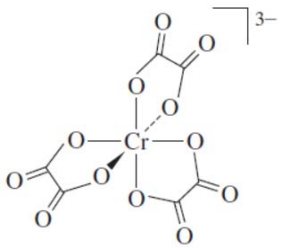
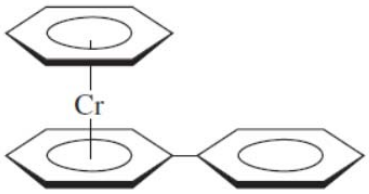
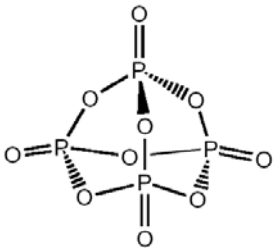
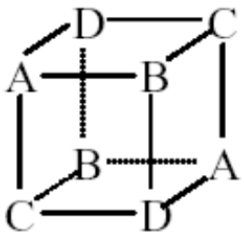
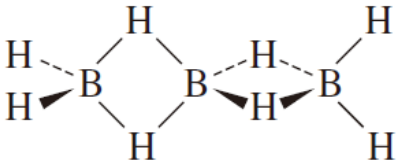
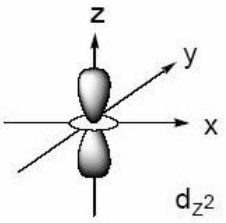
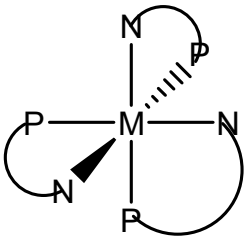
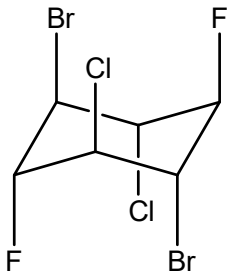
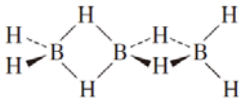
2020 CHEM754 Final

Name _____ ID number _____

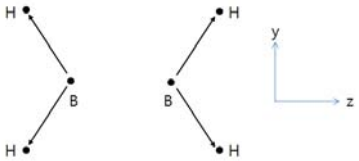
1. (10) Point groups?

Structure	Point group	Structure	Point group
$[Cr(ox)_3]^{-3}$ 			
$P_4O_{10}^{-4}$ 			
B_3H_8 			
			
H_2O			

2. (10) Following is the structure of diborane.



To derive the terminal B-H stretching vibrational modes, 4 terminal B-H stretchings are depicted as following.



(a) Find the reducible representation ($\Gamma_{str(B-H)}$) for the 4 terminal B-H stretchings of the figure.
(b) Reduce the reducible representation ($\Gamma_{str(B-H)}$).
(c) Sketch the Raman-active vibrational modes and identify their symmetry types.
(d) Sketch the IR-active vibrational modes and identify their symmetry types.

3. (15) Following is the method to construct the MOs of NH_3.

(a) Derive the group orbitals of three outer H 1s orbitals by using projection operator method. Sketch the group orbitals.

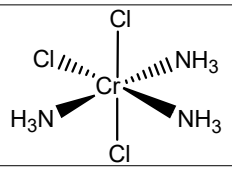
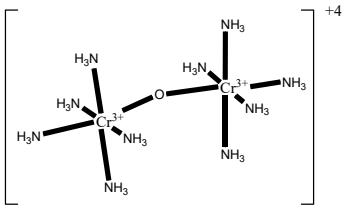
(b) What are the symmetry types of the valence orbitals of N atom.

(c) Draw the MO energy level diagram of NH_3.

(d) What is the name of LUMO of NH_3? Sketch the shape of LUMO.

4. (10)

(a) Fill the blanks.

Nomenclature	Structure or Chemical formula
	
tetracyanonickelate(II)	formula
	$[Co(en)_2CO_3]Br$
	
trans-$[Pt(NH_3)_2BrCl]$	structure

(b) Draw all the isomers of ***mer*-[M(ABC)(NH_3)(H_2O)Br]**. (ABC = H_2N-C_2H_4-PH-C_2H_4-AsH_2 = N—P—As tridentate ligand) Boxes are given more than needed. If there is enantiomer pair(s), draw the pair(s) side by side as in the table.)

enantiomer pair		enantiomer pair	

5. (15) Let's construct the MO energy level diagram of a **trigonal bipyramidal** complex (ML_5) by using ligand field theory. **(L is a σ-donor ligand.)**

(a) Determine the symmetry types of 3d, 4s, 4p orbitals of metal M.

$3d_{z2}$		$3d_{x2-y2}$		$3d_{xy}$		$3d_{yz}$		$3d_{xz}$	
4s		$4p_x$		$4p_y$		$4p_z$			

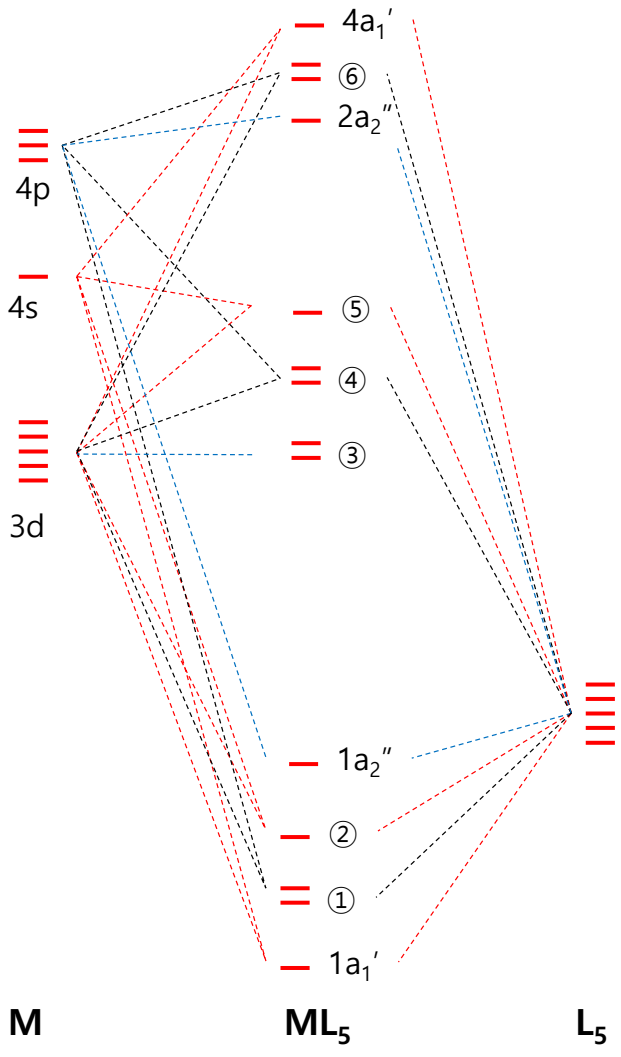
(b) Find the reducible representation(Γ) for the 5 σ-donor orbitals of ML_5.

	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v
Γ	5					

(c) Reduce the irreducible representation.

Γ	

Right is the MO energy level diagram of ML_5.



(d) What are the names of the orbitals?

①	②	③
④	⑤	⑥

(e) Sketch the shapes of orbitals $4a_1$' and ③. (For $4a_1$', assume there is no contribution of 3d orbital. For ③, specifiy the axes on your sketches.)

$4a_1$'	

③-1		③-2	

6. (10) Let's construct the orbital energy level diagram of a **trigonal bipyramidal** complex (ML_5) by using angular overlap model. (**L is a π-acceptor ligand.**)

(a) Calculate the strength of σ-interactions of d orbitals.

(b) Calculate the strength of σ-interactions of ligands.

(c) Calculate the strength of π-acceptor interactions of d orbitals.

(d) Calculate the strength of π-interactions of ligands.

(e) Draw the orbital energy level diagram of ML_5.

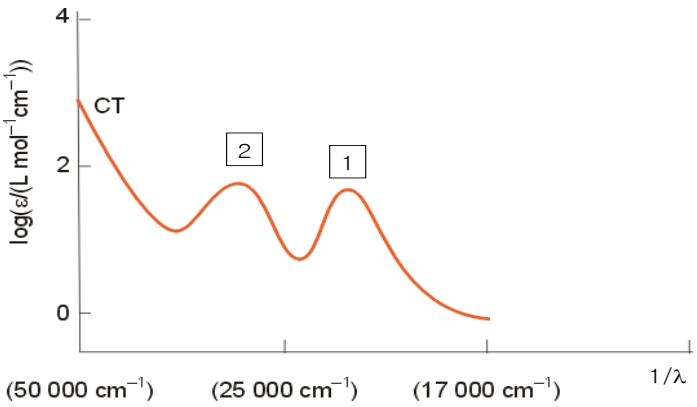
7. (10) Fill the blanks. (All complexes are octahedral.)

Complexe	number of unpaired electrons	LFSE(Δ_o)	Jahn-Teller Effect (yes or no)	Free ion term symbols of metal ion (ground state)
$[Fe(CN)_6]^{4-}$				
$[Mn(H_2O)_6]^{3+}$				
$[Co(H_2O)_6]^{3+}$				
$[Cu(en)_2(H_2O)_6]^{2+}$				
$[Ni(H_2O)_6]^{3+}$				

8. (5) Fill the blanks.

term symbol	S	L	number of microstates
	0	1	
^3P			
^4F			
$^4A_{2g}$			
$^2T_{2g}$			

9. (15) Figure is the UV/VIS absorption spectrum of $Cr(NH_3)_6^{3+}$. Table 1 is the microstate table for d^3. (x is a microstate.)



(a) Write alll the electron configurations for M_S = 1/2, M_L = 2. (as in the box of M_S = -1/2, M_L = 5)

(b) Write all the term symbols of free Cr^{3+}.

Table 1.

M_L \ M_S	3/2	1/2	-1/2	-3/2
5		x	(2+,2-,1-)	
4		x x	x x	
3	x	x x x x	x x x x	x
2	x			x
1	x x	x x x x x x x	x x x x x x x	x x
0	x x	x x x x x x x	x x x x x x x	x x
-1	x x	x x x x x x x	x x x x x x x	x x
-2	x			x
-3	x	x x x x	x x x x	x
-4		x x	x x	
-5		x	x	

(c) Fill the blanks for Cr^{3+}.

	Free ion term symbol	Term symbol(s) in octahedral field
Ground state		
Excited state(s) with the same spin multiplicity as the ground state		

(d) Mark the d-electron configure of $^4A_{2g}$ and $^4T_{2g}$ terms using arrows on the figure below and calculate LFSE.

Term	electron configuration	LFSE(Δ_o)	Term	electron configuration	LFSE(Δ_o)
$^4A_{2g}$	— — e_g — — — t_{2g}		$^4T_{2g}$	— — e_g — — — t_{2g}	

(e) Identify the transitions corresponding to the absorption bands 1 and 2 of the UV/VIS absorption spectrum of $Cr(NH_3)_6^{3+}$, respectively.

1		2	

(f) Estimate ligand splitting parameter(Δ_o) of $Cr(NH_3)_6^{3+}$.

Δ_o = _____ cm^{-1}