LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

THIRD SEMESTER – **APRIL 2022**

PCH 3602 – PHYSICAL CONCEPTS IN INORGANIC CHEMISTRY

Date: 24-06-2022 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

Part-A

Answer ALL questions. **(10 × 2 = 20)**

1. State Laporte selection rule.
2. Why is it customary to measure Stokes lines in Raman spectroscopy?
3. NMR spectra of paramagnetic materials is always difficult to measure and it is often done with diamagnetic dilution method. Why?
4. What is zero-field splitting? Cite an example.
5. Write the possible coordination mode exhibited by CO_3^{2-}.
6. Write the disadvantages of using dropping mercury electrode.
7. A solution of cadmium ions of concentration, 1.04 mM, has the diffusion current 8.76 μA and the capillary constant is found to be 1.987. Calculate the diffusion coefficient of Cd^{2+} ions.
8. Show that photoracemisation of chromium complexes follow an intramolecular mechanism.
9. What is a spectroelectrochemical technique? Cite its significance.
10. Sketch the energy level diagram for any one general scheme of photoinduced electron transfer reactions.

Part-B

Answer any EIGHT questions. **(8 × 5 = 40)**

11. Arrive all possible electronic term symbols for d^9 ion.
12. Describe the various possible coordination exhibited by sulphate and perchlorate ion. How are they differentiated by vibrational spectroscopy?
13. How are Racah parameter useful in quantify the covalency in the transition metal complexes?
14. The Mössbauer spectrum of $K_4[Fe(CN)_6]$ consists of one line whereas that of $K_3[Fe(CN)_5(NO)]$ consists of two lines with large quadrupole splitting value. Justify
15. Explain the origin of contact shift. Show that how they are useful in predicting covalency of metal-ligand bond.
16. How does light energy is converted to chemical energy using lamellar solids and thin films?

17a. Illustrate the importance of Randles-Sevick equation in voltammetry.

b. Mention the role of supporting electrolyte in voltammetric techniques. (3+2)

18. Explain the working of Honda cell for the photolysis of water.

19. Describe the photocarbonylation of hydrocarbons using $[RhCl(CO(PMe_3)_2]$.

20. State Adamson's rule and predict the product formed on the photo aquation of the following complexes.

(a) *Cis*-$[Cr(CO)_2(NH_3)_4]^{3+}$ (b) *Trans*-$[CrCl_2(NH_3)_4]^{+}$

21. Discuss Marcus theory of electron transfer reactions.

22. How do inner sphere complexes act as acceptors and donors in electron transfer reactions? Illustrate with examples.

Part-C

Answer any FOUR questions. **(4 × 10= 40)**

23a. The electronic spectrum (d-d) of the $[Ti(H_2O)_6]^{3+}$ is broad in nature. Why?

b. Construct the Tanabe-Sugano diagram for d^2 ion. (3+7)

24a. Draw the energy level diagram for a system with S = 5/2 and show the possible transitions in the presence and absence of applied magnetic field.

b. Illustrate the significance of isomer shift and quadrupole splitting values in studying oxidation state of the following iron complexes: $FeSO_4.7H_2O$ and $FeCl_3$. (5+5)

25a. Explain the significances of Jahn-Teller distortion in studying the electronic spectra of the transition metal complexes.

b. How many hyperfine lines would you expect in the EPR spectrum of $(NH_3)_5CoO_2Co(NH_3)_5$? (6+4)

26a. Describe the mechanism involved in the working of dye sensitised solar cells.

b. Write the principle of AC polarography and cite its advantages. (5+5)

27. Discuss the mechanism for the photosynthetic evolution of oxygen by manganese complexes.

28a Explain the electrochemistry and photophysics of monoquat (N-methyl-4,4'-bipyridine) Ru Complex.

b. What are metal-organic dyads? Explain the photoinduced electron transfer mechanism of any one type of meal-organic dyads. (5+5)

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