Reading For Today: 16.8-16.11 in 4th and 5th editions
Reading for Lecture #29: same as above

Topic: I. Introduction to Crystal Field Theory
II. Crystal Field Theory: Octahedral Case
III. Spectrochemical Series

I. Introduction to Crystal Field Theory

Crystal field and ligand field theories were developed to explain the special features of transition metal coordination complexes, including their beautiful colors and their magnetic properties. Coordination complexes are often used as contrast agents for magnetic resonance imaging (MRI) and other types of imaging.

Basic idea behind theories:
When a metal ion with a given oxidation number (Mn+, where M is a metal and n+ is its oxidation number) is placed at the center of a coordination sphere defined by a set of ligands, the energy levels of the d orbitals housing the metal electrons are different from those in the free metal ion.

Crystal field theory is based on an ionic description of the metal-ligand bond.

Ligand field theory includes covalent and ionic aspects of coordination. It is a more powerful description of transition metal complexes. It is, however, beyond the scope of this course. (Take 5.03 if you are interested in this topic).

Crystal Field Theory considers ligands as point charges and considers the repulsion between the negative point charges and the d-orbitals, and even though this theory is simple, a number of properties of transition metals can be explained.
II. Crystal Field Theory: Octahedral Case

- Ligand (L) point charges are directed right toward the \( d_z^2 \) and \( d_x^2 \) orbitals of metal (M\(^{n+}\)), resulting in a **large** repulsion.

- The \( d_z^2 \) and \( d_x^2 \) orbitals are **destabilized**, and they are destabilized by the same amount. \( d_z^2 \) and \( d_x^2 \) are ________.

- The \( d_z^2 \) and \( d_x^2 \) orbitals are destabilized relative to \( d_{xy} \), \( d_{xz} \), and \( d_{yz} \).

- Ligand point charges are directed in between \( d_{xy} \), \( d_{xz} \), and \( d_{yz} \) orbitals (not directly toward them), resulting in ________ repulsion.

- The \( d_{xy} \), \( d_{xz} \), and \( d_{yz} \) orbitals are **stabilized** relative to \( d_z^2 \) and \( d_{x^2-y^2} \) orbitals, and they are stabilized by the same amount.

- \( d_{xy} \), \( d_{xz} \), and \( d_{yz} \) orbitals are degenerate with respect to each other.
Octahedral Crystal Field Splitting Diagram

\[ \Delta_o \] is the overall splitting between \( e_g \) and \( t_{2g} \) orbitals = octahedral field splitting energy ("o" in \( \Delta_o \) is for octahedral)

Because the overall energy is maintained, the energy of the three \( t_{2g} \) orbitals are lowered by \( \frac{2}{5} \Delta_o \) and the energy of the two \( e_g \) orbitals are raised by \( \frac{3}{5} \Delta_o \) relative to the spherical crystal field.

What determines the magnitude of \( \Delta_o \)? Answer: the ____________ of the ligand.

III. Spectrochemical Series

The relative abilities of common ligands to split the d-orbital energy levels generate what is known as the spectrochemical series.

**Strong field ligands** - produce ________ energy separations between d-orbitals (big \( \Delta_o \))

**Weak field ligands** - produce small energy separations between d-orbitals (small \( \Delta_o \))

\[ \begin{align*}
I^- & < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < CO < CN^- \\
\text{weak field ligands} & \quad \text{strong field ligands}
\end{align*} \]

\( \Delta_o \) is small \( \quad \Delta_o \) is large

**Example 1.** Consider two different iron compounds: \([Fe(H_2O)_6]^{3+}\) and \([Fe(CN)_6]^{3-}\).

(a) Figure out the oxidation number of Fe

(b) Figure out d count
(c) Draw octahedral crystal field splitting diagrams

Small $\Delta_o$ (___________ field)

\[
\begin{array}{c}
\downarrow d_{x^2-y^2} \quad \downarrow d_{z^2} \\
\uparrow \quad \uparrow \\
\downarrow d_{xy} \quad \downarrow d_{xz} \quad \downarrow d_{yz} \\
\end{array}
\]

\[\Delta_o \quad \Delta_o \]

\[\frac{+3}{5} \quad \frac{-2}{5} \quad \Delta_o \]

\[d_{x^2-y^2} \quad d_{z^2} \quad (e_g) \]

\[\Delta_o \]

\[d_{xy} \quad d_{xz} \quad d_{yz} \quad (t_{2g}) \]

\[\Delta_o \]

\[\frac{+3}{5} \quad \frac{-2}{5} \quad \Delta_o \]

\[d_{x^2-y^2} \quad d_{z^2} \quad (e_g) \]

\[\Delta_o \]

\[d_{xy} \quad d_{xz} \quad d_{yz} \quad (t_{2g}) \]

\[\Delta_o \]

\[\frac{+3}{5} \quad \frac{-2}{5} \quad \Delta_o \]

Compound is ______________

Large $\Delta_o$ (___________ field)

\[d_{x^2-y^2} \quad d_{z^2} \quad (e_g) \]

\[\Delta_o \]

\[d_{xy} \quad d_{xz} \quad d_{yz} \quad (t_{2g}) \]

\[\Delta_o \]

\[\frac{+3}{5} \quad \frac{-2}{5} \quad \Delta_o \]

\[d_{x^2-y^2} \quad d_{z^2} \quad (e_g) \]

\[\Delta_o \]

\[d_{xy} \quad d_{xz} \quad d_{yz} \quad (t_{2g}) \]

\[\Delta_o \]

\[\frac{+3}{5} \quad \frac{-2}{5} \quad \Delta_o \]

Compound is ______________

(d) Place electrons. There are two ways to place electrons: (1) singly to the fullest extent possible before pairing (i.e. using both $t_{2g}$ and $e_g$ orbitals) or (2) only fill $t_{2g}$ before pairing.

The decision is made based on whether $\Delta_o$ is greater or less than the pairing energy (PE): energy of electron-electron repulsion.

When $\Delta_o$ is small, $\Delta_o < PE$
Electrons are placed singly with parallel spins to the fullest possible extent in $t_{2g}$ and $e_g$ orbitals.
This arrangement of electrons gives the maximum number of unpaired electrons (high spin).

When $\Delta_o$ is large, $\Delta_o > PE$
Electrons are paired in lower energy $t_{2g}$ orbitals. $e_g$ orbitals are not both occupied until $t_{2g}$ orbitals are filled.
This arrangement of electrons gives the minimum number of unpaired electrons (low spin).

(e) Write $d^n$ electron configuration:

(f) Predict Crystal Field Stabilization Energy (CFSE) - ________________ relative to that of the hypothetical spherical crystal.

CFSE =

**Practice Questions**

1. Place electrons correctly for an octahedral Co$^{2+}$ ($d^7$) weak field complex.

\[
\begin{array}{c}
\downarrow d_{x^2-y^2} \quad \downarrow d_{z^2} \\
\uparrow \quad \uparrow \\
\downarrow d_{xy} \quad \downarrow d_{xz} \quad \downarrow d_{yz} \\
\end{array}
\]

\[\Delta_o \quad \Delta_o \]

\[\frac{+3}{5} \quad \frac{-2}{5} \quad \Delta_o \]

\[d_{x^2-y^2} \quad d_{z^2} \quad (e_g) \]

\[\Delta_o \]

\[d_{xy} \quad d_{xz} \quad d_{yz} \quad (t_{2g}) \]

\[\Delta_o \]

\[\frac{+3}{5} \quad \frac{-2}{5} \quad \Delta_o \]
2. Predict the CFSE of a high spin octahedral Mn$^{3+}$ (d$^4$) complex ________________

\[ \begin{align*}
\Delta_o & \quad \frac{+3}{5} \\
\frac{+2}{5} \Delta_o & \quad \frac{t_{2g}}{(e_g)}
\end{align*} \]

\[ \begin{align*}
d_{x^2-y^2} & \quad d_{z^2} \\
d_{xy} & \quad d_{xz} \quad d_{yz}
\end{align*} \]

**Back to [Fe(H$_2$O)$_6$]$^{3+}$ and [Fe(CN)$_6$]$^{3-}$**

Predict whether these compounds are paramagnetic (attracted by a magnetic field) or diamagnetic (repelled by a magnetic field).

Based on the above diagrams, they are likely to be ________________ (i.e. have ________________ electrons).

**Predict the colors of these two iron complexes**

**Light Absorbed and Emitted by Octahedral Coordination Complexes**

A substance absorbs photons of light if the energies of the photons ________________ the energies required to excite the electrons to higher energy levels.

\[ E_{\text{light}} = h\nu = \Delta_o \]

\( E = \) energy of light absorbed; \( h = \) planck’s constant

\( \nu = \) frequency; \( \Delta_o = \) octahedral crystal field splitting energy

If **low** frequency light is absorbed, the wavelength of the absorbed light is ________.

(yellow/orange/red end of spectrum)

If **high** frequency light is absorbed, the wavelength of the absorbed light is ________.

(violet/blue/green end of spectrum)

\[ c = \lambda\nu \]

\( c = \) speed of light

\( \lambda = \) wavelength

\( \nu = \) frequency

<table>
<thead>
<tr>
<th>violet</th>
<th>blue</th>
<th>green</th>
<th>yellow</th>
<th>orange</th>
<th>red</th>
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<td>400nm</td>
<td>430nm</td>
<td>490nm</td>
<td>560nm</td>
<td>580nm</td>
<td>620nm</td>
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Color of transmitted light is ________________ to the color of absorbed light.

**Going back to our example: high spin [Fe(H$_2$O)$_6$]$^{3+}$ and low spin [Fe(CN)$_6$]$^{3-}$**

High spin [Fe(H$_2$O)$_6$]$^{3+}$ **absorbs** low frequency/long wavelength light and **transmits** ________ wavelength light. It can appear pale violet to yellow brown.

Low spin [Fe(CN)$_6$]$^{3-}$ **absorbs** high frequency/short wavelength light and **transmits** ________ wavelength light. It is bright red-orange.
Which coordination complexes are colorless?

All d-orbitals are ____________. ___________ d-d transitions in the visible range possible.

Examples:

Will Co^{3+} be colorless?

Which vitamin contains cobalt?

**Cobalt Flower Demonstration**

Predict the color of \([Co(H_2O)_6]^{2+}\) (\(\Delta_o = 239 \text{ kJ/mol}\))

(a) Calculate the wavelength of absorbed light

\[
\lambda = \frac{hc}{\Delta_o} = \frac{(6.626 \times 10^{-34} \text{ J s}) (2.997 \times 10^8 \text{ m/s})}{(239 \text{ kJ/mol})(1000 \text{ J/kJ})(1 \text{ mol/6.022 \times 10^{23}})}
\]

\([Co(H_2O)_6]^{2+}\) absorbs ___________ light.

(b) Predict the color of the transmitted light ___________.

In solution, CoCl\(_2\) + H\(_2\)O -> [Co(H\(_2\)O\(_6\))]\(^{2+}\) color =

In the solid state, CoCl\(_2\) + H\(_2\)O \(\rightarrow\) trans-[CoCl\(_2\)(H\(_2\)O)\(_4\)] color = blue

So we can go between _____ and blue by adding water (hydrating) or removing water (dehydrating).