

[Ru(bpy)₃](Cl)₂ in dichloromethane. 2

8. a) The self-exchange rate between the couple Co(NH₃)₆³⁺/Co(NH₃)₆²⁺ is slow but that for Co(H₂O)₆³⁺/Co(H₂O)₆²⁺ is fast. Explain. 4
- b) Thermodynamically Cr(H₂O)₆²⁺ is a better reducing agent than V(H₂O)₆²⁺ but kinetically V(H₂O)₆²⁺ reduces Co(III) or Ru(III) complexes faster than Cr(H₂O)₆²⁺. Explain. 3
- c) MnO₄⁻/MnO₄²⁻ exchange rate in aqueous media is affected by metal ions in the order : Cs⁺>K⁺ or Na⁺>Li⁺. Comment. 2
- d) State any inner-sphere electron transfer reaction where bridging ligand is retained with the oxidizing centre. Discuss with proper reasoning. 3½

M. SC. CHEMISTRY EXAMINATION, 2019

(4th Semester)

INORGANIC CHEMISTRY SPECIAL

PAPER - XIV - I

Time : Two hours

Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - I - 4141

Answer *any five* of the following questions :

1. a) Why the contribution of diamagnetism due to the spinning motions of electrons and nucleus is negligible? 2
- b) Define magnetic permeability and susceptibility and establish their relationship. 3
2. a) Draw the nature of magnetic susceptibility vs temperature plot for dia-, paraferro- and anti-ferromagnetic systems. 2
- b) Discuss about the calculation of the Curie and Weiss constant from experimental temperature variation molar magnetic susceptibility data. 3
3. a) Derive the equation of orbital magnetic moment of an electron. 2

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- b) Calculate the magnetic moment (μ_J) of Nd^{3+} (f^3) and Sm^{3+} (f^5) systems. Comment on the values by comparing with the experimentally determined magnetic moment values ($\mu_{\text{exp}} = 3.5 - 3.6 \text{ B.M}$ for Nd^{3+} and $1.5 - 1.6 \text{ B.M}$. for Sm^{3+}) 3
4. a) Oxides of early elements of 3d (TiO, VO and CrO) are diamagnetic whereas latter element of 3d (MnO, FeO, CoO, NiO) are paramagnetic at high temperatures and exhibits ordered magnetic behaviour at low temperature. Explain. 3
- b) Write down with examples about metamagnetism. 2
5. a) Critically discuss about the nature of magnetic interaction observed in $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{Cu}(\text{HCOO})_2 \cdot 4\text{H}_2\text{O}$. 3
- b) Ferromagnetic properties of metals are independent of crystal structures. Explain with examples. 2
6. a) For the A and E ground state, μ_{eff} may be greater or less than μ_{spin} depending on the d^n configuration but for the T ground state, μ_{effect} is always greater than μ_{spin} . Explain. 2
- b) Define the following terms : Spin Canting, Remanent magnetization. magnetic frustration parameter. 3

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UNIT - I - 4142

Answer *all* the questions.

7. (a) What do you mean by Light Emission Sensitizers (LES)? Show schematically how LES function? What are the essential criteria of an ideal LES? 3
- (b) A cell consisting of two identical compartments separated by sintered glass disk contains a Pt electrode and aqueous solution of $[\text{Ru}(\text{bpy})_2]^{+2}$ and Fe^{3+} . What happens when one compartment is illuminated and the other is kept in the dark. Write your answer with appropriate reactions and scheme. 2
- (c) What do you mean by zero-zero spectroscopic energy (E_{0-0})? How E_{0-0} value of chemical species can be estimated? $1 \frac{1}{2}$
- (d) What happen if the photo-excited $^*[\text{Ru}(\text{bpy})_3]^{2+}$ complex is treated with $[\text{Cr}(\text{CN})_6]^{3-}$ and $\text{Cr}(\text{bpy})_3^{3+}$? 2
- (e) What do you mean by chemiluminescence? How does it differ from photoluminescence? 2
- (f) $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$ is photochemically inert in water but $[\text{Ru}(\text{bpy})_3](\text{Cl})_2$ is photochemically labile in dichloromethane at room temperature. Suggest a probable reason of the experimental finding and predict the final product that can be obtained from

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