(b) State how many ^1H NMR signals will be shown by $(CH_3)_2CHCH_2Cl$. Draw schematic diagram to show the signals. Indicate the ratio between the peak areas. Indicate spin-spin coupling citing reasons. 1+1+3=5

Or

(c) Consider the two ^1H NMR signals shown by CH_3OH. Explain which protons will show resonance at down field compared to the other if the energy of the radiation is kept constant and the magnetic field is swept. Discuss whether the position of the signals will change or not if the magnetic field is kept constant and the radiation is swept. 3+2=5

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

(e) Write two reasons for using TMS as reference in non-aqueous solvents in ^1H NMR spectroscopy. 2

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2018

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 the following in brief : 1×7=7

(a) State which of the following radiations is associated with NMR spectroscopy :

X-ray, infrared, γ-ray, radiowave

(b) Find the normal modes of vibration in case of C_2H_6.

(c) State why IR radiation cannot induce electronic transition.

(d) Some relationships between the components of moment of inertia are given below :

(i) $I_A = I_B = I_C$

(ii) $I_A \neq I_B \neq I_C$

(iii) $I_A = 0,\ I_B = I_C$

(iv) $I_A \neq 0,\ I_B = I_C$

State which of these combinations represents CO_2 molecule.

(e) Considering a diatomic molecule as the vibrating rotor, write the selection rule.

(f) Draw a schematic diagram to show different components of a mass spectrometer.

(g) Name the quantities which are used to present the mass spectrum of a compound.

2. Answer any *four* questions : 2×4=8

(a) Taking the example of butane, write in brief about the electron ionization process used in mass spectrometry.

(b) Distinguish between molecular ion peak and base peak in mass spectrometry.

(c) Show how the McLafferty rearrangement takes place in pentanal and identify the species with $m/z = 44$.

(d) Indicate the specie responsible for the molecular ion peak and the base peak observed in the EI mass spectrum of ethanol. Find m/z values corresponding to these two peaks.

(e) In the mass spectrum of 2-methyl pentane, two prominent peaks are observed at m/z values of 71 and 43 respectively. Identify the specie showing fragmentation.

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

(i) The energy of a hypothetical quantum mechanical system is given by $An^2(n+1)$, where A is constant and $n = 1, 2, 3, \ldots$. The selection rule for the system is $\Delta n = \pm 1$. Calculate the energy of the radiation required for the transition to take place. 3

(ii) Write how the population of states affects the intensity of spectral line. 2

Or

(iii) Identify with reasons the IR active and microwave active molecule(s) from the following : 3

HCl and CO_2

(iv) A particular molecule is considered to undergo spectroscopic transition between the ground state and the excited state. If the lifetime in the excited state is about 0·1 s, calculate the width of the spectral line in Hz. 2

(b) Consider a diatomic molecule to be an anharmonic oscillator and write its energy as wave number. Deduce the expressions for energy needed for allowed vibrational transitions. Indicate fundamental absorption and overtones. 1+3+1=5

(c) In the pure rotational spectra of ^{14}NO and ^{15}NO, the first lines appear at 3·4 cm^{-1} and 3·2815 cm^{-1} respectively. If the atomic masses of ^{14}N and O are 14·004 amu and 15·9994 amu respectively, find the atomic mass of ^{15}N. 5

Or

The spacing between the consecutive *S*-branch lines in the pure rotational Raman spectrum of H_2 is 243·2 cm^{-1}. Calculate the bond length of H_2. 5

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

(a) Considering the diatomic molecule to be non-rigid rotator, find an expression for the energy required in wave number for rotational transitions to take place. Write what difference in the spectra is expected if the molecule is considered to be a rigid rotator. 3+2=5

(b) What do you mean by fingerprint region in IR spectroscopy? Explain with example. 3

(c) Sulphur dioxide shows three bands around 519 cm^{-1}, 1151 cm^{-1} and 1361 cm^{-1} in both the Raman and the IR spectra. Explain what information you can draw from this observation regarding the structure of the SO_2 molecule. 2

Or

(d) Show that the Raman lines in the pure rotational Raman spectrum of a diatomic molecule appear at wave number

$$\bar{\nu} = \bar{\nu}_0 \pm 2B(2J+3)$$

where $\bar{\nu}_0$ is the wave number of the Rayleigh line. Draw the schematic diagram to show the Stokes lines and the anti-Stokes lines. 4+1=5

(e) Taking the example of H_2O, write how many normal vibrational bands you may expect. Explain why the number of the IR bands of H_2O is much more than that indicated by the normal vibrational modes. 1+2=3

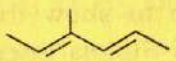
(f) Using a monochromatic radiation of wavelength 435·8 nm, the Raman line of C_2H_2 (g) is observed at the wavelength of 511 nm. Find the wave number of the vibrational band corresponding to this observation. 2

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

(a) Write the selection rules associated with the electronic transition of atom. Hence explain the fine structure of the spectrum of H-atom. 5

(b) Discuss with diagram what you mean by v' progression in connection with vibrational coarse structure of electronic spectra of diatomic molecule. 3

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



Or

(d) Electronic transition is accompanied by vibrational and rotational transitions. Discuss with diagram how the vibrational bands associated with the electronic spectrum of a diatomic molecule will appear if—

(i) the internuclear distance in the ground and the excited states is the same;

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

(e) State what type of electronic transition may be observed in CH_4. Write how the λ_{max} value of this transition varies in CH_3NH_2. 2

(f) A radiation with wavelength 58·4 nm ejects a photoelectron from Ar and the kinetic energy of the photoelectron is 5·4 eV. Calculate binding energy. 3

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

(a) Deduce an expression for the energy difference between the two spin states of an electron in an applied magnetic field in the z-direction. Write how transition from the lower to the upper spin state may be affected. State the selection rule involved. 3+1+1=5

2018

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) The ionic radii of Cs^+ and Cl^- ions are 1·69 Å and 1·81 Å respectively. Predict the coordination number of Cs^+.

(b) Yttrium barium copper oxide superconductor is often referred to as the 123 superconductor. Why?

(c) Arrange the following in increasing order of their effectiveness in coagulating ferric hydroxide sol :

Na_2SO_4, KCl, $K_3[Fe(CN)_6]$

(d) When a freshly prepared precipitate of $Fe(OH)_3$ is treated with water and a small amount of $FeCl_3$ solution, $Fe(OH)_3$ is converted to colloidal solution. What is the role of $FeCl_3$ in this process?

(e) Why should one always use purest monomer in free-radical polymerization?

(f) What do you mean by dominant configuration?

(g) The weight average and number average molecular weight of a polymer is 60000 kg mol^{-1} and 40000 kg mol^{-1} respectively. What will be the poly-dispersity index of the polymer?

2. Answer the following : 2×4=8

(a) Lithium borohydride, $LiBH_4$ crystallizes in an orthorhombic system with 4 molecules per unit cell. The unit cell dimensions are $a = 6{\cdot}81$ Å, $b = 4{\cdot}43$ Å and $c = 7{\cdot}17$ Å. If its molar mass is $21{\cdot}76$ g mol^{-1}, calculate the density of the crystal.

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

(c) Explain the difference between accuracy and precision with examples.

(d) 100 ml of a colloidal solution is completely precipitated by addition of 5 ml of 1 *M* NaCl solution. Calculate the coagulation value of NaCl.

3. (a) How does electrical conductivity of a metal and a semiconductor vary with temperature? What do you mean by *n*-type and *p*-type semiconductors? Explain with appropriate diagram and example. 1+4=5

Or

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

(b) Deduce an expression for the entropy of monoatomic perfect gas in terms of partition function. 5

Or

Derive an expression for rotational partition function. The rotational constant of gaseous HCl, determined from microwave spectroscopy is $10{\cdot}59\ cm^{-1}$. Calculate the rotational partition function of HCl at 100 K. 3+2=5

(c) Distinguish between repeatable and reproducible results. Analyzing of a sample of iron ore gave the following percentage values for the iron content :

7·08, 7·21, 7·12, 7·09, 7·16, 7·14, 7·07, 7·14, 7·18, 7·11

Calculate the mean, standard deviation and coefficient of variations for the values. 1+4=5

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

(a) A reflection from the (111) planes of a cubic crystal was observed at a glancing angle of 11·2° when CuK_α X-rays of wavelength 154 pm were used. What is the length of the side of the unit cell? 3

(b) Show that for an atom to occupy a tatrahedral void, its radius must be 0·225 times the radius of the sphere. 4

(c) Non-stoichiometric cuprous oxide, Cu_2O can be prepared in laboratory. In this oxide, copper to oxygen ratio is slightly less than 2 : 1. How will you account for the fact that this substance is a *p*-type semiconductor on the basis of the above stated information? 3

(d) What is radius-ratio? How does radius-ratio help in determining the structure of ionic solids and coordination number of ions? Explain. 1+3=4

(e) Why does zinc oxide exhibit enhanced electrical conductivity on heating? 2

(f) Explain the following terms with examples : 2×2=4

(i) Ferrimagnetism

(ii) Piezoelectricity

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

(a) Discuss the osmotic pressure method for determination of molar mass of polymers. Why does this method give number average molar mass only? 4+1=5

(b) The intrinsic viscosity of myosin is $217\ cm^3\ g^{-1}$. Calculate the appropriate concentration of myosin in water if it has a relative viscosity of 1·5. 3

(c) What are lyophilic and lyophobic sols? Give one example of each. 1+1=2

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

(e) In a polymer sample, 30% molecules have a molar mass 20000, 40% have molar mass 60000 and the rest have 30000. Calculate weight average and number average molar mass of the polymer. 3

(f) Account for the origin of charge on colloidal particles in detail. 3

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

(a) Derive the Boltzmann distribution law. Give its physical significance. 5+1=6

(b) Distribute three energy quanta among three particles. Calculate the probability of each distribution. 4

(c) Using the concept of partition function, deduce an expression for the internal energy of a monoatomic perfect gas.

Hence find an expression for the heat capacity at constant volume. Graphically show how heat capacity of diatomic molecules varies with temperature. 3+2+1=6

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

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(iii) What is protein? Discuss the various levels of structure of protein. 5

(d) (i) What is mutarotation in glucose? Draw the α- and β-anomer of D(+)-glucose in pyranose form and hence explain anomerism. 1+2+2=5

(ii) Write a short note on biosynthesis of DNA. 3

(iii) What is nucleotide? Draw the structure of guanylic acid. 2

(e) (i) Explain why both glucose and fructose reduce Fehling's solution. 2

(ii) What is the cause of photo-isomerization of olefin? 2

(iii) How will you prepare paracetamol and sulphapyridine? 3

(iv) Give example of synthetic rubber and plan its synthesis. 3

(f) (i) Give the name and structure of a neutral, acidic and basic amino acid. What is zwitterion? 3

(ii) Describe Watson-Crick model for the structure of DNA. 4

(iii) What are the fractions of starch? Give the structures. 3

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2018

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) What is photostationary state?

(b) Mentioning the main source of citral, name one of the methods of extraction of citral from the source.

(c) Give the name and structure of a female sex hormone.

(d) What is the monomer of Teflon?

(e) Write the structure of ala-gly.

(f) What is isotactic polymer?

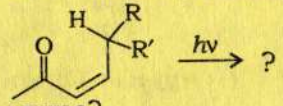
(g) Draw the structure of an energy-rich compound in biochemical reaction.

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

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

(b) Stating the condition of Norrish type-II reaction, explain why cyclohexanone does not give this type of reaction.

(c) Write down the following product :



(d) What is lysozyme?

(e) Write the structure of adrenaline and mention one of its function.

(f) How will you establish the presence of pyridine in nicotine?

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

(a) What is special isoprene rule? Plan a synthesis of citral starting from 6-methylhept-3-ene-2-one. Also draw the geometrical isomer of citral. 1+3+1=5

(b) What is isoelectric point of amino acids? Mention the use of Sanger's reagent in N-terminal amino acid determination. 1+4=5

(c) State and explain Wigner spin conservation rule by taking triplet-triplet energy transfer in photo-sensitization process. What is optical pumping? 4+1=5

(d) Draw the general structure of the penicillin and discuss the mechanism of action. 1+4=5

(e) Draw the structures of the bases present in RNA. 5

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

(a) (i) Complete the following reaction and write the mechanism :

$$\phi_2CO + Me_2CHOH \xrightarrow{h\nu} ?$$

What is the role of isopropyl alcohol here? 3+1=4

(ii) What is glycolysis? Mention the various steps involved. 1+3=4

(iii) Write the general mechanism of action of sulpha drugs. 2

(b) (i) Draw the Jablonski diagram to show IC, ISC, F and P. 3

(ii) Name and give the structure of any two antipyretic or analgesic. Write the general mechanism of action of such drugs. 4

(iii) Discuss briefly the effect of denaturation on the structure and activity of protein. 3

(c) (i) Plan a synthesis of the peptide gly-ala. 3

(ii) Explain why most of the photo-chemical reactions of ketone occur via T_1-state. 2

(d) (i) The electronic spectrum of $[VCl_4(bipy)]$ shows a single asymmetric band at 21300 cm^{-1} of moderate intensity ($\varepsilon < 800\ L\,mol^{-1}$) with a shoulder at lower energy (17400 cm^{-1}). How many absorption bands are expected if this complex is regarded as a perfect O_h? 2

(ii) Explain why MnO_4^- is intensely purple coloured while ReO_4^- is not highly coloured. 3

(iii) Discuss the separation of the lanthanides via ion-exchange chromatography. 5

(e) (i) How does neutron activation analysis (NAA) work? What types of archaeological samples can be analyzed by NAA? 2+3=5

(ii) Write notes on the following (any *two*) : 2½×2=5

(1) Vibronic-coupling

(2) Orgel diagram

(3) Nuclear belt of stability

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2018

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 : 1×7=7

(a) Silica gel contains $[CoCl_4]^{2-}$ as an indicator. When activated, silica gel becomes dark blue while upon absorption of moisture, its colour changes to pale pink. This is because

(i) Co(II) forms kinetically labile while Co(III) forms kinetically inert complexes

(ii) Co(II) changes its coordination from tetrahedral to octahedral

(iii) Co(II) changes its oxidation state to Co(III)

(iv) tetrahedral crystal field splitting is not equal to octahedral crystal field splitting

(b) In carbon dating application of radio-isotopes, ^{14}C emits

(i) β-particle

(ii) α-particle

(iii) γ-radiation

(iv) positron

(c) The correct *d*-electron configuration showing spin-orbit coupling is

(i) $t_{2g}^3 e_g^2$

(ii) $t_{2g}^6 e_g^0$

(iii) $t_{2g}^4 e_g^0$

(iv) None of the above

(d) In photosynthetic systems, the redox metalloproteins involved in electron transfer are cytochrome (cyt *b*),

cytochrome *bf* complex (cyt *bf*) and plastocyanin (PC). The pathway of electron flow is

(i) PC → cyt *b* → cyt *bf*

(ii) cyt *bf* → cyt *b* → PC

(iii) cyt *b* → cyt *bf* → PC

(iv) PC → cyt *bf* → cyt *b*

(e) Which one of the following statements is true for half-life of radioactive matters?

(i) It depends on amount of the matter

(ii) It depends on types of the matter

(iii) It depends on phase of the matter

(iv) It depends on temperature of the matter

(f) The lanthanide(III) ion having the highest partition coefficient between tri-*n*-butylphosphate and concentrated HNO_3 is

(i) La(III)

(ii) Eu(III)

(iii) Nd(III)

(iv) Lu(III)

(g) The activity of a radioactive source is measured in

(i) sievert

(ii) gray

(iii) becquerel

(iv) watt

2. Answer the following : 2×4=8

(a) Explain why, in terms of electronic transitions, substituting two of the NH_3 in $[Cr(NH_3)_6]^{2+}$ by bipy to form $[Cr(NH_3)_4(bipy)]^{2+}$ leads to more intensely coloured ($\varepsilon > 45000\ L\ mol^{-1}\ cm^{-1}$) complex.

(b) Potassium thiocyanate solution is used as a very sensitive test for the presence of iron(III) ions in solution. Discuss the chemistry behind the test.

(c) Metal ions are often used for diagnostic medical imaging. Explain the fact giving suitable examples.

(d) If the decrease in mass of a radioactive material between 18 and 24 years is 4 g, find the initial mass of the material (half-life of the material is 6 years).

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

(a) What are spectroscopic term symbols? Discuss how Hund's rule determine the term symbols of ground electronic states. 2+3=5

(b) What is meant by lanthanide contraction? Discuss how this phenomenon influences the properties of the transition elements immediately following the lanthanides. 1+4=5

(c) What is a radioactive disintegration series? Specify the different steps involved in the disintegration series of thorium. Why does the thorium series also known as 4*n* series? 1+3+1=5

(d) Name the metal ion present in the metalloenzyme carbonic anhydrase. Discuss the structure and functions of carbonic anhydrase. 1+4=5

(e) (i) What do you mean by labile and inert complexes? How does the *d*-electron configuration affect the labile/inert nature of complexes? 1+2=3

(ii) How will you prepare $K_3[Rh(ox)_3]$ from kinetically inert $K_3[RhCl_6]$? 2

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

(a) (i) Write the basic principle of conductometric titrations. Discuss the conductometric titration curve of sulphuric acid versus dilute ammonia. 2+3=5

(ii) What are the major roles of metal ions in biological systems? 3

(iii) Match the following metal salts with their prospective medicinal uses : 2

Metal salts	*Medicinal uses*
(1) Li_2CO_3	(I) Disinfectant
(2) *cis*-$[Pt(amine)_2X_2]$	(II) Antiulcer; antacid
(3) $AgNO_3$	(III) Manic depression
(4) Bi(sugar) polymers	(IV) Anticancer agent

(b) (i) When does induced radioactivity occur? Write a nuclear equation for the creation of ^{56}Mn through the bombardment of ^{59}Co with neutrons. 2+3=5

(ii) Discuss the ligand substitution mechanism in octahedral complexes. Sketch the reaction profile for the reaction

$$[Co(NEt_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NEt_3)_5(H_2O)]^{3+} + Cl^-$$

Clearly indicate intermediates and transition states. 2+3=5

(c) (i) The fusion reaction given below is one of the final stages in the fusion process that occurs in the Sun :

$$^2_1H + ^3_1H \rightarrow ^4_2He + ?$$

(1) Complete the reaction identifying the missing particle. 1

(2) Calculate the energy released in the fusion reaction using the following information (the mass number of the other particle is also required) : 2

$$^2_1H = 3{\cdot}345 \times 10^{-27} \text{ kg}$$
$$^3_1H = 5{\cdot}008 \times 10^{-27} \text{ kg}$$
$$^4_2He = 6{\cdot}647 \times 10^{-27} \text{ kg}$$

(ii) What do you mean by BOD and COD? What is their significance? 2+2=4

(iii) Carbon monoxide is more dangerous than carbon dioxide. Why? 3