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M.Sc. DEGREE EXAMINATION, NOVEMBER 2010

Third Semester

Faculty of Science

Branch III - Chemistry

Paper IX - INORGANIC CHEMISTRY - III

(Common with Paper IX of Branch IV-A. Analytical Chemistry)

Time: Three Hours

Maximum: 75 Marks

Section A

Answer any ten questions. Each question carries 2 marks.

- Sketch the unit cell of CaF₂.
- 2. Give the local symmetries of the As and NI atoms in a typical nickel arsenide structure.
- 3. Distinguish between fluorite and antifluorite structures. Give typical examples.
- 4. Sketch the first two brillouin zones of a square lattice in K-space.
- 5. Distinguish between piezoelectricity and ferroelectricity.
- Explain how Fe₃O₄ behaves on a ferrimagnetic material.
- 7. What are Pascal's constants? Comment on their utility in the studies of magnetic properties.
- 8. What are Ferritins?
- 9. Explain why calcium binding proteins are typically rich in asportate and glutamate structures.
- Give the co-ordination environment of cobalt in Vitamin B_{12(r)} and B_{12(s)}.
- How oxidative addition of dihydrogen take place in Wilkinson's catalyst during the hydrogenation of olefins.
- 12. Explain the functions of CuCl2 in the Wacker process.
- 13. Early transition metal halides can function as good Zeigler-Natta catalyst along with aluminium alkyls but not late transition metal halides. Explain, why?

 $(10 \times 2 = 20 \text{ marks})$

Section B

Answer any five questions. Each question carries 5 marks.

- Explain with suitable examples different types of intrinsic point defects in solids and suggest methods for determining the types of defects.
- Diffusion of atoms and ions in solids is considered as an activated process and the diffusion coefficients are generally dependent on the presence of defects. Justify the above statement.

Turn over

- Explain the origin of diamagnetic susceptibility in atoms and molecules and show that diamagnetic susceptibility is independent on H and T and dependent on radius of electron orbit.
- What are Bohr Magneton and Gyromagnetic ratio. Explain their significance in describing magnetic properties of materials.
- Considering the oxidation state and co-ordination environment of iron explain how the oxygen intake, transport and storage are achieved in Hemoglobin and Myoglobin.
- 19. What are ionophores? Give typical examples and explain their importance.
- Give the catalytic cycle for the convertion of propene to n-butyraldehyde using the catalyst HRh(CO)₄.
- 21. Suggest a suitable mechanism for the following reactions.
 - (a) $CH_3Mn(CO)_5 + CO \rightarrow (CH_3CO) Mn(CO)_5$
 - (b) $L_nM H + RCH = CH_2 \rightarrow L_nM CH_2 CH_2R$

 $(5 \times 5 = 25 \text{ marks})$

Section C

Answer any two questions. Each question carries 15 marks.

- 22. (a) Show that the energy of the free electrons in crystalline solids is related to the wave vector in a parabolic manner. (Assume that the potential energy is constant inside the solid).
 - (b) When a periodically varying potential field exist in a solid crystalline material. Show that there are allowed and forbidden zones for the movement of electrons in the wave vector diagram.

(7 + 8 = 15 marks)

- 23. (a) Explain the term spin-orbit coupling in the case of transition metal complexes and how is it determined. State its importance in describing magnetic properties.
 - (b) State and explain the Lande interval rule.
 - (c) Explain how spin-orbit coupling occur on A,E and T terms in octahedral field. (6 + 4 + 5 = 15 marks)
- 24. (a) Give the active sites of cytochrome C and discuss the mechanism of electron transport through cytochrome C.
 - (b) What are blue copper proteins? Give their active sites and explain their important functions. (7 + 8 = 15 marks)
- 25. (a) WCl₅ + [FtALCl₂]₂ can homogeneously catalyse alkene metathesis in ethanol. Give the mechanism of the reaction which invokes a carbene complex as the effective catalyst.
 - (b) Discuss the mechanism of mansanto acetic acid process. (8 + 7 = 15 marks) $(2 \times 15 = 30 \text{ marks})$