

CHEMISTRY – HONOURS

Part – I (1st Year)

First Paper (Physical Chemistry)

(Group – B)

CHT – 13a

Unit I: Kinetic theory and the gaseous state

1. Deduce the probability distribution function for speed of gas molecules moving on a plane. Assume that the velocity distribution function for 1 dimensional gas is $f(u) = Ae^{-Bu^2}$ (Terms have their usual significances and A and B are constants). Using that speed distribution function, find an expression for the most probable speed of the gas molecules. Also evaluate the most probable velocity of such gas molecules. Comment on the difference in the most probable values of speed and velocity of gas molecules.

2. Deduce the probability distribution function for speed of gas molecules moving along a straight line. Assume that the velocity distribution function is $f(u) = Ae^{-\frac{mu^2}{2kT}}$ (Terms have their usual significances and A is a constant to be evaluated). Using that speed distribution function, evaluate the average translational kinetic energy of the gas molecules. Compare the expression with that predicted by classical equipartition theorem for one-dimensional mono-atomic gas.

3. A gas obeys the following equation of state :
$$p = \frac{RT}{V_m} - \frac{B}{V_m^2} + \frac{C}{V_m^3}.$$

Find the critical volume, pressure and temperature for the gas in terms of B and C. Will the gas exhibit critical behavior if it obeys a modified version of the above equation of state where the last term is dropped?

4. State the principle of equipartition of energy and apply it to calculate the molar heat capacity of N₂O , NO₂ and NO at constant pressure.

5. A gas obeys the following equation of state:

$P = \frac{RT}{(V_m - \beta)} \exp\left(-\frac{\alpha}{V_m RT}\right)$, where α and β are constants and other terms have their usual significances. Show that it behaves as a van der Waals gas at low and moderate pressure. Find the dimensions and S.I. units of α and β .

Given: $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$

6. Plot Maxwell's distribution function for the velocities of two different one-dimensional gases with molecular weights M and $2M$. Derive an expression for the average speed of a hypothetical two-dimensional gas using Maxwell's distribution for the speed of gas molecules.
7. State and explain the observed behaviour of C_p values of gases with temperature.
8. Calculate the root mean square deviation of speed of oxygen molecules at 300 K.
9. A gas obeys the following equation of state: $PV = RT\left(1 + \frac{B}{V}\right)$, where B is a constant. Will it be possible to liquefy it? Justify your answer. Find the dimension of B and the initial slope of the compressibility curve.
10. Assuming ideal behaviour, calculate the ratio of final to initial wall collision frequencies, when temperature is doubled keeping pressure constant, and vice versa.
11. Plot Maxwell's distribution function for translational kinetic energy of gas molecules at two different temperatures. In the graph, depict the fraction of gas molecules possessing energies lesser than a particular value ϵ and state briefly how this value can be calculated mathematically.
12. Can you obtain the most probable energy of gas molecules from the knowledge of most probable speed? Justify your answer.
13. Which of the three van der Waals attractive forces depend on temperature and why?

14. In an equimolar mixture of Helium and Hydrogen gas what will be the ratio of rates of effusion? How will this ratio change when the molar ratio is 1:4? (Assume ideal behavior)
15. Name the types of intermolecular forces contributing to attraction between the molecules in a mixture of Argon and HCl.
16. What will be the probability that the speed of an ideal gas molecule lies within ± 0.005 of 300 ms^{-1} at 27°C ? (Assume that the molecular weight of the gas is 28).
17. A gas obeys the following equation of state: $(P + a/TV_m^2)(V_m - b) = RT$, where 'a' and 'b' are two constants. State with reason whether the gas shows critical behaviour or not.
18. What is critical compressibility factor? What is its value for a gas obeying van der Waals equation of state?
19. Express van der Waals equation of state in the virial form and hence deduce an expression for the Boyle temperature of a gas obeying this equation of state.
20. Formulate an expression for the temperature at which an ideal gas has the same fraction of molecules moving with speeds C_1 and C_2 . Plot the molecular speed distribution curve for such a gas and depict the above-mentioned fractions on the graph.
21. The second virial coefficient of a gas is $13.7 \text{ lit mol}^{-1}$ at 273 K . Calculate the volume of the gas at NTP.
22. Calculate the root mean square deviation of translational kinetic energy of oxygen molecules at 298 K (assuming ideal behavior). What does it signify?
23. Does the mean free path of a gas molecule depend on temperature? Justify your answer. For N_2 at 350 K and 2 atm pressure, find the number of molecular collisions with the container wall of area 1 cm^2 per second.

24. The critical temperature and pressure for Xenon are 289.73 K and 5.84 MPa, Find the value of compression factor Z for xenon at reduced pressure 1.75 and reduced temperature of 1.35. Does it obey van der Waals equation of state at this state?
25. A real gas obeys the equation of state: $Z = A_1 + A_2P + A_3P^2$, and Z vs P curve shows a minimum at P_0 at temperature T_1 , which is lower than the Boyle temperature of the gas. Find i) A_1 , ii) the signs of A_2 and A_3 . Also find the dimensions of the virial coefficient.

UNIT-II: Thermodynamics-I

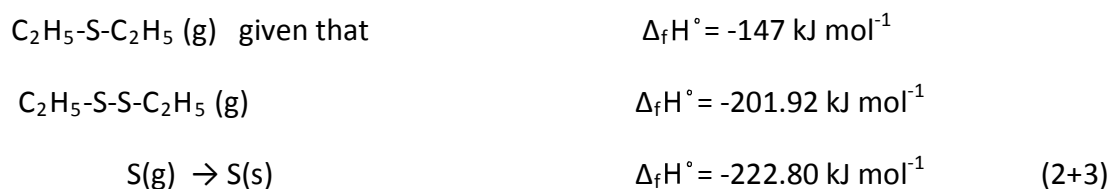
- Mention the conditions of thermodynamic equilibrium. How does the equilibrium state differ from a steady state? (2+3)
- a) Show that $(\frac{\delta P}{\delta T})_v = \frac{\alpha}{\beta}$ where α = coefficient of thermal expansion and β = coefficient of compressibility.
b) Distinguish bond enthalpy and bond dissociation enthalpy. (2+3)
- One mole of an ideal gas at 27°C and 1 MPa pressure is expanded adiabatically to a final pressure of 0.1 MPa against a constant opposing pressure of 0.1MPa. Calculate the final temperature, Q, W, ΔU and ΔH . (given $C_v = \frac{3}{2} R$) (5)
- (a) Under what conditions Heat (Q) is a state function?
(b) 2.0 mol of an ideal gas at 300K and 0.507 MPa are expanded adiabatically to a final pressure of 0.203 MPa against a constant pressure of 0.101 MPa. Calculate the final temperature, q, w, ΔU and ΔH . (1.5+3.5)
- (a) What is Joule coefficient? Show that it is given by the relation,

$$\eta = -1/C_v (\delta U/\delta V)_T = 1/C_v \{P - T(\delta p/\delta T)_v\}$$

(b) Show that $(\delta H/\delta P)_T \approx V$ for solids and liquids
(3.5+1.5)

6. (a) Justify or criticize whether $[\delta(G/T)/\delta(1/T)]_p$ is a state function or not.

(b) Find the bond enthalpy of S-S bond from the following data:



7. i) Show that $(\delta U/\delta V)_p (\delta V/\delta P)_T = -(\delta U/\delta T)_p (\delta T/\delta P)_V$

ii) One mole of chlorine gas undergoes adiabatic free expansion from 1 dm^3 to 10 dm^3 . If the initial temperature of the gas was 273 K, calculate T final, Q, W, ΔU and ΔH if the gas is considered as van der Waals gas. Given : $a = 655 \text{ dm}^6 \text{ kPa mol}^{-2}$, $b = 0.055 \text{ dm}^3 \text{ mol}^{-1}$, $C_{v,m} = 33.91 \text{ JK}^{-1} \text{ mol}^{-1}$.
(2+3)

8. i) Taking V is a state function, derive the equation of state for which $\alpha = (V-a)TV$ and $\beta = 3(V-a)/4PV$ where a is constant.

ii) Under what conditions heat (Q) becomes a state function?
(3+2)

9. The bond dissociation enthalpies of $H_2(g)$ and $N_2(g)$ are $+435.95 \text{ kJ mol}^{-1}$ and $+941.8 \text{ kJ mol}^{-1}$ and enthalpy of formation of $NH_3(g)$ is $-46.024 \text{ kJ mol}^{-1}$.

(a) What is the enthalpy of atomization of $NH_3(g)$?

(b) What is the average bond enthalpy of N-H bond?
(2+3)

CHT-13b

Unit-I: Thermodynamics-II

1. i) Prove that for n moles of **van der Waals gas** $(\delta S/\delta P)_T = (V-nb) / [2naV^3 R^{-1} (V-nb)^2 - T]$

ii) For Daniel cell calculate ΔH if $E = 1.10$ volt at 25°C and $n = 2$; $F = 96500$ Coulomb. (3+2)

2. i) Prove that the coefficient of performance of refrigerator $= T_2 / (T_1 - T_2)$; where $T_1 =$ High temperature reservoir and $T_2 =$ Lower temperature reservoir.

ii) A cup hot coffee is kept on a table at room temperature and it will gradually cool down at room temperature. So total entropy change will be negative – justify or criticize the statement.

(3+2)

3. i) Explain the Joule Thomson effect by plotting temperature(T) vs pressure (P) diagram for real gases.

ii) Prove that $(\delta V/\delta T)_S = -1 / (\gamma - 1) [(\delta V/\delta T)_P]$ where the terms have their usual meanings.

(2.5+2.5)

4. i) Explain the fact “ entropy as a measure of the microscopic but not macroscopic disorder”- explain .

ii) The Joule- Thomson coefficient for a van der Waals gas is given by $\mu_{JT} = [(2a-RT)-b]/C_{p,m}$. Calculate the value of ΔH for the isothermal change, 300 K, compression of 1 mole of nitrogen from 1 to 500 atm: $a = 0.136 \text{ m}^6 \text{ Pa mol}^{-2}$; $b = 0.0391 \text{ dm}^3 \text{ mol}^{-1}$. (1.5+3.5)

5. i) Sketch the **diagram H vs S** for the reversible **Carnot cycle** for an ideal gas.

ii) A typical 500 megawatt (500 megawatts = 500 MJ sec^{-1}) coal fired power plant burns about 200 tons of bituminous coal per hour (50 kg sec^{-1}) with a heating value of 12,500 btu. 1b^{-1} ($28,700 \text{ kJkg}^{-1}$). The high –temperature boiler operates at 538°C while the heat exchanger cools the condensed steam to about 50°C . Calculate the theoretical (maximum) efficiency of the process and compare with the efficiency that is actually achieved. (2+3)

6. a) What is inversion temperature? Show that for a vander Waals gas

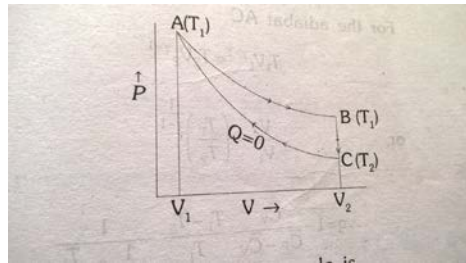
$$\mu_{JT} = 1/C_{p,m} [2a/RT - b - 3abp/R^2T^2]$$

b) Show that at moderate low pressure and high temperature, the above expression reduces to $\mu_{JT} = \frac{1}{C_{p,m}} \left(\frac{2a}{RT} - b \right)$ (3.5+1.5)

7. (a) Plot temperature (T) vs pressure (P) diagram under isoenthalpic condition for real gases and explain it. How does the plot appear for an ideal gas.

(b) Show that $C_p = C_v$ for water at 4 °C. Given that density of water is maximum at 4 °C. (2.5+2.5)

8. (a) One mole of an ideal gas is allowed to undergo the following cyclic process:



Show that the efficiency of the cycle is, $\eta = 1 - \frac{T_1 - T_2}{T_1} \ln \frac{T_1}{T_2}$

(b) Draw a Carnot Cycle for E vs V and H vs T diagrams with explanations. (3+2)

9 (a) Prove that $(\delta G / \delta T)_S = V C_p / T (\delta V / \delta T)_P - S$

(b) For an ideal gas $(\delta V / \delta S)_P = (\delta T / \delta P)_S$ (3.5+1.5)

10. (a) Entropy is a measure of the microscopic but not macroscopic disorder- explain.

(b) Calculate the entropy change of the universe as a result of each of the following processes: (i) An aluminium block of 500 gm mass of total heat capacity at constant pressure of 496.2 J/deg. at 100 °C is placed in a lake at 10 °C.

(ii) The same block at 10 °C is dropped on the lake from a height of 200 meters

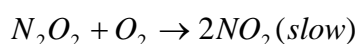
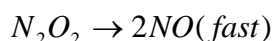
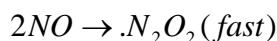
(iii) Two such blocks at 100 and 0 °C are joined together (2+3)

CHT-13b

Unit II: Chemical kinetics

1. Acid catalysed inversion of sucrose was carried out in presence of i) 0.5 M HCl and ii) 0.5 M acetic acid. Will the rates and rate constants be different?

2. The reaction $2NO + O_2 = 2NO_2$ proceeds through the following elementary steps:



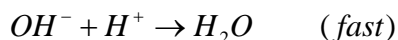
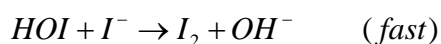
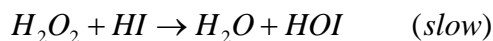
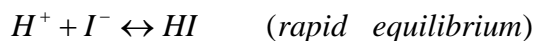
Predict the order of the reaction. The overall rate constant is found to decrease with rise in temperature. Why?

3. What will be the SI unit of pre-exponential factor of Arrhenius equation for a second order reaction? For another reaction, the plot of $\log(k/s^{-1})$ vs $1/T$ gives an intercept 13.5. Slope of the line is -5500 K. State the order of the reaction and calculate the energy of activation as well as the Arrhenius pre-exponential factor.

4. The rate law for the reaction $A \rightarrow \text{products}$ is $-\frac{d[A]}{dt} = k[A]^{\frac{1}{2}}$. Integrate this rate equation, find the dimension of the rate constant and show the plot of $[A]^{1/2}$ against time.

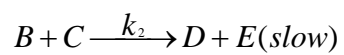
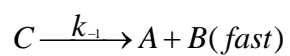
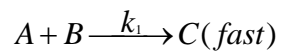
5. A substance decomposes with a rate constant $5 \times 10^{-3} \text{ Lmol}^{-1}\text{s}^{-1}$. Establish a relation between the half life and the initial concentration of the reactant. Calculate the half life of the substance when the initial concentration is 0.04 M

6. The reaction $H_2O_2 + 2H^+ + 2I^- \rightarrow I_2 + 2H_2O$ proceeds through the following steps:



Find the rate law predicted by this mechanism, mentioning the approximations made. If the concentration of I^- is kept constant during the reaction, what would be the order of the reaction?

7. For a reaction the plot of $\log t_{1/2}$ versus $\log a$ is a straight line with positive slope and intercept, which makes an angle of 45° with the $\log a$ axis. (Terms have their usual significances). What is the order of the reaction?
8. The rate of the reaction $2A + B \rightarrow 2D$ is doubled when the concentration of B is doubled, and increases by a factor of eight, when the concentration of both the reactants are doubled. What is the overall order of the reaction?
9. For a second order reaction, $A + B \rightarrow X$, involving two reactants at the same initial concentration, find an expression for the concentration of X as a function of time. Show that this expression reduces to the initial concentration of the reactants when a long time has elapsed.
10. A reaction has a rate constant equal to $0.015 \text{ mol L}^{-1} \text{ s}^{-1}$ at a certain temperature. If the initial concentration of the single reactant is 1 M, predict the change in concentration of the reactant (absolute value) after 5 seconds at that temperature. Draw a graph showing the dependence of this change in the concentration of reactant on temperature, assuming a positive value of overall activation energy.
11. Formulate Michaelis-Menten equation for a simple enzyme catalyzed two-step reaction scheme where the product formation step is practically unidirectional.
12. Draw a graph showing the dependence of rate constant of a reaction on temperature. Identify activation energy on the graph. In the same graph, show the change expected when a catalyst is added to the reaction mixture.
13. In a graph, depict the dependence of rate constant of
 - i) an acid catalysed reaction, and
 - ii) a base catalyse reactionon the pH of the reaction medium.
14. The reaction $A + 2B \rightarrow D + E$ is found to be a first order reaction with respect to A and B:



Is the above mechanism acceptable? What will be the order of reaction if the first two steps are slow and the third one is fast?

15. Consider the following parallel reaction scheme:



At 313 K the predominant product is B, while at 423 K the predominant product is C. Comment on the relative values of the rate constants with reason.

Chemistry Honours

Part II (2nd Year) Physical Chemistry

Third Paper

(Group – B)

CHT – 23a

Full Marks - 50

Unit – I: Thermodynamics and Equilibrium

Q1. Show that partial molar quantities are additive and hence derive the following expression:
 $U = \sum n_i U_i$; i is equal to 1 to n ; where terms have their usual meanings. (5)

Q2. How can the quantity $-\left(\frac{\partial G}{\partial \xi}\right)$ be viewed as a “driving force” towards chemical equilibrium - discuss. (5)

Q3. Sketch G vs ξ for a reaction for which $\Delta G^\circ < 0$. What are the roles of both ΔG° and the mixing Gibbs energy in determining the equilibrium position. (5)

Q4. a) Ammonium carbonate dissociates as, $\text{NH}_2\text{COONH}_4(\text{s}) \rightleftharpoons 2\text{NH}_3(\text{g}) + \text{CO}_2(\text{g})$. In a closed vessel containing ammonium carbamate in eqm. with its vapour, ammonia, is added such that the partial pressure of NH_3 now equals the original total pressure. Calculate the ratio of the total pressure now to the original pressure.

b) The vander Waals constants for CO_2 gas are $a = 3.59 \times 10^6 \text{ cc}^2 \text{ atm} / \text{mole}^2$ and $b = 42.7 \text{ cc} / \text{mole}$. Calculate the fugacity and fugacity coefficient of the gas at 100 atm pressure and 50 °C.

(2.5+2.5)

5. a) Show that in the low pressure range, the pressure of a real gas is the geometric mean of the ideal pressure and fugacity.

b) The solubility of CaF_2 at 27 °C is 3.55×10^{-11} . Using Debye – Huckel limiting law. Calculate the solubility of CaF_2 at 27 °C in moles / lit. (3+2)

6. a) The fugacity of a certain gas is given by the expression

$$f = P + \alpha P^2 \text{ where } \alpha = v_{\text{ideal}} - v_{\text{real}}$$

Show that $Pv_m/RT = 1 + \alpha P/(1 + \alpha P)$

b) The vapour pressure of $\text{NH}_4\text{HS(s)}$ at 25°C is 50.1 cm. Calculate the total pressure when $\text{NH}_4\text{HS(s)}$ dissociates at 25°C in a vessel already containing 32 cm pressure of NH_3 .



7. a) Prove thermodynamically “ the progress of a reaction in equilibrium will increase with increase in temperature (at constant pressure condition) provided it is in endothermic in nature.”

b) Does the equilibrium constant of a reaction depends upon (i) the standard state chosen for the reactants and products, (ii) stoichiometric representation of the reaction? Justify your answer? (2.5+2.5)

8. a) Explain – “The neutralization of all bases by acids do not necessarily occur at pH 7”

b) Using Debye-Huckel limiting law calculate the mean activity co-efficients of 0.001(M) aq. solutions of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$; assuming Debye-Huckel constant = 0.51. (2+3)

CHT – 23a

Unit – II : Liquid State and Viscosity of Fluids

6.a) The liquid state is characterized by short range order and long range disorder – explain.

b) Graphically represent the velocity profiles for fluid flow in a pipe: i) laminar flow;

(ii) turbulent flow with respect to the centre of a pipe.

(2+3)

7. a) Distinguish Newtonian fluid and non-Newtonian fluid with examples.

b) Two soap bubbles of radius 4 cm and 5 cm are joined together so as to have a common surface. Find the radius of the surface. (2+3)

8. a) What is the origin of gas viscosity and liquid viscosity?

b) For a water – air interface at 25 °C and 1 atm, calculate the capillary rise in a glass capillary tube with inside diameter of 0.200 mm. The surface tension of water at 25 °C is 72.0 dynes / cm. The densities of air and water at 25 °C and 1 atm are 0.001 g / cm³ and 0.997 g / cm³. (2.5+2.5)

9. What is meant by the contact angle of a liquid on a solid surface? State the factors on which the magnitude of the contact angle depends. (2.5+2.5)

CHT- 23b

Unit I: Quantum Chemistry I

1. For a particle in a 1-dimensional box, calculate the probability that the particle will be found in the middle third of the box: $L/3 \leq x \leq 2L/3$. From the general formula for arbitrary n , find the limiting value as $n \rightarrow \infty$
2. Predict the wavelength (in nm) of the lowest-energy electronic transition in the following ion: $(\text{CH}_3)_2\text{N}^+ = \text{CH} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{N}(\text{CH}_3)_2$
Assume that all the C–C and C–N bond lengths equal 1.40 Å. Note that N^+ and N contribute 1 and 2 π -electrons, respectively.
3. Determine the order of magnitude of nuclear energies. Assume that a nucleus can be represented as a cubic box of side 10^{-14} m. The particles in this box are the nucleons. Calculate the lowest allowed energy of a nucleon. Express your result in MeV (1 MeV = 10^6 eV = 1.602×10^{-13} J and mass of proton = 1.67×10^{-27} kg)
4. Consider two “cube-atoms” which may be represented by two electrons held in two cubic potential boxes of length a . Now consider a hypothetical reaction in which two atoms fuse to form a “molecule-box”. Calculate the energy change in this reaction assuming no interaction between the electrons. Comment on the feasibility of such a reaction based on your result.
5. As a variant on the free-electron model applied to benzene, assume that the six π electrons are delocalized within a square plate of side a . Calculate the value of ‘ a ’ that would account for the 268 nm ultraviolet absorption in benzene.

6. For a particular quantum mechanical operator no two eigenfunctions can have the same eigenvalue - Justify or criticize.
7. Planck's constant has the same units as that of angular momentum - Justify or criticize.
8. The momentum of a particle in a one dimensional box cannot be measured exactly – Justify or criticize.
9. Electron diffraction makes use of 40 keV electrons. Calculate their de Broglie wavelength. (1 eV = 1.602×10^{-19} J)

10. A certain one-dimensional quantum system in $0 \leq x \leq \infty$ is described by the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - \frac{q^2}{x} \quad (q \text{ is a constant})$$

One of the eigenfunctions is known to be

$$\psi(x) = A x e^{-\alpha x}$$

where A is a constant and $\alpha = \frac{mq^2}{\hbar^2}$

- a) Write down the Schrödinger equation and carry out the indicated differentiation.
- b) Find the corresponding energy eigenvalue (in terms of \hbar , m and q).
- c) Find the value of A which normalizes the wavefunction.

$$\text{Given: } \int_0^{\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

11. Consider the eigenvalue equation $\hat{A}\psi(x) = \alpha \psi(x)$

The physical significance of the eigenvalue α is that it is the statistical average of a large number of measurements of A on identical systems. Justify or criticize the above statement.

12. State the salient features of photoelectric effect that cannot be explained from the standpoint of classical physics.
13. Derive an expression for the total energy of a particle held in a one dimensional potential box using the de Broglie formula.
14. Assuming that the electron in hydrogen atom is a matter-wave, show that Bohr's postulate regarding the angular momentum of electron in a stationary orbit is justified.

15. Indicate with reason the functions from among the following that are acceptable as wave functions over the given intervals:

i) e^{-x} $[-\infty, \infty]$

ii) $e^{-|x|}$ $[-\infty, 0]$

iii) e^{-x} $[0, \infty]$

iv) $\sin^{-1}x$ $[-1, 1]$.

(ii) $1/x$ $[a, \infty]$

(iii) $\cos^{-1}x$ $[-1, 1]$

iv) xe^{-x} $[0, \infty]$

v) $\ln x$ $[0, a]$

Normalize the acceptable wave functions.

16. Evaluate the commutator $[x, p_x^2/2m]$ and comment on your result, where x and $p_x^2/2m$ are position and kinetic energy operators for a 1-particle 1-dimensional system.

17. Determine the values of $\Delta x = \{ \langle x^2 \rangle - \langle x \rangle^2 \}^{1/2}$ and $\Delta p = \{ \langle p^2 \rangle - \langle p \rangle^2 \}^{1/2}$ for the ground state of a particle held in a one-dimensional potential box in terms of measurable quantities and comment on the importance of these values with reference to Heisenberg's uncertainty principle. (The terms have their usual meanings).

18. For a particle held in a one dimensional potential box, the lowest observed transition frequency is $2.0 \times 10^{14} \text{ s}^{-1}$. Find the length of the box. [Given: Mass of the particle = $9.1 \times 10^{-28} \text{ gm}$]

19. Find out the degeneracy of the first two energy levels for a particle held in a three dimensional box of dimensions $l_x = l_y = 2 l_z$

20. Derive an expression for the energy of a particle of mass 'm' held in a one dimensional potential box of length 'L' assuming that the particle can be described by a standing de Broglie wave within the box. Using the expressions for energy for a particle in a cubical box of the same length, given the condition: $n_x + n_y + n_z = 4$, indicate the level of degeneracy, if any, and find the degeneracy of the energy level that is three times higher than that of the lowest level.

21. Is $\cos ax \cos by \cos cz$ an eigen function of the Laplacian operator?

22. Work out the operator $(\hat{A})^2$ and state whether $(\hat{A})^2$ commutes with the position operator x , if

$$\hat{A} = \left(\frac{d}{dx} + x \right)$$

23. The lifetime of an excited state of a nucleus emitting γ -rays is about 10^{-12} s. What is the uncertainty in the frequency of the γ -ray produced from it? If we locate an electron within 50 pm (the Bohr radius), what will be the uncertainty in its speed? Comment on your result.

24. Show that $\langle E^2 \rangle - \langle E \rangle^2 = 0$ for a particle in a box of length 'L' represented by the wavefunction $\psi(x) = (2/a)^{1/2} \sin(n\pi x/L)$, ($0 \leq x \leq L$; $n = 1, 2, 3 \dots$). What does this result imply?

25. Set up time independent Schrödinger wave equation for a particle of mass 'm' moving in a one-dimensional potential box extending from '-a/2' to 'a/2', where 'a' is a finite length along x axis. Find the energy eigenfunctions.

26. A particle in a 1 dimensional box of length 'L' is represented by the wavefunction $\psi = \phi_2 + 2\phi_4 + \phi_6$ where ϕ_n s are the normalized wave-functions for $n=2,4,6$ eigenstates of the system. Is ψ an eigenfunction of the Hamiltonian for the system?

27. ψ is a solution to the time-independent Schrodinger equation for a particle executing motion in 1-dimensional space. Will the function $g(y)$ ~~be another~~ $g(y)$ is any function of y ? Calculate the uncertainty in frequency for an electron de-excitation from an excited state of life time 10^{-8} s.

28. Benzene may be regarded as a 4.0 \AA square box containing 6 π -electrons. Calculate the wavelength of radiation required to promote a π -electron to the first excited state.

29. If Ψ is a wave-function representing a two-particle, 3-dimensional system, what is the physical significance of Ψ ? State the normalization condition for Ψ when the space coordinates vary from $-L$ to $3.5L$.

30. What is Compton wavelength?

CHT – 23b

Unit II: Electrochemistry

- State and explain the Kohlrausch's law of independent migration of ions. How does it help in determining the molar conductivity at infinite dilution of a weak electrolyte?
 - Explain why conductivities of H^+ and OH^- ions in aqueous medium are rather abnormally high.
 - Explain, why ionic molar conductivity at infinite dilution increases in the order of Li^+ , Na^+ , K^+ and Rb^+ , etc.
- Define ionic mobility. What is its unit? How does it differ from ionic speed?
 - Explain why the amide ion in liquid ammonia has abnormally high transport number.
 - "Transport number of Cl^- ion in aqueous solution of HCl is 0.16 and it is 0.62 in aqueous solution of NaCl" – explain the difference.
- Discuss the nature of the following conductometric titration curves:
 - $Ba(OH)_2$ versus $BaCl_2$ solution
 - NH_4Cl solution versus NaOH solution.
- The conductivity of a saturated solution of CaF_2 at $18^\circ C$ was found to be $4.2 \times 10^{-5} S\ cm^{-1}$. The conductivity of water used for making the solution was $2 \times 10^{-6} S\ cm^{-1}$. The molar ionic conductivities at infinite dilution of Ca^{+2} and F^- are 104.0 and 48.0 $S\ cm^2\ mol^{-1}$, respectively. What is the solubility and solubility product of CaF_2 ? (Assume that only Ca^{+2} and F^- are present in the solution.)
- Construct the galvanic cell for each of the following reactions and write down the corresponding expression for the cell potential.
 - $AgCl(s) + I^-(aq) = AgI(s) + Cl^-(aq)$
 - $Ag(s) + 1/2 Br_2(l) = AgBr(s)$
 - $Ag^+(aq) + Cl^-(aq) = AgCl(s)$
 - $HgO(s) + H_2(g) = Hg(l) + H_2O(l)$

6. Starting from the Gibbs – Helmholtz equation and the relation $\Delta G = -nFE$; derive the following expressions of ΔH and ΔS .

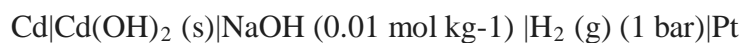
$$\Delta H = -nF[E - T(\delta E/\delta T)_P]; \quad \Delta S = nF(\delta E/\delta T)_P$$

7. a) Show that the standard equilibrium constant of the cell reaction at 298 K can be computed from the relation

$$\text{Log } K^\circ = n(E^\circ/\text{volt})/0.05913$$

b) Show that the essential condition for a cell reaction to be at equilibrium is $E_R = E_L$.

8. Given the cell



With $E_{\text{cell}} = 0.0\text{V}$ at 298°K . If $E^\circ_{\text{Cd}^{+2}|\text{Cd}} = -0.40\text{V}$. Calculate (a) K_{sp} for $\text{Cd}(\text{OH})_2$ and (b) ΔG , ΔH and ΔS for the cell reaction if $(\delta E/\delta T)_P = 0.002 \text{ V K}^{-1}$.

SEVENTH PAPER
(Group –A)
Full Marks - 75

CHT- 33a

Unit-I: properties of solids, interfaces and dielectrics

- 1.a) What is the lowest limit of wavelength of X ray used to produce reflection spectra?
- b) Using X- rays of wavelength, $\lambda = 170.0$ pm, a metal produces reflection at $2\theta = 47.2^\circ$. If this is a first order reflection from the 110 planes of a body centered cubic lattice, what is the edge length of the cube?
(2+3)
- 2.a) The distances between two successive parallel planes in a cubic crystal cannot be $1/\sqrt{7}$ - Comment.
- b) Explain qualitatively why the reflections from (hkl) planes are either all odd or all even for f.c.c. and h+k+l is even for b.c.c. solids?
(2+3)
3. a) Distinguish between physical adsorption and chemisorptions.
- b) Adsorption of a gas on solid surface is an exothermic process-Justify or criticize.
(2+3)
- 4 a) Explain Kraft temperature. Discuss the effect of addition of electrolyte on Zeta potential.
- b) “The orders of heterogeneous catalytic reaction changes if the pressure changes”-Justify (2+3)
5. a) The dielectric constant of a liquid compound of molecular weight 84.16 is 2.033; its refractive index (D line) is 1.427 and its density is 0.778 g cm^{-3} at 20°C . Determine its molar and electronic polarizations. Comment on the polarity of the molecule from these results.
- b) Explain why lyophilic sols are more stable than lyophobic sols?
(3+2)

Questions (Module CHT 33a, Unit II)

1. The energy levels of a linear harmonic oscillator are non-degenerate – Justify or criticize.
2. We usually solve Schrödinger wave equation for linear harmonic oscillator in Cartesian coordinates, but for hydrogen atom we always choose spherical polar coordinates. Why?

3. Show that $e^{im\phi}$ is an eigenfunction of the one-particle orbital angular momentum operator \hat{L}_z in spherical polar coordinates, normalize it, and complete the equation: $\hat{L}_z^3 Y_l^m = ?$ (The angular momentum quantum numbers are $l = 0, 1, 2, \dots$ and $m = l, l-1, \dots, 0, \dots, -l+1, -l$. The functions Y_l^m are spherical harmonics).
4. What is the energy of the ground state of a rigid rotor? Does it violate Heisenberg's uncertainty principle?
5. The radial wave-function for the 2s state of hydrogen atom is given by $R_{2s} = \frac{1}{\sqrt{32\pi}} \left(\frac{1}{a_o}\right)^{3/2} \left(2 - \frac{r}{a_o}\right) e^{-\frac{r}{2a_o}}$ (where a_o is Bohr radius and r is distance from the nucleus). Locate the node(s) in R_{2s} . Plot R_{2s} and the corresponding radial distribution function against r/a_o .
6. Bohr's theory assumed that the angular momentum of electron in the ground state is equal to \hbar . What is the value predicted using quantum mechanical calculations?
7. Show that \hat{L}_z, \hat{L}^2 and $\hat{H}_{relative}$ for hydrogen atom commute with each other (the terms have their usual significances). Comment on the consequences of such commutation properties.
8. Justify the non-zero energy of a molecular harmonic oscillator at the $v=0$ state from the standpoint of Heisenberg's uncertainty principle.
9. Write down and normalize the radial distribution function for the 1s state of hydrogen atom.
10. What is the expectation value of $\frac{1}{r}$ for a hydrogen-like atom in the 1s state?

Given:
$$\int_0^{\infty} e^{-x} x dx = 1$$

11. Show that the function e^{-gx^2} is a solution of the Schrödinger wave equation for a linear harmonic oscillator. Find the value of g in terms of mass and force constant of the particle.
12. The real wave-functions ψ_{2p_x} and ψ_{2p_y} for hydrogen atom are obtained by linear combination of the states ψ_{2p_1} and $\psi_{2p_{-1}}$. State with reason, whether ψ_{2p_x} and

Ψ_{2p_y} are eigenfunctions of \hat{L}_z and \hat{L}^2 operators for hydrogen atom, when the symbols have their usual significances

13. What is the origin of quantization of the z-component of orbital angular momentum in hydrogen atom?
14. Write down the wave function for the 1S orbital of a hydrogen atom in terms of Bohr radius. Depict graphically, with explanation, the plots of (i) ψ_{1s} against r, (ii) $4\pi r^2 \psi_{1s}$ against r.
15. Why should a harmonic oscillator have a zero-point energy?
16. What is the physical significance of the radial distribution function of a particular state of hydrogen atom.
17. Find the most probable distance of the 1s electron from the nucleus in a hydrogen atom.
18. A particle on a ring is described by the wavefunction $\psi = ae^{i\phi} + be^{2i\phi} + ce^{3i\phi}$. Calculate its mean kinetic ene

CHT 33b

Unit I: Phase equilibrium and colligative properties

9. a) In a single graph, draw the μ -T plots for solid and liquid phases of (i) pure solvent and (ii) solvent in solution. Mention the thermodynamic basis for the depression of freezing point.
 b) Elevation of freezing point is observed sometime for solutions- justify. (3+2)
10. What do you understand by an azeotrope? Calculate the degree of freedom for an azeotrope in a two component liquid- vapour equilibria. (3+2)
11. Starting from the appropriate form of the Duhem- Margules equation deduce Konowaloff's rule and discuss its significance. (5)
12. 100 g of a 1: 1 (by weight) mixture of water and phenol is taken at 40 °C. It shows two layers: (i) Phenol (9.2%) in water and (ii) water (35%) in phenol. Find the amount of the two layers. Also mark the above three % values of phenol (w/w) in proper T - wt% of phenol diagram. Assume CST =66 °C, wt% of phenol at CST = 33 (5)

13. Derive thermodynamically a relation between the osmotic pressure of a dilute solution of a solute and its molar concentration. State the assumptions and approximations involved. (5)

Unit II: Statistical thermodynamics and the third law

14. State the third law of thermodynamics relating entropy of a perfectly crystalline solid at zero Kelvin. Show that the statement is perfectly consistent with the statistical definition of Entropy. Comment on the value of S at $T = 0^\circ\text{K}$ for CO (3+2)
15. For a collection of equispaced non-degenerate levels, evaluate the partition function and from it get an expression for internal energy of the system. (5)
16. Give definition and significance of Einstein's characteristic temperature. Explain why Einstein's theory of heat capacity of solids fails to explain the experimental temperature heat capacity entirely. (5)

Questions (Module CHT 33c, Unit I)

1. According to the collision theory of elementary bimolecular gas phase reactions, the pre-exponential factor of Arrhenius equation should be independent of temperature– Justify or criticize.
2. When the reaction between potassium persulphate and potassium iodide are carried out using two different initial concentrations, the rate constants differ. – Justify or criticize.
3. What is photo-sensitized reaction? Discuss with a suitable example.
4. State whether there is any exception to the Stark-Einstein law of photochemical equivalence.
5. For the photolysis of gaseous HI to produce hydrogen and iodine using light of wavelength 254 nm, quantum yield is 2. Calculate the number of moles of HI decomposed when 300 J of light is absorbed.
6. While setting up a calibration curve for the determination of concentration of dichromate ions in aqueous solution using a spectrophotometer, what would be the criteria for choosing the concentrations of the standard solutions?
7. What are internal conversion and inter-system crossing? Explain with the help of a Jablonsky diagram.
8. Why phosphorescence is observed at low temperature and in solid matrix?
9. State and explain Frank-Condon principle with a suitable diagram.
10. What is photo-stationary state? Discuss with a suitable example.
11. What is the physical basis of 'vertical transition' in electronic spectroscopy?
12. State three basic assumptions of transition state theory of chemical reactions.

13. While setting up a calibration curve for the determination of concentration of Mn^{2+} ions in solution using a spectrophotometer, is it necessary to record absorbance at the λ_{max} of permanganate ion?
14. Why is phosphorescence lifetime much greater than fluorescence lifetime?
15. The acid-base indicator Bromo-cresol green (BCG) in strongly alkaline solution transmits 20% of the incident monochromatic radiation of wavelength 570 nm. Under identical experimental conditions, the transmittance was 72% for a buffer solution at pH 4, with the same concentration of added BCG indicator. Calculate the pK_{In} of the indicator.
16. Define fluorescence quantum yield. The photodecomposition of HI was carried out with radiation of wavelength 2820 Å. Absorption of each calorie produced 1.995×10^{-5} g of hydrogen gas. Calculate the quantum yield.
17. During experiments in spectrophotometry, it is advised to keep the percentage transmission above 15 and within 70-75. Why?
18. State the assumptions for the collision theory of bimolecular gas phase reactions, indicating the one which is not valid in most real systems. Explain the following: The value of the probability factor in the expression of rate constant of the bimolecular gas phase reaction

$$K + Br_2 = KBr + Br \quad \text{is much greater than 1.}$$

Questions (Module CHT 33c, Unit II)

1. For the molecule HI, the force constant and anharmonicity constant are 314 Nm^{-1} and 0.0172 respectively. Predict the intensity of the first hot band relative to that of the fundamental at 300 K.
2. A linear molecule has formula AB_2 . How would you ascertain whether the molecule has the structure BAB or ABB using spectroscopy as a tool?
3. Calculate the relative intensity of the 5th and the 2nd microwave absorption line of HCl molecule at 300 K. Which will be the most populated state at that temperature? (Given: $B=10.593 \text{ cm}^{-1}$)
4. 'A harmonic oscillator can absorb photons of different energies, corresponding to changes to different energy states' – Justify or criticize.
5. The rotational constant for the linear molecule $^{16}\text{O}^{12}\text{C}^{32}\text{S}$ is 0.202864 cm^{-1} . Calculate the moment of inertia of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$. If the moment of inertia of $^{16}\text{O}^{12}\text{C}^{34}\text{S}$ is 1.024637 times that of $^{16}\text{O}^{12}\text{C}^{32}\text{S}$, calculate the bond lengths of the species assuming that isotopic substitution does not affect bond length.
6. Justify or criticize: 'The ground state rotational energy of a rigid rotator is non-zero'.
7. What are fundamentals, overtones and hot bands in vibrational spectroscopy?

8. H^{80}Br molecule has a bond length of 142.3 pm and is observed to have absorption at 2559 cm^{-1} . Calculate the force constant of HBr molecule in SI unit assuming harmonic oscillation. Do you expect DBr to vibrate with a greater or lower frequency? Justify your answer.
9. 'A molecule with zero dipole moment cannot change its rotational state' – Justify or criticize.
10. The rotational constant for $^{12}\text{C}^{16}\text{O}$ is $3.83 \times 10^{-23}\text{ J}$. Calculate B in cm^{-1} unit. Find the value of B for $^{12}\text{C}^{18}\text{O}$.
11. Justify or criticize the following statement: Aqueous medium is not suitable for IR spectroscopy.
12. The fundamental and first overtone transitions of NO molecule are centered at 1876 and 3724 cm^{-1} respectively. Evaluate the equilibrium vibrational frequency and the zero point energy.
13. Using 435.8 nm lines of mercury as source of radiation a Raman line was observed at 444.7 nm. What is the Raman shift? Which is the most populated level of ICl ($B=0.114\text{ cm}^{-1}$) at 298 K?
14. State with reasons which of the following molecules show i) Microwave spectrum, ii) Infra-red spectrum, iii) Raman spectrum. HCl , Br_2 , CO_2 , CCl_4 , C_2H_4
15. The vibrational Raman spectrum of $^{35}\text{Cl}_2$ molecules show a series of Stokes lines separated by 0.98 cm^{-1} and a similar series of anti-stokes lines. Calculate the Cl-Cl bond length.

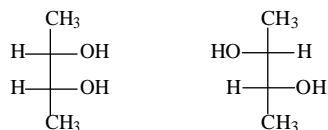
CHEMISTRY HONS
ORGANIC CHEMISTRY

Year -I (PART-I)

Paper IA (CHT 12a)

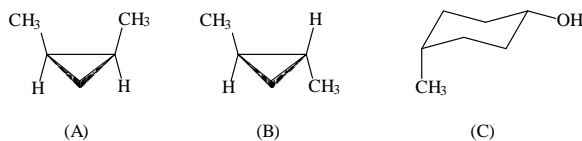
Unit-1

1. Indicate the relationship between the following two structures as Identical or enantiomer or diastereomer? And indicate the chiral centers as 'R' or 'S'.



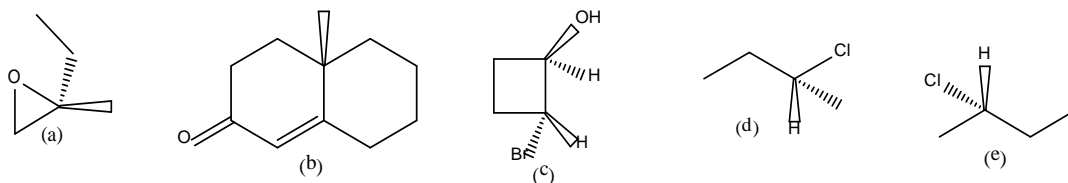
2. The specific rotation of pure (R)-2-butanol is -13.5° . What % of a mixture of the two enantiomeric forms is (S)-2-butanol if the specific rotation of this mixture is -5.4° ?

3. Which of the following molecules is chiral? Assign (D) and (E) as 'E' or 'Z'.

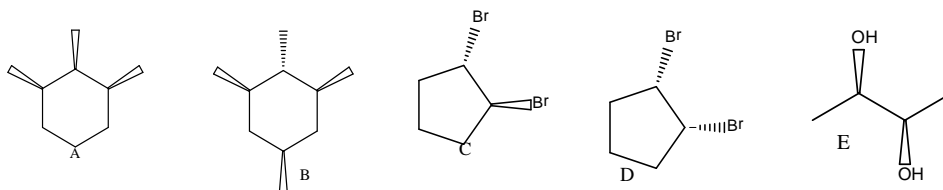


4. Write all the possible conformational structures for n-butane and draw the energy profile diagram showing the rotation between $C_2 - C_3$ bond in Newman Projection structures.

5. Determine the configuration (R or S) around the asymmetric center(s) in each of the following compounds.

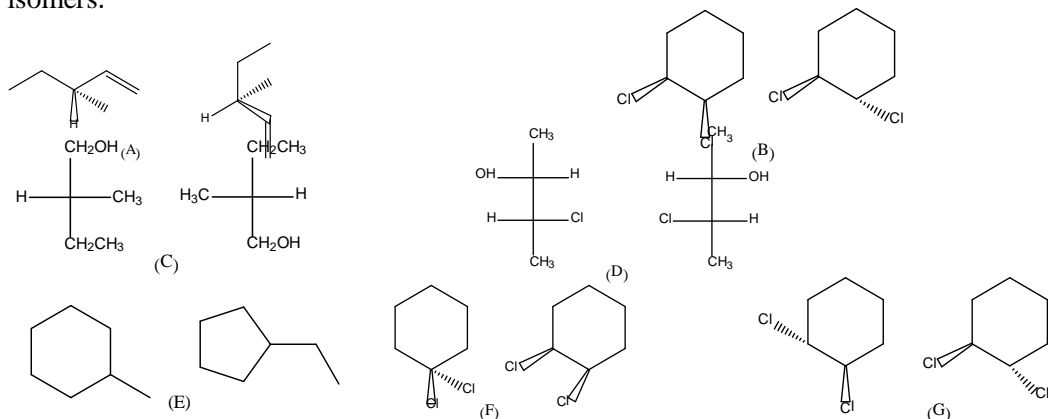


6. Identify the meso compounds and show the plane of symmetry.

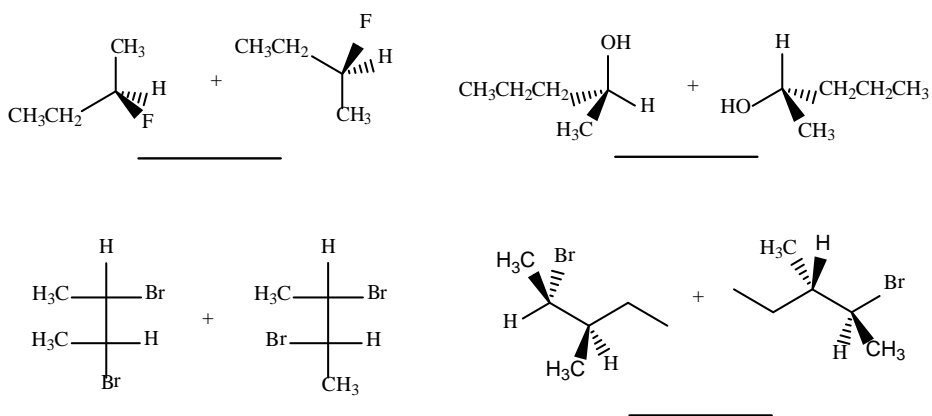


7. Draw all stereoisomers of 1,2,3,4,5-pentanepentol.

8. Identify if the following pairs of compounds are identical, enantiomers, diastereomers or constitutional isomers.

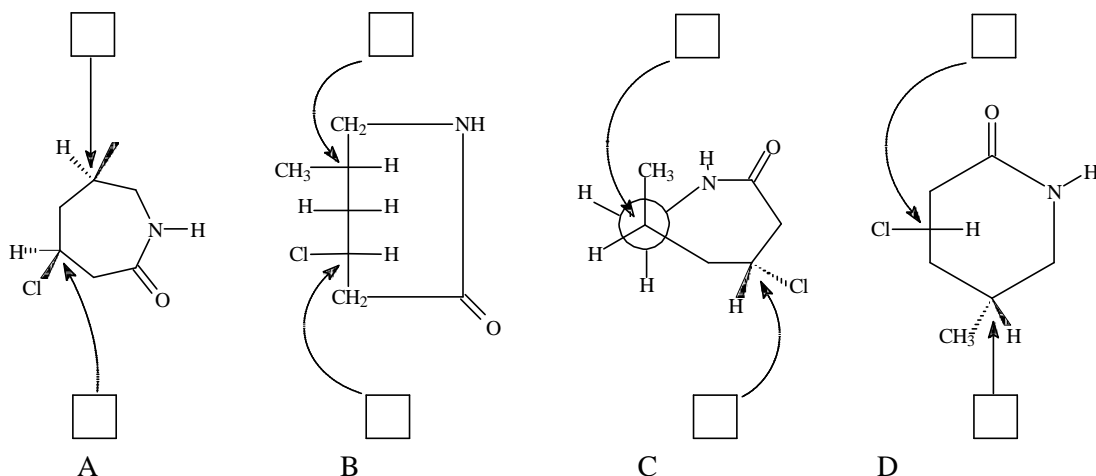


9. Using Newman projections, draw the three staggered conformations of 1-bromobutane and 3-ethylheptane formed from rotation along the C1-C2 bond and the C3-C4 bond respectively. Mention the most stable conformation in each case.
10. Indicate whether the following pairs of molecules are identical, enantiomers, diastereomers or stereochemically unrelated. Mention any meso compounds.



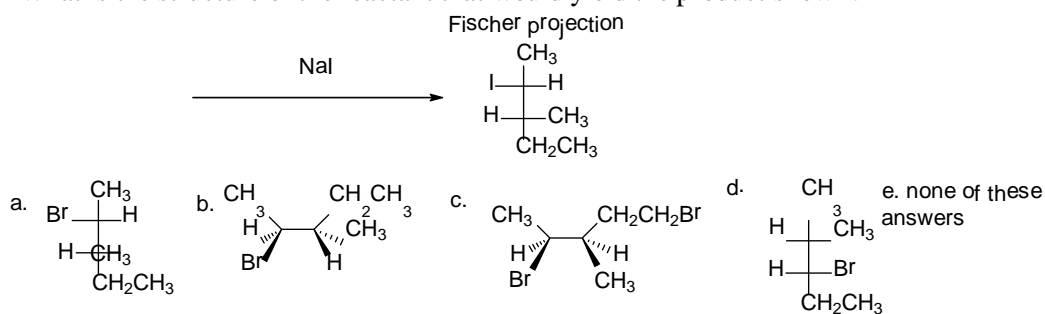
11. Draw the indicated stereoisomer, clearly showing the stereochemistry
- (a) *cis*-4-chlorocycloheptanol, (d) (*E*)-1-bromo-3-chloro-2-methoxy-2-pentene
- (b) (*Z*)-3-hexen-3-amine, (e) (2*S*,3*R*)-3-methylpentan-2-ol
- (c) (*S*)-3-methylpent-1-ene
12. Draw the Fischer and Newmann projection structures in their most stable conformation of (2*R*, 3*R*)-2,3-dibromopentane.

13. Consider the molecules below and answer the following questions.



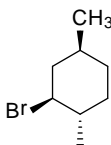
- i) In the boxes provided, assign the configuration R or S to each chiral atom above.
- ii) Identify the relationship between the following pairs using one of: enantiomers, diastereomers, mesomer, same compound or no relationship.
(A,B); (A,C); (B,C); (B,D).

14. . What is the structure of the reactant that would yield the product shown?



15. How many (max. no.) of possible stereoisomers (enantiomers + diastereomers) are there of the molecule shown below

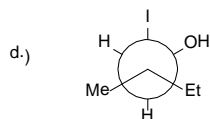
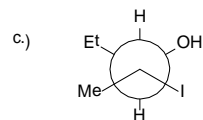
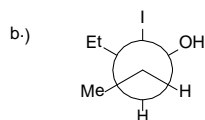
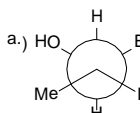
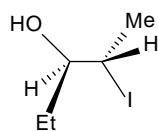
- a) 1 b) 2 c) 8 d) 5 e) 4



16. Provide the IUPAC name for the molecule shown below:



17. Which is the enantiomer of this compound?



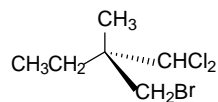
e.) none of these answers

. Which is the identical molecule of the compound shown in question 18?

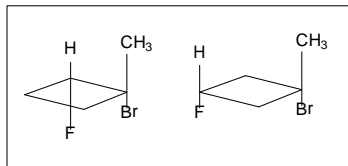
20. Which is the constitutional isomer of the compound shown in question 18?

21. Which is the diastereomer of the compound shown in question 18?

22. Assign a configuration (R or S) to the following molecule.

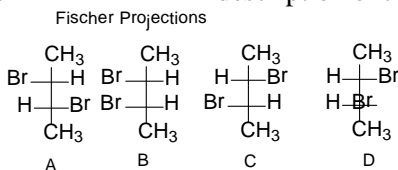


23. What is the correct stereochemical description of the relationship between this pair of molecules?



a) identical b) constitutional isomer c) enantiomers d) diastereomers e) none of these

24. What is the correct stereochemical description of the relationship between structures A and B?



(a) Identical (b) constitutional isomers (c) enantiomers (d) diastereomers (e) none of these answers.

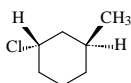
25. What is the correct stereochemical description of the relationship between structures A and C in question 24?

(a) Identical (b) constitutional isomers (c) enantiomers (d) diastereomers (e) none of these answers.

26. . What is the correct stereochemical description of the relationship between structures B and D in question 24?

(a) Identical (b) constitutional isomers (c) enantiomers (d) diastereomers (e) none of these answers.

27. Give the correct IUPAC name for the following compound

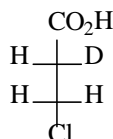


28. Optical rotation of an optically active substance having concentration 1 g/ml is found to be $+5^\circ$ when measured in a polarimeter with tube length of 1 m. Calculate the specific rotation of the sample. The specific rotation value in literature is found to be $+365^\circ$. – explain the anomaly.

29. Suggest a procedure for resolving racemic alcohols. Why racemic alcohols are not resolved by converting them into diastereomeric esters?

30. What do you mean by chiral environment? Show that the environment of an achiral substance could be chiral.

31. Find out the homomorphic ligands and also find out their topic relationship.



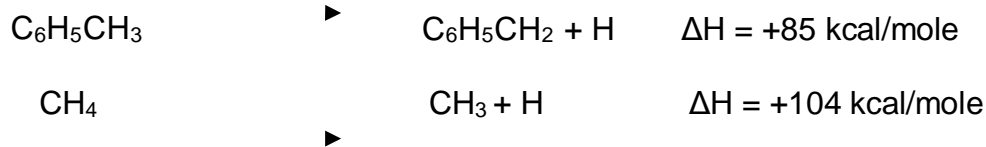
Unit II. Bonding and Physical properties

- (a) Using molecular orbital theory, show that benzene is more stable than 1,3,5-hexatriene.
(b) Apply molecular orbital theory to explain that the carbocation $\text{CH}_3\text{OCH}_2^+$ has greater stability than $\text{CH}_3\text{CH}_2\text{CH}_2^+$.
- (a) Croconic acid is as strong as sulphuric acid. – Explain.
(b) Compare the C=O bond distance in acetone, propionate and 2,3-diphenylcyclopropenone.
- (a) “Heat of combustion and not heat of hydrogenation is more suitable to compare the stabilities of 1-butene, *cis*-2-butene, *trans*-2-butene and isobutene.” – Explain.
(b) An acid has a K_a of 4.53×10^{-6} in water. Find the K_{eq} for the same acid.

CHT 12b

Unit I. General treatment of reaction mechanism

- (a) Explain why the bond dissociation energy (homolytic) for a benzylic hydrogen is less than that of a methane hydrogen.

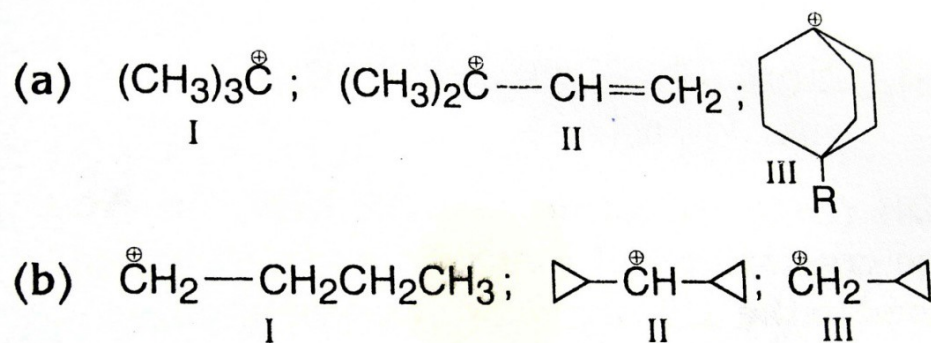


Provide an energy diagram to illustrate your answer

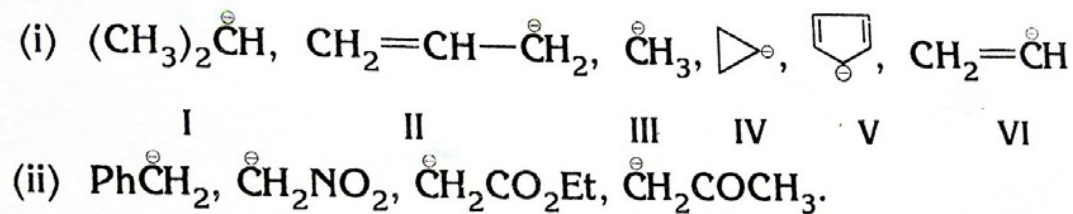
(b) When triphenylmethyl chloride (Ph_3CCl) is dissolved in benzene and then treated with Ag or Zn in the absence of air, a yellow solution is obtained, which when evaporated forms a white residue. The yellow colour of the solution disappears in the presence of O_2 and I_2 . Explain these observations.

- Explain why aryldiazonium ions are more stable than alkyldiazonium ions.
What happens when an acidic solution of an aryldiazonium salt is warmed?

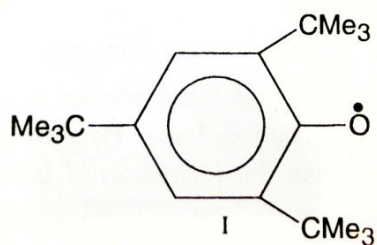
3. Arrange the following carbocations in order of their increasing stability with reasoning:



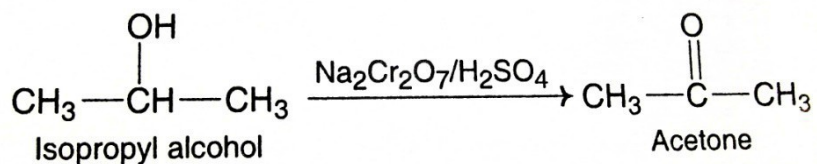
4. Arrange the following carbanions in each of the following series in order of increasing stability:



5. (a) The phenoxy radical I exists not as the dimer but in this form both in solution and in the solid state.



6. Give the mechanism of the following reaction (chromic acid oxidation of isopropyl alcohol):



Which step of this mechanism is rate-determining? Give evidence in favour of your answer.

7. What do you understand by kinetic isotope effect? What are primary and secondary isotope effects? Illustrate these techniques of elucidation of reaction mechanisms with suitable examples.

Unit 2. Nucleophilic substitution reactions

1. Account for the following observation:

(a). When (R)-2-bromopropanoate ion is treated with concentrated sodium hydroxide, (S)-2-hydroxypropanoate ion is obtained. However when the same reaction carried out with a low concentration of hydroxide ion in the presence of Ag_2O , (R)-2-hydroxypropanoate ion is obtained.

(b). β -chlorodiethyl sulphide, $\text{EtSCH}_2\text{CH}_2\text{Cl}$, undergoes hydrolysis very much faster than β -chlorodiethyl ether, $\text{EtOCH}_2\text{CH}_2\text{Cl}$.

2. What is neighbouring group participation? Discuss the mechanism and stereochemistry of the reactions involving neighbouring group participation. Why does enhancement of reaction rate (anchimeric assistance) occur in such reaction?

3. Active threo-3-bromo-2-butanol, upon treatment with HBr, gives rise to (\pm)-2,3- dibromobutane. From this observation how would you establish that the reaction proceeds not by the ordinary $\text{S}_{\text{N}}2$ or $\text{S}_{\text{N}}1$ mechanism, but by the neighbouring group mechanism (bromine acting as a neighbouring group).

4. Account for the following observation:

(a) Alkaline hydrolysis of $\text{Et}_2\text{NCH}_2\text{CHClCH}_2\text{CH}_3$ produces $\text{Et}_2\text{NCH}_2\text{CH}_2\text{OH}$.

(b) Chloroacetone undergoes $\text{S}_{\text{N}}2$ reaction faster than does n-propyl chloride, but it undergoes $\text{S}_{\text{N}}1$ reaction much more slowly.

5. Explain the following observations:

(a) β -(p-methoxyphenyl)ethyl tosylate, $p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{OTs}$, undergoes acetolysis faster than β -phenylethyl tosylate, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OTs}$, which in turn undergoes acetolysis faster than ethyl tosylate, $\text{CH}_3\text{CH}_2\text{OTs}$.

(b) Ethyl methyl ether reacts with HI to give ethanol and methyl iodide, whereas tert-butyl methyl ether is cleaved by HI to give methanol and tert-butyl iodide.

6. (a) Explain why (+)-2-iodobutane reacts with iodide ion in acetone to give optically inactive (\pm)-2-iodobutane instead of only (-)-2-iodobutane. Draw an energy diagram for this racemization process.

(b) The hydrolysis of methyl chloride takes place much faster in the presence of sodium iodide.

YEAR –II (PART –II)

CHT 22a

Unit I((Addition reactions)

- (a) Show how deuterium labelling experiments may be used to establish the mechanism of *Cannizzaroreaction*.
(b) Explain the role of Li^+ ion in the reduction of carbonyl compounds with LiAlH_4 . Give the mechanism of the reaction.

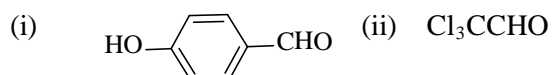
2. What is *thiamine*? Write down the mechanism of *thiamine* catalyzed *Benzoin condensation* reaction.

3. (a) Explain the concerted mechanism and stereospecificity of *Diels-Alder reaction* in terms of the principle of conservation orbital symmetry.

(b) “Cyclic 1,3-dienes are more reactive than that of an acyclic diene.” –Explain.

4. (a) On ozonolysis the optically active alkene **A** (C_8H_{16}) gives acetone as one of the products. Identify the alkene **A**.

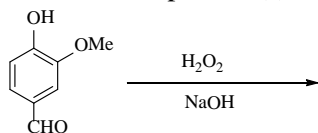
(b) Explain why the following aldehydes with no α -hydrogen atom do not undergo the *Cannizzaro* reaction.



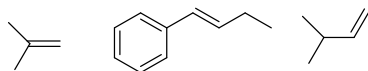
5.(a) The reaction between $\text{PH}_3\text{P}^+\text{C}^- \text{MeEt}$ and 2-butanone gives two diastereomeric products **A** and **B**. Predict the products and show the stereochemical course involved in their formations.

(b) What is phase transfer Wittig reaction?

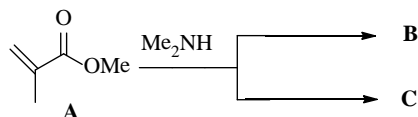
6. Predict the product(s) of the following reaction and give mechanism.



7. Predict the orientation in HCl addition to these alkenes.



8. Addition of dimethylamine to the unsaturated ester **A** could give either product **B** or **C**. Identify the products with plausible mechanisms for both reactions .

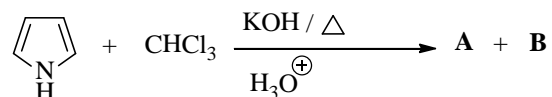


9. Cyclopropanone exists as the hydrate in water but 2-hydroxyethanal does not exist as its hemiacetal. Explain.

10. Trichloroethanol may be prepared by the direct reduction of chloral hydrate in water with sodium borohydride. Suggest a mechanism for this reaction. (Warning! Sodium borohydride does *not* displace hydroxide from carbon atoms!)

Unit II (Elimination and aromatic substitution)

11. Predict the product(s) with probable mechanism.



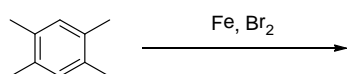
12. When Benzene is treated with $\text{CD}_3\text{CH}(\text{OH})\text{CH}_3$ in presence of BF_3 , a racemic substituted benzene is obtained. – Explain.

13. (a) How would you establish that the attacking entry in the *Reimer-Tiemann* reaction is $:\text{CCl}_2$.

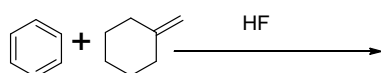
(b) Explain why potassium phenoxide is not suitable for the synthesis of salicylic acid by *Kolbe-Schmidt* reaction.

14. Predict the product(s) with mechanism for the following reactions.

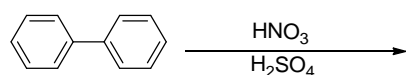
(a)



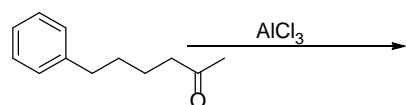
(b)



(c)

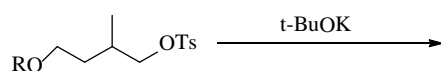


(d)

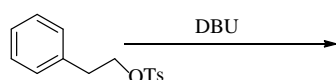


15. Determine the product(s) of the following reactions with plausible mechanism.

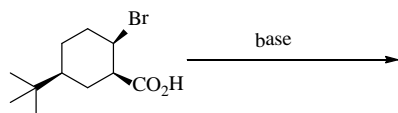
(a)



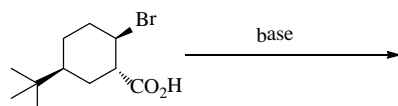
(b)



(c)



(d)



16. Aromatic $\text{S}_{\text{N}}1$ reactions are possible, but unfavourable. – Explain.

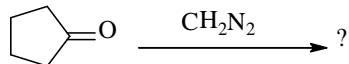
CHT 22b

Unit I. Nitrogen compounds and Organometallics

1. (a) In the *Arndt-Eistert* synthesis two equivalents of diazomethane is used. – Explain the statement using mechanism. What would happen if half equivalent of diazomethane were used?

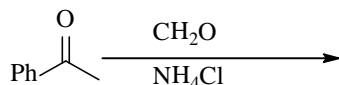
(b) Diazoacetic ester is more stable than diazomethane. – Explain.

2. (a) Predict the product(s) with mechanism.



(b) How can you distinguish chemically between *N*-methyl aniline and *N,N*-dimethyl aniline.

3. (a) Predict the product(s) with mechanism.

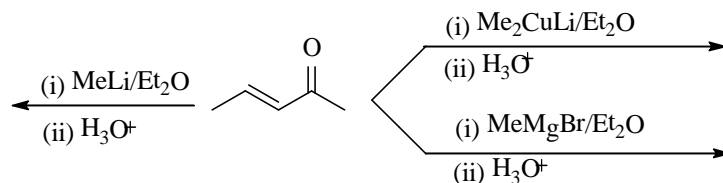


(b) Convert *p*-nitrobenzoic acid to *p*-nitroacetophenone using appropriate organometallic reagent.

4. (a) Write down the *Gabriel's phthalimide synthesis* for the preparation Et_2NH . Why the primary amine like Et_3CNH_2 cannot be prepared by above method?

(b) Phenol can be converted to Anisole using diazomethane, but aliphatic alcohols cannot be converted to the corresponding methyl ether by the same method. – Explain.

5.(a) Identify the product(s) formed in the following reactions, indicating whichever is the major product. Give explanation to your answer.

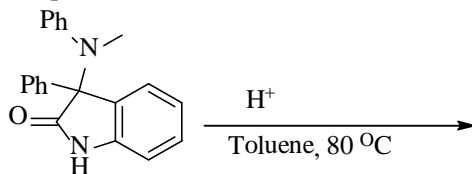


(b) Carry out the conversion: Aniline to *p*-dinitrobenzene.

Unit II. Reactions: Rearrangements

1. (a) Fries rearrangement is both intramolecular and intermolecular. Explain the reaction with supporting evidences.

(b) Predict the product(s) with mechanism.

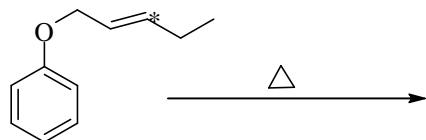


2. (a) What happens when PhCH_2COCl is reacted with CH_2N_2 and the resultant product is allowed to react with Ag_2O in water? Give the plausible mechanism.

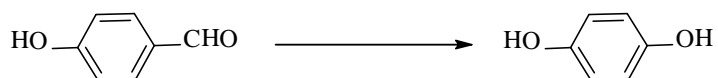
(b) Predict the product(s) with mechanism.



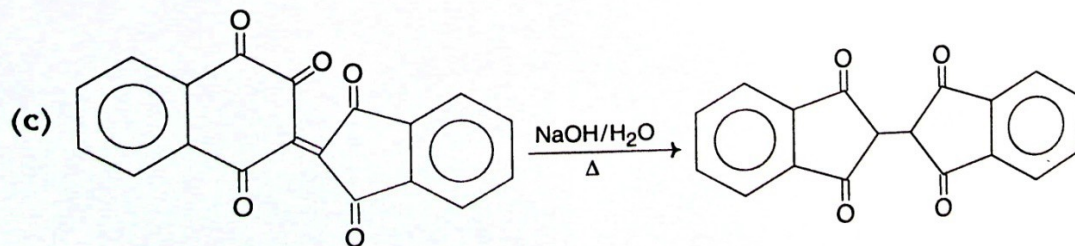
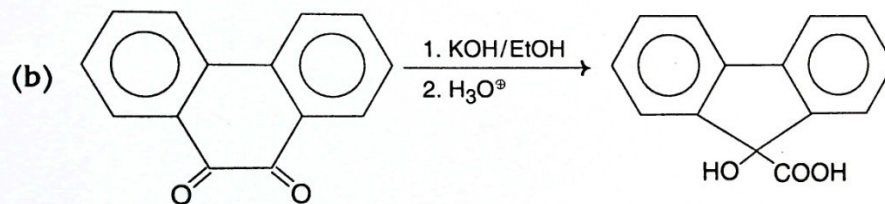
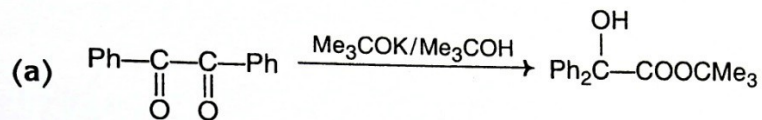
3. (a) Predict the product(s) with mechanism.



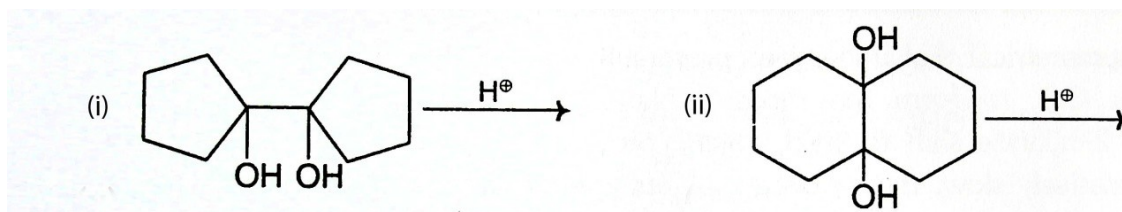
(b) Carry out the following transformation showing plausible mechanism.



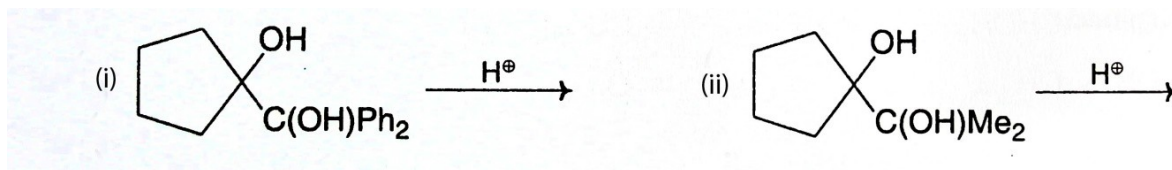
4. Outline the mechanisms of the following transformations:



5. Predict the major product and suggest a mechanism for each of the following reactions:



6. Predict the major product and suggest a mechanism for each of the following reactions:



7. Explain the following observations:

(a) N-methylpropanamide does not undergo Hofmann rearrangement when treated with aqueous NaOBr

(b) When butanamide is treated with bromine in aqueous sodium hydroxide solution, N, N-dipropylurea is recovered along with n-propylamine.

8. (a) The Curtius rearrangement involves thermal decomposition of acyl azides to isocyanates in benzene or chloroform solution. Give the mechanism of the reaction.

(b) The primary amine formed in the Curtius rearrangement carried out in water often reacts with unchanged isocyanate to form ureas, RNHCONHR. How can the formation of ureas be avoided.

9. (a) Give a suitable experiment to establish that in the Beckman rearrangement the group anti to the oxime hydroxyl migrates.

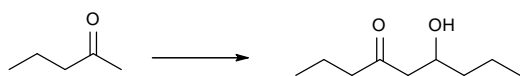
(b) How will you establish that the benzidine rearrangement is an intramolecular process.

CHT 32a

UNIT – I (Carbanion chemistry and cyclic stereochemistry)

- (a) Draw the possible conformations of *trans*-2-bromocyclohexanol. Indicate their relative proportions in the aggregate.
 (b) The *a,a*-conformer of *trans*-1,2-dibromocyclohexane is more stable in gaseous state, the *a,a:e,e* = 95:5 while the ratio is 52:48 in benzene solution. Explain.
- (a) Draw the preferred chair conformations of *cis*- and *trans*- 1,3-dimethylcyclohexane. Indicate in both cases their optical properties considering symmetry elements present.
 (b) Sodium borohydride reduction of cyclohexanone is faster than that of *di-n*-hexylketone.–Justify.

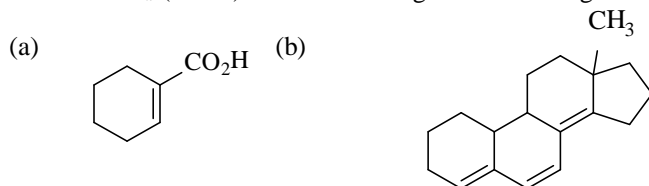
- (a) Carry out the following transformations:



- (b) Discuss the mechanism of addition of an enolate to an aldehyde with help of *Zimmerman–Traxler* model.

UNIT – II (Spectroscopy UV, IR, NMR)

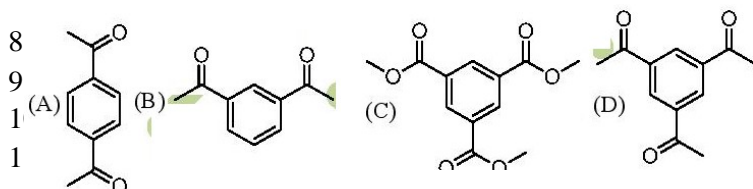
- Mention the types of shifts (hypsochromic or bathochromic) observed in UV-Vis spectra of a carbonyl group under the following conditions:
 - Substitution on the carbonyl by an auxochrome
 - Olefinic conjugation added to the carbonyl group. - Explain your answer.
- Molecules possess only quantized energy levels and UV-Vis spectra are the result of electronic transitions. Still we observe a broad band in UV-Vis spectroscopy. – Explain.
- One isomer of dimethoxybenzoic acid has the ¹H NMR spectrum 3.8 (6H, s), 6.63 (1H, t, J=2 Hz), 7.17 (2H, d, J=2 Hz). Identify the proper isomer of dimethoxybenzoic acid.
- Calculate the λ_{max} (in nm) for the following molecule using Woodward's rule.



- Substitution of an amino group on the para position of acetophenone shifts the >CO frequency from 1685 cm⁻¹ to 1652 cm⁻¹, whereas a nitro group attached to the para position yields a >CO frequency of 1693 cm⁻¹. – Explain.
- (a) Give the correct order of the ¹H NMR chemical shift values (δ) for the indicated hydrogens (in bold) in the following compounds with explanations.

(b) Arrange the following diatomic molecules in order of the fundamental vibrational frequencies: $^1\text{H}^{35}\text{Cl}$, $^1\text{H}^{37}\text{Cl}$, D^{35}Cl . Explain your answer.

7. (a) Which of the following compound(s) show(s) only two signals in ^1H NMR and a strong IR band at $\sim 1690\text{ cm}^{-1}$? Give reasons to your answer. 2



(b) An organic compound **X** ($\text{C}_9\text{H}_{10}\text{O}$) exhibited the following spectral data.

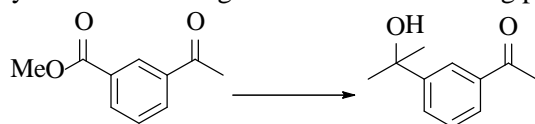
IR: 1680 cm^{-1} . ^1H NMR δ (ppm): 7.8 (2H, d, J 7.5 Hz), 7.2 (2H, d, J 7.5 Hz), 2.7 (3H, s), 2.4 (3H, s).
Compound **X** on treatment with *m*-CPBA produces two isomeric compounds **Y** (major) and **Z** (minor).
Identify **Y** and **Z**.

8. (a) If a sample of β -carotene is placed in a cell with a path length of 1.0 cm and the UV absorbance reads 0.37. Assume the concentration of β -carotene in the sample is $2.7 \times 10^{-3}\text{ mmol/L}$. Find the molar absorptivity of β -carotene.
9. (b) β -Ocimene is a pleasant-smelling hydrocarbon found in the leaves of certain herbs. It has the molecular formula $\text{C}_{10}\text{H}_{16}$ and a UV absorption maximum at 232 nm. On hydrogenation with a palladium catalyst, 2,6-dimethyloctane is obtained. Ozonolysis of β -ocimene, followed by treatment with zinc and acetic acid, produces the following four fragments:
Acetone, Malonaldehyde, Formaldehyde, Pyruvaldehyde.
- How many double bonds does β -ocimene have?
 - Is β -ocimene conjugated or nonconjugated?
 - Propose a structure for β -ocimene.
 - Write down the reactions, showing starting material and products.

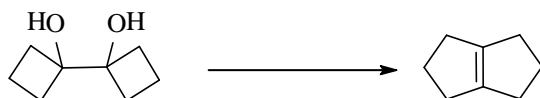
CHT 32b

Unit –I (Synthetic strategies and Asymmetric Synthesis)

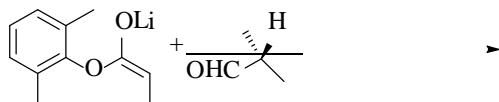
10. (a) Carry out the following transformation showing plausible mechanism.



- (b) Show the necessary steps for the following conversions giving suitable reagent(s) for each step.

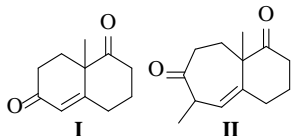


11. (a) Predict the product(s) with help of *Felkin-Anh* model.

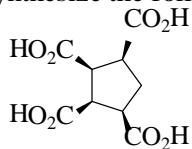


(b) When will you observe '*anti-Felkin*' product.

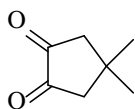
12. (a) Synthesize **II** from **I**.



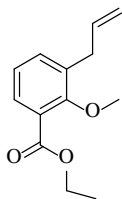
(b) Synthesize the following molecule giving retrosynthetic analysis.



13. Design a synthetic route for the synthesis of the given molecule.



14. Show the retrosynthetic analysis for the synthesis of the following molecule.



1. (a) What are called anomers? What is called the anomeric effect? Comment on the effect of solvent on anomeric effect.
 (b) How do epimers and anomers differ?
 (c) Do the anomers of D-glucose have specific rotations of the same magnitude but opposite signs?
2. (a) What is called mutarotation? Explain the phenomenon of mutarotation.
 (b) Discuss the mechanism of mutarotation. How would you establish that the solvent should have both acidic and basic properties for mutarotation to take place?
3. (a) What are called reducing and non-reducing sugars. Explain with examples.
 (b) How would you distinguish between methyl D-glycopyranoside and methyl D-glycofuranoside by periodic acid oxidation? State the number of moles of periodic acid consumed in each case.
4. (a) In acid solution D-glucaric acid undergoes lactonization to yield two different γ -lactones, and under certain conditions, a dilactone. Draw their structures and explain their formation.
 (b) How would you prove that the methyl glycoside obtained by refluxing D-(+)-glucose in methanol solution in the presence of a small amount of hydrochloric acid is a six-membered ring and not a five-membered ring?
5. (a) How would you establish that all methyl pyranosides of α -D-hexose series have the same configuration and C-1 and C-5? What products would be formed from the strontium salt (obtained from methyl α -glycoside of any D-aldohexose when subjected to Jackson and Hudson's procedure) by treatment with dilute HCl? Give the mechanism of the reaction involved.
6. (a) α -D-glucopyranose is oxidized by HIO₄ more rapidly than the β -anomer at the 1,2-bond. Suggest a reason for this observation. Why periodic acid rather than lead tetraacetate is used for oxidative cleavage of carbohydrates?
7. (a) Why is periodic acid oxidation of D-mannose faster than that of D-glucose? How would you carry out the following transformation?

$$\text{CHO}-(\text{CHOH})_4-\text{CH}_2\text{OH} \longrightarrow \text{CHO}-\text{CHOH}-\text{CO}-(\text{CHOH})_2-\text{CH}_2\text{OH}$$
8. (a) How would you carry out selective methylation of C-3 hydroxyl group of D-glucose?
 (b) Diisopropylidene derivative of D-glucose but not that of D-galactose can be alkylated at C-3 position. Give reason.

9. (a) Show how D-glucose can be converted into D-allose by inversion of configuration at C-3.
(b) Show how methyl β -D-glucopyranoside can be converted into 2,3,4-tri-O-methyl- β -D-glucose.
10. (a) β -D-glucopyranose undergoes oxidation by bromine water 250 times as fast as that of α -D-glucopyranose. Explain this observation.
(b) Explain why bromine water is a better reagent than Tollen's reagent for the oxidation of aldose to aldonic acids.
11. (a) When optically active D-glucose is reduced with NaBH_4 optically active D-glucitol results. However, when D-galactose (the C-4 epimer of D-glucose) is reduced, the product is optically inactive. Explain these observations.
(b) Sodium borohydride reduction of D-fructose leads to both D-mannitol and D-glucitol. Explain why two products are formed.
12. (a) Write the mechanism for the base-catalyzed conversion of D-fructose into D-glucose and D-mannose.
(b) When heated with dilute alkali, D-glucose breaks down to glycolaldehyde, while D-fructose breaks down to dihydroxyacetone, glycolaldehyde, and formaldehyde. Propose mechanisms for these base-catalyzed fragmentations.
13. (a) Aldose and ketoses react with excess (three molar equivalents) of phenylhydrazine to give yellow crystalline solids called osazones. Give mechanism of these reactions and evidence in favour of the mechanism.
(b) Explain why osazone formation does not proceed beyond the first two carbon atoms.
14. (a) Explain why D-glucose, D-mannose and D-fructose form the same osazone.
(b) Osazones are useful as derivatives for characterization of sugars – why?

CHT 32C

UNIT 1. Carbocycles and Heterocycles

- (a) Write down the mechanism for the Bucherer reaction.

(b) Explain: (i) Naphthalene is more reactive than benzene.
(ii) 9-position of anthracene is more reactive than any other position.
- (a) Write notes on Bardhan – Sengupta synthesis of Phenanthrene.

(b) Explain: (i) Anthracene has a diene character.
- (a) When 1 mole hydrogen is added to 1 mole of anthracene, 9,10-dihydroanthracene is the product. However, when 2 moles of hydrogen are added to 1 mole of anthracene 1,2,3,4 – tetrahydroacene is formed- Explain.

(b) Convert: Phenanthrene \longrightarrow phenanthrene -9-carboxylic acid.
- (a) How could you convert naphthalene into 2 – nitronaphthalene?

(b) What product do you expect when phenylhydrazone of cyclohexanone is treated with boron trifluoride with acetic acid at 65 °C? Write down the mechanistic steps for the reaction.
- (a) Convert furan to pyrrolidene.

(b) How will you prepare indole in one step from easily accessible starting materials?
- (a) How will you synthesize 2,6-disubstituted pyridine from acyclic precursors.

(b) Describe the process of Fischer indole synthesis.
- (a) How can furan be prepared from mucic acid? Give the mechanism of the reaction involved.

(b) Furan-2-carbaldehyde undergoes Cannizaro reaction, whereas pyrrole -2-carbaldehyde does not. Explain.
- (a) Explain why pyrrole, furan and thiophene are more reactive than benzene toward electrophilic aromatic substitution.

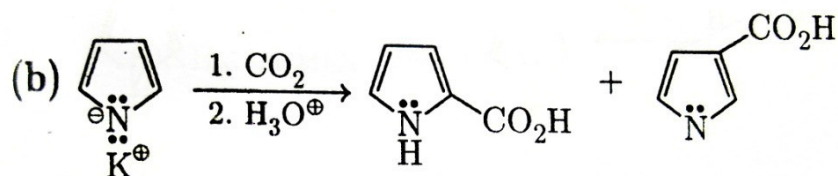
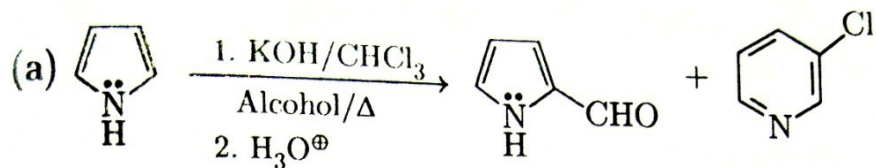
(b) Explain why the electrophilic substitution of furan, pyrrole and thiophene occurs preferentially at the 2-position.
- Explain the following observations:

(a) When phenylhydrazine is reacted with 2-butanone under conditions of the Fischer indole synthesis, a mixture of two isomeric indoles is obtained.

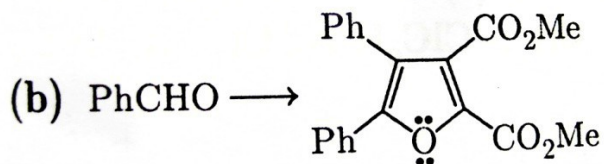
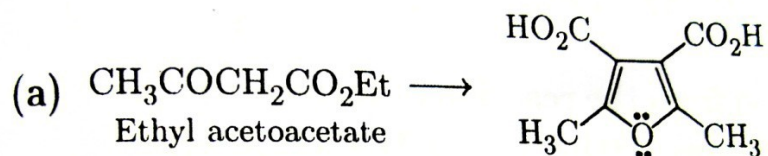
(b) When 3-methylphenylhydrazine is reacted with acetone under conditions of the Fischer indole synthesis, a mixture of two isomeric indoles are formed.
- (a) Indole undergoes electrophilic substitution predominantly at position- 3. Explain.

(b) Predict the product and suggest the mechanism of the reaction takes place when pyridine is heated with (i) n-butyl lithium and (ii) KOH

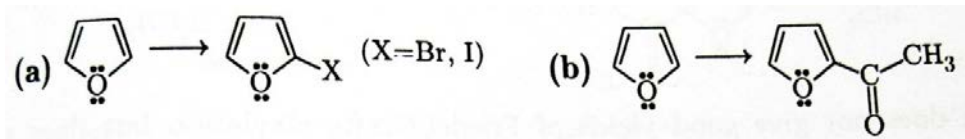
11. Suggest a mechanism for each of the following reactions:



12. How would you carry out the following transformations:



13. How would you carry out the following transformations:



CHT 32c

UNIT II. Amino acids, peptides and nucleic acids

1. (a) Synthesize cysteine from PhCH₂SH.
(b) Are all amino acids Zwitter-ionic? – Explain.
2. (a) Describe the Sanger's method for the determination of N-terminal of a peptide.
(b) What will happen if 2,4-dinitrochlorobenzene is used instead of DNFB?
3. (a) Give a route for the preparation of phenylalanine.
(b) Explain why the isoelectric point for glutamic acid is 3.2, that for alanine is 6.1 and that for lysine is 9.5.
4. (a) Most naturally- occurring amino acids have S configuration. Why is L- cysteine unique in having the R configuration?
(b) Explain the following observations:
 - i> Amino acids are non-volatile crystalline solids which decompose rather than melt at fairly high temperature.
 - ii> Amino acids are insoluble in non-polar solvents like petroleum ether, benzene or ether and are appreciably soluble in water.
5. (a) Give mechanisms of the chemical reactions involved in the identification of N –terminal amino acid of a peptide by Edman degradation. Explain why the Edman degradation is usually preferred over the Sanger method.
(b) Show how cyanogen bromide (BrCN) is used in selective cleavage of a peptide bond.
6. (a) A pentapeptide (A) did not evolve nitrogen upon treatment with HNO₂. Its complete hydrolysis gave glycine (3 moles), alanine (1 mole) and phenyl alanine (1 mole), whereas partial hydrolysis gave two dipeptides Ala –Gly and Gly –Ala. Write the abbreviated formulas of all the possible structures that fit these data; give relevant explanations.
(b) A tetrapeptide of unknown sequence, on amino acid analysis, was shown to contain ala, gly, phe and val in equimolar ratios. Determine the primary structure of the tetrapeptide from the following three experimentally determined facts:
 - i> Valine is the N –terminal amino acid.
 - ii> The tetrapeptide on hydrolysis yields a number of fragments, one of which is a tripeptide composed of Gly, Phe, and Val.
 - iii> A dipeptide containing Ala and Gly is also present in the hydrolysis mixture.

INORGANIC CHEMISTRY

Year –I (PART – I)

SECOND PAPER

CHT -11a

Unit I : Radioactivity and Atomic structure

- a) Show the mechanism of emission of β^+ and β^- from radio nuclide with the help of meson theory. (3)
b) Find the ground state term of elemental chromium. (2)
- a) How do the four quantum numbers signify the state of an electron in H-atom? (3)
b) Fission of U^{235} and Fusion of ($^2H+^3H$) evolve 200 MeV and 17.6 MeV respectively. Compare their energy efficiencies. (2)
- Explain 'Radial function and radial distribution function' of an orbital. Compare the radial distribution plots for 3S, 3P and 3d orbitals and hence comment on their relative penetrating property. (3 + 2)
- a) An electron in a hydrogen atom in its ground state absorbs 1.6 times as much energy as the minimum required for it to escape from the atom. Calculate the wave length of the emitted electron. Given, Ionization energy is 13.6eV. (3)
b) What is spallation? Give example. (2)
- a) What is exchange energy? How it explain the stability of ground state electronic Configuration of copper? (2)
b) What is half life of a radioactive element? A radioactive material of half life 20 days accidentally got spread radiation 40 times greater than the permissible safety level in a Laboratory. After how much days the laboratory would be safe for work? (3)
- a) State and explain Pauli exclusion principle. (2)
b) Distinguish between nuclear fission and nuclear fusion. Give example of each.
- a) What is magic number? Explain their significance with the help of nuclear quantum number. (3)
b) Explain how Th can be a source of nuclear energy. (2)

- a) Define binding energy and explain the significance of binding energy curve. (3)
- b) What is meant by artificial transmutation? Give example. (2)
- a) On what factors the radial part of a wave function $R(r)$ depends. What is the nodal point? (3)
- b) What is the significance of \hbar and \hbar^2 ? (2)
- a) Define with example Hund's rule of maximum multiplicity. Account for the $\pm 1/2$ value for the m_s assigned to spin quantum number. (3)
- b) Draw the radial distribution curve for : a) $n=4, l=0$; b) $n=3, l=2$ (2)
- List the main drawbacks of Bohr's Theory of atomic structure. Explain how these were overcome? (3)
- b) What is deBroglie equation and How does the equation prove one of Bohr's postulates $mvr = nh/2\pi$? (2)
- a) The ratio of ${}^{14}_6\text{C}$ to ${}^{12}_6\text{C}$ in certain piece of wood is 14.5% of that in atmosphere. Calculate the age of piece of wood if the half-life period of ${}^{14}_6\text{C}$ is 5580 years. (3)
- b) Define decay constant and derive an expression for it.
- a) What is the use of Szilard-Chalmer reaction? (2)
- b) State two safety precautions taken while handling radioactive substance. (3)
- a) Discuss the Aufbau principle with suitable example. Why the outer electronic configuration of chromium is $3d^5 4s^1$ not $3d^4 4s^2$? (3)
- b) The half life of a radioactive element is 500 days. How long it takes to convert 90% decays? (2)
- a) Define radioactive equilibrium. Explain the types of radioactive equilibrium. (3)
- b) Calculate the largest wavelength of first line of Balmer's series. (Given the Rydberg constant = 109678 cm^{-1}) (2)
- a) How can you prove that a larger amount of energy is evolved in nuclear fusion compared to nuclear fission. (3)
- b) Prove that an electron can never reside in the nucleus. (2)
- a) Define specific activity of a radioactive substance. Derive its equation. (3)
- b) State and explain Heisenberg's Uncertainty principle.

- a) What is meant by radioactive disintegration series? How is it prepared? Write the starting and end products of each series. (3)
- b) Explain the rules for determining ground state term symbol taking one suitable example. (2)

UNIT-II

Chemical Periodicity

1. Explain the reasons for classification of elements on the basis of electronic configuration. Mention general electronic configuration of each class.
2. Discuss shortly the significance of group and period.
3. Why long periodic table is constituted with 18 groups and 7 periods?
4. Explain the respective total number of element in a period.
5. Why d-block element is placed in between s and p-block?
6. Justify the successive position of s, p and d-block elements.
7. Which can follow transition properties: Ti^{2+} , Ti^{4+} , Fe^{3+} , Sc^{3+} , Mn^{4+} , Mn^{7+} , G^{6+} , Cr^{3+} , Cu^+ , Cu^{2+} , Co^+ , Cu^{3+} , V^{5+}
8. Explain the following characters of transition elements:
 - a. Catalytic activity
 - b. Conductivity (electricity and heat)
 - c. Variable valencies
 - d. High complex forming activity in cationic form
 - e. Polarising ability
9. Explain the following periodic properties (period wise and group wise) with exceptions, if any
 - a. Atomic radii
 - b. ionic radii
 - c. ionization energy
 - d. Electronegativity
 - e. Electron affinity
10. Mention the factors determining the magnitude of above periodic properties.
11. Discuss the theoretical basis of Pauling scale of electronegativity. Show the plot of electronegativity difference and percentage ionic character of a polar covalent molecule.
12. What is Alred-Rochow electronegativity? Correlate it with Pauling's electronegativity.
13. Explain Mulliken's electronegativity. Express Mulliken electronegativity to Pauling's value.
14. Compare the properties of 3d, 4d and 5d transition series.
15. Explain the electronegativity of Sulphur in SF_4 , SF_5 and SF_6 .
16. How atomic radii depend on geometry of molecule for the same central atom?
17. State Slater's rule to calculate screening constant for a particular electron.
18. Give explanation for preferential ionization of 4s electrons before 3d electron.
19. Calculate effective nuclear charge for any 3d and 4s electron in Zn atom.
20. Arrange Gr-13 elements in increasing order of electronegativity and give reasons.
21. What is inert pair effect? Explain with examples.
22. Why diagonal relationship is remarkable for 2nd and 3rd period?
23. Why Zr and Hf occur in the same mineral and it is very difficult to separate them by chemical process?

24. What is lanthanide contraction? How it affects properties of lanthanoids?

25. Rationalize the following data:

	Covalent radii (Å)	Vander Waal's radii (Å)	Ion	Ionic radii (Å)
F	0.64	1.35	F ⁻	1.36
Cl	0.99	1.80	Cl ⁻	1.81

26. Compare redox properties of Sn(IV) and Pb(IV).

27. Comment on the relative ionic radii of O²⁻, F⁻ and Na⁺.

28. Write down I.U.P.A.C. names and symbol of the elements having atomic no. 109, 111, 113, 117, 121, 123, 126.

29. Establish the relation between electron affinity of X(g) atom and ionization potential of X(g) ion.

30. Discuss Pauling univalent method to calculate ionic radii with suitable example.

31. Define Bragg-Slater radii.

CHT IIb

Unit I: Chemical bonding and structure

1. What is radius ratio rule? Explain its theoretical basis.

2. State exceptions of radius ratio rule with examples.

3. Calculate the limiting radius ratio value for:

- Tetrahedral structure
- Square planer structure
- Octahedral structure
- Cubical structure (bcc).

4. Define lattice n lattice energy. Draw Brown-Haber cycle for $M(s) + \frac{1}{2}X_2(g) \rightarrow M^+X^-(s)$ to calculate its lattice energy.

5. Define Born-Lande equation and mention Its application.

6. Explain the following:

- Polarization
- Polarisability
- Solvation energy
- Ionic potential.

7. State Fajan's rule to fix up polarization in a compound.

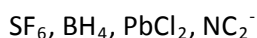
8. Trivalent cation result compound predominantly covalent – justify the statement with example.

9. Why defects in solid occur? Give example of different types of defects.

10. Compare Frenkel and Schottky defects.

11. How crystal defect is related to coordination number?

12. Applying VSEPR theory, predict the shapes of the following and indicate the types of hybridization of central atom.



13. Are the bond angles LHLH, LFLF in CF₂H₂ are equal? Explain your answer.

14. Give examples of stoichiometric and non stoichiometric defects.
15. Calculate formal charge on each atom of O_3 , N_2O , CO_3^{2-} .
16. What do you mean by equivalent and nonequivalent hybridization?
17. Apply the nonequivalent hybridization to explain the bond angles in PCl_5 , SF_6 .
18. Explain the limitation of VB theory with examples.
19. State Bent's rule. Apply it to explain the structure of PCl_3F_2 .
20. Compare dipole moment values for NH_3 and NF_3 with explanation.
21. Draw the polar structure of CO and justify the respective position of dipoles.
22. In spite of high bond polarity, dipole moment of CF_4 is zero – explain.
23. The dipole moment value of AB is 2.0 D. If its percentage of ionic character is 40, calculate the bond length.
24. The value of positive dipole on $X^{\delta+} - Y^{\delta-}$ is 2.8×10^{-10} egk. What is the percentage ionic character of XY?

Apply VSEPR rule to explain the structure of: C

CHT -11b

Unit II : Acid-base reactions

- a) Predict which way the reaction will go in gas phase with explanation.(3)

(i) $HF + NaF = HF + NaI$ and (ii) $TiF_4 + 2TiI_2 = TiI_4 + 2TiF_2$
- b) Which member between the pair given below is stronger acid.(2)

(i) H_2CrO_4 and $HMnO_4$; (ii) $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$
- a) In the light of solvent theory, justify the nature of BiN in liquid ammonia and CaO in water.(3)

b) Compare the basicity of $(CH_3)_3N$ and $(SiH_3)_3N$.(2)
- a) What is acid- base indicator? Give one example with structure in both acid and base.(3)

b) How can you chose appropriate indicator for the titration of strong acid and strong base. (2)
- a) Define hard and soft acid bases with suitable examples. (3)

b) In the light of acid base theory explain the reaction: (2)

$$6 CaO + P_4O_{10} \rightarrow Ca_3(PO_4)_2$$
- a) Using Pauling rules, calculate the pK_a values of H_3PO_4 and $HClO_4$ (2)

b) Acid strength of HF , HCl , HBr and CH_3COOH are different but all are equally strong in liquid ammonia. Explain (3)

- a) SnCl_2 can act both Lewis acid and base. Explain (3)
- b) What is magic acid? Give example. (2)
- a) Explain the acid base titration curve for NH_4OH and HCl . (3)
- b) Why ammonia is called water like solvent? (2)
- a) Can you develop a pH like scale for liquid ammonia.
(Given $K_w = 10^{-14}$ at 25°C and $K_{\text{NH}_3} = 10^{-31}$ at -50°C . (3)
- b) Explain the acidity order of BF_3 BCl_3 BBr_3 BI_3 . (2)
- a) Explain the acidity strength of oxy acid of chlorine (3)
- b) What is Pearson acid- base principle? (2)
- a) What is symbiosis? Explain with example. (2)
- b) Predict the course of the following acid base reaction (forward/ backward)
 $\text{CH}_3\text{F} + \text{CF}_3\text{H} \rightarrow \text{CH}_4 + \text{CF}_4$ (3)
- a) What is super acids ? Explain with example (2)
- b) How is hardness of a base evaluated? Why methyl mercury cation is chosen as an standard? (3)
- a) All reactions are considered as acid base reaction . Explain in the light of Usanovich concept of acid base theory. (3)
- b) Tri methyl amine is less basic than tri methyl phosphene in their reaction with diborane (2)
- a) Sulphuric acid is stronger acid than phosphoric acid. Explain (3)
- b) KNH_2 is base in liquid ammonia . Explain (2)
- a) Nitric acid is a base in sulphuric acid medium. Explain (2)
- b) Explain SHAB principle with example .(3)
- a) What is Ostwald dilution law? Derive a pH of an weak acid. (3)
- b) Calculate the pH of 0.1(M) acetic acid . (Given $K_a = 1.8 \times 10^{-5}$ mol/lit) (2)
- a) HgCl_2 is soluble in dil.HCl but HgS is not. Explain (3)
- b) What is meant by Levelling effect of water? (2)

YEAR – II (PART – II)

Fourth paper

CHT 21b

Unit I: Chemical of s and p –block elements

- a) How will you prepare diborane from sodium borohydride? (2)
b) Discuss the structure and bonding of Diborane. (3)
- a) What are phosphazenes? (2)
b) What happens when hexachloro tri phosphazene reacts with ammonia? (3)
- a) What are interhalogen compounds? (2)
b) What are general characteristics of inter halogen compounds? (3)
- a) Write the structure and hybridization of the following compounds (3)
 ClF_3 , IF_7 , ICl
b) What is inorganic graphite? (2)
- a) How will you prepare XeO_3 and XeOF_4 from xenon? (3)
b) Write down the photochemical reaction of ozone. (2)
- a) Discuss the structure and bonding of phosphazene. (3)
b) What are silicones? Give example. (2)
- a) Complete the following reaction
 (i) $\text{ClF}_3 + \text{AsF}_5 + \text{KF}_2 \rightarrow$
 (ii) $\text{N}_2\text{H}_4 + \text{KIO}_3 + \text{HCl} \rightarrow$
- a) What are pseudohalides ? Write the differences with halides. (3)
b) Discuss the structure of thiosulphate ion. (2)
- a) What happens when (i) XeF_6 is treated with aqueous caustic soda.
 (ii) Silver nitrate is added to a concentrated solution of ammonium persulphate. (2)
b) Write a short note on CFC.(3)
- a) How freones are to be prepared ? What are their uses? (3)
b) Write the different types of silicates. (2)

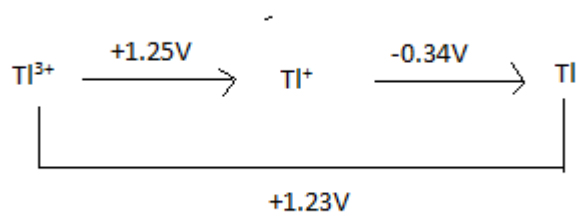
CHT 21b

Unit II: Precipitation and redox reactions

- a) Cu^+ (aq) does not exist but CuI is stable. Explain using the following data (2)

$$E^0_{\text{Cu}^{2+}/\text{Cu}}=0.153\text{V}, \quad E^0_{\text{Cu}^+/\text{Cu}}=0.521\text{V}$$

- b) Construct Frost Diagram from the following Latimer diagram (3)



- a) Balance the chemical equation using ion electron method of the reaction potassium ferricyanide to potassium ferrocyanide by hydrazine in alkaline medium. (3)

b) What is standard electrode potential? (2)

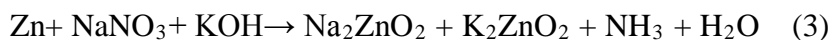
- a) What is formal potential? How does it influenced by the pH of the medium. (3)

b) Solubility of HgI_2 ($\text{X}=\text{Cl},\text{Br},\text{I}$) decreases chloride to iodide- explain. (2)

- a) Discuss the redox indicators by taking diphenylamine as an indicator. (3)

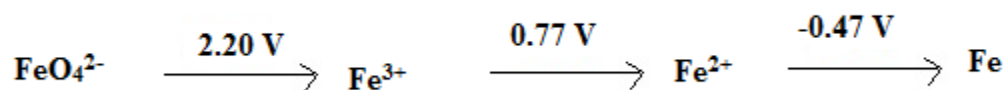
b) Derive Nernst equation and explain the term used. (2)

- a) Balance the following equation by ion electron method



b) In group IIIA precipitation of Fe^{3+} , Al^{3+} , Cr^{3+} , mixture of NH_4Cl and NH_4OH is used not NaOH . Explain (2)

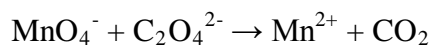
- a) Calculate E^0 for the reaction $\text{Fe}^{3+} \rightarrow \text{Fe}$, from the following reduction potential diagram: (3)



b) Compare the oxidizing property of KMnO_4 in acidic and neutral medium. (2)

- a) Define disproportionation and comproportionation reaction with example. (3)

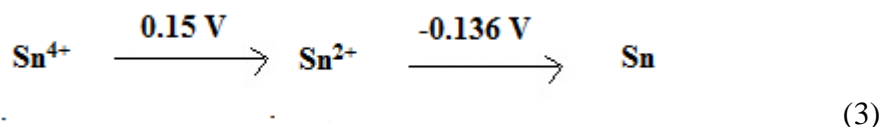
b) Balance the following by ion electron method: (2)



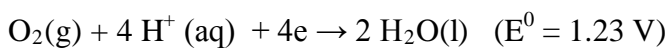
- a) Define solubility and solubility product of sparingly soluble salt (AX_2 type). (3)

b) calculate the solubility of 0.1(M) AgNO_3 in water. (Given K_{sp} of silver nitrate = 1.5×10^{-22}) (2)

- a) From the Latimer diagram, calculate the reduction potential of the reaction $\text{Sn}^{4+} \rightarrow \text{Sn}$.



b) Write down the Nernst equation for the following reaction (2)



- a) If 20 c.c of each of 0.01 AgNO_3 and 0.0004 (M) NaCl are mixed, will precipitation of AgCl occur? (Given K_{sp} of $\text{AgCl} = 1.7 \times 10^{-10}$) (3)

b) Identify the differences between the following reactions:

