

- 1.a. How many spherical (radial) nodes does $5s$ orbital have? 2%
- b. How many angular nodes does $5f_{yz}$ orbital have? 2%
- c. Select the better choice and explain your selection briefly.
- (i). Higher ionization energy: Mg or Al 3%
- (ii). Higher electron affinity: S or Cl 3%
- 2.a. Draw the molecular structure of the following species: 4%
- (i). SNF_3 (S is central) (ii). SeOCl_4 (Se is central)
- b. What is the point group of the following species: 6%
- (i). $\text{B}_3\text{N}_3\text{H}_6$ (planar) (ii). N_2H_4 (iii). BrF_5
3. Using the D_{4h} character table:
- a. Determine the order of the group. 1%
- b. Verify that the E_g irreducible representation is orthogonal to the E_u irreducible representation. 3%
- c. Determine the number of Raman active C-O stretching vibrations for *trans*- $[\text{Fe}(\text{CO})_4\text{Br}_2]$. 5%
- d. Determine the types of hybridization possible for a $[\text{PtCl}_4]^{2-}$ complex (consider hybrids used in σ bonding only). 5%

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	Rz	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x^2-y^2
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(Rx,Ry)	(xz,yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-2	0	2	0	0	(x,y)	

4. Select the better choice and explain your selection briefly. 6%
- a. Strongest Lewis acid: BF_3 BCl_3 BI_3
- b. Strongest protonic acid: $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ H_2O
- c. More basic toward BMe_3 : 4-methylpyridine 2-methylpyridine pyridine
- 5.a. Given $E^{\circ}_A = 0.34 \text{ V}$ for $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ and K_{sp} for $\text{Cu}(\text{OH})_2$ is 1.6×10^{-19} . Calculate the *emf* for $\text{Cu}(\text{OH})_2 \rightarrow \text{Cu}$ in 1 M base. 5%
- b. Calculate the ideal ratio of r_M/r_X for cation-anion and anion-anion contact for an octahedral arrangement of anions around a cation. (Hint: the NaCl structure) 5%

- 6.a. Determine the number of unpaired electrons and calculate the magnetic moment for the spin-only contribution and the LFSE for $[\text{Ru}(\text{NH}_3)_6]^{3+}$. 6%
- b. For which d^n configurations would **no** Jahn-Teller splitting be expected for the tetrahedral case (ignore possible low-spin cases)? ($n = 1\sim 10$) 4%

- 7.a. Identify the ground-state terms with the spin multiplicity for Fe^{2+} in the following cases: 6%
- a free ion
 - an high-spin octahedral complex
 - a low-spin octahedral complex

- b. Show the number of d-d transition bands in terms of spectrum terms for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. 4%

- 8.a. Consider the half-lives (in minutes) toward substitution of the pair of complexes: 6%

Half-lives less than 1 minute	Half-lives greater than 1 day
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Fe}(\text{CN})_6]^{4-}$

Explain the differences in half-lives in terms of the electronic structures.

- b. Activation volume (ΔV^\ddagger) for acid hydrolysis of *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ is -9.5 (at 45°C) cm^3/mol . 4%
How is the value consistent with what you know about the mechanism for square-planar substitution?

- 9.a. Classify the following species as *closo*, *nido*, *arachno* or *hypho* structure type. 6%
- $\text{B}_{10}\text{H}_{14}$
 - $\text{C}_4\text{B}_2\text{H}_6$
 - $\text{Rh}_6(\text{CO})_{16}$

- b. Which of the following enzymes contains Fe? 4%
- hemoglobin chlorophyll a coenzyme B₁₂ cytochrome c

10. Predict the transition metal-containing products of the following reactions:

