304/Chem.

U.G. 2nd Semester Examination - 2022

CHEMISTRY

[HONOURS]

Course Code : CHEM-H-CC-T-03

Full Marks : 40 Time : $2\frac{1}{2}$ Hours

The figures in the right-hand margin indicate marks.

Candidates are required to give their answers in their own words as far as practicable.

GROUP-A

1. Answer any **one** from the following questions:

 $1 \times 1 = 1$

- a) Write down the structure of a redox indicator.
- b) What is common ion effect?
- 2. Answer any **two** from the following questions: $2 \times 2 = 4$
 - a) Calculate the oxidation number of Cr in CrO_5 and O in F_2O .
 - b) Write down the Nernst equation for MnO^{4-} / Mn^{2+} system.
 - c) What is super acid? Give example.

- d) Does metallic copper dissolve in HCl? Give reason. $\left[E^{0}_{Cu^{2+}/Cu^{+}} = 0.4V\right]$
- 3. Answer any **one** from the following questions:

 $5 \times 1 = 5$

 a) i) Explain why Cu²⁺ ion readily liberates iodine from iodide but in presence of ethylenediamine it does not.

$$\left[E^{0}_{Cu^{2^{+}}/Cu^{+}}=0.15V,\ E^{0}_{1/2}\ I_{2}\ /\ I^{-}=0.54V\right]$$

- ii) What will be the solubility of AgCl in a solution of 0.1(M) NaCl solution? (K_{sp} of AgCl = 1× 10⁻¹⁰)
- iii) Define standard hydrogen electrode.

2+2+1=5

- b) i) 100 ml of buffer solution of pH = 9 is to be prepared by mixing 0.1 (N) HCl and 0.1 (N) NH₄OH. Calculate the volume of each solution required to prepare the buffer $(K_b = 2 \times 10^{-5}).$
 - ii) Calculate the pH of 0.1 (M) CH₃COONa solution. (Given $K_a = 1.8 \times 10^{-5}$). 3+2=5

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4. Answer any **one** from the following questions:

 $10 \times 1 = 10$

- a) i) Show that the equilibrium constant (K) of a redox reaction is given by the equation $\log K = n/0.0591 (E_1^0 - E_2^0)$
 - ii) Draw the Frost Diagram for mercury in acid solution from the given Latimer diagram.:

 $Hg^{2+} \xrightarrow{0.911V} Hg^{2+} \xrightarrow{0.796V} Hg$

Determine the slope of each line and comment on the tendency of any of the species to undergo disproportionation.

 iii) Explain the role of Zimmermann-Reinhardt solution during the titration of Fe²⁺ vs MnO⁴⁻ in HCl medium.

3+(1+1+3)+2=10

- b) i) What do you mean by buffer capacity?Show that the buffer capacity is maximum at the half-neutralization point and then prove that for an acidic buffer, pH at the half-neutralization point is equal to pKa.
 - ii) What is the condition of precipitation of a salt from a solution?

- iii) Derive the Henderson equation for the calculation of pOH of a basic buffer.
- iv) State and explain the Ostwald dilution law. (1+2+1)+2+2+2=10

GROUP-B

- 5. Answer any **one** question from the following: $1 \times 1 = 1$
 - a) What is meant by the efficiency of a heat engine?
 - b) What is temperature co-efficient of reaction?

6. Answer any **two** questions from the following:
$$2 \times 2=4$$

- a) Show that $(\partial A/\partial V)T = p$ and $(\partial A/\partial T)V = -S$.
- b) Why is the half-life for a first-order reaction independent of the initial concentration?
- c) "Entropy of the universe is always increasing." Comment on this.
- d) How does rate of a reaction vary with temperature?
- 7. Answer any **one** question from the following:

 $5 \times 1 = 5$

a) Derive the Gibbs-Helmholtz equation for a process at constant pressure and constant

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volume. What does the Clausius Inequality signify in thermodynamics? 4+1=5

 b) "Two Carnot engines working between the same temperature domains have the same efficiency."—Explain. Write the importance of Joule-Thomson co-efficient. Prove that this coefficient is zero for an ideal gas.

 $2+1\frac{1}{2}+1\frac{1}{2}=5$

- c) Write three important features of homogeneous catalysis. What is Lineweaver-Burk plot in enzyme catalysis? What is acid-base catalyst?
 2+2+1=5
- 8. Answer any **one** question from the following:

 $10 \times 1 = 10$

- a) i) Discuss the primary kinetic salt effect with a suitable example.
 - ii) Discuss Mechanism and Kinetics of Enzyme-catalyzed Reactions.
 - iii) The boiling point of water at a pressure of 50 atmospheres is 265°C. Assume the temperature of the sink to be 35°C in this case. Calculate theoretical efficiency of a steam engine operating under these temperatures. 3+5+2=10

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- b) i) The 50% of a first-order reaction is complete in 23 minutes. Calculate k and the time required to complete 90% of this reaction.
 - ii) Briefly discuss the collision theory for a bimolecular reaction.
 - iii) Explain the equivalence of Kelvin–Planck and Clausius's statements.

(1+2)+3+4=10