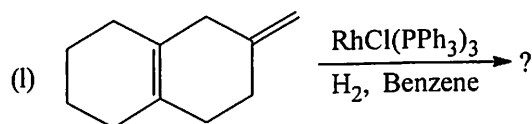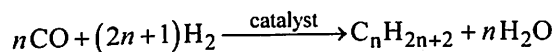# 2023

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) Among Cu^{2+}, Pb^{2+}, As^{3+} and Co^{2+}, which radical will not be precipitated by passing H_2S in hydrochloric acid medium?

   (b) What is the group reagent for precipitation of metal ions present in analytical group-IV?

   (c) Name one biological function of Mg^{2+}.

   (d) Write the formula of the precipitate obtained when disodium hydrogen phosphate is added in ammoniacal medium to Mg^{2+} solution.

   (e) Name one metalloprotein which shows cooperativity effect.

   (f) Name any two beneficial elements for the living bodies in biological system.

   (g) What is the basic function of Carboxypeptidase-A?

   (h) What is the active species in Ziegler-Natta catalyst?

   (i) Write down the IUPAC name of Zeise's salt.

   (j) What is the oxidation state of molybdenum in $[\eta^7\text{-tropylium Mo(CO)}_3]^+$?

   (k) Identify the catalyst used in the reaction given below.

   $$nCO + (2n+1)H_2 \xrightarrow{\text{catalyst}} C_nH_{2n+2} + nH_2O$$

   (l) $\xrightarrow[\text{H}_2, \text{ Benzene}]{\text{RhCl(PPh}_3)_3}$?

2. (a) Write down the procedure for the separation of Gr. II_A and Gr. II_B basic radicals. State the relevant chemical reactions.

   (b) Why is the change from deoxyhaemoglobin to the oxy-form accompanied by a decrease in the observed magnetic moment? 3+2

Please Turn Over

3. (a) Comment on the oxidation states of the metal ion in the active site of Haemoglobin and Hemerythrin with reference to oxygen transport.

 (b) Why is heating with conc. nitric acid done before precipitation of analytical group IIIA?   3+2

4. (a) Why the presence of one Zn(II) ion per mole of carboxypeptidase A is crucial for its activity? Explain.

 (b) Why is it necessary to prepare the sodium carbonate extract for the detection of acid radicals in inorganic qualitative analysis?   3+2

5. (a) What are metalloproteins and metalloenzymes? Distinguish between the terms.

 (b) How can you prepare $Fe(CO)_5$ and $Fe_2(CO)_9$?   3+2

6. (a) What is Chelation therapy? Mention its limitations.

 (b) How can you incorporate an $-NH_2$ group in ferrocene?   3+2

7. (a) Mention the role of NH_4Cl in group IV qualitative analysis. Can $(NH_4)_2SO_4$ be used instead of NH_4Cl?

 (b) Name two clinically approved drugs of platinum (II) for the treatment of cancer.   3+2

8. (a) $[Cr(CN)_5NO]^{4-}$, $\gamma(NO) = 1515$ cm^{-1}; $[Mn(CN)_5(NO)]^{3-}$, $\gamma(NO) = 1725$ cm^{-1}; $[Fe(CN)_5(NO)]^{2-}$, $\gamma(NO) = 1939$ cm^{-1} : Justify.

 (b) Discuss the role of NH_4OH in Gr. III$_B$ precipitation by H_2S.   3+2

9. (a) Draw the catalytic cycle mentioning each step for the following transformation. State the role of Cu^{2+} in the cycle. $H_2C = CH_2 + \frac{1}{2} O_2 \xrightarrow{\text{PdCl}_4{}^{2-}} CH_3CHO$.

 (b) 'Metal deficiency and metal excess both may exert toxic effects.' — Substantiate the statement with examples.   3+2

10. (a) Compare the acidity of the following compounds :

 $H_2Fe(CO)_4$, $HMn(CO)_5$ and $HCo(CO)_4$.

 (b) Explain, why ferrocene is unreactive toward iodine while cobaltocene rapidly decolorizes the colour of the iodine solution.   3+2

11. (a) Do you expect any rotation of ethylene molecule in Zeise's salt without hampering the stability of the complex? If possible, explain it.

 (b) What happens when boric acid is heated with methanol and the issuing gas is burnt? Write down the chemical reaction.   3+2

12. (a) Find out 'n' : (i) $Fe_4(CO)_n$ (ii) $[(\eta^5 - C_5H_5)_3Ni_3(\mu_3 - CO)_3]^n$.

 (b) Haemoglobin is not only an oxygen transporter but it also transports CO_2 and helps in the maintenance of pH of blood. Justify the statement.   2+3

13. (a) What is Wilkinson's catalyst? Mention the example of oxidative addition and reductive elimination with reference to the hydrogenation of alkene with Wilkinson's catalyst.

(b) Comment on the CO stretching frequencies of terminal CO, doubly bridging CO and triply bridging CO. 3+2

————————

2023

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* questions from the rest.

1. Answer *any ten* questions : 1×10

   (a) Molecular rotation about the bond axis cannot generate any microwave lines. Explain.

   (b) In vibrational spectra of a diatomics, the energy of the second overtone was found to be thrice that of the hot band. Comment on the observation.

   (c) Water can safely be used as a solvent in Raman spectroscopy but not in IR spectroscopy.

   (d) In microwave spectra, a molecule yields three different rotational constants. Comment on the symmetry of the molecule.

   (e) Identify in which of the following process/es spin inversion occur : Internal conversion, fluorescence, phosphorescence.

   (f) Name one bioluminescent chemical and one photosensitizer of plant origin.

   (g) Calculate the energy (in eV) of one Einstein radiation of wavelength 300 nm.

   (h) Define surfactant with one example.

   (i) Differentiate between absorption and adsorption.

   (j) What is Critical Micelle concentration?

   (k) Define isoelectric point for a colloid.

   (l) Dielectric constant of water (80) is much greater than air (1.00059). What is the implication of this information?

2. The rotational constant for H^1Cl^{35} is observed to be 10.5909 cm^{-1}.

   (a) Calculate the rotational constant for D^2Cl^{37}.

   (b) Find out the ratio of number of H^1Cl^{35} molecules with J = 4 to those with J = 0 at 300 K.

   2+3

Please Turn Over

3. (a) The fundamental and first overtone transition of NO molecule are found at 1876 cm^{-1} and 3724 cm^{-1} respectively. Evaluate the equilibrium vibration frequency and exact zero point energy of NO.

   (b) State the 'rule of mutual exclusion' in spectroscopy and illustrate with a suitable example.   3+2

4. (a) The Vibrational-Raman spectra of Cl_2 molecule shows a series of Stokes lines separated by 0.98 cm^{-1} along with the anti-Stokes lines. Calculate the Cl-Cl bond length.

   (b) Despite the selection rule $\Delta J = \pm 1$ and equal transition probability for all the possible transitions, why intensity of all rotational lines in a microwave spectra are not same? Explain.   3+2

5. (a) For CO_2, how many vibrational modes are there? Among them how many are IR active? Name those modes.

   (b) The rotational spectrum of HI is found to have its first line at 12.8 cm^{-1}. Find out which particular transition for HI will produce the most intense spectral line at 300 K.   3+2

6. (a) State the selection rules for both the Rotational Raman and Vibrational Raman spectroscopy. Explain, why with increasing vibrational quantum number value, the spectral lines gradually crowd together.

   (b) The fundamental vibration frequency of a homonuclear diatomic molecule is 'v_0'. Calculate the temperature at which the population of that molecule in its first excited state would be half of that of the ground state.   3+2

7. (a) 'The number of photons required to activate one molecule is called quantum yield'. Criticize the statement. If a system is found to absorb 3×10^{18} quanta of light per second to irradiate 0.002 mole of its molecules for 10 minutes, calculate the quantum yield of the process.

   (b) The fact that fluorescence wavelength is often much longer than the irradiation wavelength is a consequence of the Frank Condon principle. Explain.   3+2

8. (a) The ϵ of 'B' (MW = 180) is 4×10^3 Lmol^{-1}cm^{-1}. Now if one litre of 'C' containing 0.1358 gm of 'B' shows an absorbance value of 0.411 in a 1cm quartz cell, calculate the % (w/w) of 'B' in 'C'.

   (b) State major significances of the primary kinetic salt effect. If KCl is added to the reaction: $[PtCl_4]^{2-} + OH^- \rightarrow$ Pdts, the rate of reaction decreases. Justify the claim.   2+3

9. (a) When a mixture of Hydrogen and Bromine is exposed to radiations of 450-550 nm, although they combine, the quantum yield is found to be as low as 0.01. Explain with proper reasoning.

   (b) 0.01 molar solution of a compound transmits 20% of the Na-D line when the absorbing path is 1.50 cm. Calculate the molar extinction coefficient of the compound.   3+2

10. (a) When a capillary tube of diameter 2 mm is dipped into a liquid of specific gravity 0.8, it rises by 15 mm, making a contact angle 0° with the tube. Calculate the surface tension of the liquid in contact with the air and the glass tube. State the dimension and unit (in SI) of surface energy.

    (b) To kill mosquito larva, kerosine oil is often sprinkled on the pool water. Explain.   3+2

11. (a) If there is 2% error in the determination of rotational constant 'B' of a diatomic molecule, calculate the percentage error in its bond length measurement.

(b) Based on Stern's theory of electrical double layer, for a solid liquid interface, show how zeta potential differs from thermodynamic potential. 2+3

12. (a) Between Lyophobic and Lyophilic sols, which one is more stable and why? Explain, how the lesser stabilised one can be made stabilised using the more stabilised one.

(b) Coagulation and peptization are reverse phenomena related with the lyophilic colloids. Criticize the sentence with proper reasoning. 3+2

13. (a) Surface tension and surface energy are numerically same.— Explain.

(b) The % T of a solution of an acid base indicator (HIn) was determined at 590 nm under the following condition.

(i) At pH 4.39, %T = 20

(ii) At strong basic condition, %T = 5.4.

Assuming that at the given wavelength only the basic form (ie In^-) absorbs appreciably, determine pK_{In}. 2+3

———————

2023

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) Give example of one green reagent that can be used in Friedel-Crafts reaction instead of anhydrous $AlCl_3$.

    (b) What is PEG? Write its general formula.

    (c) Write one medical importance of nicotine.

    (d) Give one example of biodegradable polymer.

    (e) Name two carcinogenic solvents.

    (f) What is meant by hydrophobic effect?

    (g) Why is waste prevention better than waste clean up?

    (h) Write down the names of two alternative energy sources other than thermal energy used in chemical reactions.

    (i) What are the methods by which ultrasonic waves are generated?

    (j) Mention one limitation in the pursuit of goal of green chemistry.

    (k) Give one example of ionic liquid.

    (l) What is isoprene rule?

2. (a) Give one example of decarboxylation reaction using MWI. Write down the green context of the reaction.

    (b) 'Atom economy' of rearrangement and addition reactions is always 100%. Explain with one example of each.   3+2

3. (a) Outline the synthesis of hygrine alkaloid.

    (b) Why does green chemistry prefer the use of catalyst instead of stoichiometric reagents?   3+2

4. (a) Discuss the green synthesis of adipic acid, mentioning all the steps involved.

    (b) What are the advantages of green method over the conventional one?   3+2

Please Turn Over

5. (a) Discuss briefly for the green methods of the following reactions :

    (i) Fries rearrangement

    (ii) Benzoin condensation.

  (b) How a lactone can be synthesised *via* Bayer-Villiger oxidation method following an environmentally benign procedure?   3+2

6. (a) Write down the following reactions using MWI (microwave irradiation) and also mention the conditions of the reactions.

    (i) Oxidation of toluene

    (ii) Conversion of methyl benzoate to benzoic acid.

  (b) Write down the green context of the above reactions [stated in Q. 6(a)].   3+2

7. (a) Consider the following reaction :

$$\text{Sc-CO}_2 \quad 49.5 - 11T \text{ bar} \quad 50° - 117°C \quad 3 - 24 \text{ days}$$

R = Me, ^{t}Bu
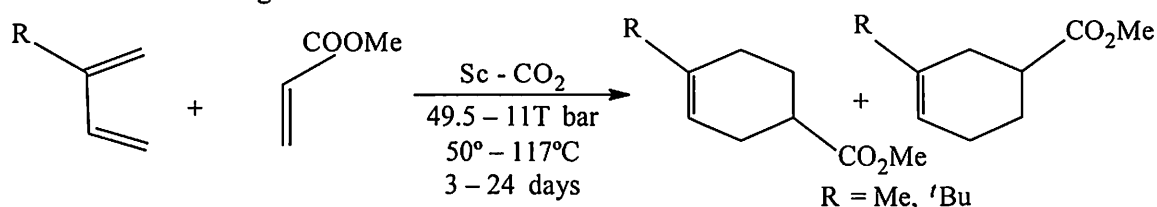
What is the role of Sc - CO_2 in the above reaction? How is its use advantageous over the conventional solvent?

  (b) Give an example of an organic reaction where PEG acts as a phase transfer catalyst.   3+2

8. (a) Mention three advantages of solvent-free synthesis over conventional methods.

  (b) Give one example each of two solid support syntheses.   3+2

9. (a) Give any one green approach of aldol condensation. Mention one important advantage of this method over classical method.

  (b) What are the limitations of MW heating?   3+2

10. (a) What are the emerging areas on which the future trends of green chemistry depends?

  (b) Mention four disadvantages of the common oxidation processes.   3+2

11. (a) What is biomimetic synthesis?

  (b) Which oxidation catalyst is used for the green oxidation of alcohol to carbonyl compounds? Write down the reaction.   3+2

12. (a) Write the disadvantages of the conventional method of the Beckmann rearrangement. Elaborate one example about the green approach of the reaction.

  (b) Mention the advantages of using ultrasonics in the medical field over other techniques.   3+2

13. (a) How can the functional nature of oxygen present in an alkaloid chemistry be detected?

  (b) Write down the medical importances one for each of quinine and cocaine.   3+2