

Five Year Integrated M.Sc. Examination, 2019

Semester - IV

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

(Chemistry)

Time: Three Hours

Full Marks: 60

Questions are of value as indicated in the margin.

Group-A

Answer **any two** questions

1. a) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic, whereas $[\text{CoF}_6]^{3-}$ is paramagnetic –Explain in the light of valence bond theory. 4
b) What is the pH of pure water at 100 °C? K_w at 100 °C is 5.6×10^{-13} . 2
c) What are the basic assumptions of Crystal Field Theory? What are the parameters which decide the extent of splitting in a crystal field? 2+2
2. a) What are hydric acids and oxo-acids? How does their acidity vary down a group with respect to the heteroatom attached? 1+2
b) 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? 2
c) Draw the structures of *cis*- and *trans*-isomers of $[\text{Pt}(\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NH}_2)_2]^{2+}$. 2
d) A solution contains KCl and KI, both in 0.1 M concentration. Silver nitrate solution at 0.01 M concentration is added drop wise with stirring.
i) Which will be precipitated first, AgCl or AgI? 3
ii) What will be the concentration of I^- in solution when AgCl begins to precipitate? K_s for AgCl = 1.5×10^{-10} ; for AgI = 10^{-16} . 3
3. a) Demonstrate ligand isomerism with appropriate example. 2
b) State and explain with appropriate example Werner's coordination theory. 3
c) Derive the expression for pH of a solution containing a salt obtained from a weak acid and strong base. 3
d) With the help of appropriate theory explain the direction of the following reactions:
(i) $\text{LiI} + \text{CsF} \rightarrow \text{LiF} + \text{CsI}$ (ii) $\text{CH}_4 + \text{CF}_4 \rightarrow \text{CH}_3\text{F} + \text{CHF}_3$ 2

Group-B

Answer **any two** questions

4. Carry out the following transformations (**any four**): 2.5×4
a) Benzene to salicylaldehyde
b) Benzene to salicylic acid
c) Benzene to *p*-nitrophenol
d) Propylene to *n*-propanol (propan-1-ol)
e) Acetic acid to acetone
5. a) Show the energy profile diagram of any aromatic electrophilic substitution reaction. 3
b) Compare the rate of nitration among the following substrates 4
 C_6H_6 , C_6D_6 , $\text{C}_6\text{H}_5\text{CH}_3$ and $\text{C}_6\text{H}_5\text{NO}_2$
c) Explain why nitrobenzene is not good substrate for Friedel Craft alkylation reaction. 3
6. Write down the mechanism of the following reactions (**any four**): 2.5×4
a) Hydroboration oxidation
b) Diazo coupling reaction
c) Reimer – Tiemann reaction
d) Fries rearrangement
e) Gatterman – Koch reaction

P.T.O.

Group-CAnswer *any two* questions

7. a) For an elementary reaction
 $aA + bB = cC + dD$
 Write the rate equation of the reaction. 2
- b) The half-life for the decomposition of the radioactive element (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? 2+3
- c) For a first order process: $A \rightarrow P$, show that the number of molecules at a time 't' is given by
 $N_t = N_0 \left(\frac{1}{2}\right)^{t/t_{1/2}}$, where, N_0 is the number of molecules at $t = 0$ and $t_{1/2}$ is the time for half decomposition. 3
8. a) What is chain reaction and what is its essential condition to occur? Show that the rate of polymerization of polyethylene is directly proportional to the initial concentration of ethylene and square root of the initiator (I) concentration. 2+3
- b) Show that the Michaelis-Menten rate law 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? 4+1
9. a) What is the difference between physical adsorption and chemisorption? Write down the assumptions which were considered for deriving the Langmuir adsorption isotherm. Show that the rate of a heterogeneous catalytic reaction follows first order kinetics at very low pressure. 2+2+2
- 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
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