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University Examinations 2023/2024

FIRST YEAR, FIRST SEMESTER EXAMINATION FOR THE DEGREE OF MASTER OF SCIENCE CHEMISTRY

SCH7112: ADVANCED COORDINATION CHEMISTRY

DATE: DECEMBER 2023 **TIME:3 HOURS**

INSTRUCTIONS: *answer question one and any other two questions*

TANABE SUGANO DIAGRAMS ARE ATTACHED.

QUESTION ONE (30 MARKS)

a) Explain why $[Mn(H_2O)_6]^{2+}$ is pale colored while $[MnCl_4]^{2-}$ is intensely colored. (4 marks)

b) Consider the electronic structure of the complex $[Fe(CN)_6]^{4-}$ and $[Fe(F)_6]^{4-}$ to answer the following questions

i. What is the ground state term of $[Fe(CN)_6]^{4-}$? (2 marks)

ii. What is the ground state term of $[Fe(F)_6]^{4-}$? (2 marks)

iii. Which transitions are spin allowed for $[Fe(F)_6]^{4-}$? Which transitions are spin allowed for $[Fe(CN)_6]^{4-}$? (6 marks)

c) Determine the electronic transition responsible for the purple color of the complex ion $[Ti(H_2O)6]^{3+}$. If the wavelength light required for this transition is 492.61nm calculate the amount energy associated with the electronic transition. ($h=6.626 \times 10^{-34}$j.s; 3.0×10^{8}m/s) (4 marks)

d) State franck-condon principle and explain its significance in absorption spectroscopy.

e) Explain why the emission spectra of molecules can be used in chemical analysis of substances.

f) Discuss three criteria of identifying the charge transfer band

g) Discuss the following two types of charge transfer

(i) Ligand-to-metal charge transfer

(ii) Metal-to-ligand charge transfer

h) Explain 'nephelauxetic effect'? (2 marks)

i) Place the following ligands in order of increasing nephelauxetic effect H_2O, I^-, F^-, en, CN^-, NH_3 (2 marks)

QUESTION TWO (15 MARKS)

a) With examples, explain what is meant by pi acceptor and pi donor ligands (4 marks)

b) Using relevant molecular orbital energy level diagrams of octahedral metal complexes, illustrate how ligand field theory accounts for spectrochemical series (11 marks)

QUESTION THREE (15 MARKS)

a) Determine the number of microstate in V^{3+} (4 marks)

b) Derive the microstates in V^{3+} and classify them into terms and provide their term symbols (6 marks)

c) Use hund's rule to arrange the terms obtained in (b) above in order of increasing energy (3 marks)

d) Splits the ground state terms into state using spin-orbital coupling and identify the new ground state term. (2 marks)

QUESTION FOUR (15 MARKS)

a) Use the value of pascal's constant in the table below to answer questions that follow.

The value of pascal's constant for different atoms and bonds	
$XM^{D\text{-atomic}}(10^{-6}cm^3mol^{-1}$	
H	-2.9
C	-6.0
C(aromatic)	-6.2
N	-5.6
N(aromatic)	-4.6
O	-4.6
Cl	-20.1

Calculate the molar diamagnetic susceptibility (XM^D) for

i) Pyridine (2 marks)

ii) Acetone (2 marks)

b) Explain the following terms

i) Magnetic permeability (1 mark)

ii) Magnetic Susceptibility (1 mark)

c) For each of the following state $^{2}D_{3/2}$, $^{3}F_{2}$, and $^{5}D_{0}$, determine effective magnetic moment where:

i) The resultant orbital motion (L) and resultant spin motion (s) contribute independently (3 marks)

ii) The resultant orbital motion (L) and resultant spin motion (s) couple with each other (3 marks)

iii) The resultant spin motion (s) contribute but resultant orbital motion (L) is quenched (3 marks)