ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE - 27
B.Sc. CHEMISTRY - V SEMESTER
END-SEMESTER EXAMINATION - OCTOBER 2019
CH 5215 - CHEMISTRY V

Time: 2 1/2 hours Maximum marks: 70

Note: This question paper has three parts and 21 questions.
All parts are compulsory.

Part A

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

1. State Kohlrauch's law of independent migration of ions.

2. Molar conductance of NH_4OH solution at infinite dilution is 271.4 x 10^{-4} S m^2 mol^{-1} at 25°C. Molar conductance of 6 x 10^{-5} M NH_4OH solution is 115 x 10^{-4} S m^2 mol^{-1}. Calculate the degree of dissociation of 6 x 10^{-5} M NH_4OH solution.

3. Account for the abnormally high ionic mobility of H^+ ions using Grotthus mechanism.

4. What is liquid junction potential? How do you eliminate it?

5. Give the mathematical expression of Born-Oppenheimer approximation.

6. What are the consequences of elastic and inelastic scattering in Raman spectroscopy?

7. State Beer-Lambert's law.

8. Explain photosensitization with an example of a photosensitizer.

Part B

Answer any **EIGHT** questions from the following. (6 x 8 = 48 marks)

9. a) The resistance of 0.5 M solution of an electrolyte in a cell was measured to be 45 Ω. Calculate the molar conductance (in SI units) of the solution if the electrodes in the cell are 2.3 x 10^{-2} m apart and have an area of 3.8 x 10^{-4} m^2.

b) Define specific conductance. Mention its SI unit. [4 + 2]

10. a) For the following cell reaction: $2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+}$
i) Given $E^o_{Fe3+ / Fe2+}$ = 0.77V and $E^o_{Sn2+ / Sn4+}$ = 0.15V, identify the anode and the cathode.
ii) Calculate E^o_{Cell}.
iii) Write the Cell notation.

b) Draw and label a diagram of standard hydrogen electrode. [4 + 2]

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. [4 + 2]

12. What is quinhydrone electrode? How do you determine the pH of a solution by coupling it with a saturated calomel electrode? Give the cell notation.

13. What is the relation between free energy change for a cell reaction and the cell emf? Derive Nernst equation for an electrochemical reaction, $aA + bB \rightleftharpoons cC + dD$.

14. a) Write an expression for the rotational energy in terms of wave number. Draw an energy level diagram and depict the spectral transitions using selection rules. Show that the rotational lines are equally spaced.

b) Which of the following exhibit microwave spectra: H_2, HCl, N_2, CO. [4 + 2]

15. a. Write the expression for (i) vibrational energy and (ii) zero point energy. Explain the terms. What is the significance of zero point energy?

b) Name the region of the electromagnetic spectrum associated with the change in (i) vibratonal state (ii) electronic state. [4 + 2]

16) a) Give the pictorial representation of the fundamental vibrations of CO_2 molecule and indicate the IR active modes.

b) The fundamental vibrational frequency of HCl is 2890 cm^{-1}. Calculate the force constant of this molecule. Given: reduced mass = 1.626×10^{-27} kg; c = 3×10^8 ms^{-1}.

[4 + 2]

17. a)Mention the gross and quantum selection rules of a molecule to be IR active. Give two differences between IR and Raman spectroscopy.

b) Define quantum yield of a photochemical process. [4 + 2]

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 weak base (NH_4OH) and strong acid (HCl) in the following cases:

(i) When NH_4OH is taken in the conductivity cell.

(ii) When NH_4OH is taken in the burette.

20. a) For N_2O molecule, all the vibrations are simultaneously Raman and IR active.
For CS_2 molecule, all the vibrations that are Raman active are IR inactive and vice versa.

Based on mutual selection rule and the above spectral data,

(i)what is the structure of N_2O? N–N–O or N–O–N ? Justify your answer.

(i)what is the structure of CS_2? C–S–S or S–C–S ? Justify your answer.

b) What happens to the intensity of the following when the temperature is increased from 25°C to 35°C (i) Stokes' line (ii) anti-Stokes' line. [3 + 2]

21. Give reasons:

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.

b) We observe an abnormal change in the transport number of cadmium in cadmium iodide solution at higher concentrations. [3 + 2]
