

Inorganic Chemistry 411/511 Final Exam Name _____
 115 minutes; 200 points total Show your work for partial credit.

1. Draw the molecular geometry and indicate any deviations from ideal VSEPR coordination angles. Give the point group for each molecule.

(a) [10 pts] PCl_3

Tri pyr, C_{3v}
 $\text{ClPCl} < 109^\circ$

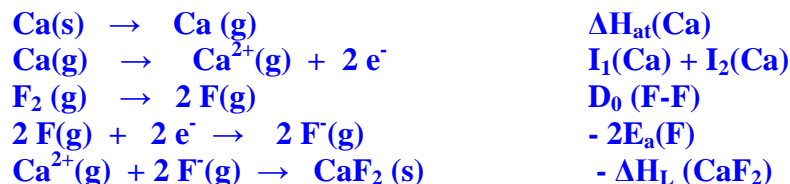
(b) [10 pts] XeF_5^+

square pyramidal, C_{4v}
 $\text{FXeF} < 90^\circ$

(c) [7 pts] Is either of the above molecules chiral? Explain using symmetry rules.

No, they both have mirror plane operations.

2. (a) [12 pts] Write down a Born-Haber analysis (give all the reaction steps) needed to estimate ΔH_f for $\text{CaF}_2(\text{s})$ from the elements in standard states. Label each reaction step with an appropriate energy term (such as I , E_a , ΔH_L , etc, be sure to indicate a negative sign where needed).



Correct reactions steps [5]

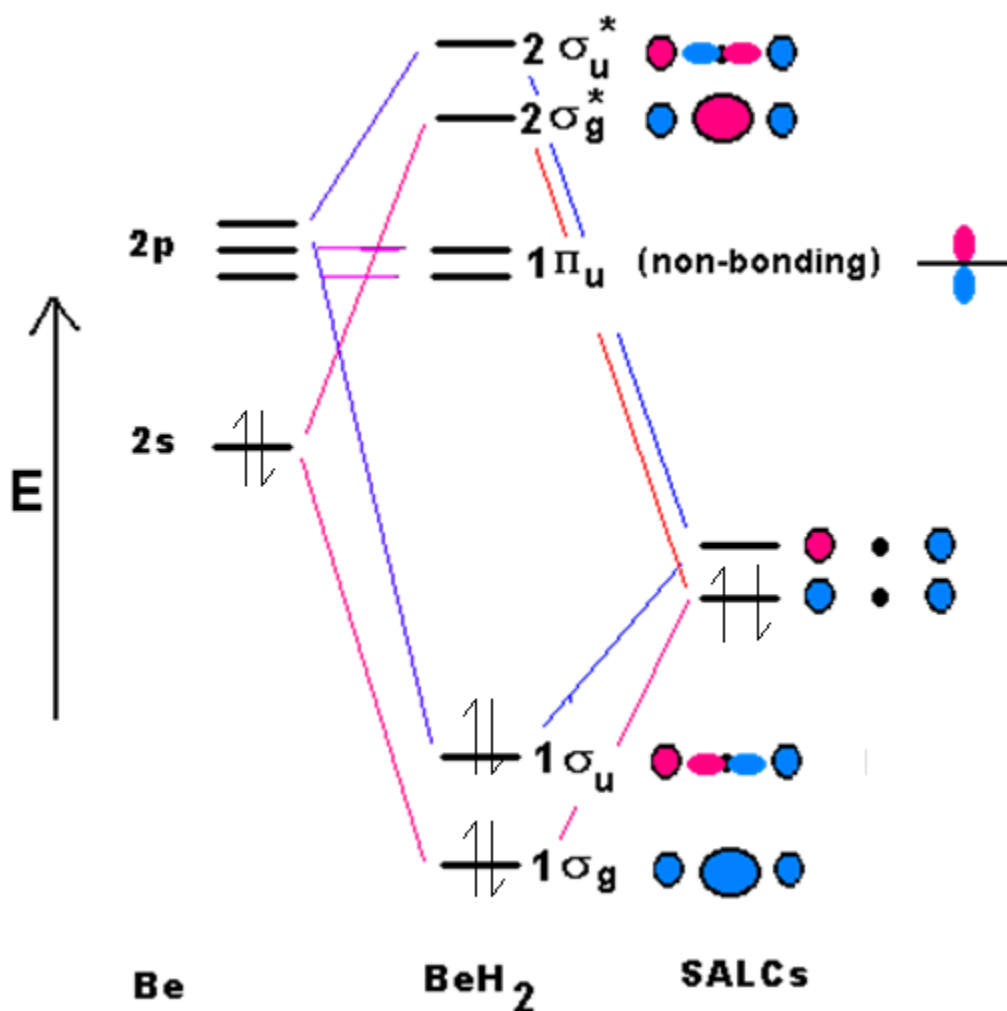
Correct label for energetics (I , E_a , ΔH_L , etc) [4]

Correct summation and signs [3]

(b) [7 pts] Predict whether $\text{CaF}_2(\text{s})$ more or less soluble in water than $\text{KF}(\text{s})$, and explain why.

Much less soluble. CaF_2 has a much larger lattice enthalpy due to the higher ion charge on Ca^{2+} , this opposes ion solvation.

3. (a) [14 pts] Construct an MO diagram for the BeH_2 (g), including valence atomic and molecular orbitals, symmetry labels, and the electron filling of the atomic orbitals and MO's.



- (b) [6 pts] Draw a figure showing the geometry of the HOMO orbital in BeH_2 .



- (c) [4 pts] Using MO concepts instead of VSEPR, explain why BeH_2 is linear but OH_2 is bent.

Adding electrons above the first sigma levels will be more favorable when the occupied levels have a central atom p-lobe contribution oriented towards the in-phase ligand combination (i.e. an a1 type orbital rather than a pi type orbital).

4. A Latimer diagram for V at pH=14 is:



(a) [10 pts] What is the standard potential for reduction of VO_4^{3-} to V at pH=14 ?

$$[2.19 + 0.54 + (-0.49) + 2(-0.82)] / 5 = +0.12 \text{ V}$$

(b) [10 pts] Does VO disproportionate spontaneously in aqueous base? Explain.

No. The reaction $\text{VO} \rightarrow \text{V}$ is -0.82 V , when combined with $\text{VO} \rightarrow \text{V}_2\text{O}_3$ ($+0.49 \text{ V}$) or any other oxidation, gives an overall negative potential.

(c) [10 pts] Write a balanced half-reaction for the oxidation of V to VO_4^{3-} in basic solution.



(d) [5 pts] Will the potential for the oxidation in part (c) increase or decrease when the pH is decreased from 14 to 12? Explain.

The potential will decrease. As pH decreases, $[\text{OH}^-]$ decreases. Since OH^- is a reactant, this makes the reaction less favorable.

(e) [7 pts] Using your results from parts (a) and (c) above, calculate the potential for the half-reaction in part (c) at pH = 12.

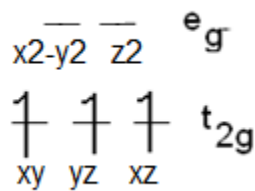
The Nernst equation is $E = E^0 - (0.059 \text{ V} / n) \log Q$

$$E = -0.12 \text{ V} - (2)(8)(0.059) / 5 = -0.31 \text{ V}$$

5. (a) [6 pts] Write out the full name of the octahedral complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$

hexamminechromium (III) or hexaamminechromium(3+)

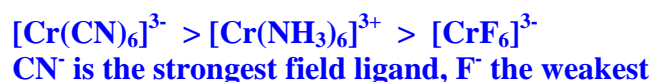
- (b) [8 pts] Write a d orbital energy level diagram for $[\text{Cr}(\text{NH}_3)_6]^{3+}$. Label the d-orbitals with (z^2 , x^2-y^2 , xy , xz , and yz) and also give the orbitals symmetry labels.



- (c) [6 pts] Calculate the ligand field stabilization energy (LFSE) in terms of Δ_O for the electron configuration in part (a).

$$\text{LFSE} = 1.2 \Delta_O$$

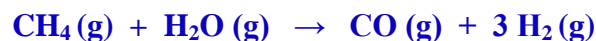
- (d) [8 pts] Rank the following in terms of high LFSE to low LFSE; $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{CrF}_6]^{3-}$, and $[\text{Cr}(\text{CN})_6]^{3-}$, ? Explain.



- (e) [6 pts] How could you experimentally confirm the relative Δ_O values in part (d)?

Analysis of uv-vis absorbance spectroscopy can give the splitting parameters.

6. (a) [10 pts] Write a balanced reaction showing how H_2 is generated on an industrial scale.



Or



Or, electrolysis is OK

- (b) **[8 pts]** Describe briefly 2 important ways that hydrogen bonding affects our daily lives.

1. Lower density of ice than water
2. DNA replication
3. High bp of liquid water.

7. **[4 pts each]** Circle the ONE best choice.

- (a) The NiAs structure has the stacking sequence of (AcBc)_n, where uppercase letters are anions and lowercase are cations. What is the coordination geometry around anions in the lattice?
 (1) tetrahedral (2) square planar (3) octahedral
(4) trigonal prismatic (5) linear (6) pyramidal
- (b) The following complexes are all high spin. Which has a ligand field stabilization energy equal to zero?
 (1) [Fe(OH₂)₆]²⁺ (2) **[Fe(OH₂)₆]³⁺** (3) [Mn(OH₂)₆]³⁺
 (4) [Co(OH₂)₆]²⁺ (5) all these complexes have the same LFSE
- (c) Which of the following octahedral complexes has the most geometric isomers?
 (1) [FeCl(OH₂)₅]²⁺ (2) [IrCl₃F₃]²⁻ (3) [RuCl₄(bipy)]²⁻
(4) [CoBr₂Cl₂(NH₃)₂]⁺ (5) [W(CO)₆] (6) [CrCl₅(NH₃)]²⁻
- (d) Which ligand will form the strongest complex with Au⁺ ?
 (1) O²⁻ (2) F⁻ **(3) S²⁻** (4) OH₂
 (5) all complexes will have the same K_f
- (e) Which ligand is a π-donor with a weak ligand field effect?
 (1) N(CH₃)₃ (2) H⁻ (3) CN⁻ **(4) Cl⁻** (5) NH₃ (6) P(CH₃)₃
- (f) Based on d electron configurations, which of the following is NOT likely to be square planar?
 (1) [IrCl₄]³⁻ (2) [AuF₄]¹⁻ (3) [Pd(CN)₄]²⁻ (4) [RhF₄]³⁻ **(5) [AgCl₄]²⁻**
- (g) The anion XeF₅⁻ shows only a single ¹⁹F NMR peak over a wide temperature range (ignoring coupling to ¹²⁹Xe). Which geometry is consistent with this data?

- (1) trigonal bipyramidal (2) square pyramidal
(3) pentagonal planar (4) linear
 (5) rhomboidal (6) cubic

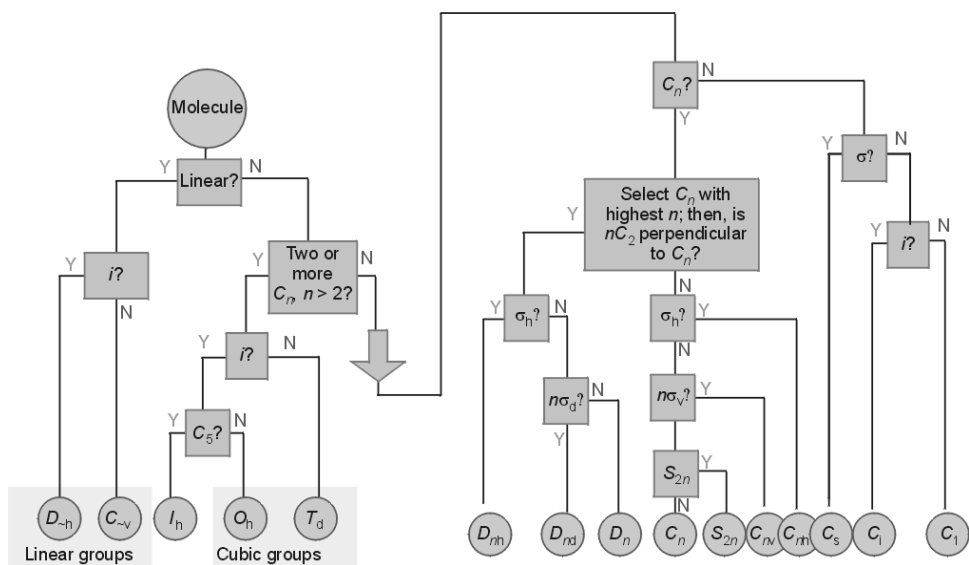
(h) Which of the following will rapidly react with water to form H_2 ?

- (1) O_2 (2) Cl_2 (3) HF **(4) LiH** (5) SF_6 (6) $Ca(OH)_2$

(i) Using Pauling's rules, what is the expected pK_a for hypochlorous acid?

- (1) 0 (2) 1 (3) 3 (4) 5 (5) 7 **(6) 8**

1 H																	18 He	
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac	104	105	106	107	108	109	110	111	112							
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		



O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
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	
E_g	2	-1	0	0	2	2	0	-1	2	0	(z^2, x^2-y^2)
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	