This paper contains THREE printed pages and THREE parts

PART-A

Answer any SIX questions from the following.

- 1. What is a comproportionation reaction? Give an example.
- 2. Mention two advantages of quinhydrone electrodes.
- 3. What is a photosensitizer? Give an example.
- 4. State Grotthus Draper law in photochemistry.
- 5. Represent diagrammatically the unit cell for a simple cubic lattice. How many atoms are present per unit cell?
- 6. Mention two advantages of potentiometric titrations.
- 7. Draw and indicate the four-fold axes of rotation in a cubic unit cell.
- 8. What is meant by the term 'quantum efficiency'?

PART-B

Answer any EIGHT questions from the following.

9. a) The molar conductance of 0.025M aqueous solution of methanoic acid (HCOOH) is 4.61 x 10⁻³ Sm²mol⁻¹ at 25°C.

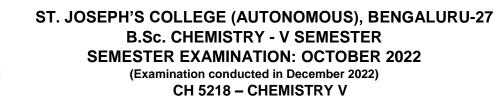
The molar conductance at infinite dilution of H⁺ and HCOO⁻ are given as:

- $\lambda^{\circ}_{H_{+}} = 34.6 \text{ x } 10^{-3} \text{ Sm}^2 \text{mol}^{-1} \text{ and } \lambda^{\circ}_{HCOO_{-}} = 5.46 \text{ x } 10^{-3} \text{ Sm}^2 \text{mol}^{-1}$
- (i) Calculate molar conductance at infinite dilution of methanoic acid.
- (ii) Calculate the degree of dissociation of 0.025M methanoic acid (HCOOH).
- (iii) Give reason for the change in value of molar conductance of methanoic acid upon dilution?
- b) What is transport number? Account for the abnormal change in the transport number of cadmium in cadmium iodide solution at higher concentrations.

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[3 + 3]

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Time: 2 ¹/₂ Hours

 $(6 \times 8 = 48 \text{ marks})$

 $(2 \times 6 = 12 \text{ marks})$

Max Marks: 70

Registration number:

Date:

- 10. a) State and explain Kohlrausch's law of independent migration of ions.
 b) Molar conductance values at infinite dilution of ammonium chloride (NH₄Cl), sodium hydroxide (NaOH) and sodium chloride (NaCl) are 14.97x10⁻³, 24.81x10⁻³ and 12.64x10⁻³ Sm²mol⁻¹ respectively. Find the molar conductance at infinite dilution of ammonium hydroxide (NH₄OH). [3 + 3]
- 11. a) Explain (i) asymmetry effect (ii) electrophoretic effect.
 - b) Write the mathematical expression of Debye-Huckel-Onsager equation for aqueous solutions of 1:1 electrolytes. Explain the terms. [3 + 3]
- 12. What is electrochemical series? Discuss any two applications.
- 13. In a copper-silver electrochemical cell, the Cu²⁺ ion concentration in is 0.1M and Ag+ ion concentration is 0.07M at 25°C.

If $E^{\circ}(Ag^{+}/Ag) = 0.80V$ and $E^{\circ}(Cu^{2+}/Cu) = 0.34V$,

- (i) Identify the cathode and anode.
- (ii) Obtain the overall redox equation.
- (iii) Calculate E^o_{cell}.
- (iv) Calculate E_{cell} (at 25°C).
- 14. a) Derive the Bragg's equation for X-ray diffraction.
 - b) What are Miller indices? A crystal plane cuts at intercepts of 1a, 2b and 3c. Determine the Miller indices of the plane. [3 + 3]

15. a) Write the equation for the redox reaction between $Cr_2O_7^{2-}$ and Fe^{2+} in acidic medium and balance the equation. $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$

b) Using the given Latimer diagram for oxygen, show that disproportionation of H_2O_2 into O_2 and H_2O is spontaneous under acidic conditions.

Latimer diagram of oxygen:

0.68 V 1.77 V O₂ ------ H₂O₂ ------ H₂O

The two half reactions are:

$$\begin{array}{ll} H_2O_2 + 2H^+ + 2e^- \to 2H_2O & E^\circ = +1.76V \\ O_2 + 2H^+ + 2e^- \to H_2O_2 & E^\circ = +0.70V & [3+3] \end{array}$$

16. a) Define the terms (i) phase (ii) component (iii) degree of freedom.

b) Give the mathematical expression of condensed phase rule. Mention one example of a two component solid – solid systems that is studied using condensed phase rule. [3 + 3]

- 17. Discuss the phase diagram of water system with a neat labelled diagram. Apply Gibb's phase rule to the various areas, curves and triple point in the phase diagram of water.
- 18. Draw Jablonski diagram and indicate the various photophysical processes. Explain fluorescence and phosphorescence using the above diagram.

PART-C

Answer any TWO questions from the following. (5 x 2 = 10 marks)

19. Draw and explain conductometric titration curve between a strong acid (HNO_3) and strong base (KOH) in the following cases:

(i) When HNO_3 is taken in the conductivity cell.

(ii) When HNO_3 is taken in the burette.

20. Consider the Latimer diagram of thalium (TI).

1.26 V 0.34 V TI³⁺------ TI⁺ ------ TI

- (i) Construct a Frost diagram in your answer script using centimetre scale. (Graph sheet will not be provided)
- (ii) Explain the stability of TI⁺.
- (iii) Which among the three species is a strong oxidizing agent?

21. a) The quantum yield is high for the photochemical combination of H_2 and CI_2 , but low in the case of H_2 and Br_2 . Explain the reason based on the mechanisms of these reactions.

b) Give reasons:

i) KCl or NH_4NO_3 are usually used to prepare a salt bridge.

ii) H^+ and OH^- have abnormally high conductance values.

[3 + 2]
