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4 SEM PG CHM (CBCS) PC-IV 405

2026

(June)

CHEMISTRY

Paper : 405

(Physical Chemistry-IV)

Full Marks : 60

Time : Three hours

***The figures in the margin indicate
full marks for the questions.***

UNIT-I

(Marks : 35)

(Advanced Electrochemistry)

1. Discuss the significance of electrochemical series in predicting the feasibility of redox reactions. Explain why :

(a) Cu(I) ions are unstable in aqueous solution.

- (b) Fe^{3+} is a stronger oxidizing agent than Fe^{2+} . 1+2+2=5

OR

A copper electrode is immersed in Cu^{2+} solution at 25°C. Calculate the electrode potential when the concentration of Cu^{2+} ions changes from 1.0 M to 0.01M. Discuss the trend using the Nernst equation. 5

2. Explain the principle and experimental setup of cyclic voltammetry (CV). Draw a typical voltammogram for a reversible system and explain the significance of peak current and peak potential. 3+2=5

OR

Discuss how cyclic voltammetry can be used to determine :

- (a) Capacitance behavior.
(b) Electrochemical band gap of a material. 5

3. Discuss the different types of catalysis with suitable examples. Explain the Sabatier principle and its importance in electrocatalyst design. 3+2=5
4. Describe the working principle of a photovoltaic (solar) cell. Explain the mechanism of electron-hole pair generation and separation in a $p-n$ junction. Mention *two* advantages of solar energy conversion. 3+2=5
5. What is electrochemical impedance ? Derive the basic expression of impedance and explain its physical significance. 2+3=5

OR

Explain Nyquist and Bode plots used in Electrochemical Impedance Spectroscopy (EIS). Discuss their features and differences. 3+2=5

6. What are fuel cells? Describe the construction and working of a hydrogen-oxygen fuel cell with electrode reactions.

2+3=5

OR

Explain the mechanism of current generation in a $p-n$ junction solar cell, highlighting the role of the electric field and charge carrier movement. 5

7. Define conducting polymers. Explain the mechanism of electrical conductivity in conjugated polymers with one suitable example. 2+3=5

UNIT-II

(Marks : 25)

(Non-Equilibrium Thermodynamics)

8. Answer **any two** of the following : 2×2=4

(a) Discuss Transformation properties of fluxes and forces of irreversible processes with the help of coupled reactions.

(b) "The diagonal coefficients of the phenomenological equations are always positive." Prove it.

(c) What is the importance of phenomenological equation? Give *two* examples of transport processes where the equation may be applied.

9. Answer **any three** of the following :

4×3=12

(a) Discuss the non-equilibrium thermodynamical treatment to thermoelectric phenomena. Identify the forces and fluxes of these phenomena.

(b) Verify the Onsager's reciprocal relationship with the help of cyclic chemical process of coupled type.

(c) Determine the entropy production due to heat transfer between two phases with (i) two phases at different temperature and (ii) a gradient of temperature along the normal of isothermal surface. Also determine the force of each heat transfer. 2+2=4

- (d) Discuss the application of phenomenological equation in chemical reaction with multiple elementary reactions.

10. Answer **any three** of the following :

$$3 \times 3 = 9$$

- (a) What is Onsager's reciprocity? Derive the Onsager's reciprocal relationship.

$$\frac{1}{2} + 2\frac{1}{2} = 3$$

- (b) State the transformation properties of fluxes and forces of irreversible processes. Verify the transformation properties of fluxes and forces in coupled reactions.

$$\frac{1}{2} + 2\frac{1}{2} = 3$$

- (c) What do you mean by coupled reactions? Derive entropy generation due to chemical reactions in the system.

- (d) What do you mean by "force" and "flux" in irreversible processes? Give *four* examples of irreversible processes and mention the force and flux of each.

$$1 + 2 = 3$$