M.Sc.Examination, 2018

Semester-I

Chemistry

Course: CH-701

(Inorganic Chemistry)

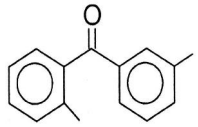
Time: Three Hours **Full Marks: 40**

Questions are of value as indicated in the margin.

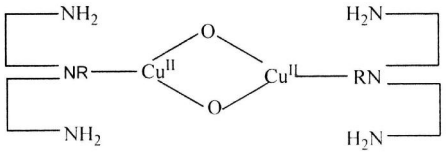
Answer ***any four*** questions.

1. a) What is the origin of diamagnetic correction? What are the utilities of Pascal constants? 2+2

   b) Calculate diamagnetic corrections of the following molecule using Pascal's constants. (Note you may use, C = –6.0, H = –2.93, O = –4.6, N(open chain) = –5.6, C=O = +6.3, C(ring portion) = –0.24, O(ketone) = +1.7, C=C = +5.5, N(aromatic) = –4.61, C(aromatic) = –6.24 etc., all units are in 10^{-6}c.g.s. units). 3



   c) The following is the relationship between Cu....Cu separation and magnetic exchange J values:



L = Separation beteween two Cu atoms

L (Å)	*J (Cm^{-1})*
2.601(1)	-10.2
2.701(1)	-18.1

On the basis of above data predict the type of magnetic exchange with explanation (Note: variations of bond distances due to different substitution in R; consider other parameters unchanged). 3

2. a) Calculated and Experimental Magnetic Moments for the following trivalent rare earths ions are:

Element	*Configuration*	$\mu_{eff(calculated)}$ *in B.M.*	$\mu_{eff(found)}$ *in B.M.*
Ce^{3+}	$4f^1$	2.54	2.5
Nd^{3+}	$4f^3$	3.58	3.5
Sm^{3+}	$4f^5$	0.84	1.5

Explain with detail justification (Note: Calculations should be provided). 2+2+2

   b) Explain the term High spin (HS), low spin (LS) and intermediate spin (IS). Predict the condition(s) including geometrical preferences of their (HS, LS and IS) existence? Take suitable example(s) to justify existence of HS, LS and IS systems. 4

3. a) The absorption energies of $K_3[TiBr_6]$, $Na_3[TiCl_6]$, $K_3[Ti(CN)_6]$ and $[Ti(H_2O)_6](ClO_4)_3$ are respectively at 10.5, 13.0, 22.3 and 20.3 kK (1 kK = 1000 cm^{-1}) – Explain. Predict the expected magnetic moment of these compounds. 3

P.T.O.

b) Compare qualitatively characteristics of d-d spectra with that of f-f (lanthanide only) spectra. The spectral characteristics of actinides before and after the Am-Cm region are different why? 2+2

c) $[Mn(H_2O)_6](ClO_4)_2$ and $KMnO_4$ respectively have molar extinction coefficient (M^{-1} Cm^{-1}) of $\in < 0.1$ and $\in >> 1,000$ – Explain. The magnetic moments are respectively 5.90 and 0.18 B. M. (at 300 K) – Explain. 3

4. a) What are the metal 'd' orbitals involved in sp^3d^2 covalent octahedral hybrid for directional bond formation and why? 2

b) Write down the six equivalent octahedral hybrid orbitals formed from two 'd' orbitals, the s-orbital and the three p orbitals. 4

c) Covalent compounds of Co(II) decomposes water with the liberation of hydrogen – Explain the fact employing VBT model. 2

d) Ni(II) undergoes dsp^2 to adopt square planar geometry rather than tetrahedral – Explain. 2

5. a) The greater strength of dsp^2 bonds over sp^3 bonds is the determining factor to adopt the geometry in Cu(II) complexes – Explain. 2

b) Write down the basic principle of VSEPR theory in adopting the geometry in complexes. 4

c) Write down the octahedral spliting of metal 'd' orbitals and why it remains as such after complexation?
The regular octahedral geometry gets disturbed in Ni(II) and Cu(II) to convert into square planar – Explain in terms of CFT. 4

6. a) What is spectrochemical series? Discuss the drawbacks of CFT in explaining the series. 3

b) What are the metal orbitals are used in σ-bonds in an octahrdral (O_h symmetry) complex? Classify their symmetry and degeneracy. 2

c) Give the MO diagram of $\left[Co\left(NH_3\right)_6\right]^{3+}$ and discuss the importance of this diagram in explaining the spectral and magnetic properties various d^n-systems. 3+2+5

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