(b) Consider the ^1H NMR spectra of the following compounds :

(i) Cl_2CHCH_2Cl

(ii) $ClCH_2CH_2Cl$

How many signals will be shown by each of the compounds? Which protons will show resonance at the highest downfield and why? Explain in which of the compounds spin-spin coupling will be observed and show schematically the splittings of the signals. 1+2+2=5

(c) Explain what you mean by diamagnetic shielding in ^1H NMR spectroscopy. Deduce an expression for the chemical shift. State why chemical shift values are independent of the applied magnetic field or frequency. 2+2+1=5

(d) Calculate the strength of magnetic field at which a free proton will show resonance when a radiofrequency of 100 MHz is used. 2

Given g for proton $= 5 \cdot 585$ and $\beta_N = 5 \cdot 047 \times 10^{-27}$ J T^{-1}.

(e) Discuss about the hyperfine structure of the ESR spectrum of H-atom. 3

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2019

CHEMISTRY

(Major)

Paper : 6.1

(Spectroscopy)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

Symbols signify their usual meanings

1. Answer in brief : 1×7=7

(a) For the transition of a molecule between the stationary states ψ_m and ψ_n, write the expression for the transition moment.

(b) Which of the following will be Raman active, but not IR or microwave active?

HCl, CO_2, O_2, H_2O

(c) State how the components of moment of inertia of a symmetric top molecule are related.

Or

Write how the components of moment of inertia of the molecule OCS are related.

(d) Let the spacings between the adjacent molecular electronic, vibrational and rotational levels be $\Delta\varepsilon_{elec}$, $\Delta\varepsilon_{vib}$ and $\Delta\varepsilon_{rot}$. Arrange these spacings in increasing order.

(e) State how the spectral line is affected by the lifetime of the excited state of a molecule.

(f) In the mass spectrum of a primary alcohol, a strong peak is observed at $\frac{m}{z} = 31$. Identify the species corresponding to this peak.

Or

The EI mass spectrum of an organic compound containing C, H and N shows the molecular ion peak with even mass. What information can be drawn regarding the number of N atoms in the molecule from this observation?

(g) Write the selection rule for pure rotational Raman spectrum of a diatomic molecule.

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

(a) In the IR spectrum of pure butan-1-ol, a broadband is observed within the range 3500 cm^{-1} – 3200 cm^{-1}. But a dilute solution of the compound in CCl_4 shows an additional band at 3650 cm^{-1}. Explain this observation.

Or

Write how you will distinguish between acetone and acetic acid by using IR spectroscopy.

(b) Calculate the energy difference in joule between the two rotational levels of a molecule if it absorbs a photon of wavelength 10 cm.

(c) In mass spectrometry, it is generally observed that a molecular ion with even mass cleaves to give fragment ions with odd mass and vice versa. But the EI mass spectrum of pentanal (molecular mass = 86 a.m.u.) shows a strong peak at $\frac{m}{z} = 44$. Explain this observation.

Or

The mass spectrum of an organic compound containing chlorine shows two peaks at $\frac{m}{z}$ values of 64 and 66. The peak at $\frac{m}{z} = 66$ is of one-third intensity as compared to the peak at $\frac{m}{z} = 64$. Which one should be the molecular ion peak? Account for the origin and intensity of the other peak.

(d) Discuss about the fragmentation of acetone to show the formation of the species responsible for the base peak.

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

(i) The energy of a hypothetical quantum mechanical system is given by $an(n+4)$, where a is some positive constant and $n = 1, 2, 3, \cdots$. The selection rule is $\Delta n = \pm 3$. Find a general expression for the energy required for the transition to take place. 3

(ii) Explain how the path length of sample affects the intensity of spectral line. 2

(iii) Taking the example of HCl, explain how the component of dipole moment along a particular direction varies with time due to rotation of the molecule. 3

(iv) A monochromatic radiation of wavelength 400 nm is allowed to pass through a solution with concentration 2 mol m^{-3} taken in a curette of 1 cm width. The solution transmits 20% of the incident radiation. Calculate molar extinction coefficient. 2

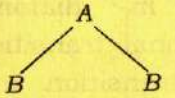
(b) In mass spectrometry, ions are detected according to their mass-to-charge $\frac{m}{z}$ ratios. Deduce the expression for $\frac{m}{z}$ and hence explain how the different ions are detected. 3+2=5

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

(i) The fundamental absorption and the first overtone bands of HCl appear at 2886 cm^{-1} and 5668 cm^{-1} respectively. Calculate the force constant of the bond in HCl. The atomic masses of H and Cl are 1·008 a.m.u. and 35·45 a.m.u. respectively. 5

(ii) The C—H stretching of an alkane appears at 2960 cm^{-1}. If the Raman spectrum of the compound is observed using a monochromatic radiation of 435·8 nm, predict the wavelength of the Stokes line corresponding to this band. 3

(iii) Write how you can differentiate between the following two structures by using IR and Raman spectroscopy : 2



and B—A—B

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

(a) Discuss the origin of the P and R branches in the rotation-vibration spectrum of a diatomic molecule. Show schematically the P and R branches. 4+1=5

(b) Write the quantum mechanical theory of Raman spectroscopy. Show schematically the Rayleigh lines, Stokes lines and anti-Stokes lines. 4+1=5

(c) Considering the diatomic molecule to be a rigid rotator, deduce an expression in wavenumber unit for the energy required for rotational transition to take place. Explain how the spectrum will differ if the molecule is considered to be a non-rigid rotator. 3+2=5

(d) Find the normal vibrational modes of CO_2. Out of these, how many are stretching and how many are bending vibrations? Explain which vibrations are IR active and which are not. 1+1+3=5

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

(a) Write the selection rules for electronic transition in diatomic molecule. The vibrational transitions along with electronic transition are represented in terms of (v', v'') numbers. Explain how the variation in intensity of (v', v'') transitions can be explained. 1+4=5

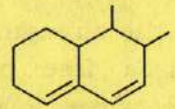
(b) The photoelectron ejected from N_2 with a radiation of wavelength 58·43 nm has kinetic energy of 5·63 eV. Calculate the ionization energy of N_2. 3

(c) Write how a polar solvent affects the $\pi \rightarrow \pi^*$ transition of a compound. 2

(d) Name the main electronic transitions observed in organic molecule and indicate the regions of wavelengths where these transitions may be observed. Name the electronic transitions that may be observed in carbonyl chromophore. Define auxochrome. 3+1+1=5

(e) Explain which of ethene and hexa-1,3,5-triene will have the higher λ_{max} value of $\pi \rightarrow \pi^*$ transition. What do you mean by redshift of λ_{max} value? 2+1=3

(f) Using the Woodward-Fieser rules, predict the λ_{max} value of the following compound : 2



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

(a) Show schematically how the spin states of an electron split up in an applied magnetic field. Find the energy difference between the two spin states. State what is done in ESR spectroscopy in order to get the spectrum. 1+3+1=5

(f) Consider a system of six distinguishable particles. One of the macrostate of the system has the following distribution of particles :

Energy level	0	1	2	3	4
Number of particles	1	0	2	1	2

Find the thermodynamic probability. 3

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2019

CHEMISTRY

(Major)

Paper : 6.2

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

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

(a) If three elements *A*, *B* and *C* crystallizes in a cubic solid with *A* atoms at the corners, *B* atoms at the cube centre and *C* atoms at the faces of the cube, what will be the formula of the compound?

(b) Calculate the Miller indices of a crystal plane which cuts through the crystal axes at (6*a*, 3*b*, 3*c*).

(c) "When an intense converging beam of light is passed through a colloidal solution kept in dark, the path of the beam gets illuminated with a bluish light." What is the name of this phenomenon?

(d) Arrange the following in increasing order of their effectiveness in coagulating AS_2S_3 sol :

$$Mg^{2+},\ Na^{+},\ Al^{3+}$$

(e) What do you mean by polydispersity index of a polymer?

(f) Using the Stirling's approximation, calculate $\ln N_A!$. (N_A is Avogadro's number.)

(g) State whether the following statement is True or False :

"In any ionic solid [*MX*] with Schottky defects, the number of positive and negative ions are same."

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

(a) Silver has a cubic unit cell with a cell edge of 408 pm. Its density is 10·6 g cm^{-3}. How many atoms of silver are there in the unit cell?

(b) Distinguish between error and uncertainty in measurement.

(c) The translational partition function for hydrogen atom at 3000 K confined in a vessel of volume $2 \cdot 494 \times 10^5$ cm^3 is $7 \cdot 586 \times 10^{30}$. Calculate the thermal de Broglie wavelength.

(d) "$CH_3(CH_2)_{15}N(CH_3)_3Br$ forms micelles in aqueous solution at a lower molar concentration than $CH_3(CH_2)_{11}N(CH_3)_3Br$." Explain this observation.

3. (a) What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanisms. What type of semiconductors are the following? 4+1=5

(i) Ge dopped with In

(ii) B dopped with Si

Or

What do you mean by non-stoichiometric defects? Give one example. Explain metal excess and metal deficiency defects with examples. 1+2+2=5

(b) Deduce the relation $S = k \ln W$. 5

Or

Deduce an expression for the entropy of monatomic perfect gas in terms of partition function.

(c) Define average deviation and standard deviation. Estimation of Fe present in a sample showed the following results in a series of experiments :

Experiment	*Amount of Fe*
I	7·146%
II	7·098%
III	6·942%
IV	7·256%
V	6·593%

Find average deviation, standard deviation and coefficient of variations for the values. 2+3=5

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

(a) What do you mean by packing efficiency? Calculate the packing efficiency of face-centred cubic arrangement. 1+2=3

(b) KNO_3 crystallizes in orthorhombic system with the unit cell dimensions a=542 pm, b=917 pm and c=645 pm. Calculate the diffraction angle for first-order X-ray reflections from (1 0 0), (0 1 0) and (1 1 1) planes using radiation with wavelength 154·1 pm. 4

(c) White coloured zinc oxide turns yellow on heating. Explain. 3

(d) State Bragg's law and deduce the equation $2d\sin\theta = n\lambda$, symbols have their usual meanings. 4

(e) Explain the following : 1½×2=3

(i) Frenkel defect is not found in pure alkali metal halides.

(ii) Antiferromagnetic substances have unpaired electrons but their dipole moment is zero.

(f) Explain the origin of low temperature superconductivity in terms of Cooper pair. 3

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

(a) Discuss the viscometric method of determination of molar mass of polymers. What is viscosity number? 3+1=4

(b) A solution contains 1:2 ratio of number of particles of two substances with molar masses 5000 g mol^{-1} and 12000 g mol^{-1} respectively. Calculate the number average and weight average molar masses. 3

(c) What do you mean by critical micelle concentration? Show graphically how molar conductance, surface tension and osmotic pressure of solutions of surfactants change at the critical micelle concentration. 3

(d) Discuss the kinetics of addition polymerization. Give an example of a polymer produced by this method. 3+1=4

(e) The osmotic pressure of 1 m^3 of a solution containing 2·5 kg of a polymer is found to be 250 Pa at 298 K. Assuming that the solution does not deviate from ideal behaviour, calculate the molar mass of the polymer. 3

(f) What are protective colloids? Explain how a lyophilic colloid can stabilize a lyophobic colloid with suitable examples. 3

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

(a) From the statistical thermodynamical consideration, deduce an expression for the equilibrium constant of an ideal gas reaction equilibrium. 4

(b) If the thermal wavelength of gaseous argon at 25 °C is 16 pm, calculate its standard molar entropy at the same temperature. (Mass of Ar is 39·95 u.) 3

(c) For a diatomic molecule rotating as a rigid rotor, obtain an expression for rotational partition function. 3

(d) Consider the molecule of a gas which have two quantum states of energies 0 and ε and degeneracies g_1 and g_2 respectively. Calculate the contribution of these quantum states to the molar heat capacity of the gas at constant volume. 4

(e) The rotational constant of gaseous HCl, determined from microwave spectroscopy is 10·59 cm^{-1}. Calculate the rotational partition function of HCl at 500 K. 3

2019

CHEMISTRY

(Major)

Paper : 6.3

(Organic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

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

(a) Define quantum yield. What does it signify in the photochemical reaction?

(b) What is photosensitizer? Give one example.

(c) What is antiretroviral drug? Give one example.

(d) Write the generic name of the anticancer drug containing Pt metal used as chemotherapy drug.

(e) What are the three components of a nucleotide?

(f) Name the enzymes used for digesting proteins.

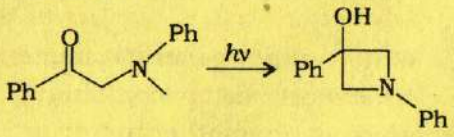
(g) Draw the structure of nicotine.

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

(a) What is quaternary structure of protein? Give two examples of protein with quaternary structure.

(b) What is Norrish type–I reaction? What are the products expected to obtain when acetone is photolyzed above 100 °C?

(c) Show the reaction mechanism of the following photochemical reaction. Name the cleavage :



(d) What is lignin? What important roles are played by lignins in plants?

(e) How does lysozyme act as antibacterial agent?

(f) Write one method of preparation of sulphonilamide.

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

(a) What are oxyhaemoglobin and deoxygenated haemoglobin? Write the functions of haemoglobin and myoglobin. What is the structural difference between haemoglobin and myoglobin? 2+2+1

(b) Name the monomer of natural rubber. Define syndiotactic and atactic polymers. What is plasticizer? Show by reaction the formation of urea-formaldehyde resins. 1+2+1+1=5

(c) Give one example of optically inactive neutral amino acid. How can it be prepared by Gabriel's phthalamide synthesis? Define essential and non-essential amino acids with one example of each type. 1+2+2=5

(d) What are the bases present in DNA? Draw the structures of the bases present in DNA. 1+4=5

(e) Discuss the mechanism of action of sulpha drugs and penicillin. 2½+2½=5

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

(a) (i) What is Paterno-Buchi reaction? Explain with a suitable example to account for the yield of the probable products. 1+3=4

(ii) What is Krebs' cycle? What are the steps of Krebs' cycle? What is the main function of Krebs' cycle? 1+2+2=5

(iii) What is special isoprene rule? 1

(b) (i) What are adrenocortical hormones? What are the main functions of these hormones? Name and draw the structures of any two adrenocortical hormones. 1+2+2=5

(ii) Explain with examples fluorescence and phosphorescence. 2+2=4

(iii) What is intersystem crossing (ISC) in photochemistry? 1

(c) (i) Give evidences to ascertain the ring structure of glucose. What are anomers? 4+1=5

(ii) What is polypeptide? Plan a synthesis of the peptide gly-ala. 1+2=3

(iii) What is asymmetric synthesis of drugs? Explain with an example. 2

(d) (i) How are terpenoids classified? Give two examples of monoterpenoids. What is carotenoid? 1+1+1=3

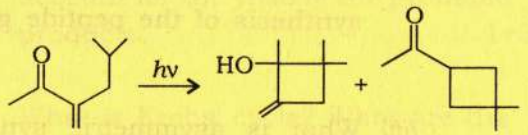
(ii) Discuss the role of RNA in protein synthesis. 5

(iii) Draw the structures of quinine and chloroquine. 1+1=2

(e) (i) What is the chemical name of vitamin B_3? Give a preparation of the compound. 1+2=3

(ii) Write the structures and preparations of aspirin and paracetamol. 2+2=4

(iii) The following photochemical reaction gives two products as shown below :



Provide the mechanism to show the formation of these two products. 3

(f) (i) What is triglyceride? Write the functions of the lipids in our body. How is lipid different from fats? 1+2+2=5

(ii) Write short notes on the following : 2½×2=5

1. Glycolysis
2. *cis-trans* isomerization of stilbene on irradiation

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2019

CHEMISTRY

(Major)

Paper : 6.4

(Inorganic Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer/Answer the following : 1×7=7

(a) The terms of an octahedral complex are labelled by the symmetry species of the overall orbital state; a superscript prefix shows the

(i) energy states of the term

(ii) multiplicity of the term

(iii) spectroscopic state of the term

(iv) coupling state of the term

(b) The correlation between electronic state energies and ligand field strength can be displayed on

(i) electronic state diagram

(ii) Orgel diagram

(iii) Tanabe-Sugano diagram

(iv) spectral diagram

(c) Haemoglobin consists of a

(i) monomer

(ii) dimer

(iii) trimer

(iv) tetramer

of myoglobin-like subunits.

(d) $[Ti(H_2O)_6]^{+3}$ absorbs the light of wavelength 5000 Å. Which of the following ligands would form Ti (III) complex absorbing the light of higher wavelength than 5000 Å?

(i) NO_2

(ii) CN^-

(iii) NH_3

(iv) F^-

(e) What disease is caused by the presence of nitrate more than 50 ppm in water?

(i) Hemolytic anemia

(ii) Sickle-cell anemia

(iii) Thalassaemia

(iv) Methemoglobinemia

(f) The ions $[NpO_6]^{-5}$ and $[PuO_6]^{-5}$ can be synthesized only in alkaline solution. Because

(i) their decompositions take place in acidic medium

(ii) in acidic solution they form unstable complexes

(iii) in alkaline solution they form stable complexes

(iv) water molecules coordinated in alkaline medium to form stable complexes

(g) Of the three isobars $^{114}_{48}Cd$, $^{114}_{49}In$ and $^{114}_{50}Sn$, which is likely to be radioactive?

2. Answer the following : 2×4=8

(a) Find out the Russell-Saunders ground-state term for Nb^{+3} ion.

(b) By applying complexometric titration, 6·5 ml of 0·0091 *M* EDTA solution was required for titration of a 50 ml sample of water for total hardness. Calculate the total hardness in terms of ppm of $CaCO_3$.

(c) How is artificial radioactivity manifested by K-electron capture?

(d) Write briefly about in vitro fixation of nitrogen.

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

(a) The logarithms of stability constant values of $[Cu(en)]^{+2}$, $[Cu(NH_3)_2]^{+2}$, $[Ag(en)]^{+}$ and $[Ag(NH_3)_2]^{+}$ complexes are 10·7, 7·8, 4·7 and 7·2 respectively. Explain why the en-complex of copper is more stable than the ammine complex, whereas the reverse is true for the corresponding silver complexes.

(b) Write the S_N2 mechanism of ligand displacement reaction of octahedral complexes.

(c) Discuss briefly the functions of haemoglobin and myoglobin in biological system.

(d) Write about the formation of coordination complex by lanthanides.

4. Answer any *three* of the following : 10×3=30

(a) *(i)* Establish a relation between stepwise formation constants and overall formation constant for a complexation reaction between $[Cu(H_2O)_6]^{+2}$ and ethylenediamine. 5

(ii) How will you explain the lability and inertness of the complexes on the basis of CFT? Which one of d^5 and d^6 ions is more inert in low-spin octahedral complex? 4+1=5

(b) (i) Write the uses of Ag, Pt and Au as medicine. 5

(ii) Write a note on chelate therapy. 5

(c) (i) Write about the consequences of lanthanide contraction. 5

(ii) The higher oxidation states are more common for actinides than for lanthanides—why? 3

(iii) Why are the observed magnetic moments of actinides lower than the calculated value? 2

(d) (i) Explain the mechanism of Na^+–K^+ pump. 5

(ii) Why do the tetrahedral complexes show intense colour than the octahedral complexes? 3

(iii) The reaction

$$[NiXL_5]^+ + H_2O \rightarrow [NiL_5(H_2O)]^{+2} + X^-$$

is much faster if L is NH_3 instead of H_2O. Explain. 2

(e) (i) State how CO affects biological system and how it can be remedied. 3

(ii) Discuss the sources and toxicities caused by copper and cadmium. 2

(iii) A museum wishes to analyze a piece of ruby for chromium content. What should be the preferred method of analysis? Write briefly about the method. 1+4=5

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