2022

CHEMISTRY — HONOURS

Paper : CC-13

(Inorganic Chemistry – 5)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question no.* 1** (Compulsory) and ***any eight*** questions from the rest (***question nos.* 2 to 13**)

1. Answer ***any ten*** questions : 1×10

(a) What masking agent can be used for the detection of Cd^{2+} in presence of Cu^{2+} ion in analytical Group II A?

(b) The chelating agent 2, 3-dimercapto-propane-1-sulfonic acid (unithiol) is used as an antidote of metal toxicity. Identify the metal.

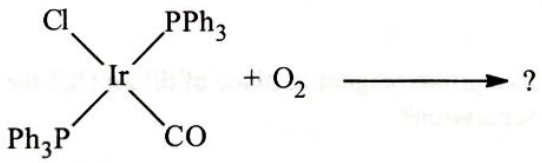
(c) Name a dinuclear iron dioxygen transport protein in biological system.

(d) Identify the first-row transition metal (M) in the following 18-electron species :
$(\eta^3 - C_5H_5)(\eta^5 - C_5H_5)M(CO)$

(e) How many ^1H NMR peaks are obtained for $Ti(\eta^1 - C_5H_5)_2(\eta^5 - C_5H_5)_2$ at $-30°C$?

(f) Name any two basic radicals with their charges present in the analytical Group II B.

(g) Draw the structure of the product of the following reaction :



(h) Which metal ion deficiency leads to pernicious anaemia?

(i) Write down the reagent(s) for the monoacetylation of ferrocene.

(j) Name two metal dependant diseases.

(k) Find out the molecular formula of the compound containing $\eta^6 - C_6H_6$, CO and Cr.

(l) Name one potential inhibitor for the activity of carbonic anhydrase (CA).

2. (a) State the roles of proximal histidine and distal histidine during the oxygenation of Haemoglobin.

(b) Compare C – C bond lengths in $[PtCl_3(C_2H_4)]^-$ and $[PtCl_3(C_2F_4)]^-$. 3+2

3. (a) What is Ziegler-Natta polymerization? Is Ziegler-Natta system homogeneous? What is the role of $Al(C_2H_5)_3$ in the catalytic process?

   (b) Discuss the difference in the active sites of carboxypeptidase A and carbonic anhydrase. 3+2

4. (a) Briefly explain the application of solubility product and common ion effect in the separation of Gr. II and Gr. III B cations.

   (b) Define reductive elimination reaction with reference to organometallic chemistry. Substantiate with an example. 3+2

5. (a) Show the valence electron count of the following :

   (i) $[(\eta^4 - C_4Ph_4)PdCl_2]_2$

   (ii) $[(\eta^5 - C_5H_5)Ir(CH_2)(PMe_3)]$

   (iii) $[Mn(SnPh_3)_2(CO)_4]^-$

   (b) Why phosphate and borate radicals are termed 'interfering'? 3+2

6. (a) Explain the principle of chelation therapy with reference to detoxification of lead, mercury and copper.

   (b) Write down the products :

   (i) $Co_2(CO)_8 + Na \rightarrow ?$

   (ii) $Mn_2(CO)_{10} + Br_2 \rightarrow ?$ 3+2

7. (a) What is the valence electron count for the blue ion $[NiCl_4]^{2-}$? Why does this tetrahedral ion not obey the 18 electron rule?

   (b) What happens when ferrocene is reacted with a hot solution of (i) sodium hydroxide and (ii) nitric acid? 3+2

8. (a) Compare the modes of binding of O_2 to the metal centres in (i) myoglobin (ii) hemerythrin (iii) hemocyanin.

   (b) Why concentrated HCl can not be used as a group reagent in place of dilute HCl for the precipitation of Group-I cations in analytical group separation? 3+2

9. (a) $Cr(CO)_5(PF_3)$ shows two C – O stretching frequencies in the range $1850 - 2125\ cm^{-1}$. Explain.

   (b) Write down the molecular formula of chromyl chloride. What happens when it reacts with NaOH solution? 3+2

10. (a) Starting from vanadium (III) chloride, how can you synthesize vanadium hexacarbonyl? Is it possible to get a dimeric carbonyl of vanadium? Justify.

   (b) Explain why EDTA or its di-sodium salt are not used in the treatment of heavy metal ion toxicity. 3+2

11. (a) What are ionophores? What are their roles in the metal ion transport across biological membrane?

(b) Give examples of one doubly bridging and one triply bridging nitrosyl compounds. 3+2

12. (a) $[V(CO)_6]$ and $[V(CO)_6]^-$ are both octahedral. Which has the shorter carbon-oxygen distance and the shorter vanadium-carbon distance?

(b) How a patient affected with Wilson's disease can be relieved by means of chelation therapy? 3+2

13. (a) Explain the biofunction of carbonate – bicarbonate buffering system.

(b) Mention one significant role in biological processes for each of the elements Cu and Ca. 3+2

R-98

2022

CHEMISTRY — HONOURS

Paper : CC-14

(Physical Chemistry-5)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question no.*** **1** and ***any eight*** from the rest.

1×10

1. Answer ***any ten*** questions :

(a) What will be the nature of the plot of total polarization (P_T) vs. 1/T for benzene?

(b) Will there be any rotational energy at absolute zero?

(c) What are the possible maximum and minimum values of optical density?

(d) Low temperature and viscous medium are suitable for observing phosphorescence— Explain.

(e) What are hot bands?

(f) Can a molecule undergoing harmonic oscillations only dissociate?— Justify or criticize.

(g) Dipole moment of HI is 0.3 Debye. Express its dipole moment in S.I. unit.

(h) Why are strong electrolytes negatively adsorbed in aqueous medium?

(i) Gold number of albumin and gelatine are 0.08 and 0.005. Which one is a better protective colloid?

(j) Draw the graph which represents the variation of amount of chemisorption of a gas by a solid with temperature under constant pressure.

(k) Colloid solution of gold prepared by different methods are of different colour.— Explain.

(l) Surface tension of water around 293 K decreases by 0.16 dyne $cm^{-1}K^{-1}$. Calculate total surface energy per sq. cm. area at 293 K. [Given : $\gamma_{H_2O} = 72.75$ dyne cm^{-1} at 293 K].

2. (a) In methyl alcohol C – O – H bond angle is 110°. Using the geometry and bond and group moments, calculate the dipole moment of methanol.

Given : $\mu_{CH_3} = 0.4D$ and it acts along C – O bond.

$\mu_{CO} = 0.7D, \mu_{O-H} = 1.6D$

(b) C–H stretching vibration in an organic compound occur at 2900 cm^{-1}. At what wave no. would C–D stretching vibration occur? 3+2

Please Turn Over

3. (a) A plausible mechanism for the dimerisation of anthracene (A) is :

$$A + h\nu \rightarrow A^*$$
$$A^* + A \xrightarrow{k_2} A_2$$
$$A^* \xrightarrow{k_3} A + h\nu'$$
$$A_2 \xrightarrow{k_4} 2A$$

Show that the maximum concentration of A_2 is determined only by the intensity of light absorbed. Compare this with that expected in the absence of light.

(b) Derive Laplace equation for the pressure difference across a spherical curved surface. (2+1)+2

4. (a) Indicate all the photophysical processes occuring from an excited electronic state with the help of Jablonski diagram.

(b) Calculate the percentage ionic character of H–I bond where the bond length of H–I bond is 1.60 Å and its dipole moment is 0.38 D. 3+2

5. (a) Pure rotational spectrum of $C^{12}O^{16}$ has two successive lines at 7.72 cm^{-1} and 11.58 cm^{-1}. Determine the 'J' values between which transitions occur in each case.

(b) The kinetics of the reaction $[Co(NH_3)_5Br]^{++} + OH^- \rightarrow [Co(NH_3)_5OH]^{++} + Br^-$ was studied in aquous solution of (A) 0.15(N) KCl and (B) 0.3(N) KCl. State with reason whether the rate constant of the reaction in the case (A) would be greater than, less than or equal to in the case of (B). 3+2

6. (a) A unimolecular gaseous reaction show 2nd order kinetics at low pressure.— Explain using Lindemann mechanism.

(b) Absorption and fluorescence spectra hold a mirror image relationship.— Comment. 3+2

7. (a) Predict the structure of NO_2^+ ion based on the following spectroscopic data. It exhibits one vibrational frequency at 1400 cm^{-1} which is Raman active but IR inactive and two frequencies at 2360 cm^{-1} and 540 cm^{-1} which are IR-active but Raman inactive. To which vibrational modes do these frequencies correspond?

(b) The density of $SiHBr_3$(MWt 269) is 2.690 gm/cc. At 25°C its refractive index is 1.578 and dielectric constant is 3.570. Estimate its dipole moment in Debyes. (neglecting atomic polarisation). (2+1)+2

8. (a) Find the number of normal modes of vibration of H_2O molecule and explain which of these vibrations are IR and Raman active.

(b) From the following data for adsorption of N_2 gas on a solid surface, calculate the constant involved in the Langmuir isotherm.

P = ∝, V = 180 cc/gm, P = 3.5 atm

V = 100 cc/gm. [V = volume of gas adsorbed]. 3+2

H → $1s^2 2s^2$..

9. (a) A mixture of dichromate and permanganate ions was analyzed spectrophotometrically at 440 nm and 545 nm. The absorbance values were 0.385 and 0.653 respectively at each wavelength for a 1 cm cell. Calculate concentration of dichromate and permanganate in the unknown mixture.

Given : $Cr_2O_7^{2-}$: $\epsilon_{440} = 370\ M^{-1}cm^{-1}$

$\epsilon_{545} = 10.8\ M^{-1}cm^{-1}$

MnO_4^- : $\epsilon_{440} = 92.8\ M^{-1}cm^{-1}$

$\epsilon_{545} = 2350\ M^{-1}cm^{-1}$

(b) Give mathematical expression for Gibbs' surface excess. Justify that it can take up both positive and negative values. 3+2

10. (a) The surface tension of dilute solution of a certain surfactant decreases linearly with concentration. At 10^{-4}(M) surfactant the surface tension has decreased by 3 dynes cm^{-1}. Calculate Γ, the surface excess at 298 K.

(b) Exlpain the term 'Tyndall effect' using a labelled diagram. How does the wavelength of the scattered light depend on the size of the colloidal particle? 3+2

11. (a) Write down the differences between the Collision theory of reaction rate and transition state theory of reaction rate.

(b) 5g of a catalyst adsorbs 400 cm^3 of N_2 at STP to form a monolayer. What is the surface area per gram if the area occupied by a molecule of N_2 is 16 Å? 3+2

12. (a) An actinometer contains 20 cm^3 of a 0.05(M) oxalic acid through which radiation of wavelength 3500 Å was passed for 2 hrs. After exposure the solution required 34 cm^3 of $KMnO_4$ to titrate the undecomposed oxalic acid. The same volume i.e. 20 cm^3 solution required 40 cm^3 $KMnO_4$ before exposure. Calculate the energy absorbed in Joules/s if quantum efficiency is 0.53.

(b) The fundamental and first overtone for $^{14}N^{16}O$ are centred at 1876.06 cm^{-1} and 3724.0 cm^{-1} respectively. Calculate the exact zero point energy of the molecule. 3+2

13. (a) How can you justify the temperature dependence of Arrhenius frequency factor (A) using the collision theory of reaction rate?

(b) Discuss briefly the discrete lines and the continuous band in case of predissociation spectra. 3+2

2022

CHEMISTRY — HONOURS

Paper : DSE-A-3

(Green Chemistry and Chemistry of Natural Products)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question no.*** **1** and ***any eight*** questions from the rest (***question nos.*** **2** to **13**).

1. Answer ***any ten*** questions : 1×10

(a) Why green chemistry prefers the use of catalyst instead of reagents?

(b) What do you mean by biocatalyst? Give one example.

(c) Arrange the following solvents in the increasing order of greenness :
Ethanol, chloroform, tetrahydrofuran, water.

(d) What is the starting material used in the green synthesis of adipic acid?

(e) Write one source each of ultrasonic sound (US) and infrasonic sound (IS).

(f) What is the basis of formation of ionic liquid?

(g) State the second principle of green chemistry.

(h) What are the necessary conditions for a molecule to be microwave active?

(i) What is commonly used solvent in cleaning industry?

(j) What is the frequency range for sonochemical reactions?

(k) Give two important uses of Sc-CO_2 as solvent.

(l) Mention one medicinal use of morphine.

2. (a) What is a phase transfer catalyst? Discuss the role of PTC in nucleophilic substitution reaction. Cite one reaction.

(b) Why are most of Diels-Alder reactions faster in water than in methanol? 3+2

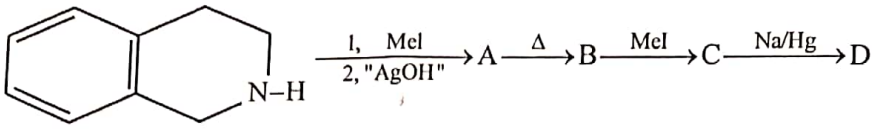
3. (a) How do you detect the presence of the followings in citral :

(i) Aldehyde group

(ii) Presence of double bond and their exact position

(iii) The hydrolysis product with aqueous potassium carbonate solution.

(b) Write down all the products (A → D) involved in the following transformations : 3+2



4. (a) Discuss the mechanism of thiamine catalysed benzoin condensation. What are the advantages of the green approach of synthesis?

(b) Give example of one green reagent along with structure which can be used in Fridel-Craft reaction instead of anhydrous $AlCl_3$. 3+2

5. (a) Give outlines of conventional and green synthesis of catechol. What are the advantages of the green method over the conventional one?

(b) How green chemistry works in sustainable development? 3+2

6. (a) Discuss in brief about biochemical and enzymatic method for the Baeyer–Villiger oxidation reaction.

(b) How combinatorial chemistry be beneficial in the context of green chemistry? 3+2

7. (a) Compare and contrast between the conventional method and any one green method of Claisen rearrangement.

(b) What are the utilities of PEG as a solvent in green synthesis? 3+2

8. (a) Discuss in brief any *one* green method of the following reactions :

(i) Michael reaction

(ii) Knoevenagel reaction

(iii) Cannizzaro reaction.

(b) Mention the reaction conditions for oxidation of toluene under microwave irradiation (MWI). Write the reaction and compare with conventional process. 3+2

9. (a) How microwave improves the yield of elimination product in 'Hofmann elimation' reaction? Explain with an example.

(b) What is hotspot in microwave irradiation? 3+2

10. (a) What is 'hydrophobic effect'? How it helps to get the activation energy necessary for the substrate molecules to react?

(b) What are micelles? 3+2

11. (a) Give one example of aldol condensation reaction carried out in a solventless benign way. Mention the substrate, reagents and conditions of the reaction.

(b) How acetanilide can be prepared *via* Beckmenn rearrangement following an environmentally benign procedure? 3+2

12. (a) Write down the product of the reaction when acrylonitrile is treated with benzaldehyde in a green way. Mention the name of the reaction, catalyst used and conditions needed for the reaction.

(b) Give an example of an oxidation catalyst. Write down one reaction showing its application. 3+2

13. (a) Why is carbon dioxide used as a supercritical fluid? Give two important uses of Sc-CO_2 as solvent.

(b) Why is an ionic liquid called a designer solvent? 3+2

2022

CHEMISTRY — HONOURS

Paper : DSE-B-3

(Polymer Chemistry)

Full Marks : 50

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Answer ***question no.*** **1** and ***any eight*** questions from the rest.

1. Answer ***any ten*** questions : 1×10

(a) A polymer mixture contains three non-dispersive polystyrene samples; A, B and C of molecular weights 10,000, 20,000 and 30,000 gm mol^{-1} respectively. Find $\overline{M}_n$, if the mixture contains equal mass of A, B and C.

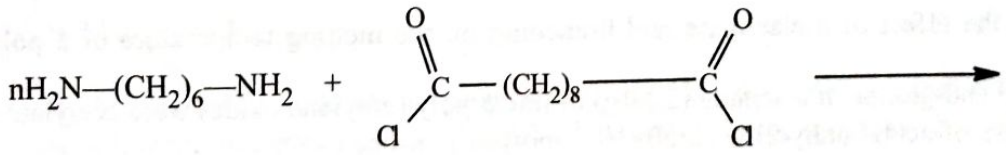
(b) In the polymerisation of phthalic anhydride (3 moles) and glycol (3 moles), what is the average functionality of the reacting system?

(c) What is the polydispersity index at stoichiometric conditions for step-growth polymerisation of two bifunctional monomers with a monomer ratio of 0·99 and number average degree of polymerisation of 66·8?

(d) Name two characteristic techniques which can be used to determine degree of crystallinity of a polymer?

(e) Compare Tg values of polyvinyl chloride and polypropylene with explanation.

(f) For the following polymerisation, write down a balanced chemical equation, showing the structure of the polymer formed, indicating the repeat unit and groups.



(g) Show $\overline{M}_n = 1\Big/\sum_i\left(\frac{W_i}{M_i}\right)$, where W_i is the weight fraction, i.e., the mass of molecules of molar mass M_i divided by the total mass of all the molecules present.

(h) Write down the chemical structure of polypyrrole. What special type of polymer is it?

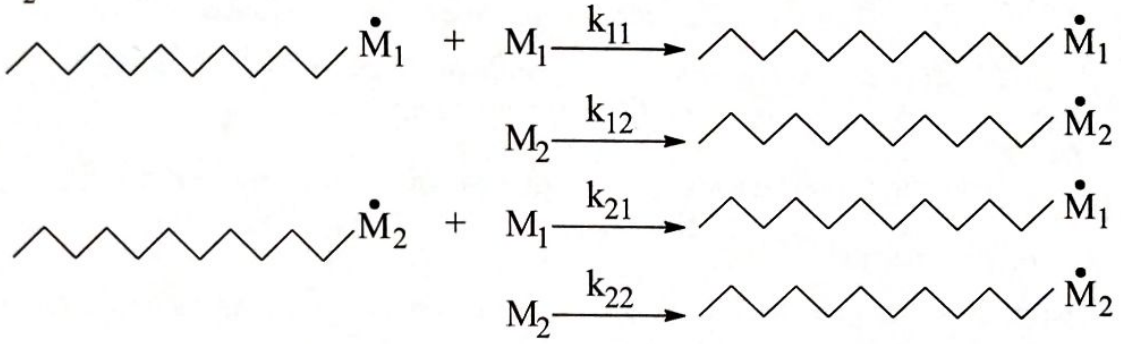
(i) Polymers generally behave as a Non-Newtonian fluid. When do they behave as Newtonian fluid?

(j) Name two methods for the determination of mass average molecular weight $\overline{M}_w$.

(k) Name the technique which permits simultaneous increase in rate of polymerisation and polymer molecular weight in the free radical polymerisation.

(l) Isobutene can be polymerised by cationic initiation, but acrylonitrile can be polymerised by anionic initiation. Explain.

2. (a) Consider the following scheme of chain growth during a radical polymerisation of monomers M_1 and M_2.



Show that, $\frac{d[M_1]}{d[M_2]} = \frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1]+[M_2]}{r_2[M_2]+[M_1]}$,

where, m_1 and m_2 be the concentrations of M_1 and M_2 respectively in the newly formed polymer, r_1 and r_2 are the copolymerisation parameters.

(b) Using the above equation, how can you experimentally determine the copolymerisation parameters, r_1 and r_2? 3+2

3. (a) The melting temperature (T_m) of a sample of poly (decamethylene adipate) with a number average degree of polymerisation $\left(\overline{X}_n\right)$ of 3 was found to be 65°C. T_m was found to be 75°C for a sample of the same polymer with $\overline{X}_n = 10$. Estimate the equilibrium melting temperature (T_m°) for poly (decamethylene adipate).

(b) Discuss the effect of molar mass and branching on the melting temperature of a polymer. 3+2

4. The hydroxyl end-groups of a sample (2·00 g) of linear poly (ethylene oxide) were acetylated by reaction with an excess of acetic anhydride ($2{\cdot}50\times10^{-3}$ mol) in pyridine :

After completion of the reaction, water was added to convert the excess acetic anhydride to acetic acid, which together with the acetic acid produced in the acetylation reaction was neutralised by addition of 23·30 cm^3 of a 0·100 mol dm^{-3} solution of NaOH. Calculate the number average molar mass for the sample of poly (ethylene oxide); given that each molecule has two hydroxyl end-groups, clearly explaining the procedure. 5

5. (a) How linear polyurethanes are prepared by polyaddition of diisocyanates with diols? Explain why the reaction proceeds quite rapidly at room temperature. Name two most commonly used diisocyanates.

   (b) How polyamides can be prepared by polycondensation? What is the difference between nylon 6.6 and nylon 6.10? 3+2

6. (a) Glass transition cannot be regarded as a true transition in the thermodynamic sense. Justify or criticise.
   Draw entropy versus temperature, and C_P versus temperature plots for a polymer indicating glass transition temperature.

   (b) Discuss the reasons for the differences in glass transition temperatures for the following pairs of polymers with similar chemical structures.

   (i) Poly (ethylene oxide) (– 41°C) and Poly (vinyl alcohol) (85°C)

   (ii) Poly (ethyl acrylate) (– 24°C) and Poly (methyl methacrylate) (105°C) 3+2

7. Show that in the self-catalysed step-growth polymerisation between a dicarboxylic acid and a diol, the average degree of polymerisation increases with square root of time but if the reaction is externally catalysed, then the average degree of polymerisation increases linearly with time. 5

8. Consider 1 : 1 stoichiometric polymerisation of 1, 4-diaminobutane with sebacoyl chloride.

   (a) Write down a balanced chemical equation for the polymerisation, and name the polymer formed by this polymerisation.

   (b) Using the Carother's equation, calculate the extent of reaction required to produce this polymer with a number average molar mass $\overline{M}_n = 25$ kg mol^{-1}. You should neglect the effects of end-groups on molar mass. 2+3

9. (a) Write down the important properties and uses of polystyrene. What is its IUPAC name?

   (b) How can you prepare polyvinyl acetate? Write down its IUPAC name. 3+2

10. Consider the following scheme for anionic polymerisation :

$$M_n^{\ominus} + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^{\ominus} ,$$

where, k_p be the rate constant of propagation, k_{dp} be the rate constant for depolymerisation. Derive the following integrated rate law clearly mentioning the assumptions involved.

$$k_p\left[\overline{M}_n\right] = \frac{1}{t}.ln\frac{\left([M]_0 - [M]_{eq}\right)}{\left([M] - [M]_{eq}\right)} ,$$

where, $[M]_0$ be the initial monomer concentration and $[M]_{eq}$ be the equilibrium monomer concentration. 5

11. Solution A consists of a 1% by weight solution of a polystyrene polymer in toluene of molar mass 20,000 g mol^{-1}. Solution B consists of a 1% by weight of solution also, but of the polymer molecule of molar mass 60,000 g mol^{-1}. Equal volume of A and B are mixed.

(a) Calculate $\overline{M}_n$ and $\overline{M}_w$ for the mixture.

(b) Calculate the viscosity coefficient of the mixture.

(Assume $[\eta] = 10^{-4} M^{1/2}$, and that the viscosity of pure toluene be 0·006 poise.) 2+3

12. Derive the following expression for the free energy of mixing of a polymer solution containing n_1 moles of solvent and n_2 moles of polymer molecule, using Flory-Huggins model.

$$\Delta G_{mix} = RT(n_1 ln\,\Phi_1 + n_2 ln\,\Phi_2 + n_1\Phi\,\chi_{12})$$

where, Φ_1 and Φ_2 be the volume fractions of the solvent and polymer respectively; χ_{12} be the Flory-Huggins polymer-solvent interaction parameter. What are the deficiencies of this theory? 5

13. (a) How can you determine the molar mass of a polymer from the osmotic pressure measurements?

(b) A plot of π/c versus c for a series of polymer solution gave a value of second virial coefficient equal to $1{\cdot}25\times10^{-4}$ $m^2\,kg^{-2}$ mol. If the molar mass is 25 kg mol^{-1}, determine the value of excluded volume. 3+2
