Modern Main Group Chemistry

Primarily, the chemistry of the p-block elements.
Group 1 - Alkali metals
Group 2 - Alkaline earth metals
Group 13 - Earth metals (Triels)
Group 14 - no name
Group 15 - Pnictogens (Pentels)
Group 16 - Chalcogens
Group 17 - Halogens
Group 18 - Noble Gases
Multiple bonds between main group elements

What do such compounds teach us about the rules of bonding?
Low oxidation state and cluster compounds
Main Group Metallocenes

$\text{Cp}^* \text{M} \ (M = \text{Be, Al, Mg})$

$\text{Cp}^* \text{B}^+$

$[\text{Cp}^* \text{Ga}^+][\text{AlCl}_4^-]$

$\text{Cp}^* \text{M} \ (M = \text{Si, Ge, Sn})$
Chem 59-651

Single-source Precursors for Materials

AlN

InP

16

17

18

19

Fig. 5: A typical poly(thio)phosphanated nanowire
Highly-reactive species: C-H and other bond activation
Concepts/Approaches that we must review

- Some aspects of periodicity (effective nuclear charge, electronegativity, the sizes of atoms and orbitals, contractions, relativistic effects)

- Valence Shell Electron Repulsion Theory (shapes)

- Valence Bond Theory (hybridization of orbitals, the use of d-orbitals)

- Molecular Orbital Theory and diatomic MO diagrams

- Symmetry and Point Groups

- Group Theory, Character Tables and polyatomic MO diagrams

You can find most of these in Inorganic text books or on my web site.
## Trends for Atomic Properties in the Periodic Table

Understanding how and why properties change from element to element requires us to consider:

1. The electron configuration of the atom or ion (the filling order)
2. The type of valence orbitals involved (size, shape, shielding and penetration)
3. The effective nuclear charge felt by electrons in valence orbitals
4. “Oddities”
Wave functions and Orbitals

Ψ = wave function

Ψ² = probability density

4πr²Ψ² = radial probability function

\[ \hat{H}\Psi = E\Psi \]

Ψ = \( R_{nl}(r) Y_{lm}(\theta,\phi) \)

\( R_{nl}(r) \) – radial function

\( Y_{lm}(\theta,\phi) \) – angular function

polar coordinates

[Diagrams showing wave functions, probability densities, and radial probability functions]
Nodes: surfaces where there is 0 probability of finding an electron

Number of radial nodes = \( n - l - 1 \)

Number of angular nodes:
- 0 for s orbitals
- 1 for p orbitals
- 2 for d orbitals (except \( d_{z^2} \))

An applet demonstrating nodes for 2D wavefunctions can be found at:
http://artsci-ccwin.concordia.ca/facstaff/a-c/bird/c241/java/drums/drums.html
s orbitals

p orbitals
d orbitals
Effective Nuclear Charge, $Z^*$

The presence of other electrons around a nucleus “screens” an electron from the full charge of the nucleus.

We can approximate the energy of the electrons by modifying the Bohr equation to account for the lower “effective” nuclear charge:

$$E_n = -R \left( \frac{Z^*}{n^2} \right)$$

$$Z^* = Z - \sigma$$

$Z^*$ is the effective nuclear charge
$Z$ is the atomic number
$\sigma$ is the shielding or screening constant
The prediction $\sigma$ and $Z^*$

Slater’s rules for the prediction of $\sigma$ for an electron:

1. Group electron configuration as follows:
   (1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p) etc.

2. Electrons to the right (in higher subshells and shells) of an electron do not shield it.

3. For $n_s$ or $n_p$ valence electrons:
   a) each other electron in the same group contributes 0.35 (0.30 for 1s)
   b) each electron in an $n-1$ group contributes 0.85
   c) each electron in an $n-2$ or lower group contributes 1.00

4. For $n_d$ or $n_f$ valence electrons:
   a) each other electron in the same group contributes 0.35
   b) each electron in a lower group (to the left) contributes 1.00
Example with a valence electron on oxygen: O, \( Z = 8 \)
Electron configuration: \( 1s^2 \, 2s^2 \, 2p^4 \)

a) \((1s^2) \, (2s^2 \, 2p^4)\)

\[
\sigma = (2 \times 0.85) + (5 \times 0.35) = 3.45
\]

\[
Z^* = Z - \sigma
\]

\[
Z^* = 8 - 3.45 = 4.55
\]

This electron is actually held with about 57% of the force that one would expect for a +8 nucleus.
Example with two electrons for nickel: $\text{Ni, } Z = 28$

Electron configuration: $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^8 \ 4s^2$

$$(1s^2) \ (2s^2 \ 2p^6) \ (3s^2 \ 3p^6) \ (3d^8) \ (4s^2)$$

For a 3d electron:

$\sigma = (18 \cdot 1.00) + (7 \cdot 0.35) = 20.45$

For a 4s electron:

$\sigma = (10 \cdot 1.00) + (16 \cdot 0.85) + (1 \cdot 0.35) = 23.95$

$$Z^* = Z - \sigma \quad Z^* = 28 - 20.45 = 7.55$$

$$Z^* = Z - \sigma \quad Z^* = 28 - 23.95 = 4.05$$
The basis of Slater’s rules for $\sigma$

$s$ and $p$ orbitals have better “penetration” to the nucleus than $d$ (or $f$) orbitals for any given value of $n$

i.e. there is a greater probability of $s$ and $p$ electrons being near the nucleus

This means:

1. $ns$ and $np$ orbitals completely shield $nd$ orbitals

2. $(n-1) s$ and $p$ orbitals don’t completely shield $ns$ and $p$ orbitals
Periodicity of Effective Nuclear Charge

Electrons outside have no effect of effective nuclear charge for electron of interest.

Electrons between electron of interest and nucleus cancel some of the positive nuclear charge.

Effective nuclear charge (Clementi) - 1s, nuclear charge units, coded by intensity of red.

Z* on valence electrons

WebElements
Shielding and Effective Nuclear Charge

The energy of valence electrons in an atom/ion changes with the loss of addition of an electron.

Slater’s rules are only approximate and can give poor predictions. For example:

They ignore the differences in penetration between s and p orbitals. Real s and p orbitals do not have the same energy.

They assume that all electrons in lower shells shield outer electrons equally effectively.
Effective nuclear charge can be used to rationalize properties such as the size of atoms and ions. Be and B+ are isoelectronic (1s² 2s²) but very different because of effective nuclear charge.
Orbital energy levels and atomic number

For atoms other than hydrogen:
Orbital energy depends on $n$ and $l$

Ordering of orbital energies:
$n_s < n_p < n_d < n_f$

Remember:
This ordering is due to the different penetrating ability of the different types of orbitals and the different effective nuclear charges felt by the electrons in those orbitals.
The 4s orbitals are lower in energy than the 3d orbitals for K and Ca.

This is only for the free atoms! In molecules 3d are lower in energy than 4s!

This is assumed to be an accident of nature but it is consistent throughout the table.
The Size of Atoms and Ions

Radii of neutral atoms

The atomic radius of an atom is defined as half the distance between the nuclei in a homonuclear bond.

In general:
- radii decrease across a period because of increasing $Z^*$.
- radii increase down a group because of the increasing distance of the electrons from the nucleus.
- increasing distance from the nucleus outweighs effective nuclear charge for atomic radii down a group.
Remember that the maximum probability for an orbital moves further away from the nucleus with increasing n.

0.1 nm = 1 Å = 100 pm

The “d-block contraction” causes Ga to be about the same size as Al. This is caused by the introduction of the 3d elements which cause a vastly larger $Z^*$ for Ga.

Bohr model for H; radius($n$) = $n^2a_0$
This is a “self-consistent” scale based on $O^{2-} = 1.40$ (or 1.38) Å.

Ionic radii depend on the magnitude of the charge of the ion and its environment.

Positively charged ions are smaller than their neutral analogues because of increased $Z^*$.

Negatively charged ions are larger than their neutral analogues because of decreased $Z^*$.

Same periodic trends as atomic radii for a given charge
The utility of covalent and ionic radii

The radii tabulated in various books (e.g. Huheey, Keiter and Keiter) allow us to predict the bond length we would expect to see for a new bond.

Example:
What is the expected bond length for a single Sb-N bond?

For N, $r_{\text{cov}} = 0.70$ Å and for Sb, $r_{\text{cov}} = 1.41$ Å

Using these values, an Sb-N bond should be 2.11 Å.

The experimental distance is 2.05 Å.

For covalent radii, the predictions will be the best for atoms that have similar electronegativities. If the electronegativities are very different, the predicted distance will be too long because it ignores the coulombic attraction.
Ionization Enthalpy, $\Delta H^\circ_{\text{ie}}$ (ionization potential)

*The enthalpy change for ionization by loss of electron(s)*

$E_{(g)} \rightarrow E^+_{(g)} + e^- \quad \Delta H^\circ_{\text{ie}}$ “First ionization potential”

$E^+_{(g)} \rightarrow E^{2+}_{(g)} + e^- \quad \Delta H^\circ_{\text{ie}}$ “Second ionization potential” > first

$E^{2+}_{(g)} \rightarrow E^{3+}_{(g)} + e^- \quad \Delta H^\circ_{\text{ie}}$ “Third ionization potential” > second

\[ \cdots \]

$\Delta H^\circ_{\text{ie}}$ increases

$\Delta H^\circ_{\text{ie}}$ decreases
Features and anomalies in the trend of first ionization energies

→ B: \([\text{He}]^2s^2 \ 2p^1\) – p orbitals are more effectively shielded than s orbitals so smaller \(Z^*\) and lower \(\Delta H^\circ_{\text{ie}}\). (also \([\text{He}]^2s^2\) is a full subshell)

→ O: \([\text{He}]^2s^2 \ 2p^4\) – first pairing of electrons causes repulsion so loss of one electron is more favourable.

→ Na: \([\text{Ne}]^3s^1\) – expected from lower \(Z^*\) and greater distance of the electron from the nucleus at the start of a new shell.
Features and anomalies in the trend of first ionization enthalpies

Group 17 is “normal” – $\Delta H_{ie}^\circ$ decreases down the group as one would expect based on the increasing distance of the electrons from the nucleus.

Group 13 has unusual features – $\Delta H_{ie}^\circ$ does not decrease down the group (and is higher for Tl than for Al, Ga or In.

$\Delta H_{ie}^\circ$ is greater than expected for Ga because of the greater $Z^*$ caused by the presence of the 3d elements.

$\Delta H_{ie}^\circ$ is greater than expected for Tl because of the “greater $Z^*$” caused by relativistic effects.
Electronegativity, $\times$

The ability of an atom in a molecule to attract electrons in a bond to itself.

$\times$ increases

Linus Pauling

First Year rule

$\Delta \times > 2$ : ionic

$2 > \Delta \times > 0.5$ : polar

$\Delta \times < 0.5$ : covalent

Traditional scale goes from 0 to 4 with $\times$ of F set to 4.
Electronegativity, $\times$

(note: $\Delta \!H_a^{\text{d}}(A-B) = D_{(A-B)}$)

Pauling’s definition:

Pauling reasoned that the dissociation energy of a purely covalent bond $A-B$ should be the mean of the dissociation energies for the homonuclear bonds $A-A$ and $B-B$. Any additional energy must be caused by electrostatic attraction between $A$ and $B$ (attributed to ionic character in a bond). The ionic character must be related to the difference in the electronegativities of $A$ and $B$. He calculated this difference as follows:

$$D_{(A-B),\text{theory}} = \frac{1}{2} (D_{(A-A)} + D_{(B-B)})$$

$$\Delta'(A-B) = D_{(A-B),\text{experimental}} - D_{(A-B),\text{theory}}$$

$$X_A - X_B = 0.102 \ (\Delta'(A-B))^{\frac{1}{2}}$$

$\Delta'(A-B)$ is the ionic resonance energy in kJ/mol ($\Delta_{(A-B)}$ is in eV)

A-B $\leftrightarrow$ A$^+$ B$^-$

0.102 is a conversion from kJ/mol to eV
Mulliken’s definition:

Mulliken figured that the electronegativity of an element must be related to the energies of gaining and losing electrons. Specifically an atom that binds its electrons strongly (large $\Delta H^\circ_{ie}$) and gains other electrons readily (very positive EA or very negative $\Delta H^\circ_{ea}$) should do the same in molecules. Thus Mulliken calculated the electronegativity of an atom as the mean of the ionization potential and the electron affinity.

For A-B, the electronegativity difference between $A^+B^-$ and $A^-B^+$ is given by:

$$X_A - X_B = \frac{1}{2} \left( [IP_A + EA_A] - [IP_B + EA_B] \right)$$

$$X_A = \frac{1}{2} \left( [IP_A + EA_A] \right) \text{ (these are then scaled to fit the } \approx 0-4 \text{ scale)}$$

This method makes a lot of sense, but is not used because values of $\Delta H^\circ_{ea}$ have not been accurately determined for many elements.
Electronegativity, $\times$

The Allred-Rochow definition:

The assumption is that the force that will draw an electron toward an atom is proportional to the effective nuclear charge of that atom and related to the distance of the electron from the nucleus.

\[
\text{Force} = \frac{Z^* e^2}{4\pi\varepsilon_0 r^2}
\]

$Z^*$ = effective nuclear charge  
$e$ = charge of electron  
$\varepsilon_0$ = permittivity of a vacuum  
$r$ = atomic radius

The equation:  
\[ \times = 0.359 \left( \frac{Z^*}{r^2} \right) + 0.744 \]

puts the calculated values on the Pauling scale. This definition is useful because it can be applied to many more atoms and is one of the most used scales.
There are several other definitions based on different assumptions and methods, such as quantum mechanical calculations (Boyd) or spectroscopic measurements (Allen), but the values for elements usually end up around the same.

Trends in electronegativities are similar to those found for ionization enthalpies.
The trends in electronegativities and ionization enthalpies explain many features of chemistry such as the “diagonal relationship” (x) and the position of the metallic and non-metallic elements (ΔH°ie). Electronegativity also lets us predict the polarity of bonds and chemical reactivity.