3 (Sem–6) CHM M1

2020

CHEMISTRY

(Major)

Paper : 6·1

(Spectroscopy)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

The symbols, used here, signify their usual meaning.

1. Answer in brief : ***(any seven)*** 1×7=7

   (a) Why cannot IR radiation induce electronic transition ?

(b) Consider the following relationships among the components of moment of inertia :

$I_A = I_B = I_C$; $I_A \neq I_B \neq I_C$;

$I_A = 0, I_B = I_C$; $I_A \neq 0, I_B = I_C$

Which of these combinations represent CO_2 molecule ?

(c) Which of the following molecules will be simultaneously IR and microwave active ?

Cl_2, OCS, CO_2, CH_4, HBr

(d) State True **or** False :

As the vibrational quantum number increases, the spacing between two adjacent vibrational levels of a diatomic molecule decreases.

(e) In the Raman effect, the transfer of energy between the photon and the molecule lies in the range 3 to 3000 cm^{-1}. What types of transitions the molecule may undergo due to this energy transfer ?

(f) State the rule of mutual exclusion in connection with Raman spectroscopy.

(g) State in which of the following compounds will the protons show resonance at the highest downfield : CH_2Cl_2, CH_3F, CH_3I

(h) Name the transitions which are responsible for the coarse and the fine structures of the electronic spectrum.

2. Answer the following questions : 2×4=8

(a) For the transition from the energy level A to the energy level C of a quantum mechanical system a radiation with wavelength 450 *nm* is absorbed. Again transition from level B to level C of the same system requires a radiation of wavelength 850 *nm*. Find the wavelength of the radiation required for the transition from the level A to the level B.

(b) Considering a diatomic molecule to be rigid rotator, write in brief how the presence of heavier isotope affects the rotational spectrum.

(c) The Stokes' lines are more intense than the anti-Stokes' lines. Explain.

(d) The IR spectra of ethanol are taken under the following two conditions :

(i) 10% (*V/V*) in CCl_4 and

(ii) 1% (*V/V*) in CCl_4.

Discuss what difference you may observe in the two spectra.

Or

What do you mean by characteristic group frequencies in IR spectroscopy ? Explain with example.

3. (a) Answer **either** [(i) and (ii)] **or** [(iii) and (iv)] :

(i) Define transition moment. What do you mean by allowed and forbidden transitions in the context of transition moment ? 3

(ii) The lifetime of an excited electronic state is 10^{-8} s. Calculate the width of the spectral line in *Hz*. 2

Or

(iii) Discuss how the component of dipole moment along a particular direction varies with time in anti-symmetric stretching vibration of CO_2. 3

(iv) A monochromatic radiation is allowed to pass through a solution of a compound with concentration 10 $mol\ m^{-3}$ when the intensity of the radiation reduces to $\frac{1}{10}$th of the initial value. Calculate molar extinction coefficient. 2

(b) Considering diatomic molecule to be anharmonic oscillator, deduce expressions for energy needed for the allowed vibrational transitions. Explain fundamental absorption and overtones. 5

(c) Answer **either** [(i) and (ii)] **or** [(iii)] :

(i) What do you mean by symmetric and antisymmetric vibrations ? What are perpendicular and parallel vibrations ? Discuss taking the example of H_2O. 3

(ii) Using a monochromatic radiation of wavelength 435.8 *nm* the Raman spectrum of $C_2H_2(g)$ is observed. The spectrum shows one of the lines at 511 *nm*. Determine the wavenumber of the vibrational band corresponding to this observation. 2

Or

(iii) The spacing between the consecutive *S*-branch lines in the pure rotational Raman spectrum of H_2 is 243.2 cm^{-1}. Calculate bond length of H_2. 5

4. Answer ***either*** [*(a), (b)* and *(c)*] ***or*** [*(d), (e)* and *(f)*] :

(a) Write the selection rules associated with the electronic transitions in atom. Hence, explain the fine structure of the spectra of H-atom. 5

(b) A radiation of frequency $5{\cdot}14\times10^{15}$ *Hz* ejects a photoelectron from *Ar*. The kinetic energy of the photoelectron is 5.4 *eV*. Calculate binding energy. 3

(c) The $\pi \rightarrow \pi^*$ transition in ethene is observed at 170 *nm* with molar extinction coefficient of 1000 m^2mol^{-1}. Will these values vary markely in *(i)* 1,3-butadiene, and *(ii)* 1,5-hexadiene ? Explain with reason. 2

Or

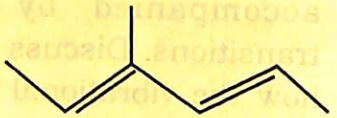
(d) Electronic transition is accompanied by vibrational transitions. Discuss with diagram how the vibrational bonds in the electronic spectrum of a diatomic molecule will appear, if—

(i) the internuclear distance in the ground and the excited electronic stages is same, and

(ii) internuclear distance in the excited state is considerably greater than that in the ground state which may lead to dissociation of the molecule. 5

(e) Define chromophore and auxochrome. What do you mean by blue shift of λ_{max} value? The $\pi \rightarrow \pi^*$ transition in aniline is observed at 230 *nm*. State how this value will change in anilinium ion. 3

(f) Using Woodward-Fieser rules predict the λ_{max} value of $\pi \rightarrow \pi^*$ transition in — 2



5. Answer ***either*** [*(a), (b)* and *(c)*] ***or*** [*(d), (e)* and *(f)*] :

(a) The two spin states of a proton are degenerated in absence of magnetic field. In presence of magnetic field, B_z, in the *z*-direction this degeneracy is lifted. Deduce an expression for the energy difference between the two spin stages. Write how transition from the lower to the higher spin state may be induced. 3+2=5

(b) Why is tetramethylsilane used as reference in NMR spectroscopy? 3

(c) Calculate the frequency of the radiation required by an electron to undergo transition from the lower spin state to the higher spin state when a magnetic field of strength $0.34T$ is used.

Given $\beta = 9.273 \times 10^{-24} JT^{-1}$ and $g = 2$. 2

Or

(d) What do you mean by hyperfine structure of ESR signals? Discuss about the hyperfine structure of the ESR spectrum of deuterium. 1+3=4

(e) Write in brief about diamagnetic shielding in ^1H NMR spectroscopy. 2

(f) State how many ^1H NMR signals will be shown by

$$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2$$

Identify the protons which will show resonance at the highest downfield. Predict the splitting of signals due to spin-spin coupling. 4

6. Answer ***either*** [*(a), (b)* and *(c)*] ***or*** [*(d), (e)* and *(f)*] :

(a) Draw a schematic labelled diagram of the mass spectrometer. What do you mean by electron ionization process? Discuss the fragmentation pattern of methanol. Identify the species responsible for the base peak. 1+3+1=5

(b) What do you mean by McLafferty rearrangement? Explain taking the example of pentanal. 3

(c) Write how the molecular mass of an organic compound can be determined by varying the energy of the bombarding electron in mass spectrometry. 2

Or

(d) In mass spectrometry generally 70 *eV* electrons are used when an organic compound undergoes fragmentation. Explain how the different ions are detected according to their $\frac{m}{z}$ values by varying the accelerating potential. 4

(e) Show the fragmentation of 2-methylbutane in electron ionization process. Identify the peaks with higher intensities. 3+1=4

(f) Write how a mass spectrum is presented. Distinguish between molecular ion peak and base peak. 2

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3 (Sem–6) CHM M 2

2020

CHEMISTRY

(Major)

Paper : 6·2

(Physical Chemistry)

Full Marks : 60

Time : Three hours

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1. Answer the following in brief : 1×7=7

(a) A substance A_xB_y crystallizes in an *fcc* lattice in which atoms *A* occupy each corner of the cube and atoms *B* occupy the centres of each face of the cube. What will be the correct formula of the substance ?

(b) A group 13 element is added in small amounts to *Ge* crystal. The doped crystal acts as _____ semiconductor.

(Fill up the gap)

(c) What is the unit of flocculation value of a coagulating electrolyte ?

(d) What happens when a freshly precipitated $Fe(OH)_3$ is shaken with little amount of dilute solution of $FeCl_3$? Give reaction.

(e) The weight average molecular weight of a polymer is 29,000. If the polydispersity index of the polymer is 0·7, what will be its number average molecular weight ?

(f) If Z is the partition function and $\beta = \frac{1}{k_B T}$, what will be the average energy of the system ?

(g) The formation of micelles takes place above a particular temperature called ——. *(Fill up the gap)*

2. Answer the following questions : 2×4=8

(a) Match crystal system/unit cells mentioned in Column I with their characteristics features mentioned in Column II :

Column I	Column II
(A) Simple cubic and face centred cubic	(p) have the cell parameters $a=b=c$ and $\alpha=\beta=\gamma$.
(B) Cubic and rhombohedral	(q) are two crystal systems.
(C) Cubic and tetragonal	(r) have only two crystallographic angles of 90°.
(D) Hexagonal and monoclinic	(s) belong to same crystal system.

(b) On passing H_2S through an aqueous solution of SO_2, a yellow turbidity is formed. Why ?

(c) Distinguish between error and uncertainty with examples.

(d) Give the physical significance of molecular partition function.

3. *(a)* What are Schottky defects ? Derive an expression for the number of Schottky defects in a crystal. 2+3=5

Or

State Bragg's law and deduce the equation

$$2d\sin\theta = n\lambda$$

The diffraction of barium with X-radiation of wavelength 2·29Å gives a first order reflection at 30°. What will be the distance between the diffracted planes ? 3+2=5

(b) Using partition function, deduce an expression for the entropy of monatomic gas. 5

Or

Using the concept of partition function, deduce an expression for the internal energy of monoatomic ideal gas. Hence find an expression for the heat capacity at constant volume. 3+2=5

(c) Write briefly about the various types of errors in measurement. An experiment was conducted to determine the amount of calcium present in dolomite. The result was found to be 21·85% while the true value is 21·73%. Find the relative error. 3+2=5

4. Answer **either** *(a)*, *(b)* and *(c)* **or** *(d)*, *(e)* and *(f)* :

(a) Explain the origin of low temperature super conduction in terms of Cooper pair. 3

(b) The first order reflection of a beam of X-rays from 100 planes of *NaCl* occurs at an angle of 6°30′. Calculate the wavelength of the X-ray. What would be the angle of reflection if X-rays of $\lambda = 1{\cdot}54$Å were used. 4

(c) What is radius ratio ? How does radius ratio help in determining the structure of ionic solids and co-ordination number of ions ? Explain. 3

(d) An element crystallizes in a body centered cubic structure with a cell edge of 288 *pm*. The density of the element is $7{\cdot}2\,gcm^{-3}$. How many atoms are present in 208 *g* of the element ? 4

(e) How does electrical conductivity of metals and semi-conductors vary with temperature ? 3

(f) Why does *LiCl* acquire pink colour when heated in *Li* vapour? 3

5. Answer **either** *(a), (b)* and *(c)* **or** *(d), (e)* and *(f)*:

(a) Discuss the light scattering method for determination of the molar mass of polymer. 4

(b) A protein sample has 35% haemoglobin $\left(M = 15{\cdot}5\,kg\,mol^{-1}\right)$, 35% myoglobin $\left(M = 17{\cdot}2\,kg\,mol^{-1}\right)$ and 30% ribonuclease $\left(M = 13{\cdot}7\,kg\,mol^{-1}\right)$. Calculate the number-average and mass-average mass of the protein. 3

(c) Discuss the origin of charge on colloidal particles in detail. 3

(d) What are super conductors? Define low and high temperature super conductors with suitable examples. 1+3=4

(e) Discuss the kinetics of condensation polymerization. 3

(f) In a polymer sample 25% molecules have molar mass 15,000, 40% have molar mass 20,000 and the rest have molar mass 25,000. Calculate weight average and number average molar mass of the polymer. 3

6. Answer **either** *(a), (b)* and *(c)* **or** *(d), (e)* and *(f)*:

(a) For a diatomic molecule vibrating as a simple harmonic oscillator, obtain an expression for vibrational partition function. 4

(b) The frequency of absorption band for *CO* associated with its vibrational transition is $6{\cdot}51\times10^{13}$ per second.

(i) At what temperature does kT become equal to the energy of the vibrational transition?

(ii) Calculate the fraction of CO molecules in the vibrational level $v = 1$ at 27°C. 2+2=4

(c) Write the expression for Boltzmann distribution. Mention the meaning of the terms involved. Gives its physical significance. 2

(d) Calculate the residual entropy of one mole of CO at $298\,K$. Discuss accuracy and precision with examples. 2+2=4

(e) Calculate the translational partition function of H_2 molecule confined to a $1000\ cm^3$ vessel at $25°C$. 3

(f) Calculate the internal energy of 1 mole of He at $25°C$. 3

Total number of printed pages–7

3 (Sem–6) CHM M 3

2020

CHEMISTRY

(Major)

Paper : 6·3

(Organic Chemistry)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions : 1×7=7

(a) What is atactic polymer ?

(b) State the Einstein's law of photochemical equivalence.

(c) What is protein ?

Contd.

(d) What are ribozymes ?

(e) Write the name of a zinc-containing metalloenzyme.

(f) What is Wigner spin conservation rule ?

(g) What is Special isoprene rule ?

2. Answer ***any four*** of the following : 2×4=8

(a) How is phosphorescence different from fluorescence ?

(b) What are elastomers ? Name a synthetic elastomer and give its structure.

(c) Give the names and structures of the sugar components present in RNA and DNA.

(d) What are essential and non-essential amino acids ? Give *one* example of each.

(e) D-fructose is a ketohexose, yet it reduces Fehling's solution. Explain.

(f) Give an example each of narrow-spectrum and broad-spectrum antibiotics.

3. Answer ***any three*** of the following : 5×3=15

(a) Discuss photochemical *cis-trans* isomerisation. What is photostationary state ? 4+1=5

(b) Why benzophenone acts as a good photosensitizer ? Explain with an example, the process of photosensitisation of organic compounds. 2+3=5

(c) How will you establish the pyranose ring structure of glucose? 5

(d) Write in brief, how a polypeptide chain is biosynthesised by the process of translation. 5

(e) What are antibiotics? How are these classified? What is the possible mode of antibacterial activity of β-lactam antibiotics? 5

4. Answer *(a)* **or** *(b)*, *(c)* **or** *(d)* and *(e)* **or** *(f)*: 10×3=30

(a) (i) How is photochemical process, the Norrish type-I different from the Norrish type-II? Give examples and mechanism. 5

(ii) What is glycolysis? Describe the glycolytic pathway of degradation of glucose into pyruvic acid. 2+3=5

(b) (i) Write the Zwitterionic structure of aspartic acid. Write *three* important properties of α-amino acids due to their Zwitterionic structure. 2+3=5

(ii) Propose a mechanism for the polymerisation reaction leading to the formation of polystyrene from the corresponding monomer. Write the reaction involved in the formation of urea-formaldehyde resin. 3+2=5

(c) (i) How phospholipids differ from triglycerides? Discuss the role of phospholipids in the formation of biological membranes. Which part of these lipid molecules determines the hardness or fluidity of the membrane? 1+3+1=5

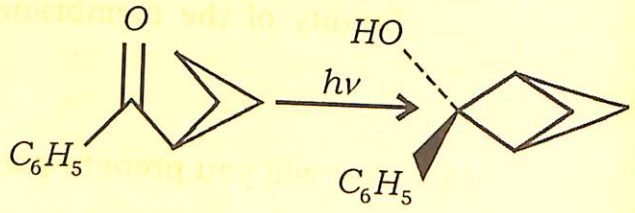
(ii) How will you prepare paracetamol and sulfapyridine? 3

(iii) Give an example of a chiral drug and draw its structure. 2

(d) (i) What are thermosetting and thermoplastic materials? Give examples. Discuss the structural differences of fibres and elastomers. 3+2=5

(ii) What are the characteristic properties of alkaloids? Comment on the possible roles of alkaloids in plant kingdom. Write the structure of nicotine and write the reactions by which the nature of the heteroatoms and heterocyclic rings of nicotine have been established. 1+1+1+2=5

(e) (i) Provide the mechanism of the following reaction : 3



(ii) Explain with examples, how nucleosides and nucleotides differ. 2

(iii) Why citral is called a monoterpenoid? Show the isoprene units which build the molecule. Write a synthesis of citral. 1+1+3=5

(f) (i) What is the structural unit present in sulfa drugs? Explain the mechanism of action of sulfa drugs. 1+2=3

(ii) Point the structural differences between haemoglobin and myoglobin. 2

(iii) Draw Jablonski diagram of the process of photoexcitation and energy dissipation of organic compounds. 3

(iv) Discuss the importance of Sanger's reagent in peptide chemistry. 2

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