RAMAKRISHNA MISSION VIDYAMANDIRA
(Residential Autonomous College under University of Calcutta)

SECOND YEAR
B.A./B.SC. THIRD SEMESTER (July – December), 2012
Mid-Semester Examination, September 2012

Date : 10/09/2012

CHEMISTRY (Honours)

Time : 2 pm – 4 pm   Paper : III   Full Marks : 50

[Use Separate Answer Script for each Group]

<u>Group – A</u>

(*Answer <u>**any one**</u> question*)

1. a) Write the I.U.P.A.C name of the followings :   [1]
   - i) $[Cr(H_2O)_5Cl]Cl_2$
   - ii) $Na_2[Fe(CN)_5NO]$

   b) Distinguish between—   [3]
   - i) Inert complex and Labile complex
   - ii) Ambidentate ligand and Flexidentate Ligand

   c) Give a concise account on "Inner-metallic complex".   [2]

   d) State the postulates of Werner's co-ordination theory and how can it be verified.   [3]

   e) Compare the limitations of Valence Bond Theory. Arrange the stabilities of O_2^{2-}, O_2^+ and O_2^- ions.   [3]

   f) Can $KMnO_4$ oxidise chloride, bromide and iodide at pH = 3? Given $E^o_{MnO_4^-/Mn^{2+}} = 1.51V$;

   $E^o_{Cl_2/2Cl^-} = 1.36V$; $E^o_{Br_2/2Br^-} = 1.07V$; $E^o_{I_2/2I^-} = 0.54V$.   [3]

   g) Why is solutions of ferrous salt always prepared and preserved in an aqueous acidic solution? — Explain. $E^o_{Fe^{3+}/Fe^{2+}} = 0.77V$; K_{SP} of $Fe(OH)_3$ and $Fe(OH)_2$ are 4×10^{-38} and 2×10^{-15}.   [3]

2. a) i) pK_a for $H_3AsO_4 = 2.3$ and for $H_3AsO_3 = 8.2$ from the above pK_a values predict the structure of H_3AsO_4 and H_3AsO_3.   [2]

   ii) $CaO + SiO_2 \rightarrow CaSiO_3$, Explain the acid-base reaction interms of Lux-Flood Definition.   [2]
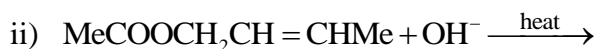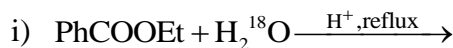
   OR

   a) i) Complete the following reactions—   [1+1]

   $$NH_4I + BiN \rightleftharpoons \qquad ; \qquad NH_2-\overset{\overset{O}{\|}}{C}-NH_2 + NH_3 \rightleftharpoons$$

   ii) Mention the limitations of HSAB principle.   [2]

   b) Draw the molecular orbital diagram of CO molecule. From the diagram show that CO molecule is a π-acid ligand.   [4]

   c) Stability of a chelate complex is greater than that of a non chelated complex. —Justify.   [2]

   d) Will iodide be oxidised to iodine by ferric at pH =4.5? $E^o_{Fe^{3+}/Fe^{2+}} = 0.77V$; $E^o_{I_2/2I^-} = 0.54V$ K_{SP} of $Fe(OH)_3$ and $Fe(OH)_2$ are 1×10^{-38} and 1×10^{-16}.   [3]

   e) Can metallic silver displaces hydrogen from 1(N) HI solution? $E^o_{Ag^+/Ag} = 0.80V$; K_{SP} of AgI is 1×10^{-16}; $E^o_{I_2/2I^-} = 0.54V$.   [2]

   f) Write down the structural change of the indicator barium diphenylamine sulphonate during red-ox titration.   [1]

Group – B

*(Answer **any one** question)*

3. a) Give the principal products of the following reactions and write the plausible mechanism for each of reaction. [4×2]
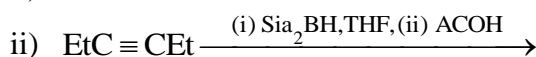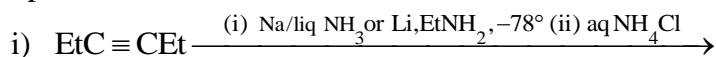
   i) $PhCOOEt + H_2^{18}O \xrightarrow{\ H^+, reflux\ }$

   ii) $MeCOOCH_2CH = CHMe + OH^- \xrightarrow{\ heat\ }$

   iii) $MeCOOCMe_3 \xrightarrow{\ H_3O^+\ }$

   iv) $2,4,6 - Me_3C_6H_2COOEt \xrightarrow{\ OH^-\ }$

   b) Benzoin gives PhCH(OH)COAr (Ar = Me —⟨O⟩+) when treated with paramethylbenzaldehyde in presence of KCN/EtOH. Explain. [3]

   c) In Perkin reaction styrene is a side product along with Cinnamic acid. Propose a mechanism which can explain both the products. [3]

   d) Predict the product of the following reaction. Give mechanism. [2]
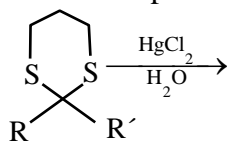

4. a) Complete the following reactions and write mechanism in each case and mention stereochemistry of products. [3]

   i) $EtC \equiv CEt \xrightarrow{(i)\ Na/liq\ NH_3 or\ Li,EtNH_2,-78°\ (ii)\ aq\,NH_4Cl}$

   ii) $EtC \equiv CEt \xrightarrow{(i)\ Sia_2BH,THF,(ii)\ ACOH}$

   b) Write out the products of 1,2 addition and 1,4 addition of (a) HBr and (b) DBr to 1,3-cyclo-hexadiene. What is unusual about the products of 1,2- and 1,4- addition of HX to unsubstituted cyclic 1,3- dienes? [2·5]

   c) Give the major product for each of the following reactions with suitable mechanisms. [2·5]

   i) $MeCH = C = CH_2 + HCl \rightarrow$

   ii) $PhCH = C = CH_2 + HCl \rightarrow$
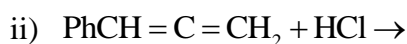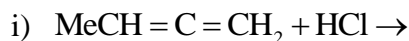
   d) Carry out the following conversions. Mechanism is not necessary. [4×2]

(2)
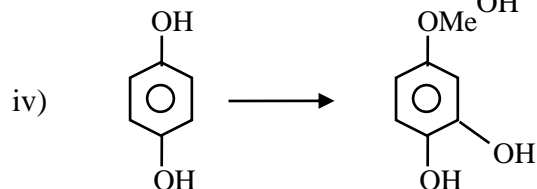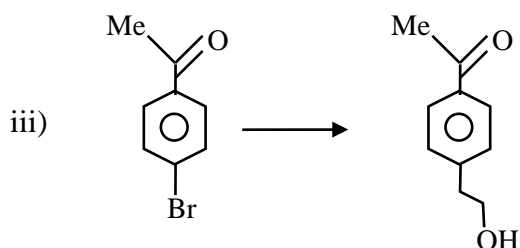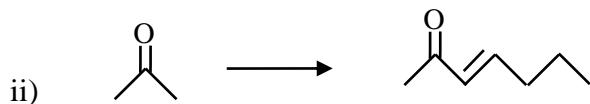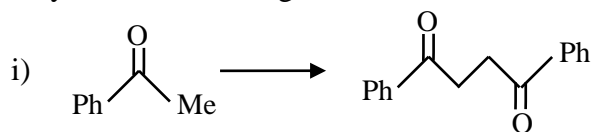
Group – C

(*Answer **any one** from each unit*)

Unit - I

5. a) How does one explain the generation of viscosity from molecular point of view? [2]

    b) Calculate the terminal speed of fall in water at 25°C of a spherical ball of diameter 1·00mm and density 7·8 gm cm^3. Mention the assumptions made for this method. [3]

    c) As temperature increases, the surface tension between liquid and solid is expected to change. Justify or criticize it. Comment on the equivalency of surface energy and surface tension. [3]

6. a) True or False? Newton's viscosity law fails at extremely high flow rates. [2]

    b) i) Arrive at the equation of pressure drop across a curved surface, relating the surface tension of liquid. [3]

        ii) What pressure in atmospheres is required to prevent water from rising in a 10^{-4}cm diameter capillary at 25°C at 1 atm^2. [1]

    c) Account for the role of Reynold Number for streamline or turbulent flow. [2]

Unit - II

7. a) Arrive at the expression for the equilibrium constant of a generalized chemical reaction in terms of the standard free energy change of the reaction at a constant temperature. [3]

    b) Explain with reason whether this equilibrium constant could have any unit. [1]

    c) Next derive the necessary relationship that shows how equilibrium constant varies with temperature. [2]

    d) Explain the fact that the dissociation of acetic acid gets enhanced upon addition of neutral salts like NaCl to the solution. [2]

8. a) A reaction at equilibrium is perturbed with an infinitesimall change of —
        i) pressure at constant temperature and
        ii) temperature at constant pressure.

        Show that in the two cases the direction of the advancement of the reaction depends upon—
        i) volume change and
        ii) enthalpy change of the reaction respectively. [3]

    b) Define fugacity for a real gas. [1]

    c) At what condition the fugacity of a real gas reduces to its pressure. [1]

    d) A gas which obeys the law $P(V - b) = RT$. Show how the fugacity of this gas is related to its pressure. [3]

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