule with its domains.
7. a) Indicate whether each of the following statements are true or false with proper justification.
- i. The presence of both IgM and IgD on a single B-cell violates one of the tenets of clonal selection the unispecificity of a given B-cell.
 - ii. Serum IgM cannot activate complement by itself
 - iii. A hapten can stimulate antibody formation but cannot combine with antibody molecules.
 - iv. Antigen presenting cells express both Class I and Class II MHC molecules on their membrane.
 - v. Hypoxanthine is added to HAT medium to prevent cell growth by the salvage pathway.
8. a) What is the basic principle for delayed type hypersensitivity.
 b) Distinguish between antibody affinity and antibody avidity.
 c) Draw a schematic diagram of a typical IgG molecule labeling its parts and domains.
 d) What do you mean by histocompatibility?
9. a) If you treat IgG with papain, pepsin and β -macaptoethanol separately, show what fragments that would be produced in each case.
 b) What is immunotoxin? Explain with the help of an example.
10. Explain briefly whether the following statements are true or false.
- i. Precipitation tests are generally more sensitive than agglutination tests.
 - ii. A single molecule of IgG can activate the C1q components of the classical pathway.
 - iii. Most pollen allergens induce type IV hypersensitivity
 - iv. A hapten can stimulate antibody formation by itself.
 - v. The concentration of hapten can be determined by Ouchterlony method.
11. Indicate whether each of the following statements are true or false. If you think a statement is false, explain why.
- i. C4 deficient individuals have difficulty eliminating immune complexes.
 - ii. APC express both class I and class II MHC molecules on their membranes.
 - iii. IgG functions more effectively than IgM in bacterial agglutination.
 - iv. Antihistamines are effective for the treatment of type III hypersensitivity.
 - v. Individuals with hemolytic anemia produce antibodies to intrinsic factor.
12. What is Rhogan? Where and why is it required?

PAPER VI
MODULE XII

1. Which amino acid residue is in abundance in histones? Which histone is not part of the nucleosome?
2. What is the role of helicase in DNA replication?
3. Briefly explain the principle of Southern Blotting.
4. Why is DNA synthesis continuous on one strand and discontinuous on the opposite strand? Explain.
5. Why is primer necessary for DNA replication?
6. If the molar amount of G in a DNA (ds) sample is 20%, what is the molar amount of T in that sample?
7. a) Define codon. Write the role of following enzymes :
 - i. Helicase, ii. Topoisomerase, iii. Reverse Transcriptase and iv. DNA Polymerase I
- b) What are shuttle vectors and what are their advantages?
- c) Write a short note on Southern Blotting technique.
8. a) Explain why DNA synthesis continuous on one strand and discontinuous on the opposite strand.
- b) Write a short note on Splicing.
- c) What result would you get if you run two separate PCR reactions, one with dNTP and one with a mixture of dNTP and di-deoxy NTP?
- d) What do you mean by positive and negative control of Lac operon?
9. a) Briefly describe the following terms:
 - i. Capping ii. Polyadenylation, iii. Nucleotide Excision repair
- b) What are phagemids? Cite one example.
10. a) Define the term Ischizomers and Neoschizomers.
- b) What is Shine Dalgarno sequence and what is its role in protein synthesis?
- c) Describe in detail the different types of restriction and modification systems.
- d) What is star activity of an enzyme?
- e) What are minor and major grooves of a DNA double helix?
- f) What would have been the possible consequence of having uracil as a nucleotide in DNA instead of thymine.
- g) What is the difference between RNase A and RNase H?
11. Explain the following:
 - a) DNA replication is a semi discontinuous process.
 - b) Transcription initiation requires formation of an open complex.
12. Where and how do the following compounds act?
 - i. Rifampin
 - ii. Actinomycin D
- a) What is selectable marker? Give one example.
- b) Give a single construct of a cloning vector?
- c) Briefly state the characteristics of Type III endonucleases.

13. Name the components of replisome. State its function. What is Kornberg's enzyme?
14. What is the energetic cost, in ATPs, for the *E. coli* synthesis, if a polypeptide chain of 100 residues starting from a \bar{a} and mRNA? Assume that no losses are incurred as a result of proof reading.
15. Describe briefly the Meselson-Stahl experiment demonstrating that DNA replication is semi-conservative in nature.
16. Give a strategy for the production of human insulin in *E. coli* cells using RDT.
17. Mention specific features of the SOS repair system that distinguish it from all other DNA repair systems.
18. What are the roles of the various exonuclease activities of the DNAP during DNA replication.
19. What is meant by catabolic repression? Explain.
20. What is the difference between an open-promoter complex and a closed promoter complex?
21. Distinguish the role of Pol I and Pol. III in DNA replication.
22. a) Mention the specific features of the SOS repair system that distinguish it from other such DNA repair system?
 b) Distinguish between prokaryotic and eukaryotic mRNA.
 c) Name 2 inhibitors of protein synthesis.
 d) Give a strategy for the production of human insulin in *E. coli* cells using Recombinant DNA Technology?
23. Explain how lactose molecules first enters an uninduced $i^+p^+o^+z^+y^+$ cell to induce β -galactosidase synthesis.
24. a) The gene encoding an *E. coli* t-RNA containing the anticodon 5'-GUA-3' mutates so that the anticodon is now 5'-UUA-3'. What will be the effect of this mutation? explain your answer.
 b) Describe the reactions involved in the amino acylation of a t-RNA molecule.
 c) What are the two mechanisms involved in repair of thymine dimer formation after exposure to ultraviolet rays?

OR

25. a) What is a shuttle vector? Why is it used?
 b) The lac operon is an inducible operon, whereas the trp operon is a repressible operon. Discuss the differences between these two operons.
 c) Draw the restriction map of the following recombinant plasmid pBR32 which is cut with three different restriction enzymes. The following fragments were obtained on agarose gel

<i>EcoRI</i>	:	8.0 and 6.0kb
<i>HindIII</i>	:	5.4, 4.5 and 4.0kb
<i>HindIII + EcoRI</i>	:	4.0, 3.5, 3.0, 2.5 and 1.0kb
26. a) How are the prokaryotic initiation complexes formed in replication?
 b) In 1958, Meselson and Stahl experimentally proved semi conservative replication of DNA in *E. coli*. Briefly describe the experiment with a special note on the role of N^{15} in this experiment.

- c) What type of products would you expect with the following partial heterozygotes of *E. coli* for lac operon in presence or absence of lactose and why?

Genotype	Uninduced		Induced	
	β -gal(z)	β -per(y)	β -gal(z)	β -per(y)
i) $\frac{i^+p^+o^c z^+y^-}{i^s p^+ o^+ z^+ y^+}$				
ii) $\frac{i^+ p^+ o^+ z^+ y^+}{i^- d p^+ o^4 z^+ y^-}$				
iii) $\frac{i^- p^+ o^+ z^+ y^+}{i^+ p^+ o^+ z^+ y^+}$				

What is a palindromic sequence?

27. What do you mean by restriction modification system?
28. What do you mean by Nick-translation.
29. Mention the type of restriction endonuclease, which are commonly used in laboratory. Give one example.
30. What do you mean by replisome and primosome.
31. What is meant by an "expression vector"?
32. The restriction enzyme EcoR-I cuts DNA at the sequence GTTAAC and the enzyme Hae III cuts DNA at the sequence GGCC. On an average, how frequently will these enzymes cut a double stranded DNA?
33. What do you mean by silent mutation?
34. What are plasmids?
35. What is catabolite repression?
36. What is post-transcriptional processing? Briefly discuss the ways by which it takes place?
37. Explain how an intercalating agent can cause mutation
38. State the use of the following enzymes in RDT :
 - a. Polynucleotide kinase
 - b. T4 DNA ligase.