RAMAKRISHNA MISSION VIDYAMANDIRA

(Residential Autonomous College affiliated to University of Calcutta)

B.A./B.Sc. SECOND SEMESTER EXAMINATION, MAY 2017

FIRST YEAR [BATCH 2016-19]

Date : 26/05/2017 **CHEMISTRY (General)**

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

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

(*Attempt <u>one</u> question from <u>each Unit</u>*)

Group - A

Unit I [13 marks]

1. a) Draw the qualitative MO diagram for CO molecule and comment that CO is a pi-acid ligand. [3+2]
   b) Explain the reaction in terms of acid-base concept : $CaO + SiO_2 = CaSiO_3$. [2]
   c) Describe the conductivity, semiconductivity and insulator properties of metals by Band theory of metals with pictorial representation. [3]
   d) From the following pick out the Lewis acid (s) and Lewis base (s) or both with reason : PCl_3, PCl_5 and SO_2. [3]

2. a) Write the conjugate acid (if) and base (if) or both of the followings : CH_3OH, HCO_3^-, NH_4^+ and PO_4^{3-}. [2]
   b) Draw the qualitative MO diagram for N_2 molecule and comment that N_2 is chemically inert. [3]
   c) Name one important redox indicator and give the mechanism of its indictor action. [3]
   d) Arrange the following Lewis acids in increasing order and explain its Lewis acidity. [2·5+2·5]
      i) BCl_3, BI_3, BF_3, BBr_3
      ii) SnF_4, $SnCl_4$, SnI_4, $SnBr_4$

Unit II [12 marks]

3. a) A certain reaction is of first order, after 540 s, 32·5% of the reactant remains.
      i) Calculate the rate constant for the reaction.
      ii) What length of time would be required for 25% of the reactant to be decomposed? [2+2]
   b) Derive the integrated form of the rate law for a first order reaction. [3]
   c) Explain why H^+ or OH^- has remarkably high ion conductance value compared to the other cation/anions. [2]
   d) Can the value of α (α = degree of dissociation) increases with dilution for a weak electrolyte? Explain with suitable law and equation. [3]

4. a) (From Ohm's law) define the following quantities :
      conductance, specific conductance, equivalent conductance, equivalent conductance at infinite dilution. [4]
   b) Explain the effect of dilution on specific conductance and equivalent conductance for both weak and strong electrolytes. [3]
   c) Deduce the relation between rate constant and half life time of a 1^{st} order reaction. [3]
   d) A sample of milk kept at 298 K is found to sour 40 times as rapidly as when it is kept at 277 K. Find out the activation energy for the souring process. [2]

Group - B

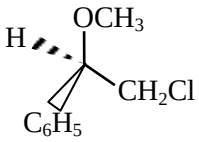
Unit III [15 marks]

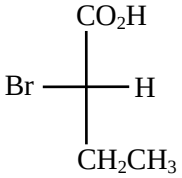
5. a) Classify the following species as electrophile and nucleophile. [2]

$\overset{\oplus}{NO_2}$, $Cl^{(-)}$, SO_3, $H_2C=CH_2$

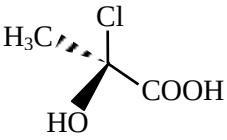
b) Nitration of nitrobenzene gives mainly metadinitrobenzene.—explain. [2]

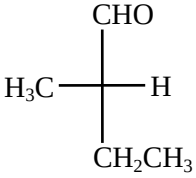
c) Give R/S configurational descriptor at the chiral centre of the following compounds. [2]

i) 

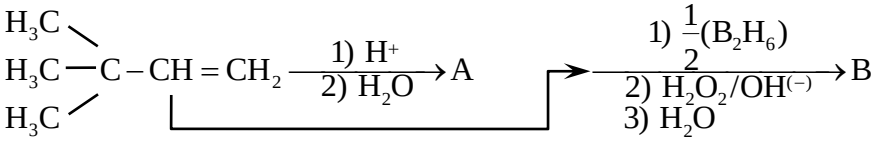
ii) 

d) Designate R/S nomenclature for the following molecules showing priority sequences. [2]

i) 

ii) 

e) Write the structures of A – D in the following reactions. [4]

i) 

ii) $H-C\equiv C-H \xrightarrow[2)\,CH_3I(1eq)]{1)\,NaNH_2(1eq)} C \xrightarrow[Hg^{2+}/H_2SO_4]{1)\,H_2O} D$

f) Discuss the mechanism of chlorination of methane in presence of uv light. [3]

6. a) Write short notes on : [2·5×2]
   i) Markownikoff's addition
   ii) Friedel-Craft's reaction

   b) Write the structure of the following compounds as indicated. [3]
   i) Mesotartaric acid (Fischer Projection)
   ii) (R)-2-bromopropanol (3D formula)
   iii) (E)-2-bromo-2-butene

   c) Discuss the mechanism of Br_2-addition to Carbon-Carbon double bond. [2]

   d) Arrange the following carbocations in order of their stability. Justify your answer. [2]

$CH_3-CH_2-\overset{+}{C}H_2$; $CH_3-\overset{+}{C}H-CH_3$; $CH_3-\overset{+}{C}H-OCH_3$

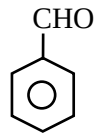
   e) Convert : [3]
   i) 1-Butene → 2-Butene ii) Benzene → Acetophenone

Unit IV [10 marks]

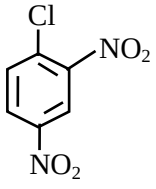
7. a) How can you chemically distinguish between benzaldehyde and acetone? Give equation. [2]

   b) Give mechanism of aldol condensation reaction of acetaldehyde. [3]

   c) Predict the product(s) of the following reactions. Mention the reaction involved in each case. [3]

i) 

$+HCHO \xrightarrow[KOH]{50\%}$

ii) 

$+NaOMe \rightarrow$

   d) Define with example : Aromatic nucleophilic substitution. [2]

8. a) Write short notes on : [2·5×2]
   i) Perkin Reaction ii) Saytzeff Elimination reaction

b) Write a short note on Claisen condensation. [2]

c) Predict the product(s) of the following reactions. Indicate major/minor if any. [3]

i) $CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5 \xrightarrow[1{\cdot}1\,\text{equivalent}]{NaOC_2H_5}$

ii) $CH_3-CH_2-CH_2-\overset{\oplus}{N}(CH_3)-CH_2-CH_3\overset{(-)}{O}H \xrightarrow{\Delta}$

Group - C

Unit V

[13 marks]

9. a) Write down the van der Waals' gas equation for 'n' moles and explain all terms involved. Find out the P_C, V_C and T_C in terms of the gas constants and R. [4]

b) What do you mean by viscosity coefficient of a liquid? How does viscosity eoefficient of a liquid vary with temperature? [3]

c) Define average velocity and 'rms' velocity of a gas molecule. Calculate the 'rms' velocity of CO_2 molecule at 50°C. [3]

d) γ for oxygen molecule is 1·4 and use equipartition theory to calculate C_V. Find out the difference between C_P and C_V. [3]

10. a) Find out the dimensions of 'a' & 'b' from n molar van der Waals' equation. [3]

b) From van der Waals' equation, establish the relation $\frac{RT_C}{P_C V_C}=\frac{8}{3}$. [4]

c) The volume of 2 moles of a real gas obeying van der Waals' equation at 35°C is 30L.What would be its pressure? [Given : a = 6·5 atm L^2mol^{-2}] [3]

d) Calculate the pressure necessary to compress a mole of O_2 at NTP to 1/10 its volume at constant T using van der Waals' equation [a = 1·36 unit, b = 0·0316 unit]. And compare it with that from 'Perfect Gas equation.' [3]

Unit VI

[12 marks]

11. a) Starting from the mathematical definition of the first law of thermodynamics show that the energy of the universe is constant. [2]

b) Prove that $C_P-C_V=\left[P+\left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$. Further show that for n moles on an ideal gas this reduces to $C_P - C_V = nR$. [3+2]

c) Joule-Thomson effect is generally accompanied by a decrease in temperature. Explain. [3]

d) Three moles of an ideal gas are compressed isothermally from 60 L to 20 L using a constant pressure of 5 atm. Calculate Q, W, ΔU and ΔH. [2]

12. a) Show that the enthalpy of the system remains constant during a Joule-Thomson experiment. [3]

b) State the first law of thermodynamics. Write down the mathematical expression for the same. [2]

c) Classify the following quantities as extensive and intensive properties: heat capacity, density, pressure, enthalpy. [2]

d) A system absorbs 990 calories of heat to perform some work equal to $8{\cdot}36\times10^9$ ergs. Calculate the change in internal energy for the system. [3]

e) Show that the work done 'w' in a reversible adiabatic expansion of one mole of an ideal gas is $W=\frac{P_1V_1-P_2V_2}{r-1}$. The terms which are used have usual meanings. [2]

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