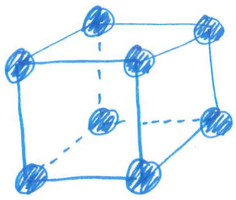
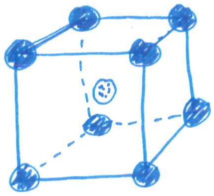
Problem Set #4 | **KEY** | Chem 417
November 14, 2012 | ***Due Friday November 30, 2012*** | Fall 2012

Solids and Transition Metal Complexes

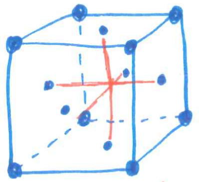
1. Sketch cubic, body-centered cubic and face-centered cubic unit cells. How many atoms are in each unit cell?



simple cubic
1 atom per u.c.



⊛ at body center
2 atom per u.c.
bcc



red lines a guide to the eye.
4 atom per u.c.
fcc

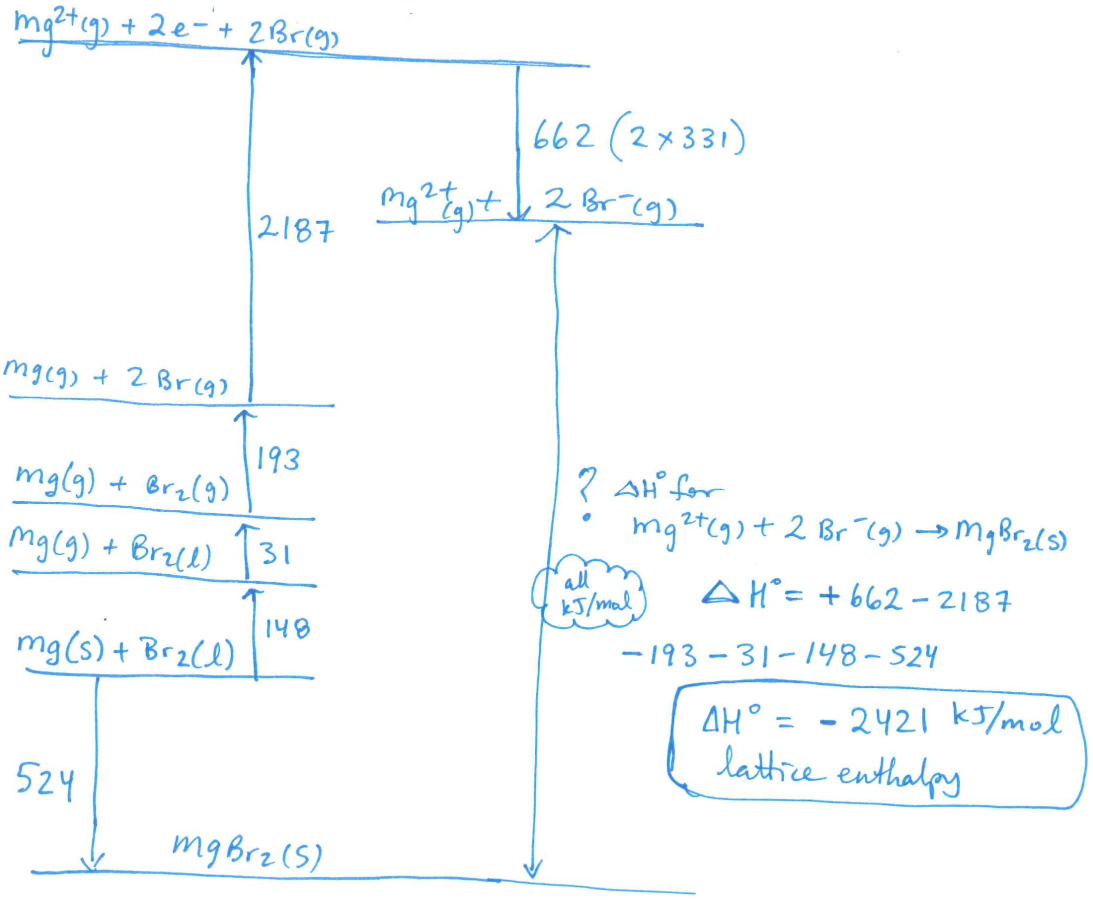
2. Describe what is meant by intrinsic and extrinsic semiconductors. Please give an example of an intrinsic semiconductor and examples of extrinsic (doped) semiconductors of different types. Explain how and why metals and semiconductors differ in their relationship of conductivity to temperature.

An example of an intrinsic semiconductor is silicon (Si). Others are germanium (Ge) and gallium arsenide (GaAs).
Extrinsic semiconductors are either p-doped or n-doped.
An example of a p-doped semiconductor is silicon doped with boron. (Boron has one less valence e^- than Silicon.) An example of an n-doped semiconductor is silicon doped with phosphorus. (Phosphorus has one more valence e^- than silicon.)
metal's conductivity decreases as temperature is raised because increased lattice vibrations give more resistance to electron flow. Semiconductor conductivity increases as temperature is raised because higher temperature means more thermal energy to promote electrons from the valence band to the conduction band.

3. Draw a Born-Haber cycle (roughly to scale) for the formation of $MgBr_2$. Also show how the problem is solved with a Hess's Law style summing of reactions. Determine the lattice enthalpy of $MgBr_2$ ($Mg^{2+}(g) + 2\ Br^{-}(g) \rightarrow MgBr_2(s)$) by both methods (which should give the same answer!).

Use the following data:

reaction	ΔH° (kJ/mol)
sublimation of $Mg(s)$	+148
ionization of $Mg(g)$ to $Mg^{2+}(g)$	+2187
vaporization of $Br_2(l)$	+31
dissociation of $Br_2(g)$	+193
electron attachment to $Br(g)$	-331
formation of $MgBr_2(s)$	-524



? ΔH° for

$Mg^{2+}(g) + 2\ Br^-(g) \rightarrow MgBr_2(s)$

$\Delta H^\circ = +662 - 2187 - 193 - 31 - 148 - 524$

$\boxed{\Delta H^\circ = -2421 \text{ kJ/mol lattice enthalpy}}$

2 × (+331)

all kJ/mol

Try it the Hess's Law way:

$$Mg^{2+}_{(g)} + \cancel{2e^-} \longrightarrow \cancel{Mg(g)} \qquad \Delta H° = -2187$$

$$2\,Br^-_{(g)} \longrightarrow 2\,\cancel{Br_{(g)}} + \cancel{2e^-} \qquad \Delta H° = +662$$

$$\cancel{Mg(s)} + \cancel{Br_2(l)} \longrightarrow MgBr_2(s) \qquad \Delta H° = -524$$

$$\cancel{Br_2(g)} \longrightarrow \cancel{Br_2(l)} \qquad \Delta H° = -31$$

$$2\,\cancel{Br(g)} \longrightarrow \cancel{Br_2(g)} \qquad \Delta H° = -193$$

$$\cancel{Mg(g)} \longrightarrow \cancel{Mg(s)} \qquad \Delta H° = -148$$

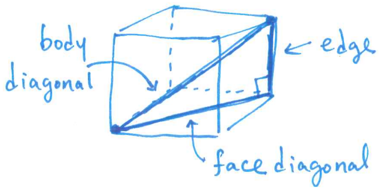
$$Mg^{2+}_{(g)} + 2\,Br^-_{(g)} \longrightarrow MgBr_2(s) \qquad \Delta H° = -2421 \text{ kJ/mol}$$

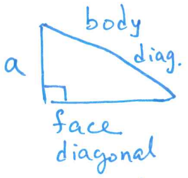
4. CaO is harder and has a higher melting point than KF. Both salts have the same type of structure (NaCl structure). Explain the difference between the two salts.

Ca^{2+} and O^{2-} have higher charges and thus higher lattice enthalpy than do K^+ and F^-.

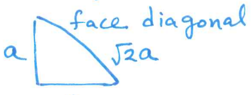
5. Use geometry and the Pythagorean theorem to determine what percentage of space in a bcc unit cell is filled by the spheres. (All spheres are the same size.)

Need the relationship between edge length and sphere radius. The spheres <u>do not</u> touch along the edges but do touch along the body diagonal. Define "a" as the edge length. The body diagonal is 4r. How to get "a" in terms of r? There is a right triangle within the cube that contains the body diagonal.





The face diagonal is in another right triangle:



So, since face diagonal is $\sqrt{2}a$, body diagonal can be found in terms of a:

$$\begin{pmatrix}\text{body}\\ \text{diagonal}\end{pmatrix}^2 = (a)^2 + (\sqrt{2}a)^2 \longrightarrow \text{body diag} = \sqrt{3}a$$

But it also equals 4r, so $a = \frac{4r}{\sqrt{3}}$ and we can write a ratio of volume of spheres to volume of cube (remember 2 spheres)

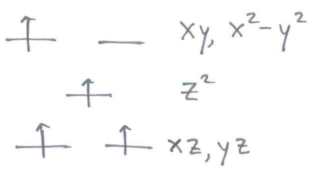
$$\frac{V_{spheres}}{V_{cube}} = \frac{2\cdot\frac{4}{3}\pi r^3}{\left(\frac{4}{\sqrt{3}}r\right)^3} = \frac{\left(\frac{8}{3}\pi\right)}{\left(\frac{4}{\sqrt{3}}\right)^3} = 0.68 \rightarrow \boxed{\text{so, space occupied is } 68\%}$$

6. Gas phase MnF_3 adopts a distorted trigonal planar geometry such that one Mn—F bond is shorter than the other two (C_{2v} symmetry). In contrast, both CrF_3 and FeF_3 have trigonal planar geometry (D_{3h} geometry, all M—F lengths equal, all ∠FMF equal). The difference for the Mn compound is attributed to the Jahn-Teller effect. Using the d-orbital splitting diagram for trigonal coordination (shown below) explain the underlying reason that MnF_3 is not trigonal planar. Draw the d-orbital splitting diagram under C_{2v} symmetry. (This problem is very similar to a suggested textbook problem. For that problem, and this one, consult the text on “Jahn-Teller effect” not covered in class.)

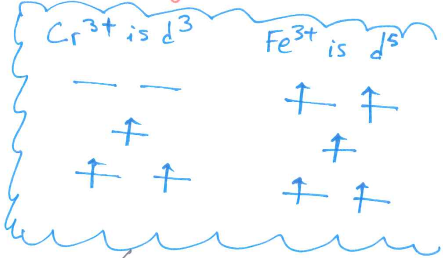
CrF_3, FeF_3 are trigonal planar (D_{3h}). MnF_3 is C_{2v}.

Jahn-Teller effect states molecules will distort to remove degeneracies so that there are no unequally occupied degenerate orbitals.

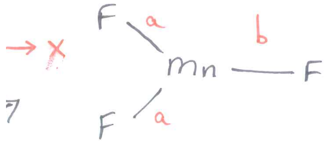
Mn^{3+} is d^4 & would fill the d-orbitals under D_{3h} symmetry as:



distort to remove this degeneracy.

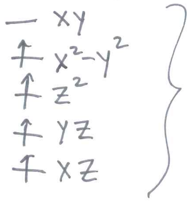


Here is C_{2v} symmetric MnF_3:



length a ≠ b (reality could be like the drawing (b > a) or it could be b < a (not shown).

For this diagram, elongation of Mn—F bond "b" along x axis will lower x^2-y^2 more than xy. (And will lower xz but not yz):

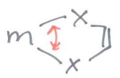


won't necessarily be evenly spaced, but none will be degenerate.

Also note that we keep the same coordinate system as we had for the D_{3h} trigonal planar hypothetical species.

7. Six-coordinate transition metal compounds are usually found in an octahedral geometry, but a few examples possess trigonal prismatic (or distorted trigonal prismatic) geometry. What are the factor(s) that favor trigonal prismatic geometry in six-coordinate metal complexes? How can one stabilize a complex in a trigonal prismatic geometry?

Sterically, the ligands are the farthest apart in octahedral. There are some examples of trigonal prismatic coordination, usually with bidentate ligands which force an angle of < 90°:



can't get 90° angle

8. A pentacoordinate complex L_5M is synthesized where L is a very large ligand. Explain on steric grounds what is the favored geometry, trigonal bipyramidal or square pyramidal.

- L_5M w/ L very large should be trigonal bipyramidal because that has only 3 90°-interactions. A square pyramid has 4 90°-interactions.

9. For which member of the following pairs of complexes would Δ_{oct} be larger and why?

(a) $[Cr(H_2O)]_6^{2+}$ or $[Cr(H_2O)_6]^{3+}$
(b) $[CrF_6]^{3-}$ or $[Cr(NH_3)_6]^{3+}$
(c) $[Co(en)_3]^{3+}$ or $[Rh(en)_3]^{3+}$
(en = 1,2-diaminoethane)

(a) $Cr(H_2O)_6^{2+}$ or [✓ $Cr(H_2O)_6^{3+}$]

higher oxidation state on same metal will have the ligands closer, and this will perturb the d-orbitals more.

(b) $[CrF_6]^{3-}$ or [✓ $[Cr(NH_3)_6]^{3+}$]

same metal, same oxidation state, look to the spectrochemical series. Fluoride is a π-donor ligand while NH_3 is not. The ammine complex should have the higher Δ_o because NH_3 is higher than F^- on the spectrochemical series.

(c) $[Co(en)_3]^{3+}$ or [✓ $[Rh(en)_3]^{3+}$]

$Rh(en)_3^{3+}$ because Δ_o gets bigger moving down a column. There is better overlap of d-orbitals with ligand orbitals and more covalent character to the bonding

10. For the following complexes, rationalize the number of unpaired electrons observed for each complex:

$Mn(CN)_6^{4-}$	1 unpaired electron
$Mn(CN)_6^{2-}$	3 unpaired electrons
$Pd(CN)_4^{2-}$	0 unpaired electrons
$CoCl_4^{2-}$	3 unpaired electrons
$NiBr_4^{2-}$	2 unpaired electrons

$Mn(CN)_6^{4-}$ has 1 unpaired e^-, confirm:

Mn^{2+} is d^5. Complex is octahedral, with strong field ligands, so L.S. d^5:

— —

↑↓ ↑↓ ↑

$Mn(CN)_6^{2-}$ has 3 unpaired e^-, confirm:

Mn^{4+} is d^3. Complex is octahedral, with strong field ligands, so L.S. d^3:

— —

↑ ↑ ↑

$Pd(CN)_4^{2-}$ has no unpaired e^-, confirm:

Pd^{2+} is d^8: this would have unpaired e^- if it were a tetrahedral geometry:

↑↓ ↑ ↑

↑↓ ↑↓

But: square planar is common for d^8 metals:

z^2 —

↑↓ ↑↓ ↑↓ ↑↓

$CoCl_4^{2-}$ has 3 unpaired e^-. Co^{2+} is d^7; tetrahedral is consistent:

↑ ↑ ↑

↑↓ ↑↓

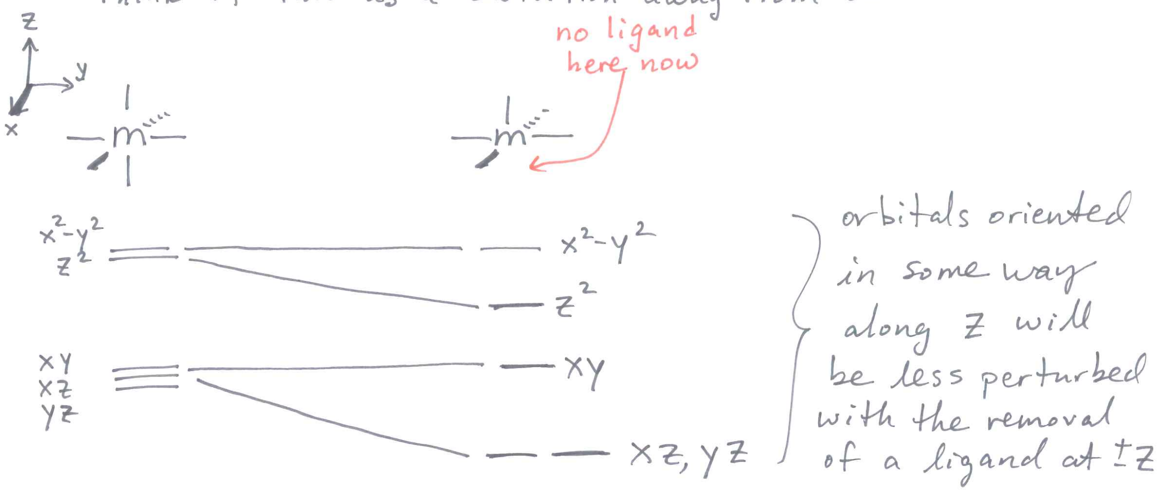
$NiBr_4^{2-}$ has 2 unpaired e^-. Ni^{2+} is d^8 & will have 2 unpaired e^- in tetrahedral geometry:

↑↓ ↑ ↑

↑↓ ↑↓

11. Prepare a d-orbital energy level diagram for a square pyramidal complex.

Think of this as a distortion away from octahedral:



orbitals oriented in some way along z will be less perturbed with the removal of a ligand at ±z

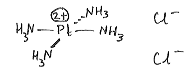
12. Consider the following series of six platinum compounds.

number	molecular formula	# of ions
1	$PtCl_2 \cdot 4NH_3$	3
2	$PtCl_2 \cdot 3NH_3$	2
3	$PtCl_2 \cdot 2NH_3$	0
4	$PtCl_2 \cdot 2NH_3$	0
5	$KPtCl_3 \cdot NH_3$	2
6	K_2PtCl_4	3

From the molecular formulas and numbers of ions produced when each compound is dissolved in water, deduce the structural formula of each compound, being explicit as to which ligands are in the coordination sphere. Draw structures for each platinum containing molecule or ion. Note that compounds **3** and **4** are isomers (one is polar, one is non-polar). All of the compounds have the same geometry at platinum—what is that geometry?

all are square planar at Pt

1



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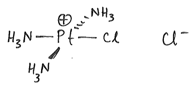
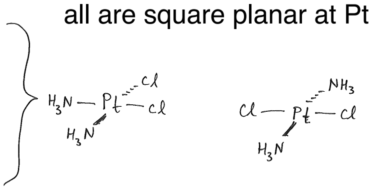
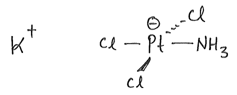


3

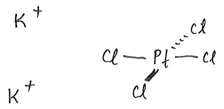
4



5



6



13. The spin-only magnetic moment (μ) of a transition metal complex is related to the number of unpaired electrons in the complex as follows:

$$\mu = \{N(N + 2)\}^{1/2}\mu_B$$

N = number of unpaired electrons
μ_B = Bohr magneton (a unit of measure)

The spin-only magnetic moment (μ) of $[Mn(NCS)_6]^{4-}$ is found to be $\mu = 6.06\ \mu_B$. Is $[Mn(NCS)_6]^{4-}$ a high spin or low spin complex?

$\mu = \sqrt{N(N+2)}\ \mu_B$ $\sqrt{5(5+2)} = \sqrt{35}$; just under 6

if μ is 6.06 μ_B, by trial & error, find this corresponds to 5 unpaired electrons. In $Mn(NCS)_6^{4-}$ where it is Mn^{2+}, a d^5 metal, it must be high spin (all e^- unpaired)

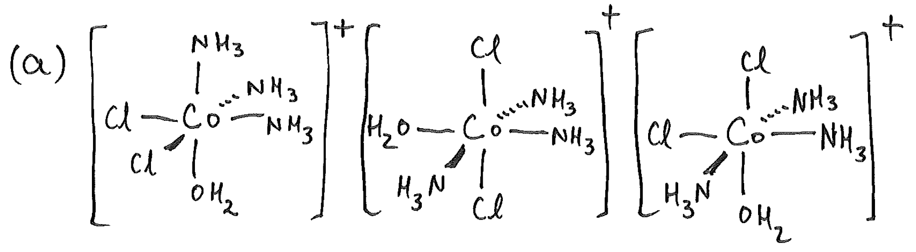
14. Which of the following is the stronger acid? Which has the higher Δ_o? Briefly rationalize your choices.

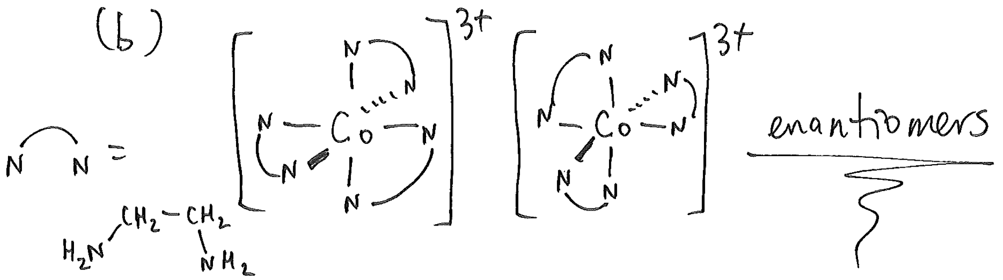
$[Ru(H_2O)_6]^{2+}$ $[Ru(H_2O)_6]^{3+}$

$Ru(H_2O)_6^{3+}$ because the higher charge on the metal more effectively polarizes the O–H bond of the water ligand, promoting ionization

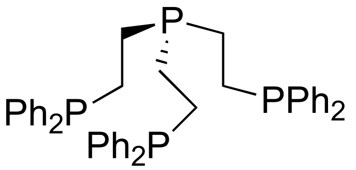
Higher Δ_o of these two ions? $Ru(H_2O)_6^{3+}$ again. Here, the higher charge brings ligands closer leading to greater perturbation of d-orbitals.

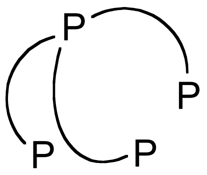
15. Provide clearly drawn structures for all isomers of the following octahedral complexes:
    (a) triammineaquadichlorocobalt(III) chloride (3 isomers)
    (b) tris(ethylenediamine)cobalt(III) chloride (2 enantiomers)



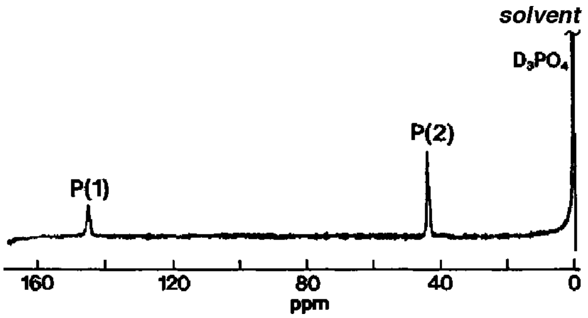


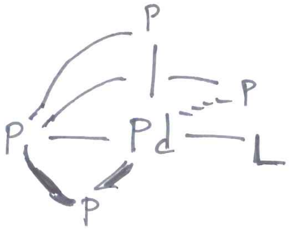
16. The tetradentate chelating ligand $P(CH_2CH_2PPh_2)_3$ (shown below as a structure and in simplified cartoon form) was used to make some cationic five-coordinate compounds of palladium. The fifth coordination site was occupied by a Lewis basic ligand like pyridine. Abbreviating the tetradentate ligand as "PP_3" and using "L" to represent the other ligand, a general representation of the ion is: $[(PP_3)Pd(L)]^+$





Generally, when five-coordinate compounds are formed, two geometries are typically observed: square pyramidal and trigonal bipyramidal. Of these two, which one is more favorable on steric grounds? How can you justify your answer?
Draw sketches of how the species $[(PP_3)Pd(L)]^+$ would look in a square pyramidal geometry and in a trigonal bipyramidal geometry. Do you see symmetry differences? Would they have a different number of ^{31}P signals in the ^{31}P NMR spectrum? Shown below is an example ^{31}P NMR spectrum for one of these species. The integration of the two peaks is in about a ratio of 3:1. Knowing how to interpret the chemical shift ***position*** is not required. Number and relative integration of signals tells the whole story here. With this information, make an argument for one geometry over the other. Show that the NMR spectrum is consistent with one of the geometries and inconsistent with the other one.





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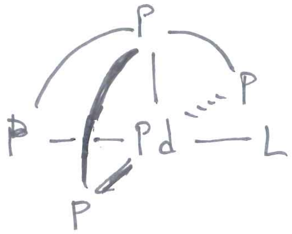
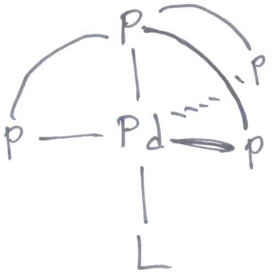


both have only mirror symmetry w/ 3 phosphorus environments



3-fold rotation axis; 2 phosphorus environments.

This one is consistent w/ NMR data.

Not these.