

Announcements

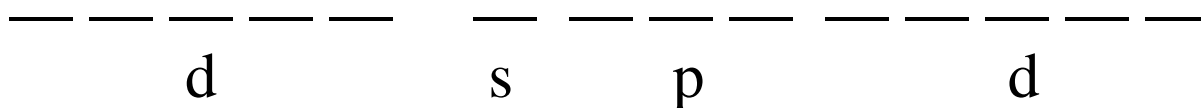
- Tuesday's quiz results are posted
- Final Exam
 - From the previous two exams, the following problems (and the topics they represented) were found to be somewhat challenging. The instructor tends to include such topics on the final
 - Exam 1
 - #3-common ion effect and solubility
 - #4-[]s is solutions of polyprotic acids
 - #6-Krxn and acid-base reactions running downhill
 - #8d-acid-base properties of conjugates
 - #9a-choosing a buffer and properly identifying the formulas of the conjugate pairs
 - 13.-LeChatelier and solubility
 - Exam 2
 - #1-temperature dependence of spontaneity
 - #7-proper identification of the reaction and the desired species
 - #8,9-standard cell representation

Transition Metal Complexes

- $A + :B \rightleftharpoons A:B$ Lewis acid-base adduct
- A metal with a vacancy in a d level in any of its oxidation states is called a “transition metal”
- Recall that when metals in the transition series form ions, they never have s electrons
- Metal cations are Lewis acids
- $:L$ =ligand which will be a Lewis base
- $M^{x+} + n :L \Rightarrow ML_n^{x+}$ transition metal ligand complex
- What makes these interesting:
 - they tend to be colored and considerable color variation is seen dependent on the metal, the oxidation state and the ligand
 - there is considerable variation in the electronic state of the complexes, including many which have multiple unpaired electrons.
 - variable valence and differing structures (octahedral, tetrahedral, and square planar) are seen
 - Given the nature of the possible ligands as well as other factors, metal ligand complexes are often quite labile. That is, ligands are added/removed/replaced relatively easily
 - The “traditional” bonding approach (Lewis Octet Theory), does not readily explain the observed properties of these materials.

Valence Bond Theory

- VBT descriptions of TM complexes are relatively straightforward, but one must keep in mind that they are not predictive, but rather constructed based upon known properties of the complex (its structure, magnetism, etc)
- In constructing the description there are two primary issues
 - The metal cation is stripped of its valence s electrons. It is of primary importance that the metal electron count be properly determined.
 - The ligand and metal electrons do not “mix” as the ligand is bringing in **electron pairs** in the formation of the Lewis acid-base adduct
- There are 14 orbitals available to the metal d s p d



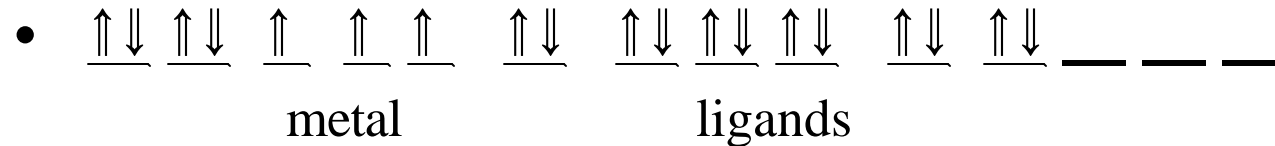
For a first transition series metal these would be 3d 4s 4p 4d

Example

- A Co^{2+} complex is octahedral and has 3 unpaired electrons-what is its VBT description
- Co^{2+} is d^7
- The metal electrons are placed in the d orbitals in accordance with the stated spin information



- Next, the six electrons pairs from the ligands are added



the complex is described as high spin, outer sphere, sp^3d^2

- An Fe^{2+} complex is octahedral and has no unpaired electrons-what is its VBT description
- Fe^{2+} is d^6
- The metal electrons are placed in the d orbitals in accordance with the stated spin information
- $\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---} \text{---}$
- Next, the six electrons pairs from the ligands are added
- $\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \text{---} \text{---} \text{---} \text{---}$
metal ligands

the complex is described as low spin, inner sphere, d^2sp^3

- An Ni^{2+} complex is tetrahedral and has 2 unpaired electrons-what is its VBT description
- Ni^{2+} is d^8
- The metal electrons are placed in the d orbitals in accordance with the stated spin information
- $\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad}$
- Next, the four electrons pairs from the ligands are added
- $\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \uparrow\downarrow \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad} \quad \underline{\quad}$

metal
ligands
- the complex is described as high spin, sp^3

- An Ni²⁺ complex is square planar and has no unpaired electrons-what is its VBT description
- Ni²⁺ is d⁸
- The metal electrons are placed in the d orbitals in accordance with the stated spin information

- ↑↓ ↑↓ ↑↓ ↑↓ ___ ___ ___ ___ ___

- Next, the four electrons pairs from the ligands are added

- ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ___ ___ ___ ___ ___

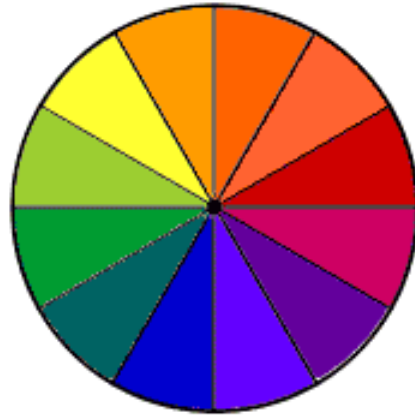
metal ligands

the complex is described as low spin, dsp²

Metal Bonding VBT Summary

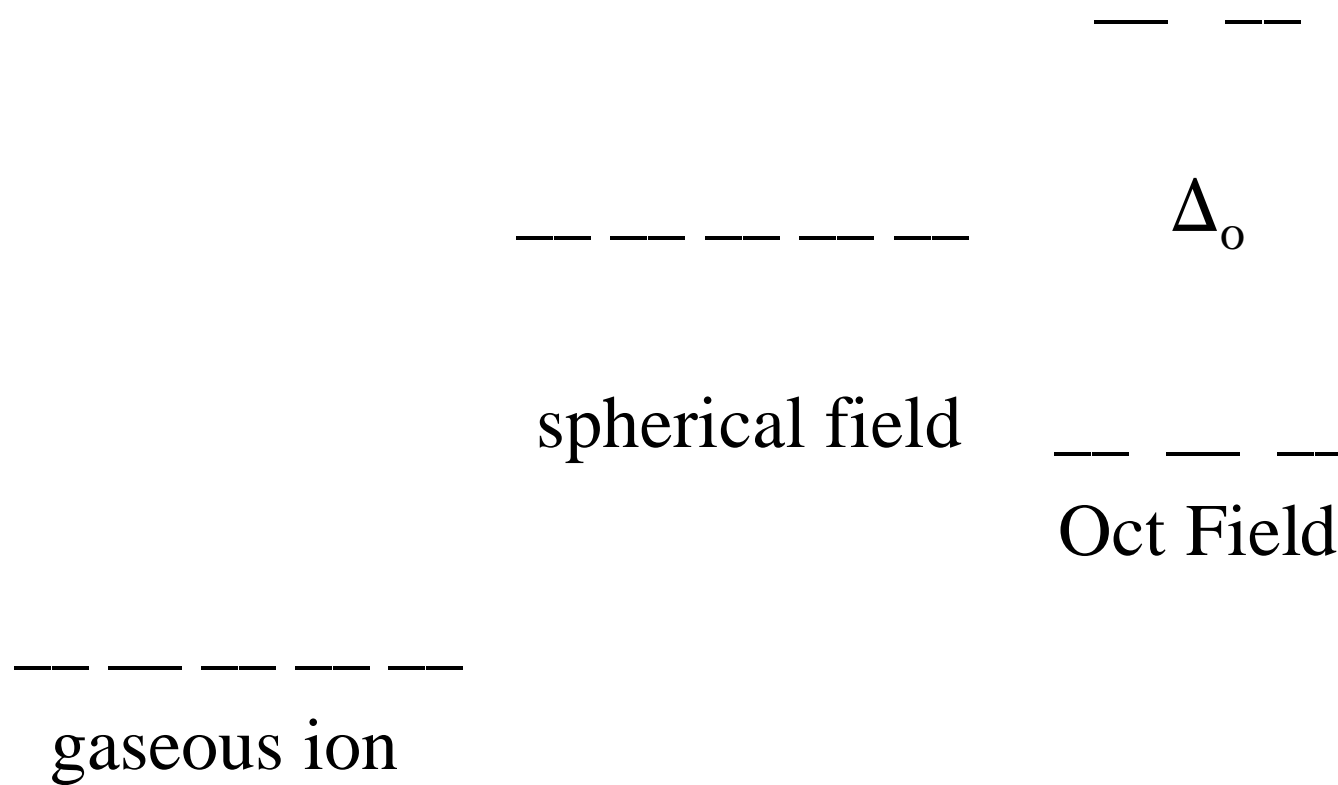
- The unique properties of TM complexes require a different bonding description than that used for other compounds
- VBT approaches the problem by dividing the electrons into two groups-the metal valence electrons and the electron pairs provided by the ligands
 - The metal electrons are distributed among the valence metal orbitals according to identified properties of the complex:
 - structure:octahedral, tetrahedral or square planar
 - high spin or low spin-or the number of unpaired electrons
 - inner or outer sphere
 - The ligand electron pairs are then placed in the next available orbitals
- Since it seems to work well, what's wrong with VBT?
- Although it generally leads to a correct distribution, it is “after the fact” and not predictive. Further, it provides no real basis for why the complexes vary or the source of the color variation-a defining property of such compounds

Why does something appear colored?



- The complex must be able to selectively absorb visible radiation
- There must, therefore, be some type of energy differential within the compound whose energy corresponds to such radiation $\Delta E = hf$
- The only available processes with these characteristics are electronic transitions-remember the visible spectra of the elements.
- Therefore, there must be a vacant electronic energy level(LUMO-lowest unoccupied level) whose “energetic distance” from the highest occupied level(HOL) corresponds to visible light
- TMs have vacancies in d orbitals. Also d^0 and d^{10} complexes are colorless
- Crystal field theory removes the degeneracy of the d orbitals by placing two of them in different environments as a result of the charges due to the ligands.

Splitting the d orbitals-CFT

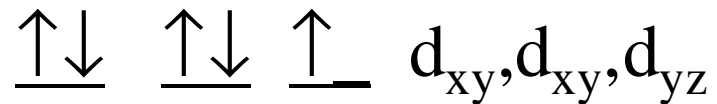
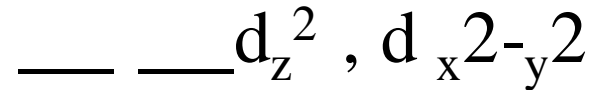


The issue of how the electrons are distributed becomes a matter of the relative sizes of the crystal field splitting (Δ_o) and the pairing energy (PE)-the repulsion caused by putting two electrons in the same orbital.

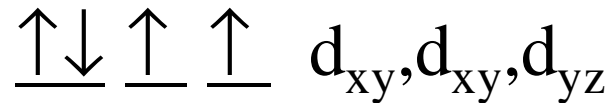
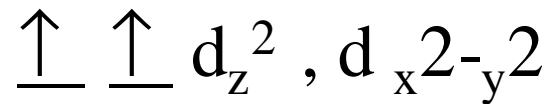
If the $PE > \Delta_o$ splitting one gets a high spin complex. This is also called the weak field case

If $PE < \Delta_o$ one gets the low spin complex. This is also called the strong field case

- Two quick examples:
low spin Mn^{2+} complex
the metal is d^5



- Weak field Co^{3+} complex
metal is d^6



Tetrahedral

- Reverse of octahedral but $\Delta_t = 4/9\Delta_o$ (Why?).
All tetrahedral complexes are high spin.

— — — t_{2g}

Δ_t

— — e_g

Square Planar

— $d_{x^2-y^2}$

Square planar complexes are low spin

Δ_o

— d_{xy}

— d_z^2

— — d_{xz}, d_{yz}

The Spectrochemical Series

- Ligands have been ranked based upon their abilities to split the metal energies. This is called the spectrochemical series. Below is an abbreviated list in order of increasing field strength.
- $I^- < Br^- < F^- < OH^- < NH_3 < NO_2^- < CN^- < CO$
- ligands low on the series would yield high spin complexes while those at the top of the series will produce low spin compounds.

Of course, CFT doesn't work either

- Without bothering with the details, suffice it to say that close scrutiny of CFT leads to the conclusion that it is not an adequate explanation for the properties of the TM complexes
- Everything comes down to MO theory-as it should
- Quick summary
 - the d orbitals in the metal are divided as follows:
 - if the ligand is only a σ base
 - the e_g orbitals are σ^* and raised in energy
 - the t_{2g} orbitals are non bonding and their energies are unchanged
 - the resultant difference is Δ_o
 - if the ligand is also a π base (Cl⁻ ion) there is an added effect that results in the t_{2g} orbitals becoming π^* and increasing in energy. This decreases Δ_o
 - if the ligand is a π acid (CO) there is an added effect that results in the t_{2g} orbitals becoming π bonding and decreasing in energy. This increases Δ_o