RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, MAY 2014

FIRST YEAR

Date : 30/05/2014 **CHEMISTRY (General)**

Time : 11 am – 2 pm Paper : II Full Marks : 75

(Use a separate Answer Book for each group)

Group – A

(*Answer **one question** from each Unit*)

Unit - I

1. a) Explain the effects of following ionisation processes on bond orders and bond lengths
   i) $O_2 + e \rightarrow O_2^-$ ii) $O_2 - e \rightarrow O_2^+$ iii) $N_2 + e \rightarrow N_2^-$ iv) $N_2 - e \rightarrow N_2^+$ [4×1]
   b) Define Lewis acids and Lewis bases. Give examples. What are the limitations of the theory? [2+2+1]
   c) Explain with examples—
   i) conductors ii) semiconductors iii) insulators [3×1]
   d) Mention two limitations of Lewis acid base concept. [1]

2. a) Draw the MO energy level diagram for N_2 molecule. Calculate bond order and explain the diamagnetism of the molecule. [3+2]
   b) Explain Lux-Flood theory of acids and bases. [3]
   c) BDS is a suitable redox indicator for the estimation of Mohr salt using $K_2Cr_2O_7$ in acid medium, explain. [2]
   d) What is meant by disproportionation of an ionic species? Give example. [3]

Unit - II

3. a) Define order, molecularity and rate of a reaction. Distinguish between order and molecularity of a reaction. [1+1+1+2]
   b) State and explain Ostwald's dilution law. Show that the dissociation constant of a weak acid is twice the concentration at which it is 50% dissociated. [4+2]
   c) What do you mean by homogeneous catalysis? [1]

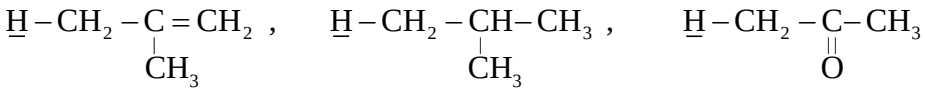
4. a) Derive the expression for rate constant of a first order reaction. Show the relation between rate constant and half life. The rate of a first order reaction is 0·04 mole $L^{-1}sec^{-1}$ at 10 minutes and 0·03 mole $L^{-1}sec^{-1}$ at 20 minutes respectively after initiation. Find the half life of the reaction. [4+2]
   b) Explain that enzymes can act as catalyst. [2]
   c) Discuss the variation of specific conductance and equivalent conductance with dilution for strong and weak electrolytes. [3]
   d) Give one example of pseudo unimolecular reaction. [1]

Group – B

Unit – I

(*Answer **any three** questions*)

5. a) Compare and account for the acidity of the underlines H in— [3]



(A) (B) (C)

b) Arrange the following carbocations according to their increasing stability, Explain

i) $CH_3CH_2CH_2\overset{+}{C}H_2$ ii) $(CH_3)_3\overset{+}{C}$ iii) $CH_3CH_2\overset{+}{C}HCH_3$ [2]

6. a) Which of the following compounds show optical isomerism :

i) $CH_3CH(Br)CH_3$ ii) $CH_3CH(CH_3)CH_2CH_3$ iii) $CH_3CH(OH)COOH$ [1]

b) Which of the following compounds show geometrical isomerism :

i) $CH_3CH=CH_2$ ii) $CH_3-CH=CH-CH_3$ [1]

c) Show R-and S-configuration of glyceraldehyde. Are they optically active? [3]

7. a) Write down Fischer projections of all the stereoisomers of tartaric acid,

$HO_2C-CH(OH)-CH(OH)-CO_2H$ [3]

b) Give structures of (A) and (B) : $Me_3CBr \xrightarrow[ii)\ Cu_2I_2]{i)\ Li/Et_2O} (A) \xrightarrow{PhCH_2Br} (B)$ [2]

8. a) Write mechanism of the following reaction : $H_2C=CH_2 + Br_2 \rightarrow CH_2Br-CH_2Br$ [3]

b) Identify X and Y in the following reaction :

$$CH_3-C\equiv C-CH_3 \xrightarrow[H_2O,Zn]{X} Y \rightarrow CH_3-\overset{O}{\overset{||}{C}}-\overset{O}{\overset{||}{C}}-CH_3$$ [2]

9. a) Why meso-tartaric acid is not optically active? [2]

b) Show E_ and Z_ isomerism in 1,2 dichloroethylene. [2]

c) If the specific rotation of one enantiomer of 2-butanol is +13·5° what is the sp. rotation of the other enantiomer? [1]

Unit – II

(*Answer **any two** questions*)

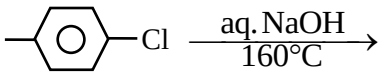
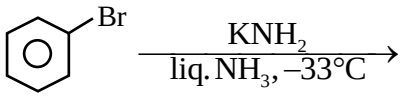
10. a) Which of the following compound reacts separately $NaHSO_3$ and Tollens' reagent? [1]

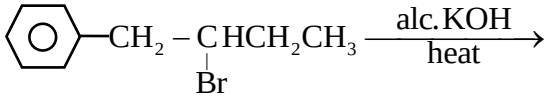
i) $CH_3CH_2CO_2H$ ii) CH_3CHO iii) $CH_3CH_2CH=CH_2$ iv) $H_3C-C\equiv C-CH_3$

b) The reaction of ethanal with one equivalent methanol and a trace of an acid will give— [1]

i) acetal ii) hemiacetal iii) ketal iv) hemiketal

c) Give the product(s) of the following reactions : [3×1]

i)  ii) 

iii) 

11. Write notes on— [2½+2½]

a) Perkin reaction

b) Benzoin condensation

12. a) What happens when— [2×1·5]

i) acetaldehyde is treated with dilute NaOH?

ii) benzaldehyde is treated with concentrated NaOH solution?

b) Discuss S_N^1 reaction with example. [2]

Group – C

(*Answer **one question** from each Unit*)

Unit - I

13. a) In a gas why all molecules are not travelling with same velocity? [1]
    b) What do you mean by the word "root-mean-square velocity"? Why it was introduced in lieu of average velocity in case of a gas. [2]
    c) Derive Dalton's law of Partial pressure from the kinetic theory of gases. [3]
    d) Calculate the temperature at which the average velocity of helium molecule shall be equal to that of hydrogen molecule at 27°C. [3]
    e) Suggest an experiment to prove that gas molecules collide amongst themself. [3]

14. a) Define Collision number and mean free path of a gas molecule.
    From the kinetic theory of gases, deduce an expression for the collision number between the molecules of the same gas at a certain temperature. [2+3]
    b) What is viscosity of a liquid?
    Define viscosity coefficient. Mention its units in CGS and SI. [2+2+1]
    c) Calculate kinetic energy of 1gm CO_2 at 27°C in ergs. ($R = 8{\cdot}314\times10^7$ ergs) [2]

Unit - II

15. a) Which of the following thermodynamic quantities are path dependent function. [2]
    i) Enthalpy ii) Work iii) Internal energy iv) Energy
    b) Indicate which of the following properties are intensive or extensive— [2]
    i) Volume ii) Surface Area iii) Density iv) Molar volume
    c) Indicate which of the following statements are true or false— [2]
    i) Most of the natural processes are reversible in nature
    ii) Work obtained in a reversible process is less than that obtained in an irreversible one
    iii) All adiabatic processes are isoenthalpic
    iv) First law of thermodynamics does not tell us a chemical reaction would take place in which direction forward or backward
    d) Calculate the maximum work in ergs when 2 moles of an ideal gas expands isothermally at 100°C from 1 litre to 10 litre. [3]
    e) Deduce the relation TV^{r-1} = constant for an adiabatic reversible change of an ideal gas. [4]

16. a) Prove that for an ideal gas $C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[P + \left(\frac{\partial PV}{\partial P}\right)_T\right]$. [5]
    b) At 18°C, the heat of solution of anhydrous $CuSO_4$ in a large volume of water is –15, 800 Cal mol^{-1}, while that of $CuSO_4$, $5H_2O$ is 2750 Cal mol^{-1}. Find the heat of reaction of the following reaction : [3]
    $CuSO_4(s) + 5H_2O(\ell) = CuSO_4, 5H_2O(s)$
    c) Joule-Thomson effect is generally accompanied by a decrease in temperature. Explain. [3]
    d) For a reaction at 25°C, enthalpy and entropy changes are $-11{\cdot}7\times10^3$ J mol^{-1} and –105 J $mol^{-1}K^{-1}$ respectively. Calculate Gibbs free energy. [2]