(b) The mass spectrum of hexanoic acid shows a peak at $m/z = 60$ involving McLafferty rearrangement. Identify the species. Write the structures of the molecular radical ion and the fragments formed. 3

(c) State what type of cleavage you may expect in the EI mass spectrometry of acetone. Write the structures of the fragments formed. 2

Or

(d) In normal EI mass spectrometry, generally 70 eV electrons are used. What happens to an organic molecule under this condition? Explain taking the example of butane. Write how the molecular mass of a compound can be determined using EI mass spectrometry. 3+2=5

(e) The mass spectrum of bromomethane shows two strong peaks at m/z values of 94 and 96 having almost equal intensity. Identify the two species involved with proper justification. 2

(f) State nitrogen rule and write the logic behind it. 1+2=3

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2017

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 meaning)

1. Answer in brief : 1×7=7

(a) State which of the following will be microwave active :

CH_4, CH_3Cl, SF_6, OCS

(b) Which of the following radiations is associated with e.s.r. spectroscopy?

Radiowave, Microwave, Infrared, X-ray

(c) For a spherical top molecule, write the relationship among the three components of moment of inertia.

(d) If the spacings between the consecutive translational, rotational and vibrational levels are $\Delta\varepsilon_{tr}$, $\Delta\varepsilon_{rot}$ and $\Delta\varepsilon_{vib}$ respectively, arrange these values in the increasing order.

(e) Find how many stretching vibrations CH_4 possesses.

(f) State which of the following nuclei possesses integral spin and which possesses half-integral spin :

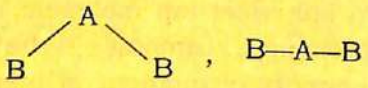
^{12}C, ^{2}H, ^{16}O, ^{13}C, ^{14}N

(g) In order to be infrared active, the dipole moment of the molecule must fluctuate with vibration. State the condition under which a molecule becomes Raman active.

2. Answer any *four* : 2×4=8

(a) Considering a diatomic molecule to be rigid rotator, find an expression in wave number for the energy required for rotational transitions to take place.

(b) Write how you can distinguish between the following two structures of the molecule B_2A using infrared and Raman spectra :



(c) Explain why Stokes lines are more intense than anti-Stokes lines.

(d) The infrared spectrum of ethanol (10% v/v solution in CCl_4) shows one sharp band at 3640 cm^{-1} and a strong broad band at 3340 cm^{-1}. But when the concentration is 1% (v/v in CCl_4), the band at 3640 cm^{-1} appears with increased intensity with simultaneous decrease in intensity of the later band. Explain this observation.

(e) Write in brief how the presence of heavier isotope affects the rotational spectrum of a diatomic molecule. Use rigid rotator concept.

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

(i) For a certain quantum mechanical system, the transition from level m to level n involves absorption of radiation with wavelength 480 nm. Again a radiation with wavelength 880 nm is absorbed in the transition from level p to level n of the same system. Find the wavelength of the radiation needed for the transition from level m to the level p.

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

Or

(iii) Write the expression for transition moment. Using this, explain what you mean by forbidden transition and selection rule. 3

(iv) A particular molecule undergoes spectroscopic transitions from the ground state to the excited state where its lifetime is about 0·1 s. Calculate the width of the spectral line in Hz. 2

(b) Explain with diagram the appearance of *P*- and *R*-branches in the rotation-vibration spectrum of a diatomic molecule. 5

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

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

Or

(ii) The infrared spectrum of thioacetic acid shows the prominent bands 2960 cm^{-1}, 2500 cm^{-1}, 1700 cm^{-1}, 1450 cm^{-1} and 1380 cm^{-1}. Indicate the groups responsible for these bands. Write what the structure of the molecule should be. 3

(iii) Write how you can distinguish between acetone and acetic acid using infrared spectra. 2

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

(a) Name the transitions that may take place along with electronic transitions in a diatomic molecule. Write how the difference in intensities of the vibrational lines associated with electronic transitions can be explained. 1+4=5

(b) The $\pi \rightarrow \pi^*$ transition in ethene is observed at 170 nm. Write in which of the following this should vary—

(i) Buta-1, 3-diene;

(ii) Hexa-1,5-diene. 2

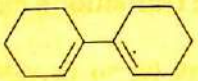
(c) The photoelectron ejected from N_2 with a radiation of wavelength 58·4 nm has kinetic energy of 5·6 eV. Calculate the ionization energy of N_2. 3

Or

(d) Name the main electronic transitions observed in organic molecules. Indicate the regions of wavelengths where these transitions may take place. What types of electronic transitions are observed in carbonyl chromophore? Mention the effect of conjugation on these transitions. 3+1+1=5

(e) Define chromophore and auxochrome. The λ_{max} value of benzene is 204 nm. State how this is affected in aniline. 2+1=3

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



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

(a) Draw schematic diagram to show the effect of applied magnetic field (B_z) on the spin states of a proton. Find an expression for the energy difference between the spin states in presence of the applied field. 1+3=4

(b) State how many ^{1}H-NMR signals will be shown by 1-chloropropane. Discuss the effect of spin-spin coupling. 1+3=4

(c) Of CH_3F and CH_3Br state protons of which compound will show resonance at more downfield compared to the protons of the other compound. Write the reason behind your answer. 2

Or

(d) Why do the protons in different chemical environments show resonance at different magnetic fields? Explain taking the example of chloroethane. Discuss what you mean by chemical shift. 2+3=5

(e) Calculate the frequency of the radiation needed for ^{1}H magnetic resonance to take place for a proton if the applied magnetic field strength is 7·05 T.

Given : $g_N = 5 \cdot 585$, $\beta_N = 5 \cdot 05 \times 10^{-27}$ JT^{-1} 2

(f) Discuss the hyperfine structure of the e.s.r. spectrum of deuterium. 3

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

(a) In the mass spectrometry experiment, the ions with different m/z values can be detected by changing the accelerating potential. Explain how this is possible. 5

2017

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) Calculate the Miller indices of crystal plane which cut through the crystal axes at $(2a, -3b, -3c)$.

(b) Find the highest order that can be observed in Bragg's reflection from a solid by X-ray.

(c) Name the crystal system with characteristics $a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$.

(d) State what you mean by critical micelle concentration.

(e) Define polydispersity index of a polymer.

(f) Define thermodynamic probability.

(g) State what you mean by isotactic polymer.

2. (a) The density of Li metal is $0{\cdot}53\ g\ cm^{-3}$ and the separation of the (100) planes of the metal is 350 pm. Determine whether the lattice is f.c.c. or b.c.c. ($M(Li) = 6{\cdot}941\ g\ mol^{-1}$) 2

(b) What is critical temperature in connection with superconductivity? What are high temperature superconductors? 2

Or

Calculate the packing efficiency of a simple cubic metal.

(c) Define partition function. What does the partition function refer to at absolute zero temperature? 2

(d) "A colloidal solution is not precipitated on the addition of an electrolyte in presence of gelatin." Explain. 2

Or

Explain how the formation of micelle affects the electrical conductivity and the osmotic pressure of the solution.

(Continued)

3. Define average deviation and standard deviation. In an experiment, the set of masses of an element obtained were 29·8 mg, 30·2 mg, 28·6 mg and 29·7 mg. Calculate the standard deviation of the individual values and the standard deviation of the mean. Express the results as absolute and relative values. 5

Or

Write briefly about the various types of errors in measurement. What do you understand by uncertainty in the measurement of physical quantities? Distinguish error from uncertainty. 2+2+1=5

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

(a) Consider six distinguishable particles distributed in three energy levels (0, ε and 2ε) in the following manner :

Energy	0	ε	2ε
Macrostate I	3	3	0
Macrostate II	2	2	2

Calculate the difference in entropy between the two macrostates. 3

(Turn Over)

(b) Calculate the translational partition function of H_2 molecule confined to a $1000\ cm^3$ vessel at 25 °C. 2

(c) Calculate the characteristic vibrational temperature of N_2 molecule, if $\bar{\nu}_0 = 2357{\cdot}6\ cm^{-1}$ for N_2 molecule. 3

(d) Consider 9 distinguishable particles divided equally among 3 non-degenerate energy levels. Find thermodynamic probability for this distribution. 2

5. Answer *either (a) or (b)* :

(a) Define number average and mass average molar mass of polymers. For a sample of polymer, which one has a larger value and why?

A solution contains 1:2 ratio of number of particles of two substances with molar masses $10{\cdot}0\ kg\ mol^{-1}$ and $20{\cdot}0\ kg\ mol^{-1}$ respectively. Calculate the values of number average and mass average molar masses. 3+2=5

(b) Discuss about the light scattering method for determination of the molar mass of polymer. 5

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

(a) What are Schottky and Frenkel defects? Write what types of compounds exhibit these defects. Discuss the effect of these defects on the density of solids. 2+1+1=4

(b) CsCl has a b.c.c. arrangement and its unit cell edge length is 400 pm. Calculate the interionic distance in CsCl. 3

(c) When NaCl crystal is exposed to Na vapours, the crystal acquires yellow colour. Explain this observation. 3

(d) Discuss the molecular interpretation of paramagnetism. 4

(e) X-ray of wavelength 0·134 nm gives a first-order diffraction from the surface of a crystal when the value of θ is 10·5°. Calculate the distance between the planes in the crystal parallel to the surface. 3

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

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

(a) For a diatomic molecule vibrating as a simple harmonic oscillator, obtain an expression for vibrational partition function. 5

(b) Deduce the relationship

$$S = k \ln W$$ 5

(c) From the statistical thermodynamical consideration, deduce an expression for the equilibrium constant of an ideal gas reaction equilibrium. 5

(d) Deduce an expression for the most probable distribution of N numbers of distinguishable particles among various energy levels. 5

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

(a) Explain the cleansing action of soaps and detergents. Which of these two is more effective in hard water and why? 3+1=4

(b) Discuss how the stability of lyophobic colloids explained with the help of DLVO theory. 4

(c) For As_2S_3 sol., the flocculation values of NaCl solution and KCl solution are almost the same, though $CaCl_2$ solution has much less flocculation value. Explain this observation. 2

(d) Discuss the kinetics of addition polymerization. 5

(e) Define relative viscosity, specific viscosity and intrinsic viscosity. The intrinsic viscosity of a polymer in water is found to be $217\ cm^3\ g^{-1}$. If the relative viscosity of the solution is 1·5, calculate the approximate concentration of the solution. 3+2=5

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2017

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 *all* questions : 1×7=7

(a) Write the zwitterion structure of glycine.

(b) Define quantum yield of a photochemical reaction.

(c) What is meant by reducing sugar? Give an example of it.

(d) Name one thermosetting and one thermoplastic polymer.

(e) What is peptide linkage?

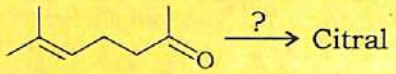
(f) Name one sulpha drug and give its structure.

(g) Write the structure of nicotine.

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

(a) What are glycosides? Describe a glycosidic linkage.

(b) Apply isoprene rule to citral molecule to show the attachment of isoprene units. How can you convert the following ketone to citral?



(c) What products are obtained when acetone is photolysed in absence of hydrogen donor?

(d) What are nucleotides? Write the name and structure of a nucleotide obtained from RNA.

(e) Why the triplet state cannot be populated directly by photoexcitation? What is meant by intersystem crossing?

(f) State the composition and functional difference between DNA and RNA.

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

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

(b) Name the monomers used in the manufacture of the following polymers :

(i) Terylene

(ii) Teflon

(iii) Bakelite

(iv) Nylon 6,6

(v) PVC

Write the polymerization reactions which give the above polymers.

(½×5)+(½×5)=5

(c) What are alkaloids? How will you establish the presence of pyridine nucleus in nicotine? Write the products of the following sequence of reactions : 1+2+2=5

$$\text{Dibromonicotine} \xrightarrow[H_2SO_4]{H_2SO_3} ?$$

(d) (i) Plan a synthesis of *cis*-platin. 2

(ii) Name an antimalarial drug and write its structure. 1

(iii) What are hormones? What is the function of insulin in the body? 2

(e) What are coenzymes? What are the biological functions of the following enzymes? 1+(1×4)=5

(i) TPP

(ii) FAD

(iii) NAD^+

(iv) CoASH

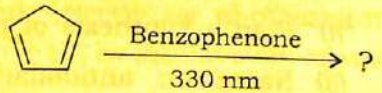
4. Answer *(a) or (b)*; *(c) or (d)*; *(e) or (f)* : 10×3=30

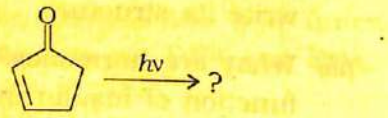
(a) (i) Draw Jablonski diagram of the process of photoexcitation and energy dissipation of organic compounds. 3

(ii) Explain why [2+2] cycloaddition of ethene is a photochemically allowed process. 3

(iii) Mention the essential differences between fluorescence and phosphorescence. 2

(iv) Find the product(s) of the following reactions : 2





(b) (i) Explain chain-growth polymerization and step-growth polymerization with a suitable example in each case. 4

(ii) What are biodegradable polymers? Give an example of an aliphatic biodegradable polyester. 2

(iii) Name the monomer units of natural rubber and neoprene. 2

(iv) Describe what you mean by vulcanization of rubber. 2

(c) (i) Name the three pyrimidine heterocycles present in nucleic acid. Write their structures. Write a general method of synthesis of a pyrimidine derivative. 3+2=5

(ii) What are the conditions under which enzymes are denatured? What do you understand by inhibition of enzyme action? 2+1=3

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

(d) (i) Point out the structural differences between hemoglobin and myoglobin. 2

(ii) Why do glucose and mannose form same osazones? 2

(iii) What are the constituents of a cell membrane? Write the general structure of a phospholipid. 2

(iv) Write short notes on helical and sheet structure of proteins. 4

(e) (i) Give a synthesis of citral. 3

(ii) Give an example each of narrow-spectrum and broad-spectrum antibiotics. 2

(iii) Name a drug which finds application both as analgesic and antipyretic. Write the reaction involved in its preparation. 2

(iv) What is the structural unit present in sulpha drugs? Explain the mechanism of action of sulpha drugs. 3

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

(ii) What is meant by glycolysis? Write the overall reaction involved in glycolysis. 2

(iii) What is Hofmann's exhaustive methylation? Explain how this reaction can be used to establish the structure of alkaloids. 4

(iv) D-fructose is a ketohexose, yet it reduces Fehling's solution. Explain. 2

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2017

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. Answer the following : 1×7=7

(a) For an atom with configuration d^2, write the possible values of L and S.

(b) Identify the ground state term in

^1P ^3P ^3F ^1G

(c) Which two metals are responsible for stabilization of DNA?

(d) What is Wilson disease?

(e) Mention one example where an actinide element is used for the identification of a soluble metal ion.

(f) In which oxidation state Ac and Th are diamagnetic?

(g) How many α and β particles will be released when $^{238}_{92}U$ successively disintegrates to be transformed to $^{206}_{82}Pb$?

2. *(a)* Give explanation that $[CoCl_4]^{2-}$ is intense coloured compound whereas $[CoCl_6]^{3-}$ is faint in colour. 2

(b) Describe the use of gold compounds in medicine. 2

(c) Why classical smog has a reducing character but Los Angeles smog has an oxidizing character? 2

Or

What are hypercalcemia and hypocalcemia? What should be the blood calcium level?

(d) Calculate Q-value for the following nuclear reaction : 2

$$^{14}_{7}N + ^{4}_{2}He \rightarrow ^{16}_{8}O + ^{1}_{1}H + Q$$

Given, $M_N = 14{\cdot}0031$

$M_O = 16{\cdot}9991$

$M_{He} = 4{\cdot}0026$

$M_H = 1{\cdot}0078$

3. *(a)* Though three electronic transitions are expected only two are observed in the visible region of $[V(H_2O)_6]^{3+}$. Discuss the aspect with the help of Orgel diagram. 5

(b) What are the causes of carbon monoxide pollution in air? Why does concentration of carbon monoxide not increase to a significant extent in atmosphere? What is the main reason for high concentration of carbon monoxide in urban areas compared to countryside? 2+2+1=5

Or

How does cyanide ion act as a poison in the human body? What is the antidote to cyanide poisoning? 3+2=5

(c) Describe one method of separation of ^{235}U and ^{238}U. 5

Or

Why is it difficult to separate lanthanide elements? Write briefly about oxidation states of lanthanides. 3+2=5

4. *(a)* The molar extinction coefficients for tetrahedral complexes are about 10^2 times greater than those for octahedral complexes. Elaborate this statement. 5

(b) Explain the use of EDTA in complexometric determination of Ca^{2+} and Mg^{2+} ions from its mixture. 5

Or

(c) Define the terms 'labile' and 'inert' of the coordination compounds. Compare these aspects with stability of compounds with appropriate examples. 2+3=5

(d) Discuss the theory of colorimetric determination of metals. 5

5. (a) Write briefly about photosynthesis in the chloroplast membrane, clearly describing the role played by PS–I and PS–II. 5

(b) What is biological nitrogen fixation? Compare it with the Haber's process of synthesis of ammonia. 1+4=5

6. (a) A radioactive substance with initial concentration N_0 disintegrates with time t. How can you establish that the radioactivity of the substance will cease to exist only at infinite time? Show that change of radioactivity with time is a straight line with amplitude and intercept. 3+2=5

(b) Give a brief description of the chemistry of uranium. 5

Or

(c) (i) How would you account for stability of He nucleus? 2

(ii) What are radioactive tracers? Give one application of it with description. 1+2=3

(iii) What is the expected electronic configuration of gadolinium? It shows only one oxidation state of +3. Give reasons. 1+1=2

(iv) A remarkable characteristic of the spectra of the tripositive lanthanide and actinide ions is the sharpness of individual colour bands. Explain this observation. 3

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