Five Year Integrated M.Sc. Examination, 2019

Semester - IV

Paper: CH-2-4-1 (Old)

(Chemistry)

Time: Four Hours **Full Marks: 80**

Questions are of value as indicated in the margin.

Group-A

1. Answer ***any ten*** questions: 10×2=20
   a) What is formal potential?
   b) Write down the structure of an optically active square planar complex.
   c) Will stannic chloride oxidize ferrous sulphate in aqueous solution? Given $E^0_{Sn^{4+}/Sn^{2+}} = 0.15$ V, $E^0_{Fe^{3+}/Fe^{2+}} = 0.77$ V.
   d) Find out the octahedral site stabilization energy (OSSE) of d^4 high spin and low spin system.
   e) Phenol is acidic in nature. Explain
   f) In Perkin reaction usually anhydride and salt of same fatty acid are used. Explain
   g) Nitro group deactivates the benzene ring towards electrophilic substitution. Explain
   h) Alkyl cyanide on hydrolysis forms acid, but alkyl isocyanides on such reaction yields amine and formic acid. Explain
   i) The specific rate constant for a reaction has the unit "$lit^2.mol^{-2}.s^{-1}$". What is the order of the reaction?
   j) What is autocatalysis? Discuss with suitable example.
   k) Elementary reaction with molecularity greater than 3 is generally uncommon. Justify.
   l) Show that the half-life of first order reaction is independent of initial concentration.

Group-B

Answer ***any two*** questions

2. a) What is redox indicator? Give an example of redox indicator and draw its structure in oxidized and reduced form. 1+3
   b) Derive the expression for Nernst equation for the couple MnO_4^-/Mn^{2+} in acidic medium. 2
   c) Consider the given portion of the Latimer diagram and check whether MnO_4^{2-} would disproportionate in solution. 4

$$MnO_4^- \xrightarrow{0.56\ V} MnO_4^{2-} \xrightarrow{2.26\ V} MnO_2$$

3. a) Write down the differences between double salt and complex salt. 2
   b) Define step-wise and overall stability constant. Hence derive the relation between these two stability constants. 4
   c) Give one example (name and structure) of each of the following: (i) Bidentate ligand, (ii) Bridging ligand, (iii) Cationic ligand, (iv) Anionic ligand, (v) Flexidentate ligand and (vi) Chelating ligand. 4

4. a) Explain the bonding nature and geometry of $CoCl_3.6NH_3$ in the light of VB theory. 4
   b) Write the IUPAC name of the following:
   (i) $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]Cl_5$ (ii) $[Pt(H_2NCH_2CH_2NH_2)_2Cl_2]Cl_2$ 2
   c) Write a brief note on crystal field theory (CFT). 4

Group-C

Answer ***any two*** questions

5. a) When benzene reacts with neopentyl chloride $(CH_3)_3CCH_2Cl$, in the presence of aluminium chloride, the major product is 2-methyl-2-phenylbutane. Explain the result. 4

P.T.O.

b) Cite one suitable example of an aromatic nucleophilic substitution reaction. 2

c) Though halogens are o-/p-directing, the rate of nitration on chloro-benzene is slower than that on benzene itself. Explain. 4

6. a) What are Grignard reagents? 2

b) Describe the preparation of methyl magnesium iodide using Grignard reagent. 2

c) How will you prepare a primary, secondary and tertiary alcohol? 2×3

7. a) Carry out the following conversions (***any two***): 4

i) Aniline → Fluoro benzene

ii) Toluene → Cinnamic acid

iii) Phenol → Salicylic acid

b) Write notes on (***any one***): 2

i) Claisen rearrangement

ii) Beckmann transformation.

c) Write notes on the following (***any two***): 4

i) Friedel craft acylation reaction

ii) Reimer-Tiemann reaction

iii) Diazo-coupling reaction

Group-D

Answer ***any two*** questions

8. a) For an elementary reaction

$$\alpha A + \beta B = \gamma C + \delta D$$

Write the rate equation and order of the reaction. 2+1

b) Write a method of determining the order of a reaction. Half life of a reaction is doubled when initial concentration of the reactant is doubled. What is the order of the reaction w.r.t. the reactant? 2+3

c) Discuss the effect of ionic strength on the following reactions:

$$S_2O_8^{2-} + 2I^- = I_2 + 2SO_4^{2-}$$ 2

9. a) Discuss the important kinetic features of the Lindemann theory of unimolecular reaction. 4

b) What is activation energy of a chemical reaction? Show that the enthalpy of a chemical reaction is the difference in the energies of the two opposing changes. 3

c) A third order reaction is 50% completed in 100 sec. Calculate the time for 75% and 100% completion of the reaction. 3

10. a) What is the difference between physical adsorption and chemisorption? Derive the Langmuir adsorption isotherm explaining the assumptions involved. 2+3

b) What is chain reaction? Write the different steps of decomposition of acetaldehyde and show that the rate of decomposition of acetaldehyde is proportional to three-half of acetaldehyde concentration. 1+4

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