RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. FOURTH SEMESTER EXAMINATION, MAY 2016

SECOND YEAR [BATCH 2014-17]

Date : 27/05/2016 **CHEMISTRY (General)**

Time : 11 am – 2 pm **Paper :** IV Full Marks : 75

[Use a separate Answer Book for <u>each group</u>]

Group – A

[***Attempt <u>one question</u> from <u>each Unit</u>***]

Unit – I

1. a) Give the name and formula of the principal ore of Nickel. How is it extracted by Mond's process? How is Nickel ion detected in solution? [4+3+2]
   b) Cupric ion is more stable in water than cuprous ion. Explain. [2]
   c) What happens when potassium iodide is added slowly and finally in excess to an aqueous solution of mercuric chloride and ammonia gas is passed after making the resulting solution alkaline? [2]

2. a) The sum of 1^{st} and 2^{nd} ionisation energies of zinc, cadmium and mercury are as follows 2639 (Zn), 2507 (Cd) and 2816 (Hg) KJ mol^{-1}. Explain this phenomenon. [3]
   b) What is meant by abnormal transport number of CdI_2? Explain. [2·5]
   c) Comment about the stable oxidation state of copper, silver and gold. [2·5]
   d) Why are bivalent copper salts more stable than monovalent ones? [2]
   e) Calculate the equivalent weight of $KMnO_4$ as an oxidant in acidic and alkaline medium. (K = 39, Mn = 55, O = 16] [3]

Unit – II

3. a) Explain the main difference between systematic error and random error. [3]
   b) How Fe^{+2} is determined by permanganometry? And also discuss the role of Z.R. reagent in this method. [3]
   c) Explain the role of ammonium bifluoride in the quantitative analysis of a mixture of iron and copper. [4]
   d) What are the roles of Ca and Mg in the complexometric titration of EDTA? [2]

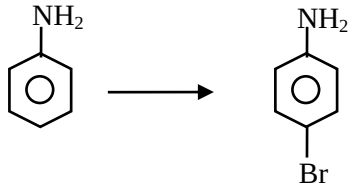
4. a) What do you mean by precision and accuracy of a chemical analysis? [3]
   b) How coprecipitation can be avoided in a gravimetric analysis? [2]
   c) Discuss the gravimetric analysis of Aluminium. [3]
   d) Explain the term solubility product with example. What do you mean by common ion effect? How does common ion effect influence precipitation reactions? [2+1+1]

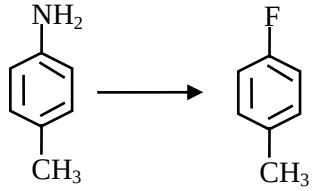
Group - B

[***Attempt <u>one question</u> from <u>each Unit</u>***]

Unit – III

5. a) Carry out the following conversions. [2×2]

i) 

ii) 

b) Give a chemical test for each to distinguish between
   i) acetaldehyde and benzaldehyde ii) aniline and nitrobenzene [2+2]

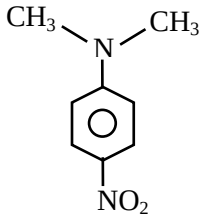
c) Explain with suitable example the $B_{AC}2$ mechanism of hydrolysis of ester. [2]

d) Write short notes on : [2×2·5]
   i) Hofmann degradation method ii) Kolbe Reaction

6. a) How will you obtain methylamine and ethylamine from acetamide? [2]

b) Discuss the process of separation of primary, secondary and tertiary amines by Heinsberg's method. Give suitable reactions. [4]

c) Which one of the following pair of compounds is more basic? Justify your choice. [2]



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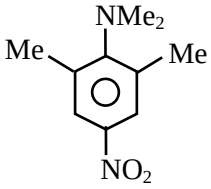

d) Write short notes on : [5]
   i) Claisen Rearrangement ii) Reimer-Tiemann reaction

e) Predict the products when *p*-toluidine is treated with $NaNO_2$/HCl and the resultant solution is added to cold alkaline β –Naphthol solution. [2]

Unit – IV

7. a) Write short notes on the following (**any one**) : [3]
   i) Osazone formation ii) Isoelectric point

b) Glucose undergoes mutarotation but methyl glucoside does not. Explain. [2]

c) How is aldopentose converted to aldohexose and vice versa? [2·5+2·5]

8. a) Give the names and structures of two α-amino acids. State with equations Gabriel pthalimide synthesis of glycine. [1+1+3]

b) Predict the product of the following reaction in Haworth projection formula. [2]

$$\alpha - D - \text{glucopyranose} \xrightarrow[0{\cdot}5\%\,HCl,\,\Delta]{CH_3OH}.$$

c) Write down the primary structure of the following tripeptide. Ala.gly.phe [1]

d) Define with example : Epimer [2]

Group – C

[***Attempt one question from each Unit***]

Unit – V

9. a) Two Carnot engines working between the same temperature domains have the same efficiency. Explain. [2]

b) Prove that all spontaneous processes are accompanied by an increase in entropy. [2]

c) 'Boiling of water is an enthalpy driven process' —mention whether this statement is right or wrong. If wrong what will be the correct form. [2]

d) A reaction is represented as $\gamma_A A + \gamma_B B \rightleftharpoons \gamma_C C + \gamma_D D$.
   i) Define equilibrium constant for the process in terms of partial pressures of A, B, C and D.
   ii) Define standard free energy change of the above reaction.
   iii) Write down the relationship between standard free energy change and equilibrium constant. [3×2]

10. a) State Le-Chatelier's principle and apply it for the following equilibrium : [1+3]

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - 17Kcal$$

b) Consider the reaction (all species gaseous) $A + 2B \rightleftharpoons C + \Delta(\text{heat})$:

i) Comment whether the equilibrium constant for the above reaction will have unit.

ii) Prove that the equilibrium constant for such a reaction (K_p) changes with temperature (T) in accordance with the following equation

$$\left(\frac{\partial \ln K_p}{\partial T}\right)_p = \frac{\Delta H^\circ}{RT^2}$$ [assume the form of Gibb's Helmholtz equation]

iii) From (ii) comment whether the equilibrium constant for the above reaction will increase or decrease with increase in temperature. [3×2]

c) Write down the relationship between entropy and thermodynamic probability. [2]

Unit – VI

11. a) i) Write down Raoult's law of vapor pressure for a solution in equilibrium with vapor.

ii) Plot solvent vapor pressure against mole fraction of the solute in case of an ideal solution.

iii) Arrange the following solutions according to the increasing boiling point of water with proper explanation. 0·1(M) sugar, 0·1(M) NaCl, 0·1(M) K_2SO_4. [3×2]

b) Draw the phase diagram of carbon dioxide system and describe the same briefly. [5]

c) What do you mean by a eutectic mixture? [2]

12. a) i) Consider the chemical equilibrium $A + B \rightleftharpoons C + D$ (all species A, B, C, D gaseous)

Determine the no. of component, no. of phases and degrees of freedom of the system.

ii) Account for the fact that CO_2 sublimates at normal atmospheric pressure but H_2O does not. [3+3]

b) State and explain Schulze-Hardy rule with a suitable example. What do you mean by the statement— 'gold number of haemoglobin is 0·05'? [3+1]

c) What do you mean by electrophoresis of colloids? Write a short note on the stability of both lyophilic and lyophobic colloids. [1+2]

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