CHEM F214: Inorganic Chemistry-II   (Closed Book)   Max. Marks: 50
Time: 70 mins.   Date: 09.03.2022

Instructions to the students:
1. There are **four questions** in all. Attempt all the questions.
2. Start answering each question on a fresh page. **Answer all parts of a question together.**
3. Write brief answers to the point with proper justifications.
4. Atomic number of Co = 27, Fe = 26, Ni = 28, Mn = 25, Cu = 29, Pt = 78, Al = 13, Cr = 24, V = 23.

Q. 1. Tetrahedral complexes of Co^{2+} such as $[CoCl_4]^{2-}$ are intensely blue in color with an intensity ε of about 600 l/mol/cm compared with the pale pink color of octahedral complexes. <u>Given</u>, the order of levels in a tetrahedral field arising from Mulliken symbols for spectroscopic term, **S:** A_1, **P:** T_1, **D:** $E + T_2$, **F:** $A_2 + T_2 + T_1$ and **G:** $A_1 + E + T_1 + T_2$. Answer the following questions. **[6+5]**

(a) Show the Orgel diagram with proper labeling and assign all the probable transitions using Mulliken symbols in $[CoCl_4]^{2-}$ complex. Identify the lowest energy electronic transition in $[CoCl_4]^{2-}$ complex.
(b) What is non-crossing rule in light of electronic spectroscopy? Is it applicable in $[CoCl_6]^{4-}$ octahedral complex while representing the energy levels during electronic transition? Justify your answer.

Q. 2. (a) In an octahedral field the electronic spectrum of $[FeF_6]^{3-}$ complex shows up to ten extremely weak absorption bands. The molar absorption coefficient ε is about 0.02 - 0.03 l/mol/cm. This accounts for the very pale violet color of the complex. Discuss in brief how ten absorption bands are possible in $[FeF_6]^{3-}$ complex. The possible terms for d^5 configuration are ^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2F, ^2D, ^2P, ^2S.

(b) Draw a crystal field splitting diagram for a complex in a linear field and justify your answer in brief for the splitting pattern. Assume that the ligands lie on the Z-axis.

(c) Explain why the difference in energy between the d_{x2-y2} and d_{xy} orbitals in a square planar field is identical to the difference between the same orbitals in the octahedral field.

(d) A solution of $[Ni(H_2O)_6]^{2+}$ is green, but a solution of $[Ni(CN)_4]^{2-}$ is colorless. Suggest an explanation for these observations. **[4+5+4+4]**

Q. 3. (a) Identify the type of distortion (natural or Jahn-Teller) in the following complex. Justify your answer (in brief) in light of additional stabilization (<u>if necessary</u>) with respect to that of the perfectly octahedral complex. $[VO(OH_2)_5]^{2+}$

(b) Justify the following statement with an example. For the d^8-system, no J.T. distortion is expected in the octahedral complexes. However, the J.T. distortion can be imposed under the conditions of strong crystal field splitting and low pairing energy.

(c) Identify the exact spinel structure of $NiAl_2O_4$ compound, where, oxide ion behave as weak ligand field. Discuss your identification in light of CFSE. **[3+4+5]**

Q. 4. (a) BCl_3 is an example of D_{3h} point group. The probable symmetry elements are E, $2C_3$, $3C_2$, σ_h, $2S_3$, and $3\sigma_v$. The expression of τ_{3N} for 3N degree of freedom of BCl_3 molecule is given below. Answer the following questions.

$$\tau_{3N} = A_1' + A_2' + 3E' + \mathbf{P}A_2'' + E''$$

Identify the number of unshifted atom and contribution per atom for S_3 symmetry operation. Calculate the value of **P** associated with A_2'' symbol in the above equation? Using the expression of τ_{vib} identify the number of Raman active modes present in BCl_3 molecule and justify your answer in favor of Raman activity. <u>Given that</u>, contribution per atom for the symmetry elements, E = 3, C_2 = -1, C_3 = 0, and σ = 1.

[6+4]

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

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