

RAJARATA UNIVERSITY OF SRI LANKA FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) Degree in Chemistry
Third Year - Semester I Examination - September / October 2019

CHE 3205 – ADVANCED INORGANIC CHEMISTRY I

Time: Two (02) hours

Answer only four (04) questions.

Use of a non-programmable calculator is permitted.

- 1. a) Consider following two complexes. Show that whether these complexes are high spin or low spin, find the number of unpaired electrons available and indicate the empty orbitals if there are any.
 - i. [Ni(CN)₄]²⁻

ii. $[Cu(NH_3)_4]^{2+}$

(30 marks)

- b) In the complex MX_6 , d orbitals are arranged in the following order in the energy level diagram from lowest to highest energy; d_{xy} , $(d_{xz} \& d_{yz})$. $d_x^2 \cdot g^2$, and d_z^2 respectively. Predict and justify the shape of the molecule and sketch the plausible electronic spectrum of the complex with the use of energy level diagram. (30 marks)
 - c) Justify the intense colour observed for the potassium permanganate. Give an approximate value for the molar absorptivity (\varepsilon) of this compound. (20 marks)
 - c) Briefly describe how electronic spectra arise.

(20 marks)

2. a) Determine the term symbol for H atom.

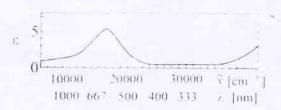
(20 marks)

b) Deduce the possible microstates for the complex [Cr(NH₃)₆]²⁺ and identify the ground state.

[30 marks]

Cont'd.

c) The complex $[Cr(H_2O)_6]^{2+}$ gives the spectrum below. Assign the transition/ transitions using an Orgel diagram.



(30 marks)

d) Defend the requirement of Tanabe-Sugano diagrams over simple Orgel diagrams in electronic spectroscopy. (20 marks)

3. a) Find the metal electron count of the each of following compounds.

i.
$$[PtCl_3(C_2F_4)]$$

11,

$$\begin{array}{c|c} & & & & \\ & & & & \\ & & & & \\ Bu^t & & & \\ Bu^t & & \\ & & & \\ Bu^t & & \\ &$$

111.

$$\begin{array}{c|c}
CI & H_2 \\
H_2N & CO & NH_2
\end{array}$$

$$\begin{array}{c|c}
H_2 & CH_2 \\
H_2C & NH_2 & H_2
\end{array}$$

(30 marks)

- b) All the transition metals (M) given are first row elements. Identify the metal in each case.
 - i. $[M(CO)_7]^+$ 18-electron species
 - ii. $[M(CO)_5]_2$ 18-electron species (assume M-M single bond)
 - iii. $[M(C_2H_4)_3]^+$ 16 electron species

(30 marks)

- c) The complex Mn(CO)₅ preferred to get dimerized. However, V(CO)₆ stay as it is. State the similarity of these two complexes and describe the reason for these two complexes to act differently.

 (20 marks)
- d) The complex[(C₅H₅)RuCl]₄ possesses a symmetrical structure with no metal-metal bonds.

 All the Ru metal sites obey the 18-electron rule. Predict the structure of this compound.

(20 marks)

- 4. a) Compare and contrast the bonding of transition metal-isocyanides and the bonding of transition metal-carbonyls. Use orbital pictures in your explanations. (40 marks)
 - b) Describe the ligand carbene. Explain Fisher type carbenes in detail. (40 marks)
 - c) Organometallic complexes formed through π electrons can be extended to metalocyclopropanes. Defend the statement using a proper example. (20 marks)
- 5. Propose a mechanism for the reaction given below which is catalyzed by the transition metal complex RhI₂(CO)₂ with trace HI. In the mechanism pathway, identify the oxidation state, coordination number and the number of valance electrons of the metal in each step. Indicate the reaction type in each step.

(100 marks)

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