Five Year Integrated M.Sc. Examination, 2017

Semester - IV

Paper: CH-2-4-1

(Chemistry)

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

Questions are of value as indicated in the margin.

Group-A

1. Answer ***any ten*** questions: 10x2=20
   a) Explain the different types of interactions giving rise to weak chemical forces.
   b) What do you understand by ligand isomerism? Explain with appropriate example.
   c) State Jahn Teller's theorem of tetragonal distortion. Out of high spin d^1, d^2, d^3 and d^4, which will show such distortion in octahedral field?
   d) Establish the potential range of an indicator across which it exhibits sharp colour contrast between the oxidized and reduced forms.
   e) Nitro group deactivates the benzene ring towards electrophilic substitution. Explain
   f) Name two rearrangement reactions where migration takes place from carbon to an electron deficient oxygen and electron-deficient nitrogen atoms, respectively.
   g) Mass spectrum of a salt of diazotized *o*-aminobenzoic acid (anthranilic acid) shows a peak having *m/e* 152. Explain
   h) Nitro-methane acts as Michael donor. Explain
   i) For the homogeneous reaction, 2A + 3B = 1C + 4D, write the unique rate expression of the reaction.
   j) Order of a chemical reaction higher than three (3) is unlikely. Why?
   k) The unit of 'k', the rate constant of a chemical reaction is lit $^{1/2}$ mol $^{-1/2}$ s $^{-1}$. Find the order of the reaction.
   l) What is autocatalysis? Discuss with suitable example.

Group-B

Answer ***any two*** questions

2. a) Draw the structures of *cis*- and *trans*-isomers of $[Pt(NH_2CH(CH_3)CH(CH_3)NH_2)_2]^{2+}$. 2
   b) $[Co^{III}(NH_3)_6]^{3+}$ is diamagnetic whereas $[Co^{III}F_6]^{3-}$ is paramagnetic. Explain the observation in terms of Valence Bond Theory. 3
   c) Name one (i) positive monodentate, (ii) ambidentate, (iii) bridging and (iv) chelating ligand. 2
   d) $Cu^{2+} \xrightarrow{0.15V} Cu^{+} \xrightarrow{0.5V} Cu$
   Explain with proper justification whether Cu^+ will disproportionate or not. 3

3. a) Complexes of cobalt namely $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$ precipitate three, two, one and no, respectively, molecule(s) of AgCl on treatment with $AgNO_3$. Establish the structure of the molecules in the light of Werner's coordination theory with proper justification. 4
   b) Establish the Nernst equation for AsO_4^{3-}/AsO_3^{3-} couple in acidic medium. Find out the formal potential of the system at pH = 8. [Given: E° for AsO_4^{3-}/AsO_3^{3-} = +0.56 V] 2+2
   c) Show the splitting patterns of *d*-orbitals in an octahedral and tetrahedral geometry. 2

4. a) Write the IUPAC name of the following:
   (i) $(NH_4)[Cr(SCN)_4(NH_3)_2]$ (ii) $[Pt(NH_3)_4Br_2]Br_2$ 2
   b) Name and draw the possible geometries for coordination number 4 and 5. 2
   c) Account for the higher melting and boiling points of H_2O compared to H_2S. 2

P.T.O.

d) What is Frost diagram? Using the following data, construct the Frost diagram for Mn up to oxidation number of 4. 1+3

$MnO_2 \xrightarrow{0.95V} Mn^{3+} \xrightarrow{1.51V} Mn^{2+} \xrightarrow{-1.18V} Mn$

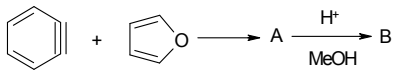
Group-C

Answer ***any two*** questions

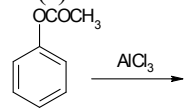
5. a) When benzene reacts with neopentyl chloride $(CH_3)_3CCH_2Cl$, in the presence of aluminium chloride, the major product is 2-methyl-2-phenylbutane. Explain the result. 4

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

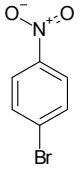
c) Write the structure of the products in the following reaction sequence. 2



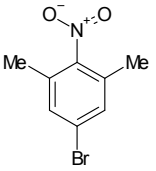
6. a) Write the structure of the product(s) with mechanism 2x2



b) Rate of nucleophilic substitution on the substrate (I) is much higher than on the substrate (II). Explain the result. 4

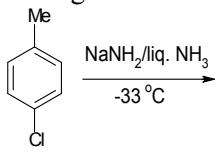


(I)



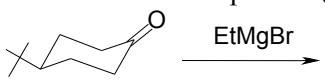
(II)

c) What will be the products of the following reaction? 2

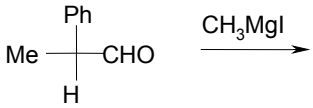


7. a) Write the structure of the product(s) (with stereochemistry where applicable). 4x2

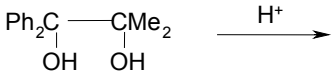
(i)



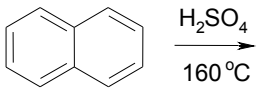
(iii)



(ii)



(iv)



b) How isocyanate intermediate is formed during Hofmann degradation reaction? 2

Group-D

Answer ***any two*** questions

8. a) Write a method by which the order of a chemical reaction can be measured. 2

b) The half-life for the decomposition of Ra is 1590 years. Calculate the rate constant in sec^{-1}. In how many years will three-quarter of the given sample of Ra have disappeared? 1+3

c) For the chemical reaction, $K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$, find the integral rate equation when the initial concentration of KI is twice that of $K_2S_2O_8$. 4

9. a) What is the chain reaction? Write the different steps involved in the chain reactions. What is the essential condition of a chain reaction to occur? 1+2+1

b) Show that the Michaelis-Menten rate law (R_o) for an enzyme catalyzed reaction is given by $\frac{1}{R_o} = \frac{1}{R_{max}} + \frac{K_m}{R_{max}} \cdot \frac{1}{[S]_o}$, where $R_{max} = k_2[E]_o$ and the other terms have their usual significance. What is turn-over number? 3+1

c) Show that for a first order reaction the time required for 75% completion is twice the time of 50% completion. 2

10. a) What is activation energy of a chemical reaction? Show that the heat of a chemical reaction is the difference in the energies of the two opposing changes. 1+3

b) What is consecutive reaction? The radioactive ^{239}U decays to ^{239}Pu through the formation of an intermediate, ^{239}Np. If the decay constants of ^{239}U and ^{239}Np are k_U and k_{Np}, respectively, find the time (t_{max}) when the concentration of ^{239}Np reaches to its maximum concentration. 1+3

c) The adsorption of a monatomic gas follows Langmuir adsorption isotherm with K = 0.85 kPa^{-1} at 25°C. Calculate the pressure at which the fractional surface coverage is 0.95. 2

_____