

RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College under University of Calcutta)

P.G. FIRST YEAR

M.A./M.SC. FIRST SEMESTER (July – December), 2012

Mid-Semester Examination, October, 2012

Date : 08/10/2012

Time : 11 am – 3 pm

APPLIED CHEMISTRY

Full Marks : 100

[Use separate answer scripts for each Unit]

Group – A

Unit – I (D.M.)

(Answer any one question)

[6]

1. a) The Lanthanides show the common oxidation state of +3. —Comment.
b) Discuss the principle of separation of Lanthanides by Ion-exchange method.
c) Give the important uses of Lanthanides in Steel Industry.
2. a) Calculate the Magnetic moment of Sm^{+3} .
b) Give suitable example of two organometallic compound of Ce^{+4} .
c) What are the main differences between 3d and 5d elements.

Unit – II (A.B)

(Answer any one question)

3. a) Write notes on (any three) : [3×2]
 - i) Wilson's disease
 - ii) Chelation Therapy
 - iii) Cis platin
 - iv) Cytochrome P-450
 - v) Gold drugs.
b) What is apoenzyme? [1]
4. a) What are cytochromes? Write down their functions. How do you classify the cytochromes? Illustrate with example. Discuss the structure of cytochrome – C. [6]
b) What are metallo enzymes. [1]

OR

- a) Write down notes on the Basic chemical reactions in Biological system. [4]
- b) Discuss the structural features of Hemoglobin and write down its important role. [3]

Unit – III (K.R)

(Answer any one question)

5. a) Find out the expressions for the Sp^2 hybridised wave functions in terms of ψ_s , ψ_{px} and ψ_{py} .
b) Mn(III) oxidises water to oxygen in acid medium but oxygen oxidises $\text{Mn}(\text{OH})_2$ to $\text{Mn}(\text{OH})_3$ in alkaline medium. Justify.

Given,

$$E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} = 1.50\text{V}$$

$$K_{\text{Sp}[\text{Mn}(\text{OH})_2]} = 10^{-13}$$

$$K_{\text{Sp}[\text{Mn}(\text{OH})_3]} = 10^{-36}$$

[3+3]

6. a) Draw the energy level diagram for carbon monoxide molecule and hence discuss the ligating property and bond order of the molecule.
- b) E° values for chlorine in different oxidation states are given in the following Latimer diagram.
- $$\text{ClO}_4^- \xrightarrow{0.36\text{V}} \text{ClO}_3^- \xrightarrow{0.33\text{V}} \text{ClO}_2^- \xrightarrow{0.66\text{V}} \text{ClO}^- \xrightarrow{0.30\text{V}} \text{Cl}_2 \xrightarrow{1.36\text{V}} \text{Cl}^-$$
- From the above diagram predict which of the above species likely to disproportionate. Justify your statement. [3+3]

Unit – IV (S.G.)

(Answer any one question)

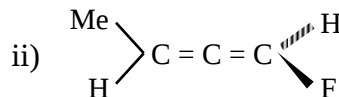
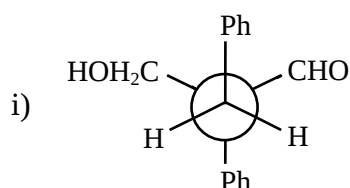
7. a) What are phosphazenes? Give the mechanism for the formation of cyclic, chlorophosphazenes (trimer). [1+2]
- b) Complete the following :
- i) $\text{S}_2\text{Cl}_2 + \text{NH}_3 \rightarrow$
- ii) $\text{S}_2\text{Cl}_2 + \text{NH}_4\text{Cl} \rightarrow$ [1+1]
- c) Write the product when B_2H_6 is treated separately with NH_3 and PH_3 . [1]
8. a) Discuss the structure and bonding of S_4N_4 . [3]
- b) How can you synthesis Xenate and perxenate ion. Give the structure of xenate and perxenate, with explanation. [1½+1½]

Group – B

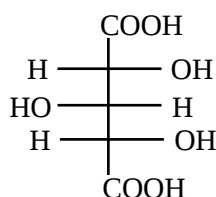
Unit – V (S.M.)

(Answer any one question)

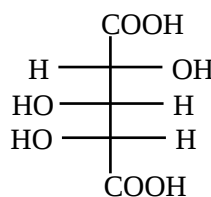
9. a) Assign R/s descriptor to the following compounds : [2]



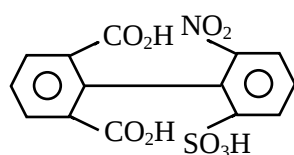
- b) How would you carry out the resolution of a racemic alcohol? Outline the reaction steps. [2½]
- c) Label the C-3 centres of the following molecules as stereogenic / non-stereogenic and chirotopic / achirotopic. Justify your answer. [2½]



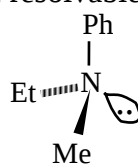
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10. a) Draw all possible stereoisomers of $\text{PhCH}(\text{OH})\text{CH}=\text{CHMe}$ and designate them by R/S and E/Z notations. [3]
- b) Draw the Newman projection formulas of the conformers of 2-methylbutane for rotation about $\text{C}_2 - \text{C}_3$ bond and compare their relative stabilities. [2]
- c) Explain whether the following compounds are resolvable or not : [1]



and



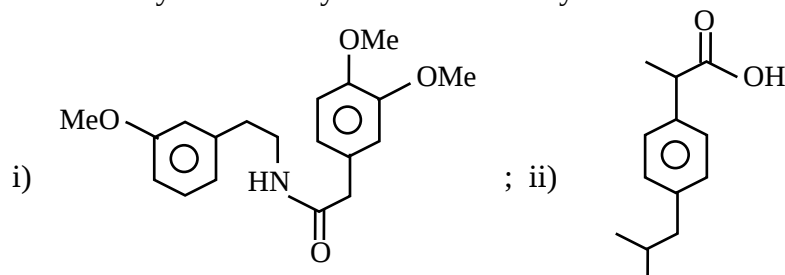
- d) Draw the Newman projection formula of the most stable conformer of ethylene glycol with reasons. [1]

Unit – VI (A.B.H)

(Answer **any one** question)

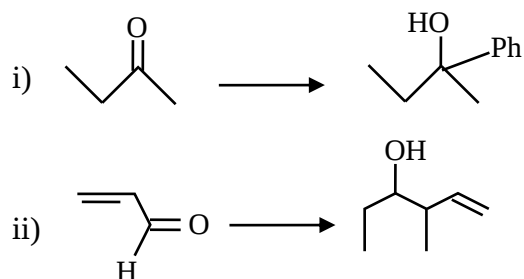
11. a) Give retrosynthetic analysis and efficient synthesis of the following

[2·5×2]



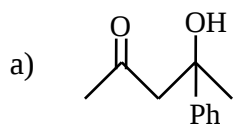
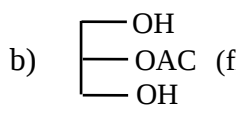
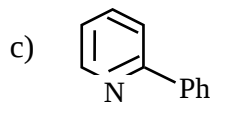
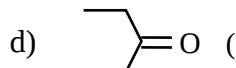
- b) Carry out the following conversions. Mechanism is not necessary.

[2·5×2]



12. Outline the synthesis of the following compounds as directed.

[4×2·5]

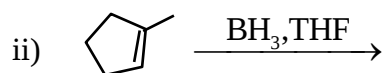
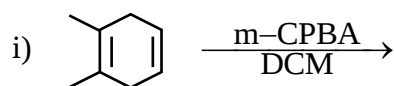
- a)  (from (EAA))
- b)  (from (glycerol))
- c)  (from (Pyridine))
- d)  (from (carbondioxide))

Unit – VII (S.B.)

(Answer **any one** question)

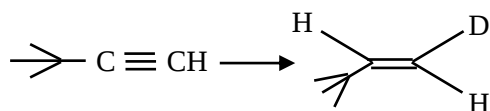
13. a) Write down the product with reason / stereochemistry—

[3]



- b) How can you effect the following transformations

[2]

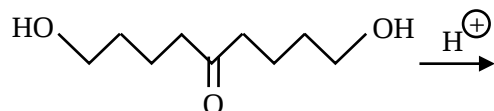


- c) Show the steps how would you convert propene into butanal.

[3]

14. a) Write down the product with mechanism—

[2]



b) How can you convert methanol into propanal?

[2]

c) Does it happen : $\begin{matrix} R \\ \diagup \\ C=O \\ \diagdown \\ R \end{matrix} \xrightarrow{NaH} \begin{matrix} R & & ONa \\ & \diagdown & / \\ & C & \\ & / & \diagdown \\ R & & H \end{matrix}$? Give reason for your answer.

[1]

d) Explain the following observed results of reduction by different $H^{(-)}$ donors :

[3]



Results :

<u>Z</u>	<u>A</u>	<u>B</u>
LAH	8%	92%
L-selectride	93%	7%

Group – C

Unit – VIII (A.S.)

(Answer any one question)

15. a) Define the term fugacity and fugacity coefficient. Derive the expression for fugacity coefficient for the equation of state, $\left(P + \frac{a}{\bar{v}^2}\right)\bar{v} = RT$ where the terms have their usual significances.

b) Show that, $\left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j's},j \neq i} = \left(\frac{\partial u}{\partial n_i}\right)_{S,v,n_{j's},j \neq i}$ [(1+1+3)+4]

16. Draw the G versus extent of reaction (ξ) plot for the following reaction,
 $A + B \rightleftharpoons C + D$

What is the difference between ΔG and $\left(\frac{\delta G}{\delta \xi}\right)_{P,T}$.

Explain the shape of the curve.

Derive the following relation for the above reaction, $\Delta G = \Delta G^\circ + RT \ln \prod_i a_i^{v_i}$

Where v_i is the stoichiometric coefficient for the i^{th} species.

[2+2+2+3]

Unit – IX (D.G.)

(Answer any one question)

17. a) A gas B_2 undergoes dissociative adsorption on the surface of a solid adsorbent. Find out the expression θ_b in terms of equilibrium pressure of the gas. [3]

b) What is meant by 'surface excess'? Find out an expression relating surface excess with molar concentration of the solution. [4]

c) Find out the dimension of the quantity $\frac{\mu^2}{kT}$. [1]

18. a) For the adsorption of a substance A from aqueous solution by charcoal at 298K, the Freundlich constants are $n = 3.0$ and $k = 0.50$ for (x/m) in grams per gram and concentration of solution in

- g/L. What weight of A will be adsorbed by charcoal from 1L of a solution containing originally 2g of the adsorbate? [3]
- b) 'Adsorption is generally an exothermic process, but sometimes it may be endothermic'. —Is this statement true? [2]
- c) The decomposition of HI(g) on gold surface is found to follow different rate laws as partial pressure of the reactant changes with time during the course of the reaction. —Explain. [3]

Unit – X (S.S.B.)

(Answer **any one** question)

19. a) Find the time required for the decomposition of $\frac{n-1}{n}$ th fraction of the initial amount of A undergoing a 1st order reaction.
- b) What is the true order of a reaction?
- c) For the rate law $r = K[A]^n$, for what values of n (indicate only $n < 1$ or $n > 1$) does the reaction goes to completion in a finite time? [2+2+4]
20. a) What do you mean by thermodynamically controlled product and kinetically controlled product (no deduction required)?
- b) Show if A reacts according to $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$ then the half life of A is given by $t_{1/2} = \frac{0.693}{k_1 + k_2}$.
- c) Discuss the kinetics of the 1st order consecutive reactions $A \xrightarrow{k_1} B \xrightarrow{k_2} C$
Represent graphically the concentration changes in case of A and B with time. [2+2+4]

Group – D

Unit – XI

21. Answer **any four** of the following [Multiple choice type questions] : [4×1]
- a) The space lattices with two lattice parameters belong to the crystal systems—
i) tetragonal ii) rhombohedral iii) hexagonal iv) all of these
- b) The unit cell with three lattice parameters is—
i) tetragonal ii) orthorhombic iii) Monoclinic iv) triclinic
- c) If the lattice parameter of Si = 5.43Å and the mass of Si atom is $28.08 \times 1.66 \times 10^{-27}$ Kg. The density of silicon in Kg m^{-3} is—
i) 2330 ii) 1115 iii) 3445 iv) 1673
- d) If the vacancy concentration in a crystal doubles itself between 25°C and 31°C the enthalpy of formation of vacancies (KJ/mole) is—
i) 138 ii) 87 iii) none of these iv) all of these
- e) The t vector is parallel to the b vector in a dislocation of the type—
i) screw ii) edge iii) mixed iv) none of these
22. Answer **any three** of the following [Short answer type questions. These questions may not have unique answers. Explain your answer with arguments] [3×2]
- a) Crystal imperfections might be perfectly designed under certain circumstances —comment
- b) Amorphous and crystalline forms of a substance may have many properties in common —explain
- c) XRD is a sophisticated tool good for looking at atomic structure but is not good for studying macrostructure. —comment
- d) Lattices in three dimensions exhibit a limited number of symmetry. —explain

23. Answer **any three** of the following questions [Long Answer/ Numerical type questions] ; [3×5]

- a) Sketch the variation of equilibrium concentration of vacancies of metallic elements as a function of their enthalpy of formation at constant temperature. (exact calculations not required).
- b) Calculate the volume of an FCC unit cell in terms of the atomic radius R. Use this information to calculate atomic packing factor for the FCC crystal structure and show that it is independent of the nature of the atom.
- c) Calculate the radius of a palladium atom, given that Pd has an FCC crystal structure, a density of 12.0 g/cm^3 , and an atomic weight of 106.4 g/mol .
- d) Calculate the number of vacancies per cubic meter in gold at 900°C . The energy for vacancy formation is 0.98 eV/atom . The density and atomic weight for Au are 19.3 g/cm^3 and 196.9 g/mol respectively.
- e) A continuous and aligned carbon fiber reinforced hardened epoxy matrix composite consists of 40vol% of carbon fibers.

Elastic modulus of carbon fibers = 400 GPa

Elastic modulus of hardened epoxy = 2.40 GPa

Density of carbon fiber = 1800 Kg.m^{-3}

Density of hardened epoxy = 1200 Kg.m^{-3}

- i) The density of the composite in Kg.m^{-3} is—

A) 1440

B) 1200

C) 1800

D) 1340

- ii) The specific modulus of elasticity of the composite in the longitudinal direction is—

A) $2.76 \text{ MPa.m}^3.\text{Kg}^{-1}$

B) 112.1 GPa

C) 161.44 GPa

D) $112.11 \text{ MPa.m}^3.\text{Kg}^{-1}$