

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

P.G. FIRST YEAR

M.A./M.SC. SECOND SEMESTER (January – June) 2013

Mid-Semester Examination, March 2013

Date : 19/03/2013

Time : 11 am – 3 pm

APPLIED CHEMISTRY

Full Marks : 100

[Use Separate Answer Books for each unit]

[Answer **any one** question from each unit except **Unit IX & XII**]

Unit – I (A.B.)

1. a) What do you mean by "Supramolecular Chemistry"? How is it different from molecular chemistry? [2]
b) What types of other chemical forces present in Supramolecular chemistry? [2]
c) What do you mean by (6–12) potential? [1]
2. a) Define Molecular recognition. [1]
b) What are alkalides and electrides? Give examples of each. [2]
c) Write notes on Crown ethers as receptors. [2]

Unit – II (S.R.)

3. a) Both cobalt, Rhodium and Iridium forms the carbonyls of formulae $M_4(CO)_{12}$, but we get two types of stretching frequencies in case of cobalt and Rhodium but not in case of Iridium. Explain. [2½]
b) Comment on the probability of carbonyls in case of scandium and copper. [2½]
4. a) Determine the structure of $Rh_6(CO)_{16}$ on the basis of total electron count, skeletal electron pairs and number of vertices. [2]
b) Using 18 electron rule as a guide determine the number of carbonyls and structure of $Co_3(CO)_xCH$. [1]
c) Metal radius play an important role for the bridging carbonyls. Explain with example (s). [2]

Unit – III (K.R.)

5. a) A deep blue solution containing Co(II) in conc. HCl gradually turns pale pink on addition of excess water. Justify. [1½]
b) Comment on the structure of $NiAl_2O_4$. [2]
c) Common oxidation state of gold is Au(III) or Au(I) but that of silver is Ag(I). Justify from CFT. [1½]
6. a) Calculate CFSE of $[Cr(H_2O)_6]^{2+}$ in high spin and low spin configurations? (Pairing energy = $23,500\text{ cm}^{-1}E$; $\Delta = 13,900\text{ cm}^{-1}$) [2]
b) In $[Cu(H_2O)_6]^{2+}$ two water molecules undergo exchange with the bulk solvent molecules much more rapidly than the other four. Explain. [1½]
c) On increasing pressure, d^5 transition metal complex may switch over from high spin to low spin state. Comment. [1½]

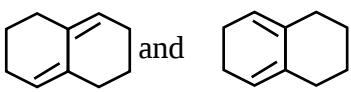
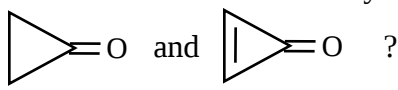
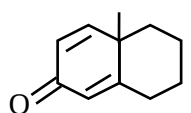
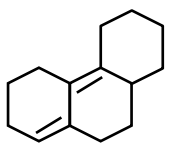
Unit – IV (D.M)

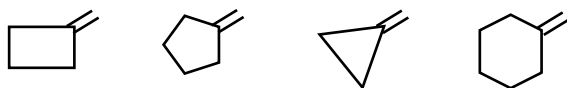
7. Discuss the band structure of transition metals. Discuss the variation of cohesive energy among transition metals. [3+2]
8. a) What are the differences between interstitial alloy and substitution alloy? [3]
b) Why diamond structure is less favourable for Sn & Pb? [2]

Unit – V (S.G.)

9. a) What do you mean by complementary and non-complementary Redox reaction? Explain each with an example. [1+2]
 b) Explain the Inner-Sphere electron transfer mechanism. [2]
10. a) $[\text{Fe}^*(\text{CN})_6]^{4-} + [\text{Fe}(\text{CN})_6]^{3-} \rightarrow [\text{Fe}^*(\text{CN})_6]^{3-} + [\text{Fe}(\text{CN})_6]^{4-}$;
 $[\text{Co}^*(\text{NH}_3)_6]^{2+} + [\text{Co}(\text{NH}_3)_6]^{3+} \rightarrow [\text{Co}^*(\text{NH}_3)_6]^{3+} + [\text{Co}(\text{NH}_3)_6]^{2+}$ For both the above two reaction, electron transfer occurs through outer sphere mechanism but the transfer of electron in the cobalt system is very slow comparing with iron system. Explain. [3]
 b) What do you mean by Labile and Inert complexes? [2]

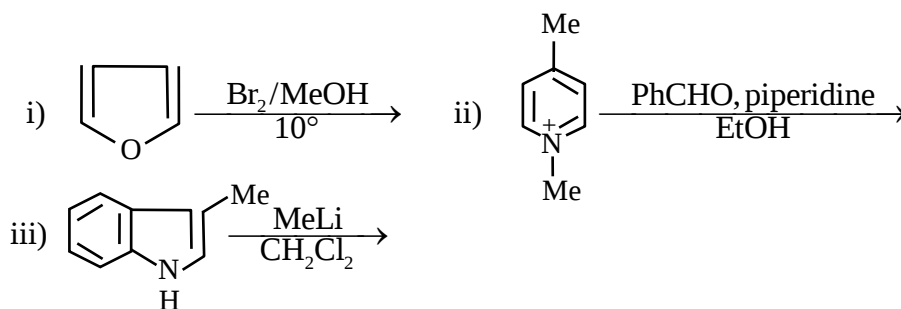
Unit – VI (S.B.)

11. a) Between the following two compounds, which one would you expect to have higher absorbance? Explain your answer. [2]

- b) Which one will show carbonyl stretching at a lower wave number between  ? [2]
- c) Estimate the maximum wavelength of UV absorption of
 (i)  and (ii)  [2]
- d) How can you differentiate between the conformational isomers of cis-cyclohexane-1, 3-diol by i.r. spectroscopy? [1]
12. a) What would be the nature of shift (Red or blue) for the R and K band of 4-methyl-3-pentene-2-one on change of solvent from n-hexane to water? Explain your answer. [2]
 b) Two isomeric compounds A and B show superimposable i.r. spectra, yet they are not identical. How can you explain it? [2]
 c) With molecular formula $\text{C}_3\text{H}_6\text{O}$, logically write two isomeric compounds which show widely different i.r absorption positions for their oxyfunctional groups. [2]
 d) Arrange with reason, the following compounds in increasing order of stretching frequency for the olefinic linkage. [1]

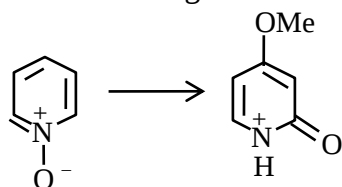


Unit – VII (S.M.)

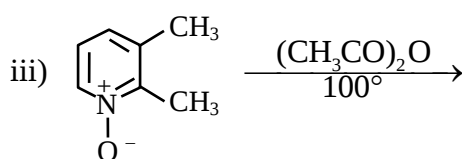
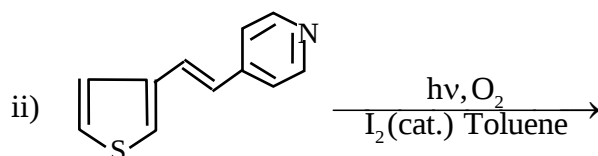
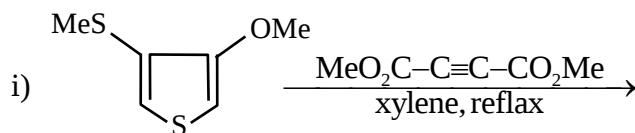
13. a) Write the structures of different pyrrolium cations resulting from protonation of pyrrole in dilute acids and compare their relative stabilities. [2]
 b) Give the product(s) with plausible mechanism in the following reactions : [2×3]



14. a) Indole undergoes electrophilic substitution primarily at C-3 but pyrrole does at C-2. Explain. [2]
 b) Carryout the following conversion : [2]

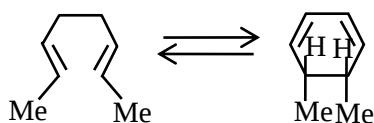


- c) Write the products(s) with suitable mechanism in the following reactions (**any two**) : [2×2]



Unit – VIII (R.D./A.B.H)

15. a) Write the help of FMO approach, explain whether the following reaction will be allowed thermally or photochemically. [2]



- b) Convert into by electrocyclic reactions. [2]

- c) Give the product of the following reaction : + C_6F_6 $\xrightarrow{200^\circ\text{C}}$ [2]

- d) Carryout the following conversions : [2×2]
 i) Phthalimidomalononic ester $\rightarrow$ Leucine
 ii) Acetamidomalononic ester $\rightarrow$ Tryptophan

16. a) Synthesize from 2-methyl-1,3-butadiene. [2]

- b) Write the structures of (A) and (B). + $\text{CH}_2=\text{CHCO}_2\text{H} \xrightarrow{\text{heat}}$ A + B [2]

- c) Give the product with configuration of the following reaction
 (2E, 4Z, 6E) – Octa – 2,4,6 - triene $\xrightarrow{h\nu}$? [3]

- d) Outline the synthesis of the following : Proline from Phthalimidomalononic ester [3]

Unit – IX (P. Roy)

[Answer **any two** questions from the following]

17. Kwong et al (J. Chem Eng Data Vol 6, No. 2, Apr 1961 p. 220) report the following P-V-T data for SO_2 at 50°C L (P given in atm)

P	2	3	4	5	6	7
Z	0.9742	0.9611	0.9478	0.9344	0.9207	0.9065
Compressibility factor						

First explain how this data can be used to obtain the second virid coefficient for SO₂ at 50°C, then use the procedure to get this value. Use graph paper for plotting. [6]

18. Kang reports P_C, T_C of SO₂ as 77°8 atm and 157·5°C, Assuming SO₂ obeys Redlich-Kwong eg of state, find compressibility of SO₂ at 50°C and 2 atm press. How does the value compare with the experimental value given in Q1 above. [6]

Obtain Redlich Kwong a and b from critical constants

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c} \quad \Omega_a = 0.42748 \quad ; \quad b = \Omega_b \frac{RT_c}{P_c} \quad \Omega_b = 0.08664$$

19. Show that Z_c for all fluids obeying Redlich-Kwong equation of state will be same (Z_c is critical compressibility factor) [6]

Unit – X (A.S.)

20. a) What are spontaneous and stimulated emission of radiation. [2]
 b) Show that for a symmetric top molecule $\epsilon_{J,K} = \frac{E_{J,K}}{hc} = BJ(J+1) + (A-B)K^2$ where terms have their usual significance. [2]
 c) Show that for diatomic molecule, the maximum population, $J_{\max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$ where terms have their usual significance [3]
21. a) What are prolato and oblato symmetric Top molecules? Give one example for each type. [3]
 b) How will you determine the bond length of a heteronuclear diatomic molecule using microwave spectroscopy. [2]
 c) Explain why it is not possible to design a two leve LASER? [2]

Unit – XI (D.G)

22. a) A system contains solid carbon, CO(g), H₂O(g) and H₂(g) at equilibrium at 1000⁰ C. Find out the number of components and the degree of freedom for this system. [1+2]
 c) A mixture of two miscible liquids A and B is at equilibrium with the corresponding vapor phase at 30⁰C. the vapor pressures of pure A and B at 30⁰C are 200mmHg and 90mmHg respectively. If the mol fraction of A in the liquid phase be 0.45, find out the total vapor pressure at equilibrium and the composition of the vapor. [3]
23. a) Draw the phase diagram of water and explain it . [3]
 c) Find out the number of components in the following ---
 i) Water at its normal freezing point
 ii) solution of iodine in benzene at equilibrium with solution of iodine in water. [3]

Unit – XII

24. State whether the following statements are TRUE or FALSE: [4x1]
 a. Molecules having molecular weight greater than 10,000 are regarded as macromolecules.
 b. Extent of polycondensation is nothing but the fraction conversion.
 c. Average degree of polymerization can be calculated as N/N₀ where N is the number of monomers left after polymerization and N₀ is the number of monomers initially present in the system.
 d. RNA is an example of biopolymer.

25. Justify the following statements:

[7x3]

- a. All crystalline polymers are actually semi-crystalline.
- b. Step growth polymerization does not have any termination step.
- c. Cage effect is observed in chain growth polymerization.
- d. T_g is not a particular temperature but the average of a temperature domain.
- e. Molecular weight of any polymer is never an absolute but an average number.
- f. Glassy state is recognized as the polymeric state where a polymer exhibit infinite relaxation time.
- g. Viscofluidic state of a polymer appears after its rubbery state.

