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M.Sc. (CBCS) DEGREE EXAMINATION,
NOVEMBER 2012.

Third Semester

Chemistry

INORGANIC CHEMISTRY — III

(For those who joined in July 2008 and afterwards)

Time : Three hours

Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

1. Charge transfer bonds are more intense than d-d transitions. Why?
2. Write the ground state term symbol for d^3 and d^5 configurations.
3. The stretching vibrations occur generally at higher frequency than the bending modes. Why?
4. What is Doppler Shift?

5. Explain the term zero field splitting.
6. Sketch the ESR spectrum of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ and interpret.
7. What is oxygen over voltage?
8. What is meant by half wave potential?
9. State the laws of absorption.
10. Convert the following :
 - (a) 50% transmission into absorbance.
 - (b) 0.5% absorbance into % transmission.

PART B — (5 × 5 = 25 marks)

Answer ALL the questions, choosing either (a) or (b).

11. (a) Describe the changes that occur when $[\text{Ru}(\text{bpy})_3]^{2+}$ is photolysed. Comment on the excited states complex, its structure and redox behaviour.

Or

(b) Write briefly on charge transfer spectra.

12. (a) Explain the term chemical shift in photoelectron spectroscopy.

Or

- (b) Explain the MB spectrum of low spin and high spin Fe(II) and Fe(III) octahedral complexes.

13. (a) Explain with suitable example how ^1H - NMR can be used to study the fluxional behaviour in molecules.

Or

- (b) Sketch the EPR spectrum of bis(Salicylaldimine) copper (II) complexes and interpret.

14. (a) Discuss in detail the electrogravimetric analysis and its importance.

Or

- (b) Discuss the principle and procedure behind the coulometric titration of arsenite by bromine.

15. (a) How will you determine vitamin B₂ by fluorimetry?

Or

- (b) Describe the principle and applications of nephelometry.

PART C — (5 × 8 = 40 marks)

Answer ALL the questions, choosing either (a) or (b).

16. (a) Explain the electronic spectrum of d^3 ion in tetrahedral and octahedral field with Orgel diagram.

Or

- (b) How are the Orgel diagrams different from Tanabe-Sugano diagrams? Draw the Tanabe-Sugano diagrams for a d^6 complex and explain the possible transitions.

17. (a) Explain briefly how IR and Raman spectra are useful in the study of metal nitrosyls, geometrical and linkage isomerism, hydrogen bonding detection.

Or

- (b) Sketch and explain XPES of N₂ and NH₃.

18. (a) (i) Explain briefly on the use of shift reagents in NMR spectra.
- (ii) Explain the spin-spin splitting in NMR with a suitable example.

Or

- (b) State and explain Jahn-Teller effect. Explain how it can be studied spectroscopically.
19. (a) Discuss the basis of amperometric titrations. Illustrate by taking suitable examples.

Or

- (b) (i) Give an example of a supporting electrolyte and mention its role in polarography.
- (ii) Discuss the instrumentation of cyclic voltammetry.
20. (a) (i) Bring out any two differences between TGA and DTA.
- (ii) Compare DSC and DTA.

Or

- (b) Distinguish between atomic absorption and atomic emission. Give a block diagram of AAS and label the various parts. Give the merits and demerits of AAS.
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