

Name of the Examination **FIVE YEAR INTEGRATED M. Sc.**Part/Semester **III****2021**Subject **CHEMISTRY THEORY**Paper/Course **CH-2-3-1**

Half

Time **Three (03) Hours**Full Marks **60**

Questions are of value as indicated in the margin

Group-A(Answer **any two** Questions)

1. (a) Comment on the boiling points trend in the following pairs of compounds. 2
(i) NF_3 and NMe_3 and (ii) CCl_4 and SiCl_4
(b) Consider the titration of 25 mL 0.1 N Fe^{2+} with 0.1 N $\text{K}_2\text{Cr}_2\text{O}_7$ being carried out at pH 1.0. Calculate the potential of the solution for the following volumes of $\text{K}_2\text{Cr}_2\text{O}_7$ added. 4
(i) 24.8 mL, (ii) 25 mL and (iii) 25.2 mL
(c) Explain why *o*-hydroxy benzoic acid is stronger than *o*-methoxy benzoic acid. 2
(d) Comment on the sizes of the tetravalent cations of titanium, zirconium and hafnium. Explain the reason behind such observation. 2
2. (a) Distinguish between alloys and interstitial compounds and explain how transition metals participate in such structures. 2
(b) HF forms stronger H-bonds than H_2O . Still ΔH_{vap} of HF is lower than that of H_2O . – Explain. 2
(c) Explain why copper displaces zinc from a solution of zinc salt in the presence of excess KCN. 2
(d) The magnitudes of standard electrode potentials are merely relative. Justify. 2
(e) Is it possible to have different geometries for a given coordination number? 2
Support your answer with appropriate examples.
3. (a) Predict the trend of increase in boiling point among the noble gases. Justify your answer. 2
(b) The Latimer diagram of silver in acid medium is 4
$$\text{Ag}^{2+} \xrightarrow{1.99 \text{ V}} \text{Ag}^+ \xrightarrow{0.80 \text{ V}} \text{Ag}$$

Predict whether Ag^+ will disproportionate to Ag and Ag^{2+} or Ag and Ag^{2+} will comproportionate to Ag^+ . Hence, calculate K for the relevant reaction.

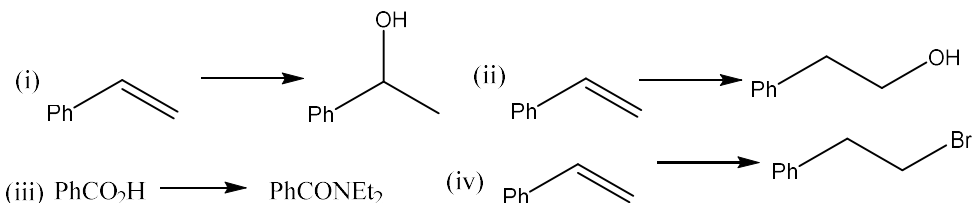
(c) Establish the expression for formal potential of $\text{MnO}_4^-/\text{Mn}^{2+}$ system in aqueous medium 2

(d) What are the ligands that can bind to a central metal ion through two different atoms called? Give examples. How do they differ from flexidentate ligands? 2

Group-B

(Answer **any two** Questions)

4. Carry out the following transformations with plausible reaction mechanism. 2.5 x 4



5. Write down the mechanism of the following reactions with supportive evidences. 2.5 x 4

- (i) Cannizzaro Reaction (ii) Michael Reaction
(iii) Diels-Alder Reaction (iv) Epoxidation of Alkene

6. (a) Give the expected major product from reaction of 3-methyl-1-butene with each of the following reagents. Explain any differences in the products mechanistically. 2 x 3

- (i) 50% aqueous H_2SO_4 ;
(ii) $\text{Hg}(\text{OAc})_2$ in H_2O , followed by NaBH_4 ;
(iii) BH_3 in THF, followed by NaOH and H_2O_2 .

- (b) Give the products of reaction of methyl pentanoate with each of the following reagents under the conditions shown. 2 x 2

- (i) NaOH , H_2O , heat; then H^+ , H_2O
(ii) CH_3MgI (excess), $(\text{CH}_3\text{CH}_2)_2\text{O}$; then H^+ , H_2O

Group-C

(Answer **any two** Questions)

7. (a) What is Reynold's number? How does this number help to ascertain the nature of flow of liquids through a narrow tube? 1+1

- (b) Consider that an incompressible liquid is flowing through a narrow tube of uniform radius (r) and length (L). The pressure difference between the two ends of the tube are P_1 and P_2 ($P_1 > P_2$). Derive the Poiseuille's equation. 4

- (c) Water flows through a tube of length 0.420 m and radius 0.00520 m. If the pressure difference across the tube is 0.0500 atm and the temperature is 20 °C, find the volume of water that flows in 1.0 hour. Assume that the flow is laminar flow. [Given 1 atm = 1.01325 kPa]. 4

8. (a) Prove that entropy (S) is a state function. 2

- (b) Write down the Gibbs-Helmholtz equation. Establish the relation, $dG = VdP - SdT$ and the corresponding Maxwell's relation. 3

- (c) Suppose a liquid is in equilibrium with its vapour phase. Derive the slope, $\frac{dP}{dT}$, of the liquid-vapour phase boundary. Write down the name of this equation. 5
From this relation, show that the ratio of the latent heat of vapourization (ΔH_{vap}) to its boiling temperature (T_b) is constant for non-associable and non-dissociable liquids.

9. (a) Define the angle of contact (θ) between a pair of liquid and solid? Droplets of liquid generally tend to form a spherical shape. But when kerosene falls on a flat and smooth solid surface it spread all over surface whereas mercury forms a 2+2

spherical droplet, does not spread over the surface. Explain why?

- (b) Find the height to which water at 20 °C will rise in a glass capillary tube of diameter 0.60 mm. [Given $\gamma = 0.07275 \text{ J m}^{-2}$]. 2
- (c) Find ΔS , ΔS_{surr} , q , w , and ΔU for the reversible isothermal expansion of 3.0 mol of argon (assume ideal) from a volume of 100.0 L to a volume of 500.0 L at 298.15 K. 4