RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Special) Degree in Chemistry
Third Year - Semester I Examination – June / July 2018

CHE 3205 – ADVANCED INORGANIC CHEMISTRY I

Answer **only four (04)** questions. **Time: Two (02) hours**

Use of a non-programmable calculator is permitted.

1. a) Transition metal complexes show different colours as well as different absorption intensities. Explain the molar absorptivity (ε) of the complexes given below.

Complex	ε (L mol^{-1} cm^{-1})
$[TiCl_6]^{2-}$	10000
$[CoBr_4]^{2-}$	500
$[Mn(H_2O)_6$	0.02

(25 marks)

b) Consider the 'd' atomic orbitals.

i. Name five types of 'd' orbitals. (5 marks)

ii. Explain the separation of 'd' orbitals into two energy levels named e_g and t_{2g} in an octahedral complex. (15 marks)

Cont.

iii. If there are only two energy levels, only one band should be observed in the UV-Vis spectrum. However, the octaheadral complex $[CuF_6]^{4-}$ shows two absorptions. Describe the observation. (25 marks)

iv. Jhan Tellar effect describes the spectra of distorted symmetry molecules. In such a molecule, if two ligands opposite to each other are compressed in an octahedral complex. Draw the orbital energy diagram. (30 marks)

2. Consider $[V(H_2O)_6]^{3+}$ complex

a) Find the 'd' electron count of the complex. (7 marks)

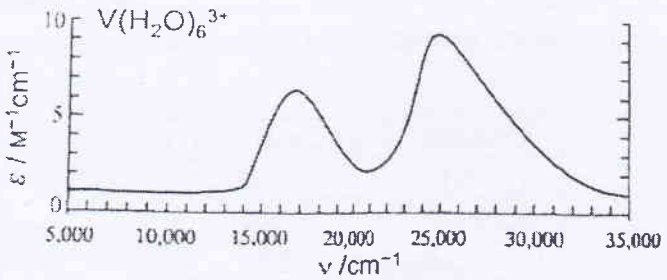
b) Obtain the spin multiplicity of vanadium in the complex. (7 marks)

c) Deduce the possible microstates. (25 marks)

d) Identify the ground state out of possible microstates and explain the reason for your identification. (23 marks)

e) Use a simplified Orgel diagram to predict the number of peaks in the electronic spectrum. (23 marks)

f) Figure given below shows the actual UV spectrum obtained. Compare and contrast the observed spectrum with your prediction. (15 marks)



3. a) State the requirement for a metal complex to be an organometallic complex. (10 marks)

b) Give the electron count of each of following compounds.

i. $[Fe(CO)_4]^{2-}$

ii. $[(\eta^5\text{-}C_5H_5)_2Co]^+$

iii. $(\eta^3\text{-}C_5H_5)\,(\eta^5\text{-}C_5H_5)Fe(CO)$

(30 marks)

c) 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)

d) Determine the specified quantity in each of the following.

i. The metal-metal bond order in $[(\eta^5\text{-}C_5H_5)Rh(CO)]_2$

ii. The expected charge, z on $[HRh(CO)(PPh_3)_3]^z$

(30 marks)

4. a) Compare and contrast the bonding of transition metal-carbonyls (M-CO) and the bonding of transition metal-phosphenes ($M\text{-}PR_3$). Use orbital diagrams in your explanations. (40 marks)

b) Transition metal complexes $[Mn(CO)_6]^+$, $Cr(CO)_6$, $V(CO)_6$ show absorption frequencies ν_1, ν_2, ν_3 respectively. Arrange three frequencies in increasing order and justify your answer. (30 marks)

c) With the use of orbital diagrams, explain the metal-ligand bonding through π electrons. Give two ligands as examples. (30 marks)

5. Propose a mechanism for the catalytic reaction given below which is catalyzed by the transition metal complex $HCo(CO)_3$.

$$CH_3CH{=}CH_2 + CO + H_2 \rightarrow CH_3CH_2CH_2CHO$$

In the mechanism pathway,

a) Identify the followings of the metal type in each step.

i) Oxidation state

ii) Coordination number

iii) Number of valance electrons

b) Indicate the reaction type in each step.

(100 marks)

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