

Unit 1

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1.1 Lecture 1: Introduction/Key Trends

- 3/29:
- Largely asynchronous, but synchronous discussions, office hours, and tests.
 - Refer to the Canvas site for all information; it's the class hub.
 - To understand transition metal trends and properties, start with *atomic* properties and trends.
 - **Electronegativity:** The energy that an atom will gain when it gains an electron.
 - Fluorine really wants to gain an electron; thus, it has high electronegativity.
 - Do you mean electron affinity?
 - Increases across a row; decreases down a column.
 - Transition metals, in general, are an exception to this rule.
 - This is because of the **lanthanide contraction**.
 - Discontinuities in the transition metals (Mn and Ni) correspond to half-filled and filled *d* shells, respectively.
 - Extra stability means less of a desire to gain an electron.
 - **Ionization potential:** The energy required to remove an electron.
 - Varies with the identity of an element *and* its oxidation state.
 - Increases across a row; decreases down a column.
 - Size:
 - Many different definitions (depending on the specific thing you're interested in, one may be more useful than another). For example,
 - Atomic radius: Specific to an element.
 - Ionic radius: Specific to an oxidation state; as in salts and coordination complexes.
 - Covalent radius: Distance that one would expect for a bond; varies with bond order.
 - Decreases across a row; increases down a column (a notable exception to the latter trend follows from the lanthanide contraction).
 - Things that affect size:
 - Oxidation state.
 - Spin state (high spin [larger; this is because the e_g orbitals are antibonding, and antibonding electrons both push the bounds of the atom and weaken bonds, increasing the covalent radius] vs. low spin [smaller]).

- **Lanthanide contraction:** In the transition metals, there is a small/no increase in size between the second and third rows.
 - This is because the shell added in between contains the f orbitals, which are small, do not extend past the noble gas core, and do not provide good shielding.
 - Z goes up a lot with little shielding, so the $5d$ orbitals are contracted; thus, $4d/5d$ orbitals are similar in size.
- **Oxidation state:** The number of electrons a metal center is below its valence.
 - Typically, the maximum oxidation state is defined by the d -count for the 0-valent metal.
- Having discussed four trends, how are they related?
 - As oxidation state increases, “electronegativity” and ionization potential will increase, and the radius will decrease.
 - This is because removing an electron \Rightarrow reduces shielding \Rightarrow higher positive charge \Rightarrow all orbitals decrease in energy \Rightarrow all orbitals decrease in size (hence radius decreases, too).
 - Watch out for discontinuities such as Mn^{2+} .
- **Magnetic properties:** Unique to the transition metals and the f block.
 - Consider $\text{Fe}^{\text{II}}\text{L}_6^{2+}$ (d^6).
 - Possible states: Low spin ($S = 0$), intermediate spin ($S = 1$; rare), and high spin ($S = 2$).
 - We predict which state dominates by the:
 - **Pairing energy.**
 - **Ligand field stabilization energy.**
- **Pairing energy:** The energy cost of putting two electrons in the same orbital. *Also known as PE.*
 - Trends with orbital size/radius.
 - Decreases down a column.
- **Ligand field stabilization energy:** *Also known as LFSE.*
 - Can be thought of in terms of crystal field theory.
 - Extra thoughts on Figure VI.10 of Labalme (2021): Donating negative charge to a free metal ion in a spherically symmetric fashion uniformly raises the energy of the d orbitals by increasing repulsions and size.
 - Low-spin LFSE: $6 \cdot -4 \text{ Dq} + 3 \text{ PE} = -24 \text{ Dq} + 3 \text{ PE}$.
 - Intermediate-spin LFSE: $5 \cdot -4 \text{ Dq} + 1 \cdot 6 \text{ Dq} + 2 \text{ PE} = -14 \text{ Dq} + 2 \text{ PE}$.
 - High-spin LFSE: $4 \cdot -4 \text{ Dq} + 2 \cdot 6 \text{ Dq} + 1 \text{ PE} = -4 \text{ Dq} + 1 \text{ PE}$.
 - Thus, the energy difference between the low-spin and high-spin configurations is $20 \text{ Dq} + 2 \text{ PE}$. It follows that if $10 \text{ Dq} > 1 \text{ PE}$, then the complex will be low spin; and if $10 \text{ Dq} < 1 \text{ PE}$, then the complex will be high spin.
 - This also explains why the intermediate spin state is rare: if Δ_o is large enough to make $10 \text{ Dq} > 1 \text{ PE}$, then it will likely take the complex all the way to a low-spin configuration (and vice versa for high spin).
 - Lastly, this means that Fe^{II} is a good **spin-crossover** ion.
- **Spin-crossover (ion):** An ion that can have both high- and low-spin states.
 - The graph of the magnetic moment χT of Fe^{II} vs. temperature T (see Figure 1.1) moves from $S = 0$ at the bottom left to $S = 2$ at the top right.
 - d^2 ions are never spin-crossover ions: $-8 \text{ Dq} + 0 \text{ PE}$ for high spin vs. $-8 \text{ Dq} + 1 \text{ PE}$ for low spin.

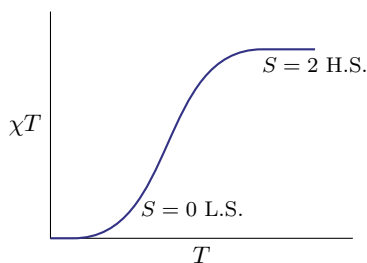


Figure 1.1: Magnetic moment vs. temperature for the Fe^{II} ion.

- Dq and PE values depend on:

- Ligand field strength.

- ΔO_h increases as σ donation increases.
- ΔO_h increases as π acceptance increases.
- ΔO_h decreases as π donation increases.
- To what extent do we need to have the spectrochemical series memorized?

- Metal center.

- Larger, more diffuse metals (i.e., second- and third-row transition metals) have better overlap with the ligands, giving rise to larger ΔO_h .
- Note that pairing energy decreases in second- and third-row transition metals (due to the larger orbitals).
- These two factors imply that second- and third-row transition metals are almost always low spin.

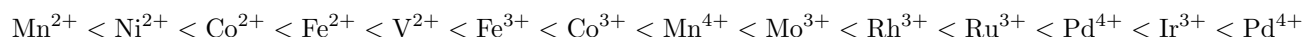
- Oxidation state.

- As oxidation state increases, ΔO_h increases (due to better energy matching, higher “electronegativity,” the role of electrostatics, and the electron configuration [d^5 is almost always high spin, and d^6 is often low spin]).
- Why do d^5 and d^6 exhibit the above behavior? Shouldn’t the stabilized orbitals be split more?
- See the below spectrochemical series for metals.

- Geometry.

- In a σ -only sense, lower coordination numbers tend to have smaller LFSEs.
- $T_d < C_{4v} \approx D_{3h} < O_h < D_{4h}$.
- $\Delta_{\text{sq. pl.}} \approx 1.74 \Delta O_h$.

- Spectrochemical series for metals (not as precise as the one for ligands, but a decent approximation):



- Hard/soft acid-base theory:

- Common Lewis acids:

- Proton: H^+ .
- Molecules with no octet: AlCl_3 , BR_3 (boranes), BeH_2 .
- Metal cations: Na^+ , Ti^{4+} .
- π acids: CO_2 , CO , PR_3 .

- Common Lewis bases:

- Carbanions: CR_3 .

- Hydrides: KH , NaH , LiAlH_4 .
 - Amines, amides, and phosphines: NH_3 , PR_4 , NH_2^- .
 - OH_2 , SR_2 , OH^- .
 - Halides: F^- , Cl^- , Br^- .
 - Carbonyl: CO (means CO is amphoteric).
 - Olefins: C_2H_4 .
- Distinguishes hard vs. soft^[1].

1.2 Office Hours (Whitmeyer)

- 3/30:
- Electron affinity, not electronegativity, for the periodic trend?
 - At higher levels, people don't really distinguish between the two.
 - To what extent do we need to have the spectrochemical series memorized?
 - You don't need to memorize them, but it's good to know some of them off the top (exams are open note, but there are time constraints).
 - In connection with oxidation state, Prof. Anderson mentioned that d^5 is almost always high spin, and d^6 is often low spin. Why? Shouldn't the stabilized orbitals be split more?
 - 5 d electrons each in their own orbital minimizes the pairing energy.
 - 6 d electrons all occupy the lower orbitals to minimize antibonding contributions.
 - Using the textbook:
 - The lectures are essential in this course, and if you don't understand something in the lecture, ask Sophie or John or read the textbook.
 - If it's in those chapters, it could be asked about, but it probably won't be if John doesn't talk about it.

¹Hard vs. soft is the basis for the solubility rules!