

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

P.G. FIRST YEAR

M.A./M.SC. SECOND SEMESTER (January – June), 2012

Mid-Semester Examination, March 2012

Date : 26/03/2012

Time : 11 am – 3 pm

APPLIED CHEMISTRY

Full Marks : 100

[Use separate Answer Books for each group]

Group – A

(Answer any five from the following)

- Find out the degrees of freedom in the following cases & give reasons for your answer in each case : [1×5]
 - a liquid at equilibrium with its vapour at 80°C
 - water at its normal boiling point
 - a saturated solution of common salt in water, in contact with the solid salt, left undissolved
 - an azeotropic mixture of ethanol and water, at equilibrium with the vapour phase, under constant barometric pressure
 - Derive the expression for absorption frequency when a transition occurs obeying the selection rule in case of a harmonic oscillator.
- Explain why ice melts but dry ice sublimates off when exposed to the atmosphere. [2]
 - Find out the number of components and degrees of freedom for an equilibrium mixture of C(graphite), CO(g), CO₂(g) and O₂(g) at 700K. [3]
- Derive Duhem-Margules equation for a binary liquid mixture in equilibrium with the vapour phase. Show that if one of the liquids obeys Raoult's law, the other liquid will also obey. [5]
- Draw a classical potential energy against internuclear distance plot for a diatomic molecule
 - when the vibration is considered purely harmonic
 - when anharmonicity is taken into account [2]
 - Write down the quantum mechanical expression for energy of the v^{th} level of a harmonic oscillator. [1½]
 - Mention what is the selection rule in this case. [1½]
- Write down the quantum mechanical expression for energy of rotation for a rigid rotor. [1]
 - Starting from the expression written above find out the spacing between two successive lines in a rotational spectra. [3]
 - Three lines are observed in the absorption spectra when a vibrational transition takes place starting from the state say $v = 0, J = 1$. —Explain. [1]
- A gas is known to obey Redlich Kwong equation of state. The following data as available.
 $T_C = 507.4 \text{ K}$; $P_C = 29.7 \text{ bar}$; $w = 0.260$
Find the molar density of the gas at 2 bar pressure and 395 K.
R – K parameters can be written as— $a = 0.4278 \frac{R^2 T_C^{2.5}}{P_C}$; $b = 0.0867 \frac{R T_C}{P_C}$ [5]
- A gas is known to follow virial equation truncated at 2nd virial coefficient, ie $Z = 1 + \frac{B}{v}$.

Find an expression for $\left(\frac{\partial P}{\partial T}\right)_v$ for this gas

[2]

- b) Methane has $T_C = 190.6 \text{ K}$, $\rho_C = 46.0 \text{ bar}$, $\omega = 0.008$ Find the value of $\left(\frac{\partial P}{\partial T}\right)_V$ for methane at 250 K and 5 bar pressure assuming that it follows virial equation
- given— $\frac{BP_C}{RT_C} = B^{(0)}(T_1) + \omega B^{(1)}(T_r)$; $B^{(0)}(T_r) = 0.083 - \frac{0.422}{T_r^{1.6}}$; $B^{(1)}(T_r) = 0.139 - \frac{0.172}{T_r^{4.2}}$ [3]
8. a) Write the definition of Pitzer's acentric factor. [1]
- b) Express Z according to van der Waals equation in a power axis of gas density $\left(\text{ie } \frac{1}{v}\right)$, and comparing with the virial equation, find out an expression of 2nd virial coefficient form in term of van der Waals parameter. [4]

Group – B

(Answer **any five** from the following)

1. a) Distinguish with examples between the followings : [1½×2]
 - i) Fluxional complex and Template complex
 - ii) Labile complex and Inert complex.
- b) Write notes on Macrocyclic effect. [2]
2. a) Discuss whether the structure of Fe_3O_4 is normal or inverted. [2]
- b) $[\text{V}(\text{CO})_6]^-$, $\text{Cr}(\text{CO})_6$ and $[\text{Mn}(\text{CO})_6]^+$ are isoelectronic species. Explain and arrange (in increasing order) the stretching frequency of carbonyl group (CO) and metal-carbon (M-C) of the above different species. [3]
3. a) $\text{Ca} + \frac{1}{2}\text{F}_2 = \text{CaF}$
 ΔH for the above reaction is negative, yet CaF undergo the disproportionation reaction $2\text{CaF} = \text{CaF}_2 + \text{Ca}$. —Explain [2]
- b) Explain semiconductance interms of band theory. [3]
4. a) What is the oxidation number of Fe in brown ring complex and also calculate the magnetic moment of Iron in that complex. [2]
- b) What are the differences of ferromagnetic & antiferromagnetic substances? Write with proper examples. [3]
5. a) The difference in energy between the $d_{x^2-y^2}$ and d_{xy} orbitals in a square planar field is identical to the difference between the same orbitals in the octahedral field. —Explain. [2]
- b) Write notes on : (**any one**) [3]
 - i) Applications of complex compounds in analytical Chemistry.
 - ii) Write down the factors for complex formation. How complex formations may be detected?
6. a) On passing ammonia through CuSO_4 solution, the complex ion $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ is formed but NiSO_4 solution under similar condition produces $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion. —Explain [3]
- b) Give I.U.P.A.C names of the following co-ordination compounds. [1×2]
 - i) $[\text{Co}(\text{N}_3)(\text{NH}_3)_5]\text{SO}_4$
 - ii) $[\text{Fe}(\text{NH}_4\text{C}_5\text{H}_4\text{N})_3]^{2+}$
7. a) Aqueous solution of Cobalt nitrate is pale pink; but the solution turns intense blue on addition of concentrated HCl. —Explain. [3]
- b) Give the structures of the following complexes. [2]
 - i) μ - amido - μ - hydroxo bis (tetraamine cobalt) (4+)
 - ii) Tris (Tetraamine - μ - dihydroxo cobalt) Cobalt(6+)

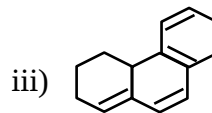
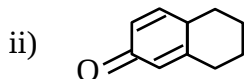
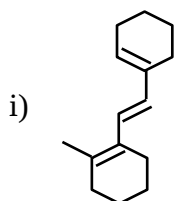
8. a) $\text{Co}_4(\text{CO})_{12}$ and $\text{Ir}_4(\text{CO})_{12}$ are example of metal cluster compounds but the carbonyl groups are not bonded in the same manner. [2]
 b) Explain the stretching frequency of terminal, μ_2 -CO and μ_3 -CO groups. [2]
 c) Ni(0) and Zn(II) are isoelectronic but nickel forms carbonyl compounds but zinc(II) does not. — Explain [1]

Group – C

Unit - I

(Answer any two from the following)

1. a) Calculate the λ_{max} values for the following compounds : [3]



- b) Arrange the methyl halides in order of increasing wave length of absorption with reason. [2]
 2. a) What is meant by vacuum uv? [1]
 b) Would you expect uv absorption to be different in terms of position (λ) and intensity (ϵ) for $\text{H}_2\text{C} = \text{CH}_2$ and $\text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{CH} = \text{CH}_2$? [2]
 c) Both of and show k-bands in respect of uv absorption, how can you differentiate between these k-bands? [2]
 3. a) Compound $\text{CH}_3\text{CH} = \text{CH} - \text{CHO}$ shown the following bands : [3]

In petrol ether : 214 nm (ϵ large)

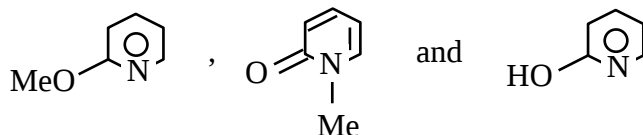
329 nm (ϵ small)

In ethanol : 220 nm (ϵ large)

322 nm (ϵ small)

Assign the bands by letter designations and explain the observed results.

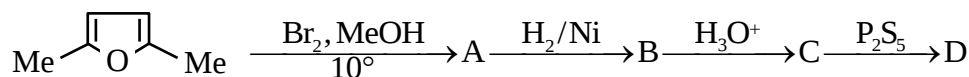
- b) Among the following three compounds, two have similar uv spectrum, identify them with reason. [2]



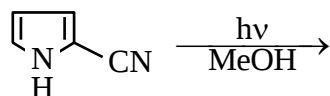
Unit - II

(Answer any two from the following)

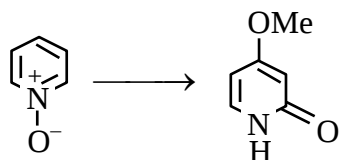
4. a) Write the structures of different pyrrolium cations resulting from protonation of pyrrole in dilute acids and compare their relative stabilities. [2]
 b) Identify A, B, C, D in the following reaction scheme : [2]



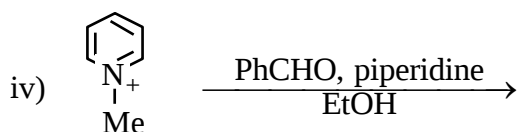
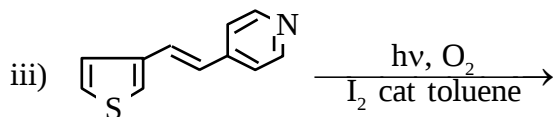
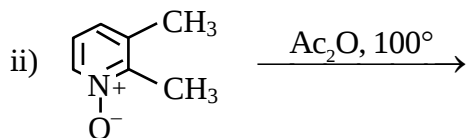
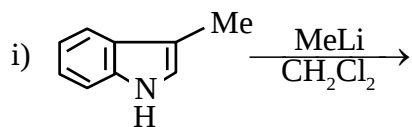
- c) Give the product with plausible mechanism in the following reaction. [1]



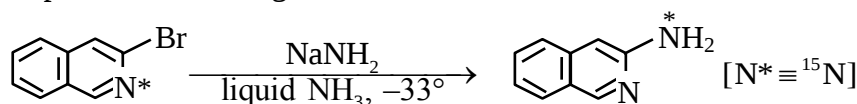
5. a) How would you carry out the following conversion : [2]



b) Give the product(s) with plausible mechanism in the following reactions (any two) : [1½×2]



6. a) Explain the following observation : [2]



b) Give the mechanism of Fischer indole synthesis and furnish an isotopic evidence in support of this. [3]

Unit - III

(Answer any one from the following)

7. a) Carry out the following conversion :
Acetamidomalonic ester → Tryptophan [3]

b) Predict the product with mechanism of the following reaction : [2]



8. What would be the configuration of the product(s) in each of the following electrocyclic reactions ?

i) cis-3, 4-dimethylcyclobutene $\xrightarrow{\text{thermal ring closure}}$?

ii) (2E, 4Z, 6E)-Octa-2, 4, 6-triene $\xrightarrow{h\nu}$?

Give reason for each.

[2+2+1]

Group – D

(Answer any five from the following)

1. Give examples of the following variety of polymers with their chemical representation: [5×1]

- A condensation polymer synthesised from a single structural unit.
- A copolymer which is elastomeric and involves styrene in its structure.
- A homopolymer which can not be synthesised directly from its monomer.
- A polymer which has natural origin.
- A copolymer which forms intra as well as inter-molecular hydrogen bonds.

2. Explain the following observations with reason: [2+2+1]
- Polymers are naturally coiled.
 - A thin rubber band gets heated when stretched.
 - Not all polymers flow immediately after its T_m .
3. Define T_g of polymers from “Segmental motion” and “relaxation” point of view. Why T_g is regarded as a kinetically controlled transition? [1.5+1.5+2]
4. Carothers equation for condensation polymers is given by: $p = 2/f (1 - 1/X_n)$ where each term bears their usual meaning. Calculate the percent conversion in following cases:
- 5 moles phthalic anhydride and 5 moles ethylene glycol is reacted
 - 3 moles phthalic anhydride and 2 moles propylene glycol is reacted. [2.5+2.5]
5. a) Explain how termination takes place in free radical polymerization.
b) What is kinetic chain length? How it is different from physical chain length? [2+3]
6. a) Explain the concept of ceiling temperature and floor temperature in polymerization.
b) What is induction period in radical polymerization? How can you correlate this with initiator efficiency? [2+3]

