## RAMAKRISHNA MISSION VIDYAMANDIRA (Residential Autonomous College affiliated to University of Calcutta) FIRST YEAR [BATCH 2018-21] B.A./B.Sc. SECOND SEMESTER (January – June) 2019 Mid-Semester Examination, March 2019 **CHEMISTRY** (Honours) : 25/03/2019 Date Paper : II Time : 11 am – 1 pm Full Marks : 50 [Use a separate Answer Book for each group] [Attempt one question from each unit] Group – A [16 marks] Unit - I Draw a reaction coordinate diagram for the following reaction when K<sub>-1</sub>>K<sub>2</sub>>K<sub>1</sub>>K<sub>-2</sub> 1. a) $A \xrightarrow{K_1} B \xrightarrow{K_2} C$ (i) Which is faster step in forward reaction? (ii) Which is the rate determining step in the forward direction? [2] The azo compound dibenzyldiazene $(Ph - CH_2 - N = N - CH_2Ph)$ decomposes thermally to b) given N<sub>2</sub> at a faster rate than di-t-butyldiazene $(Me_3C - N = N - CMe_3)$ . Explain. [2] 1,3,5 -trihydroxybenzene forms oxime with NH<sub>2</sub>OH but 1,2,3- trihydroxybenzene does not. c) Explain [2] Predict the product of the following reaction. Give mechanism. [2] d) + SO $Cl_2$ ether OH 2. a) Carry out the following conversion: (R) -2- butanol $\rightarrow$ (S) -2- butanol [2]

- b) Which one of the following is a better nucleophile? Justify your answer.
  KF or Kcl in C<sub>6</sub>H<sub>6</sub> mixed with 18-crown-6-ether.
- c) Which one of the following pair has higher enol content? Justify your answer.

[2]

[2]

[2]



d) Compare the SN' reactivity of the following compounds:



### <u>Unit - II</u>

a) Write down the structure of products when 2-methyl -1- butene reacts with the following reagents (no mechanism needed) [3]

(i) ICl/CCl<sub>4</sub> (ii) Hg(OAC)<sub>2</sub> (iii) BH<sub>3</sub>.NH<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>  $/\overline{O}H$ 

- b) Arrange the following molecules in increasing order of heat of combustion with explanation. [3]
   1-Butene, 1,3-Butadine, 2-Methylpropene, E-butene.
- c) Write down the product for the following reaction with mechanism.



- 4. a) Write down the one use of the following reagents
  - i) N- Bromosuccinimide

ii) Lead tetra acetate

b) Write down the product of following reactions with plausible mechanism  $[2\times3]$ 

(i) But-1-ene 
$$\frac{\text{CBrC}l_3,\text{hv}}{(\text{PhCO}_2)_2}$$

(ii) z-z-butane 
$$\frac{C_6H_5CO_3H}{\text{in CHCl}_3}$$

(iii) z-z-butane i) 
$$OsO_4(Cat)$$
  
NMO (l mol)  
ii) H<sub>2</sub>O

Unit - III

5. a) Consider a consecutive reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

b) Consider the parallel reaction



In an experiment it was observed that 60% decomposition of A takes place in 20 minutes and analysis of product showed that 75% of B and 25% of C. Calculate  $k_1$  and  $k_2$ .

- c) How will you determine whether a given reaction is of the first order or not? [2]
- 6. a) Why is the stoichiometry of a reaction generally not sufficient to determine reaction order? [2]
  - b) The half-life of <sup>238</sup>U is 4.5×10<sup>9</sup> years. How many disintegrations occur in 1 min from a 10 mg sample of this element? [3]

[3]

[3]

[2]

[2]

c) Show that  $t_{1/2} \propto 1/[A]_0^{n-1}$  for a reaction that is nth-order in A, where the terms have usual meaning.

#### <u>Unit - IV</u>

7. a) For a Carnot cycle  $\frac{q_h}{T_h} + \frac{q_1}{T_1} = 0$ . Prove that for a reversible cycle that uses any number of

reservoirs 
$$\sum_{i} \frac{q_i}{T_i} = 0.$$
 [4]

- b) Starting with Clausius inequality show that at constant temperature and volume for any spontaneous process  $\Delta A < 0$ . [4]
- 8. a) Derive the thermodynamic equation of state in terms of how internal energy of a system (U) varies with volume at constant temperature. [4]
  - b) Given that  $Cp Cv = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$  with the help of the thermodynamic equation of state

derived above prove that  $C_p$  is always greater that  $C_v$ .

[3]

[4]

[3]

## <u>Unit - V</u>

- 9. a) Describe alkali metal solutions in liquid ammonia. Explain why these solutions have blue colour in dilute but bronze colour in concentrated solutions. Also explain why these blue solutions have high conductivity, are paramagnetic and are strongly reducing. Give equations one in each case to show strong reducing power and metastability of the blue solutions. [1+1+1+1]
  - b) Explain why <u>(any two)</u> [2×2]

i) Linear BeCl<sub>2</sub> exists only in gas phase

ii) Li<sup>+</sup> has lower mobility and lower conductance than Cs<sup>+</sup> despite smaller size.

iii) Magnesium does not impart any colour to flame while calcium does.

- 10. a) How is beryllium extracted from its ore? Give relevant chemical equation. [3]
  - b) How does the reactivity and nature of products change from Li to Cs when the elements react with air? [3]
  - c) Giving reasons, explain

i) Which one is more basic : KOH or,  $Ca(OH)_2$ 

ii) Which one is more complexing :  $Li^+$  or  $Be^{+2}$ ?

# <u>Unit - VI</u>

- 11. a) State Bent's rule. Explain the structure of  $POF_3$  and  $PCl_3F_2$  molecules by applying Bent's rule. [3]
  - b) Using VSEPR theory predict the shapes of  $[TeCl_6]^{2-}$  ion and IF<sub>7</sub> molecule, indicating the state of hybridisation of the central atom in each case. [1.5×2]
  - c) What is radius ratio rule? Calculate the limiting radius ratio for the co-ordination number six(octahedral) (C.N. = 6). [1+2]
- 12. a)  $Na_2CO_3$  is stable whereas  $Li_2CO_3$  readily decomposes on heating.— Explain. [2]
  - b) Calculate the limiting ratio for the coordination number 8. From the radius  $r_+/r_-$  value CdS (0.52) and HgS (0.55), it is expected to adopt the NaCl structure, but they are actually crystalline with ZnS structure. Explain [2+2]
  - c) Establish the condition for a radioactive element to show spontaneous  $\beta^{-}$  decay. [2]

 $- \times -$ 

d) MgSO<sub>4</sub> is fairly soluble in water but BaSO<sub>4</sub> is water insoluble, comment. [1]