

# CHEM 20200 (Inorganic Chemistry II) Notes

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# Units

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# 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  $\text{Mn}^{2+}$ .
- **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  $\Delta_o$  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  $\text{Fe}^{\text{II}}$  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  $\chi T$  of  $\text{Fe}^{\text{II}}$  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.

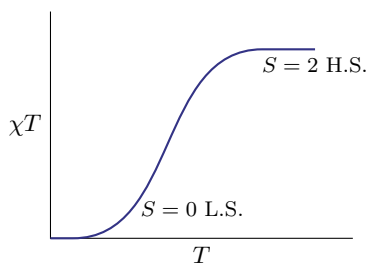


Figure 1.1: Magnetic moment vs. temperature for the  $\text{Fe}^{\text{II}}$  ion.

- Dq and PE values depend on:

- Ligand field strength.

- $\Delta O_h$  increases as  $\sigma$  donation increases.
- $\Delta O_h$  increases as  $\pi$  acceptance increases.
- $\Delta O_h$  decreases as  $\pi$  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  $\Delta O_h$ .
- 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.

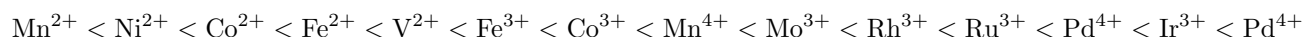
- Oxidation state.

- As oxidation state increases,  $\Delta O_h$  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  $\sigma$ -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:  $\text{H}^+$ .
- Molecules with no octet:  $\text{AlCl}_3$ ,  $\text{BR}_3$  (boranes),  $\text{BeH}_2$ .
- Metal cations:  $\text{Na}^+$ ,  $\text{Ti}^{4+}$ .
- $\pi$  acids:  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{PR}_3$ .

- Common Lewis bases:

- Carbanions:  $\text{CR}_3$ .

- Hydrides: KH, NaH, LiAlH<sub>4</sub>.
  - Amines, amides, and phosphines: NH<sub>3</sub>, PR<sub>4</sub>, NH<sub>2</sub><sup>-</sup>.
  - OH<sub>2</sub>, SR<sub>2</sub>, OH<sup>-</sup>.
  - Halides: F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>.
  - Carbonyl: CO (means CO is amphoteric).
  - Olefins: C<sub>2</sub>H<sub>4</sub>.
- Distinguishes hard vs. soft<sup>[1]</sup>.

## 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.

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<sup>1</sup>Hard vs. soft is the basis for the solubility rules!

# References

Labalme, S. (2021). *CHEM 20100 (Inorganic Chemistry I) notes* (Accessed 29 March 2021). <https://github.com/shadypuck/CHEM20100Notes/blob/master/Notes/notes.pdf>