Date:
Registration number:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27
B.Sc. CHEMISTRY - V SEMESTER
SEMESTER EXAMINATION: OCTOBER 2022
(Examination conducted in December 2022)
CH 5218 – CHEMISTRY V

Time: 2 ½ Hours **Max Marks: 70**

This paper contains THREE printed pages and THREE parts

PART-A

Answer any SIX questions from the following. (2 x 6 = 12 marks)

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. (6 x 8 = 48 marks)

9. a) The molar conductance of 0.025M aqueous solution of methanoic acid (HCOOH) is 4.61×10^{-3} Sm^2mol^{-1} at 25^oC.
The molar conductance at infinite dilution of H^+ and $HCOO^-$ are given as:
$\lambda^o_{H+} = 34.6 \times 10^{-3}$ Sm^2mol^{-1} and $\lambda^o_{HCOO-} = 5.46 \times 10^{-3}$ Sm^2mol^{-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.

[3 + 3]

10. a) State and explain Kohlrausch's law of independent migration of ions.
    b) Molar conductance values at infinite dilution of ammonium chloride (NH_4Cl), sodium hydroxide (NaOH) and sodium chloride (NaCl) are 14.97×10^{-3}, 24.81×10^{-3} and 12.64×10^{-3} Sm^2mol^{-1} respectively. Find the molar conductance at infinite dilution of ammonium hydroxide (NH_4OH). [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 Cu^{2+} ion concentration in is 0.1M and Ag+ ion concentration is 0.07M at 25°C.
    If $E^o(Ag^+/Ag) = 0.80V$ and $E^o(Cu^{2+}/Cu) = 0.34V$,
    (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:

$$O_2 \xrightarrow{0.68\ V} H_2O_2 \xrightarrow{1.77\ V} H_2O$$

The two half reactions are:

$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $\quad E^o = +1.76V$

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $\quad E^o = +0.70V$

[3 + 3]

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 (Tl).

$$Tl^{3+} \xrightarrow{1.26\ V} Tl^{+} \xrightarrow{0.34\ V} Tl$$

(i) Construct a Frost diagram in your answer script using centimetre scale.
(Graph sheet will not be provided)
(ii) Explain the stability of Tl^+.
(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 Cl_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]
