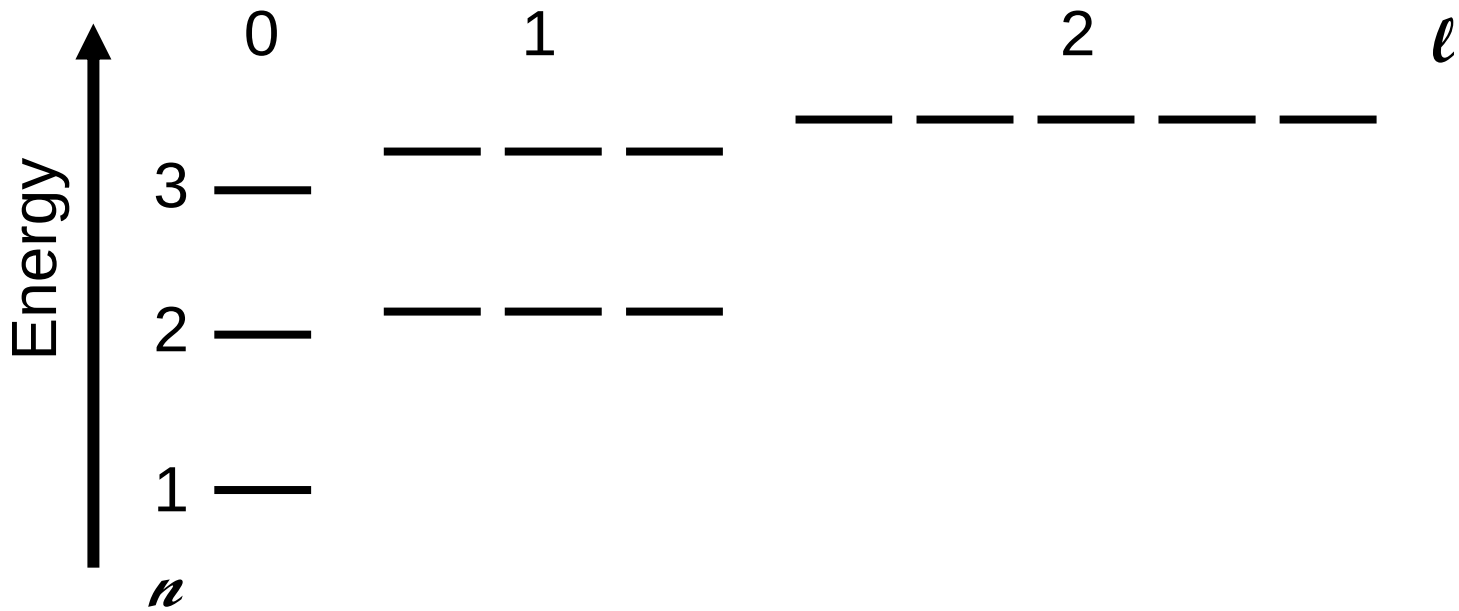
"Building up" the atoms in the periodic table

1) The *Aufbau* ("building up") principle: *lowest energy orbitals are filled first* – 1s, then 2s, then 2p, then 3s, then 3p, etc.

2) Remember the Pauli exclusion principle.

3) Hund's rule of maximum multiplicity.



Hund's rule of maximum multiplicity

"Multiplicity" is a measure of the number of unpaired electrons.
Multiplicity = number of unpaired electrons + 1

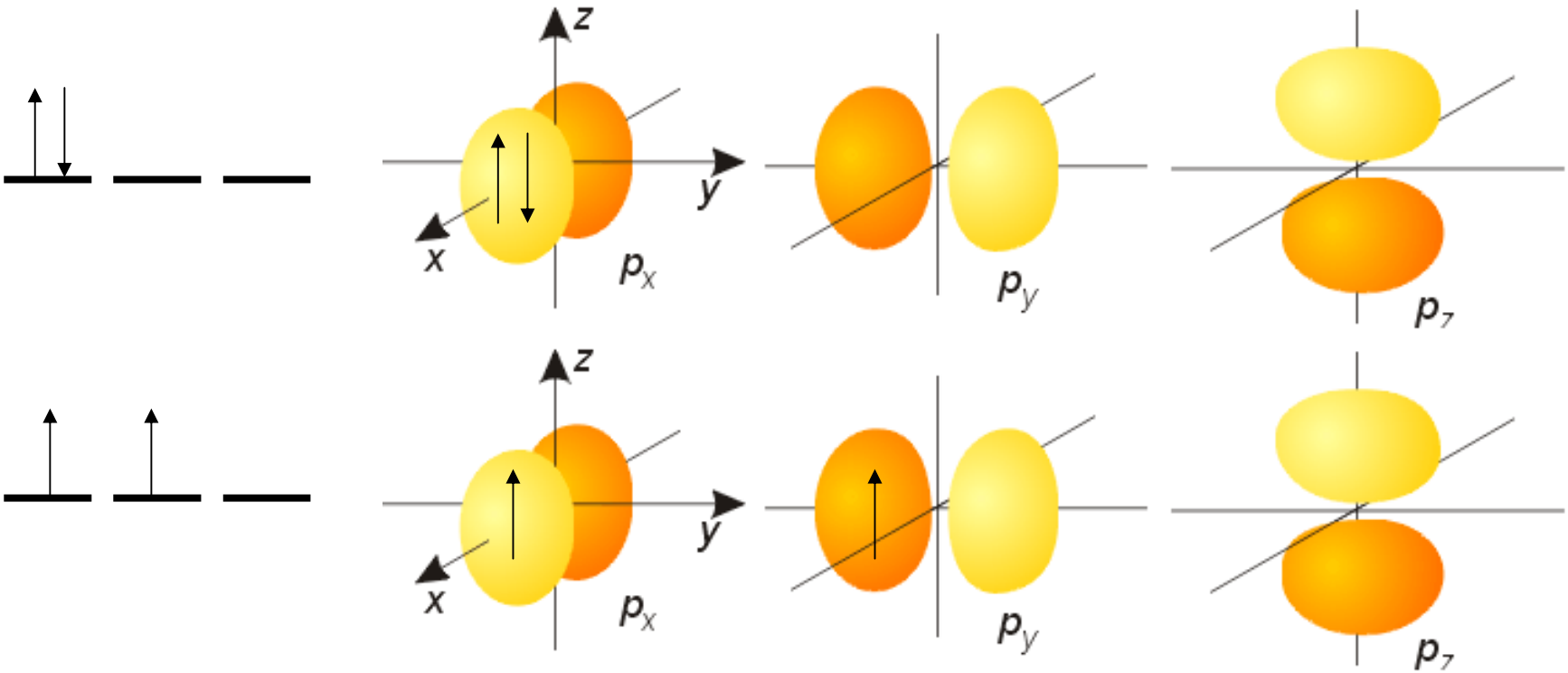
# of unpaired electrons	Multiplicity	Common Name
0	1	singlet
1	2	doublet
2	3	triplet
3	4	quartet

Hund's rule: *Electrons must be placed in the orbitals of a subshell so as to give the maximum total spin*.

i.e. put as many unpaired electrons as possible in a subshell to get the most stable arrangement.

The theory underlying Hund's rule of maximum multiplicity

1. Minimization of electron-electron repulsion
   - There is less repulsion between electrons in different orbitals (different regions in space)

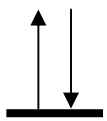


Electrons in different orbitals feel a greater Z^*, thus they are more stable

The theory underlying Hund's rule of maximum multiplicity

2. Maximization of *exchange energy* stabilization
   - This is a quantum mechanical effect that causes systems with electrons of the **same energy and spin** to be more stable.

   - The more exchanges possible, the more stable the electron configuration of the subshell

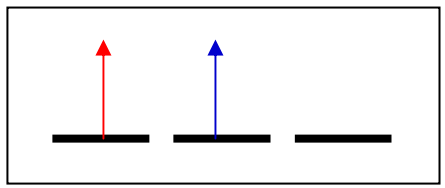


For an s-orbital (subshell), the spins must be different, so no exchanges are possible

For a p subshell, there are different orbitals of the same energy and exchanges are possible.

Two electrons of opposite spin, no exchange is possible:

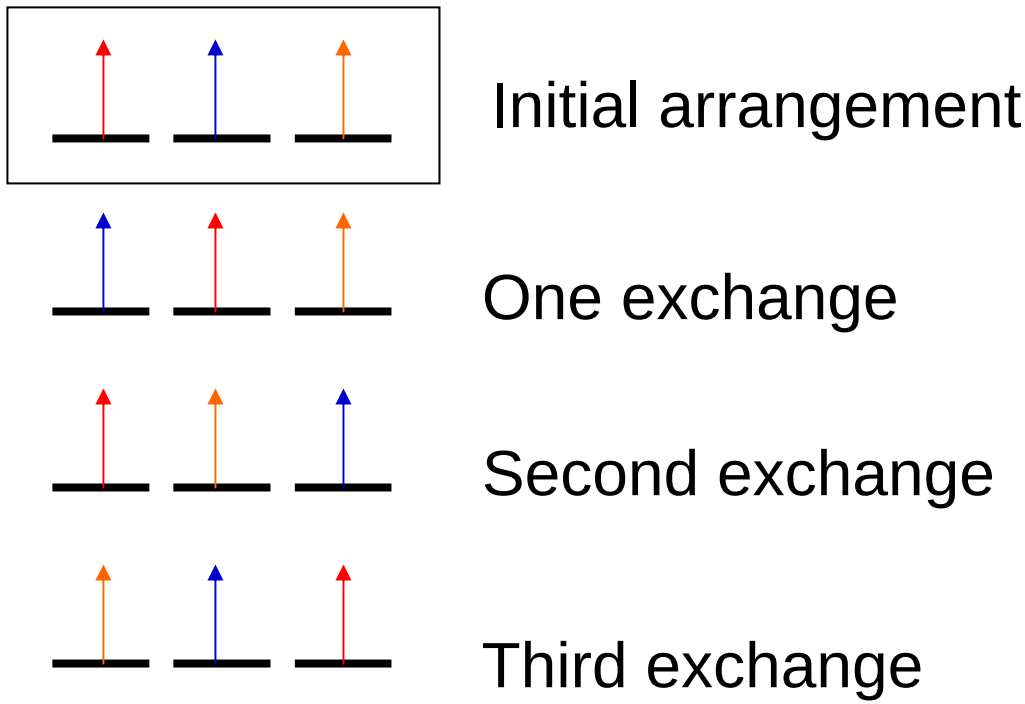
Two electrons of the same spin, one exchange is possible:



Initial arrangement

One exchange

Three electrons of same spin, three exchanges are possible:

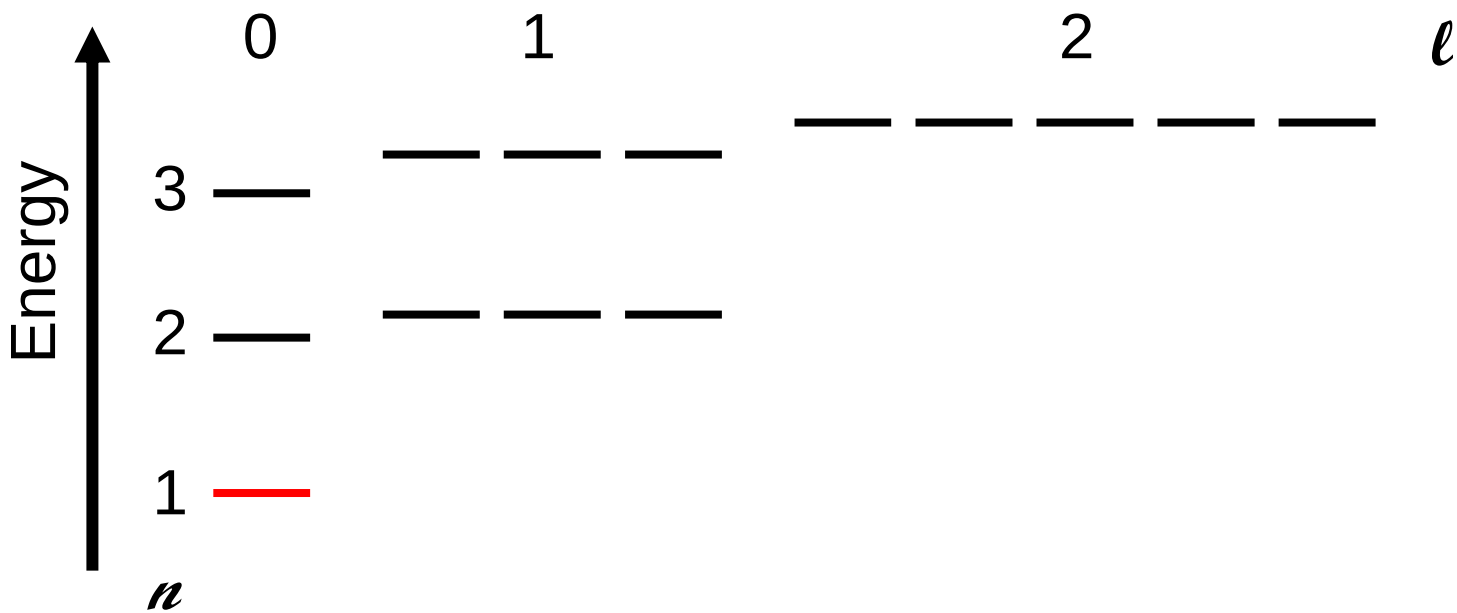


The exchange energy explains why half-filled subshells are unusually stable.

e.g. the electron configuration of Cr: $[Ar]4s^1\,3d^5$ instead of $[Ar]4s^2\,3d^4$

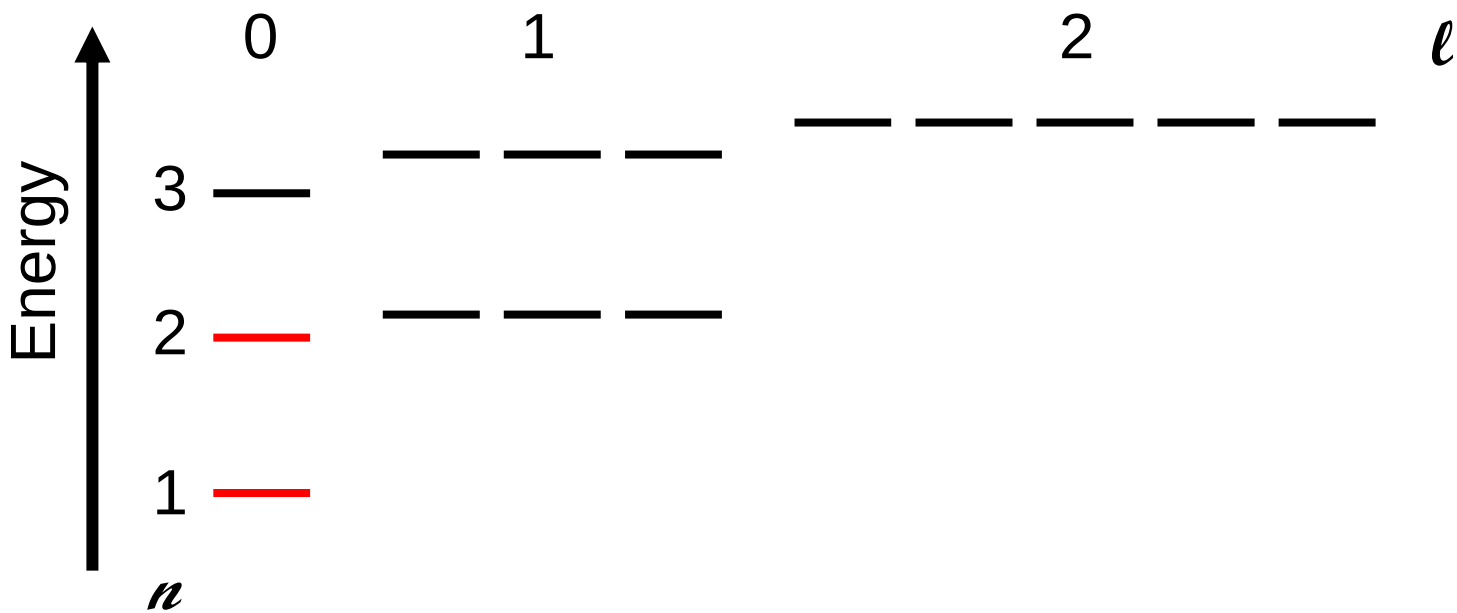
Building up the atoms in the periodic table: Period One

Z	Atom	Electron configuration	para- or diamagnetic	ΔH°_{ie} (first / eV)
1	H	$1s^1$	p	13.6
2	He	$1s^2$	d	24.6

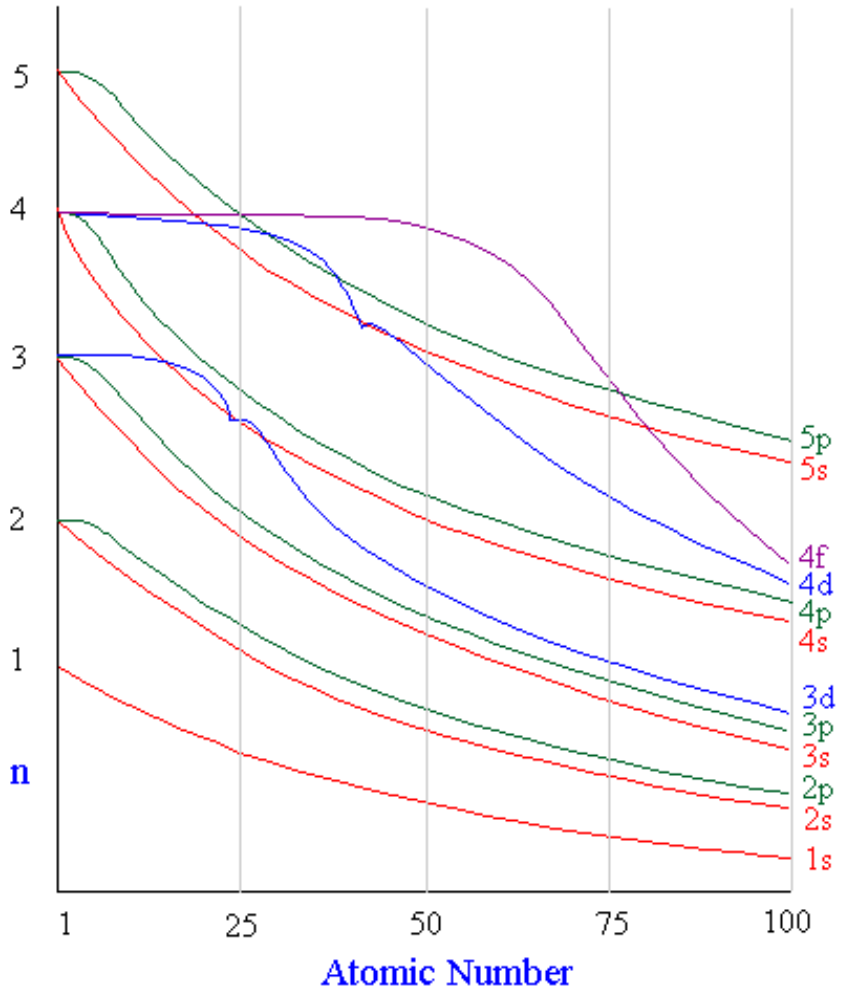


Building up the atoms in the periodic table: Period Two

Z	Atom	Electron configuration	para- or diamagnetic	$\Delta H°_{ie}$ (first / eV)
3	Li	[He]$2s^1$	p	5.4
4	Be	[He]$2s^2$	d	9.3



Orbital energy levels and atomic number



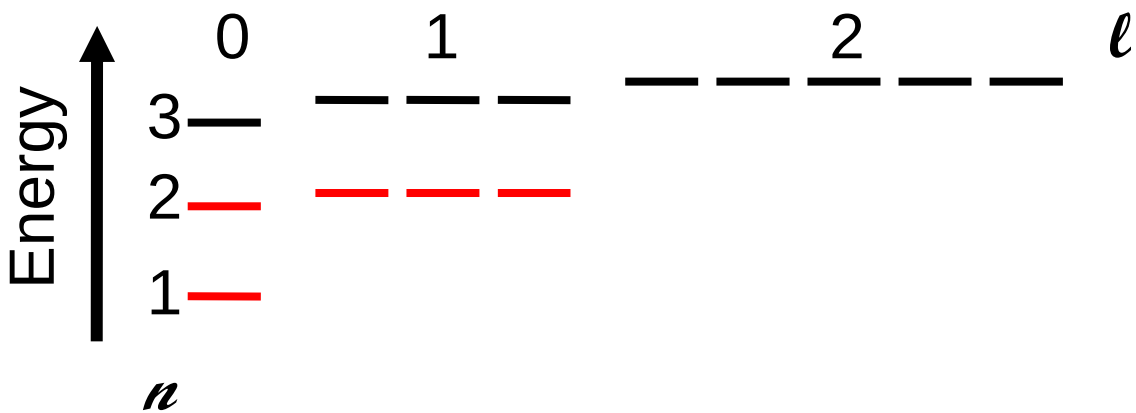
For atoms other than hydrogen:
Orbital energy depends on n and ℓ

Ordering of orbital energies:
ns < np < nd < nf

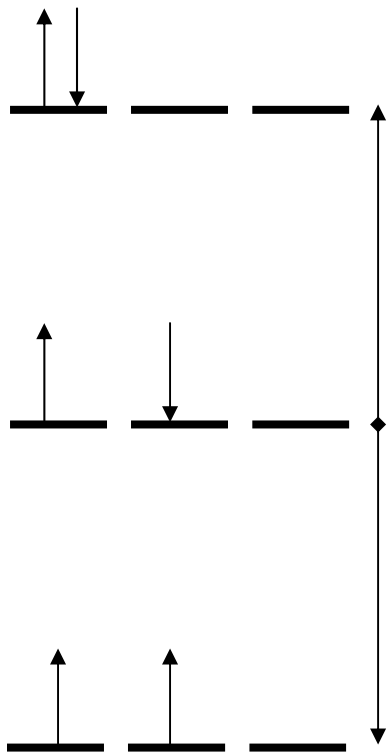
Remember:
This ordering is due to the different penetrating ability of the different types of orbitals and the different effective nuclear charges felt by the electrons in those orbitals.

Building up the atoms in the periodic table: Period Two

Z	Atom	Electron configuration	para- or diamagnetic	$\Delta H°_{ie}$ (first / eV)
5	B	$[He]2s^2\ 2p^1$	p	8.3
6	C	$[He]2s^2\ 2p^2$	p	11.3
7	N	$[He]2s^2\ 2p^3$	p	14.5
8	O	$[He]2s^2\ 2p^4$	p	13.6
9	F	$[He]2s^2\ 2p^5$	p	17.4
10	Ne	$[He]2s^2\ 2p^6$	d	21.6



The $\Delta H°_{ie}$ anomaly at nitrogen and oxygen



Π_c = Coulombic energy (destabilizing)

Hypothetical arrangement

Π_e = exchange energy (stabilizing)

C

$1\ \Pi_e$

N

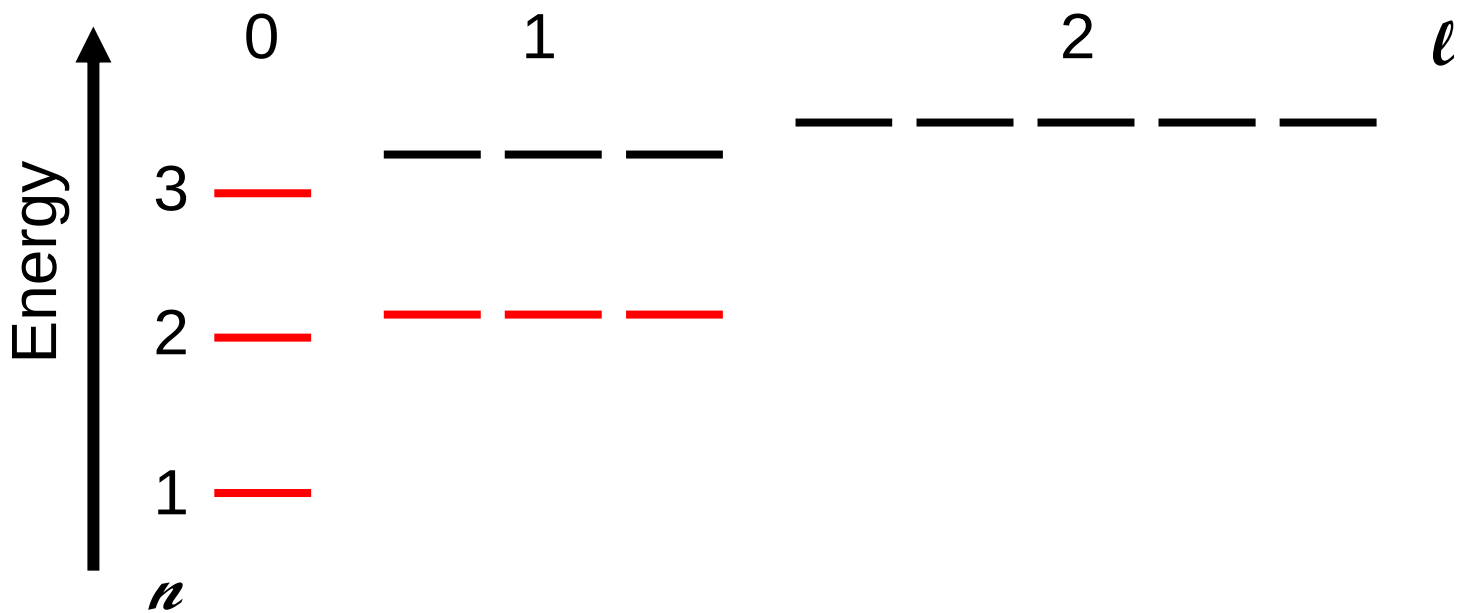
$3\ \Pi_e$

O

$1\ \Pi_c + 3\ \Pi_e$

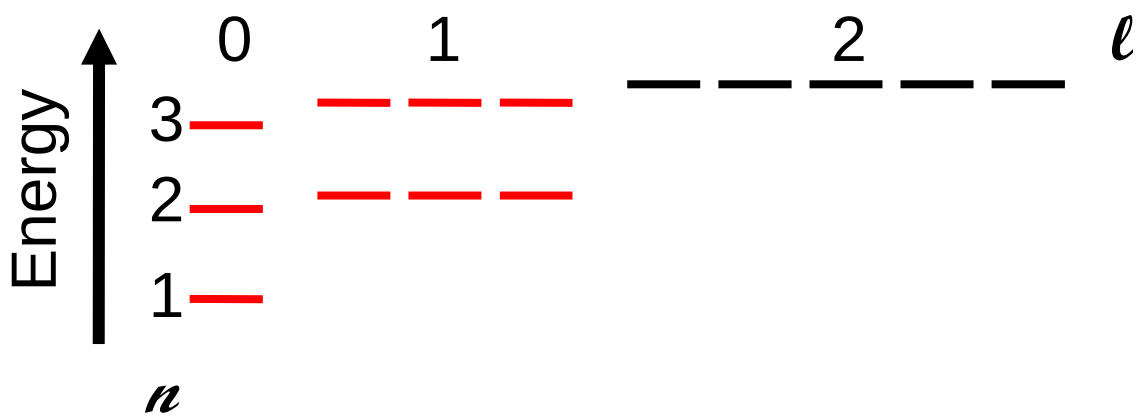
Building up the atoms in the periodic table: Period Three

Z	Atom	Electron configuration	para- or diamagnetic	ΔH°_{ie} (first / eV)
11	Na	$[Ne]3s^1$	p	5.1
12	Mg	$[Ne]3s^2$	d	7.6



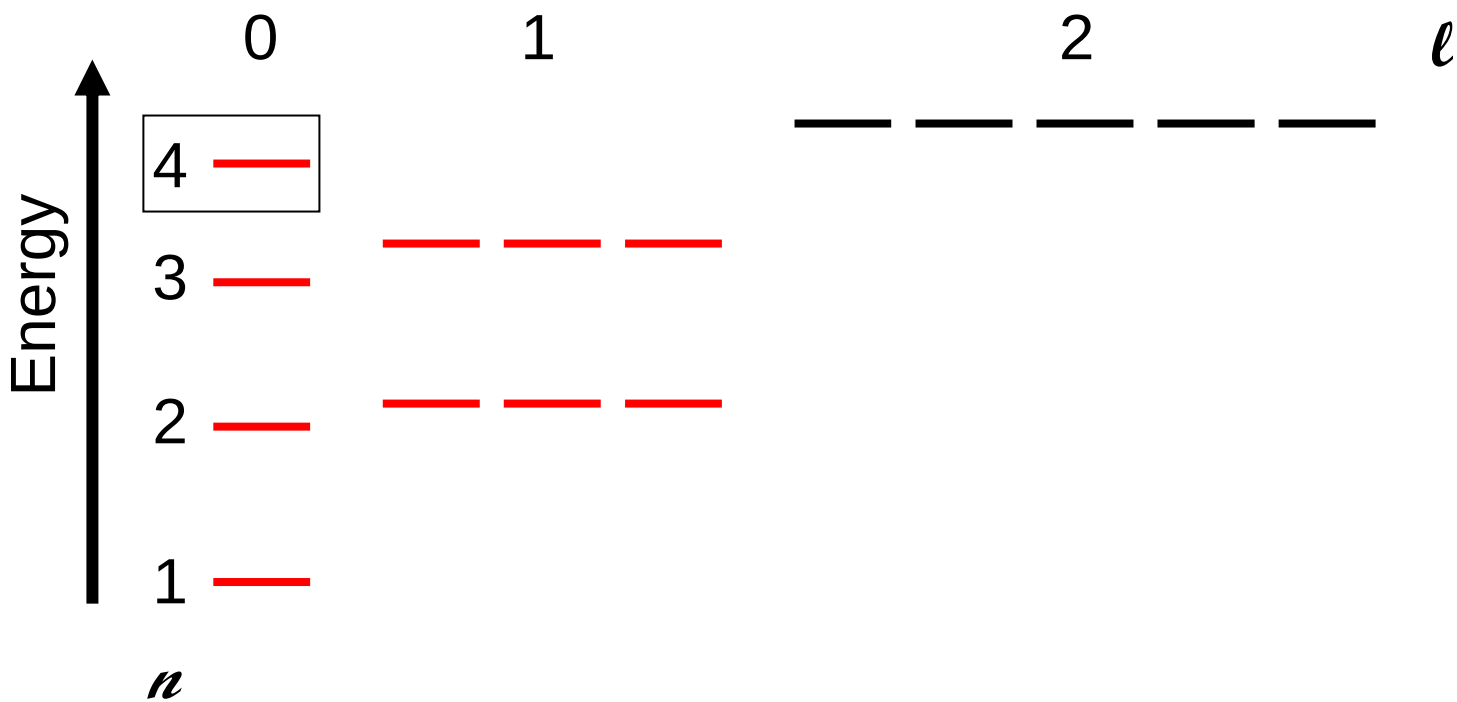
Building up the atoms in the periodic table: Period Three

Z	Atom	Electron configuration	para- or diamagnetic	$\Delta H°_{ie}$ (first / eV)
13	Al	$[Ne]3s^2\ 3p^1$	p	6.0
14	Si	$[Ne]3s^2\ 3p^2$	p	8.2
15	P	$[Ne]3s^2\ 3p^3$	p	10.5
16	S	$[Ne]3s^2\ 3p^4$	p	10.4
17	Cl	$[Ne]3s^2\ 3p^5$	p	13.0
18	Ar	$[Ne]3s^2\ 3p^6$	d	15.8

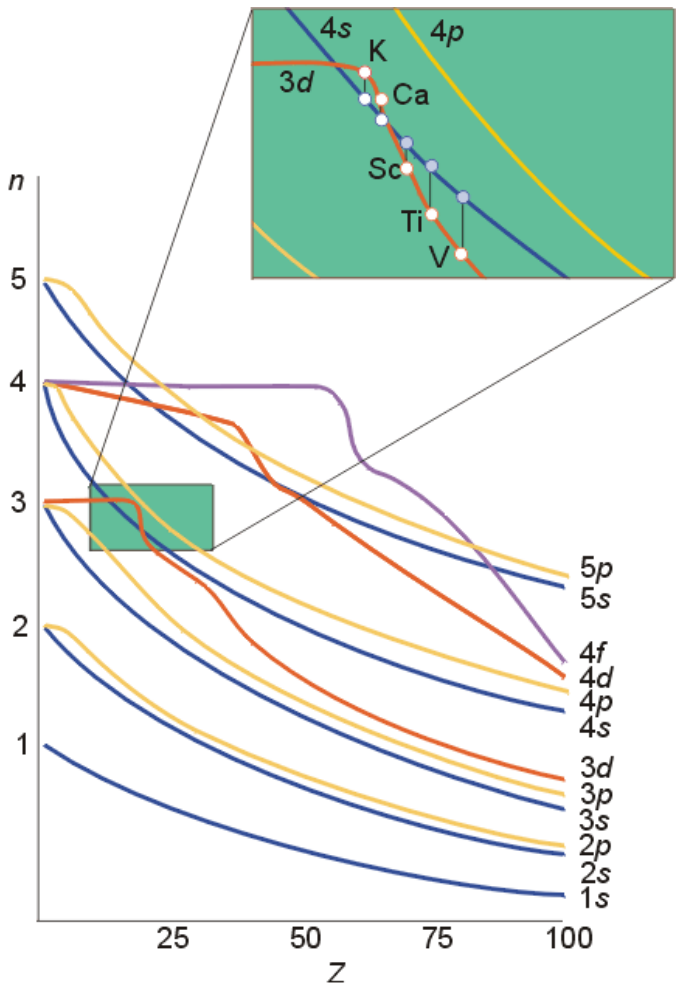


Building up the atoms in the periodic table: Period Four

Z	Atom	Electron configuration	para- or diamagnetic	$\Delta H°_{ie}$ (first / eV)
19	K	[Ar]$4s^1$	p	4.3
20	Ca	[Ar]$4s^2$	d	6.1



Chem 59-250 An anomaly of the periodic table



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.

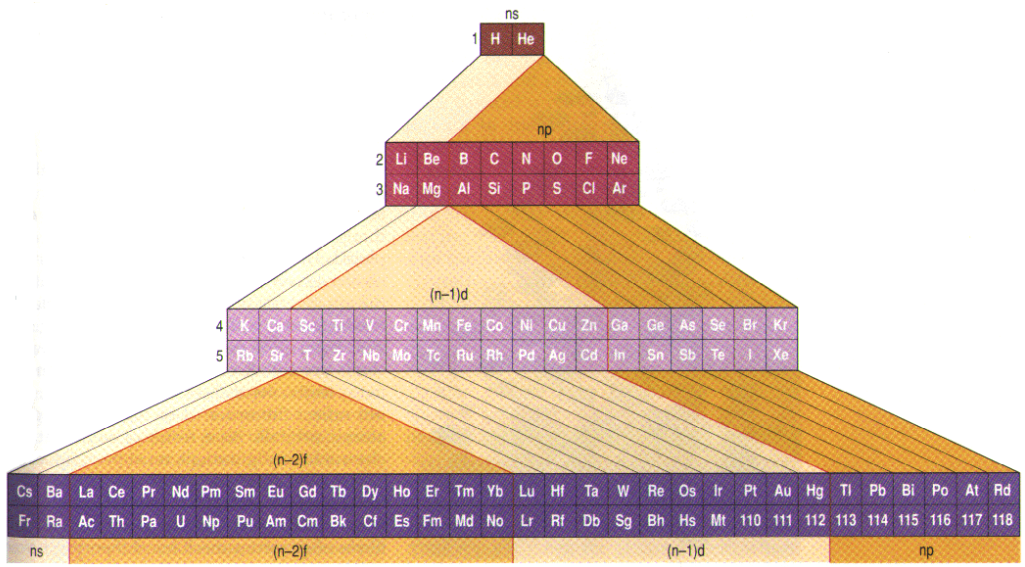


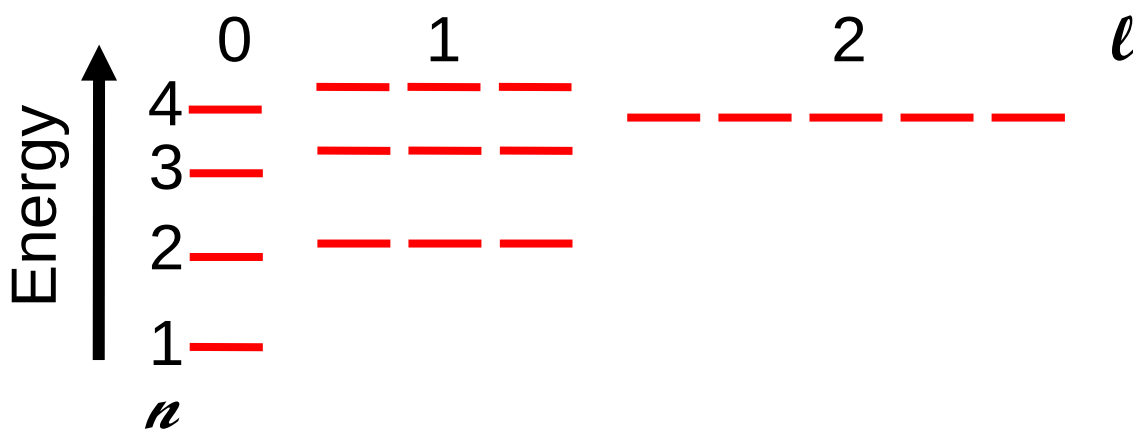
Figure 8. Alternative and updated periodic table, adapted from tables developed by Thomas Bayley, Jørgen Thomsen and Niels Bohr. These tables all depict the symmetrical nature of the periodic law regarding the increase in intervals before periodicity occurs in every other period with the exception of the first one. Tie lines denote chemical analogies.

Building up the atoms in the periodic table: Period Four

Z	Atom	Electron configuration	para- or diamagnetic	$\Delta H°_{ie}$ (first / eV)
21	Sc	$[Ar]4s^2\,3d^1$	p	6.5
22	Ti	$[Ar]4s^2\,3d^2$	p	6.8
23	V	$[Ar]4s^2\,3d^3$	p	6.7
24	Cr	$[Ar]4s^1\,3d^5$	p	6.8
25	Mn	$[Ar]4s^2\,3d^5$	p	7.4
26	Fe	$[Ar]4s^2\,3d^6$	p	7.9
27	Co	$[Ar]4s^2\,3d^7$	p	7.9
28	Ni	$[Ar]4s^2\,3d^8$	p	7.6
29	Cu	$[Ar]4s^1\,3d^{10}$	p	7.7
30	Zn	$[Ar]4s^2\,3d^{10}$	d	9.4

Building up the atoms in the periodic table: Period Four

Z	Atom	Electron configuration	para- or diamagnetic	$\Delta H°_{ie}$ (first / eV)
31	Ga	$[Ar]4s^2\,3d^{10}\,4p^1$	p	6.0
32	Ge	$[Ar]4s^2\,3d^{10}\,4p^2$	p	7.9
33	As	$[Ar]4s^2\,3d^{10}\,4p^3$	p	9.8
34	Se	$[Ar]4s^2\,3d^{10}\,4p^4$	p	9.7
35	Br	$[Ar]4s^2\,3d^{10}\,4p^5$	p	11.8
36	Kr	$[Ar]4s^2\,3d^{10}\,4p^6$	d	14.0



Building up the atoms in the periodic table:

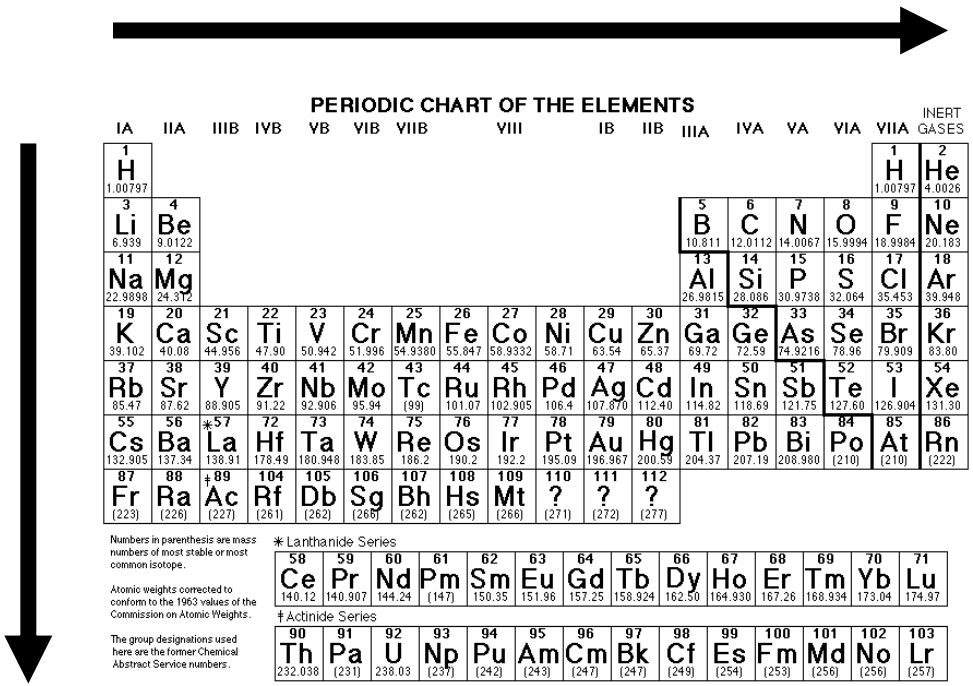
Period Five:
- analogous to Period Four

Period Six:
- analogous to Period Five with the introduction of the (4f) Lanthanides after the 6s elements

Period Seven:
- in theory, analogous to Period Six with the introduction of the Actinides (5f) after the 7s elements but little is known about the short-lived nuclei after Z=104 (Rutherfordium).

Trends for Atomic Properties in the Periodic Table

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

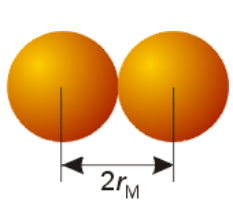


1. **The electron configuration of the atom or ion (the filling order)**
2. **The type of valence orbitals involved (size, shape, shielding and penetration)**
3. **The effective nuclear charge felt by electrons in valence orbitals**
4. “Oddities”

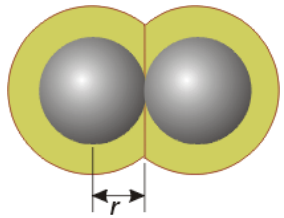
The Size of Atoms and Ions

Radii of neutral atoms

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



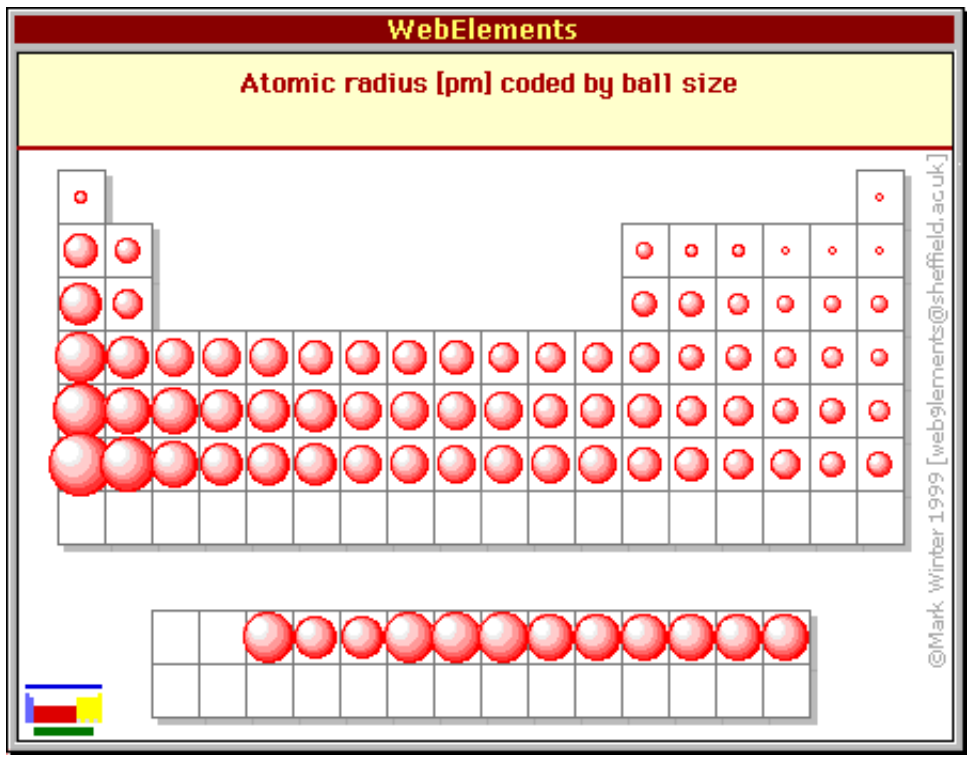
1 Metallic radius



2 Covalent radius

r decreases

r increases



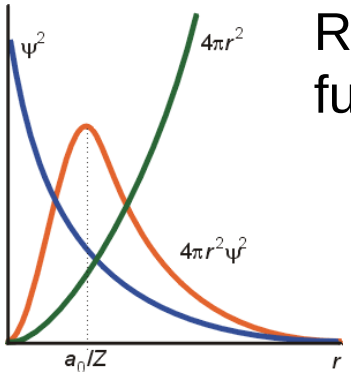
In general:

- 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.

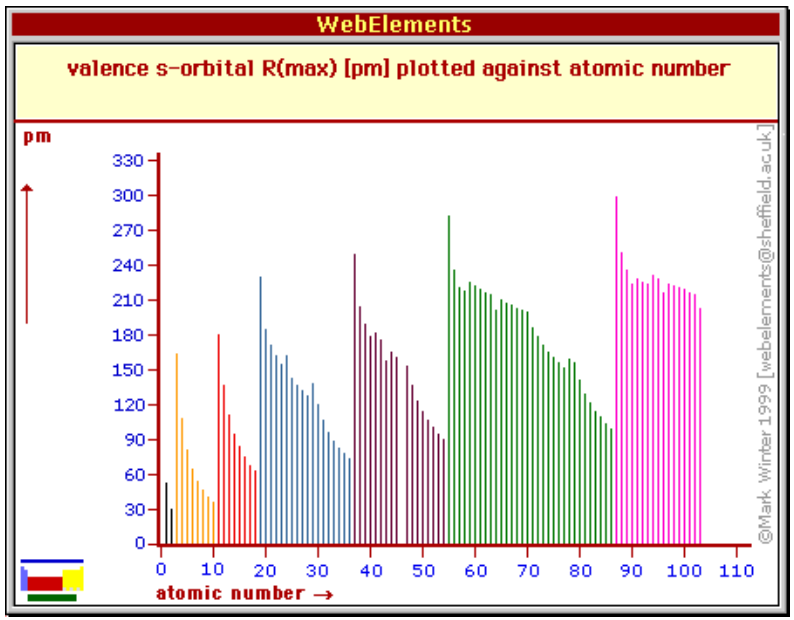
- increasing distance from the nucleus outweighs effective nuclear charge for atomic radii down a group.

Chem 59-250

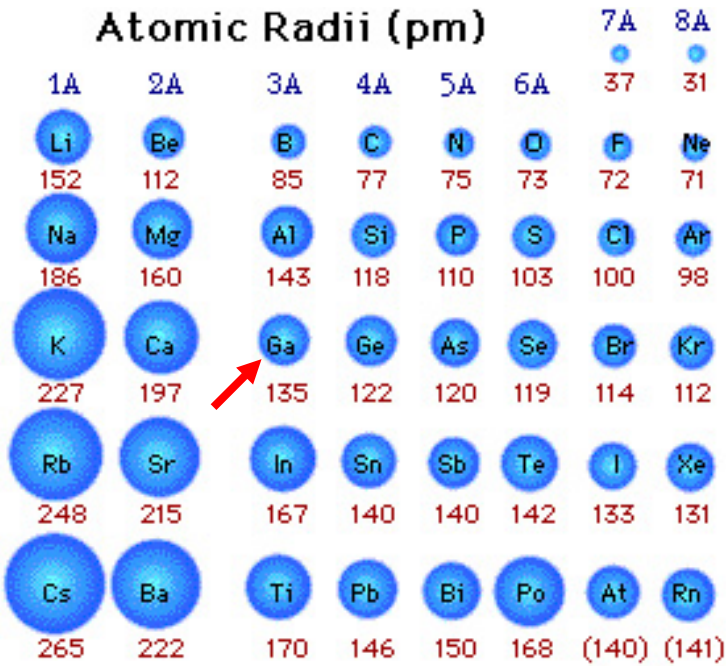


Remember that the maximum probability for an orbital moves further away from the nucleus with increasing n.

0.1 nm = 1 Å = 100 pm

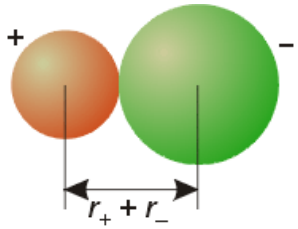


Bohr model for H; radius(n) = n^2a_0



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.

Radii of ions



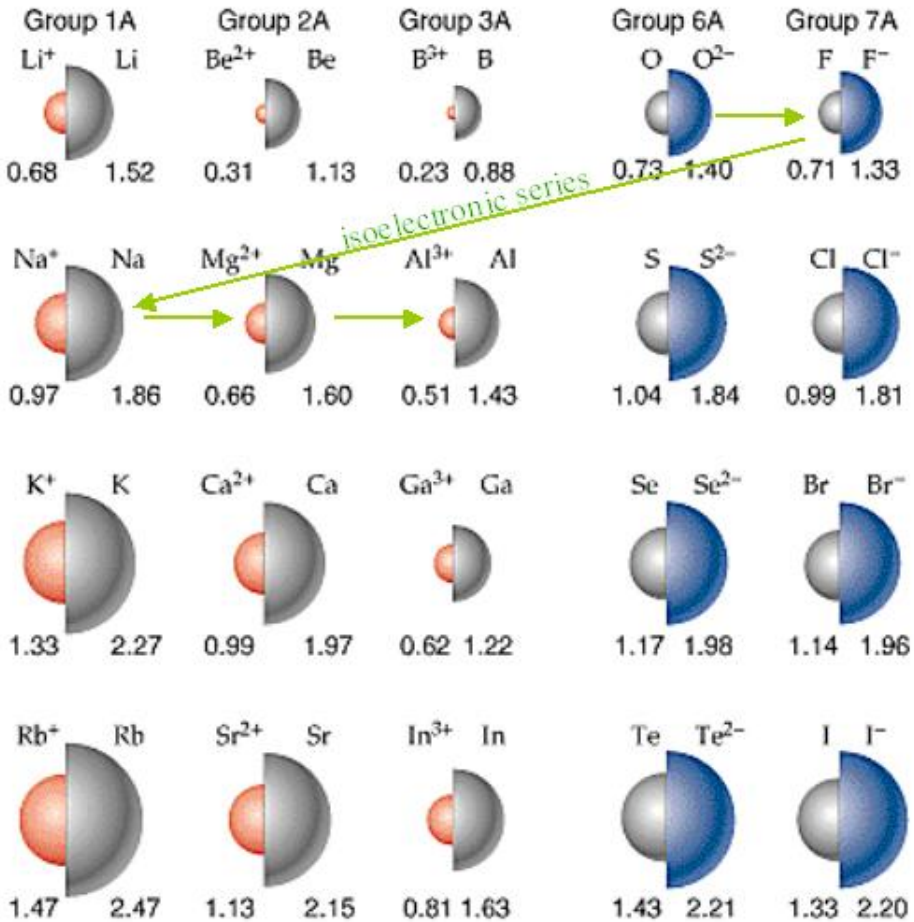
3 Ionic radius

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. (more later)

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

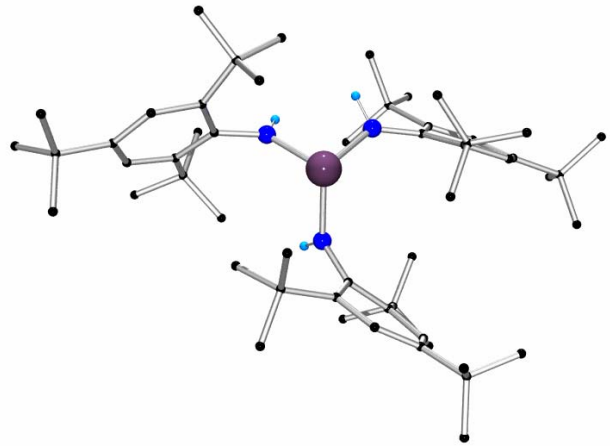
The radii tabulated in various books allow us to predict the bond length (distance between nuclei) we would expect to see for a new bond.

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

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

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

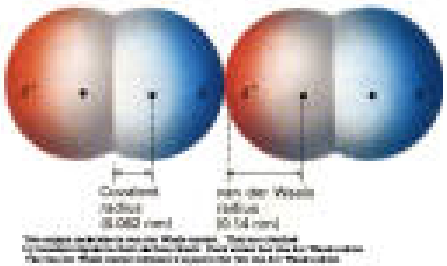
The experimental distance is 2.05 Å.



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.

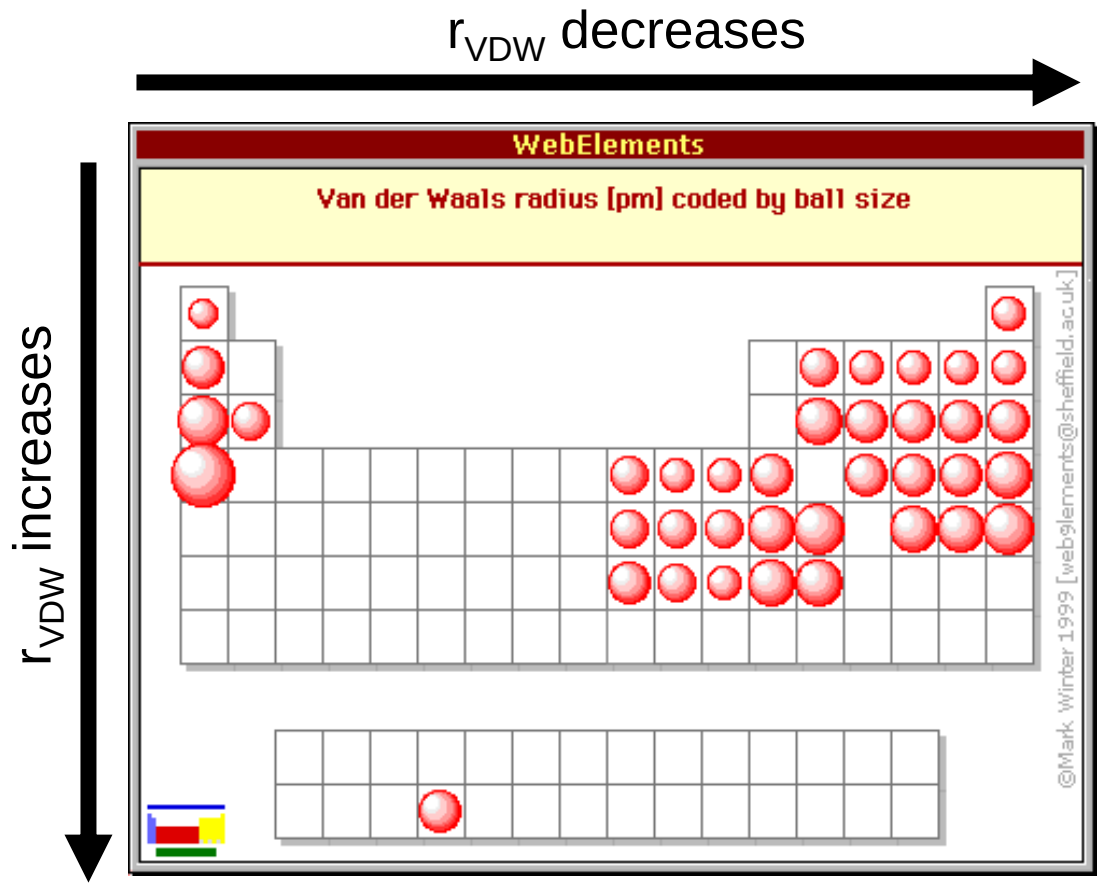
van der Waals radii

van der Waals radii are established from contact distances between non-bonding atoms in "touching" molecules or atoms



VDW radii allow us to determine whether there can be a bonding interaction between two atoms:

If the distance between the nuclei is larger than the sum of the VDW radii, then the atoms are probability not bonded.



Ionization Enthalpy, $\Delta H°_{ie}$ (ionization potential, IP)

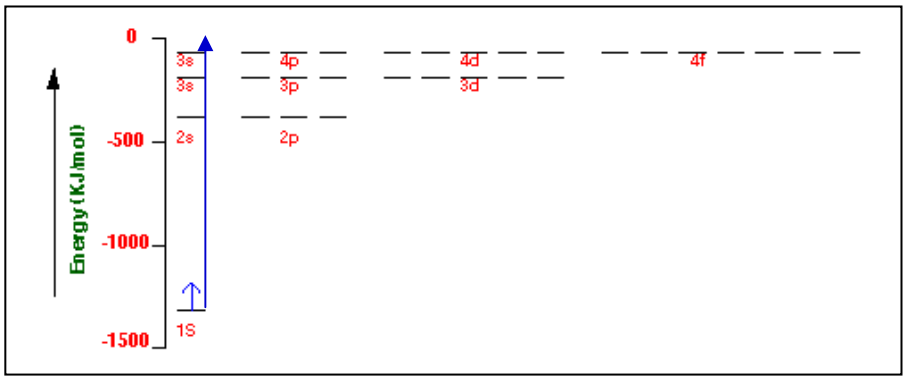
The enthalpy change for ionization by loss of electron(s)

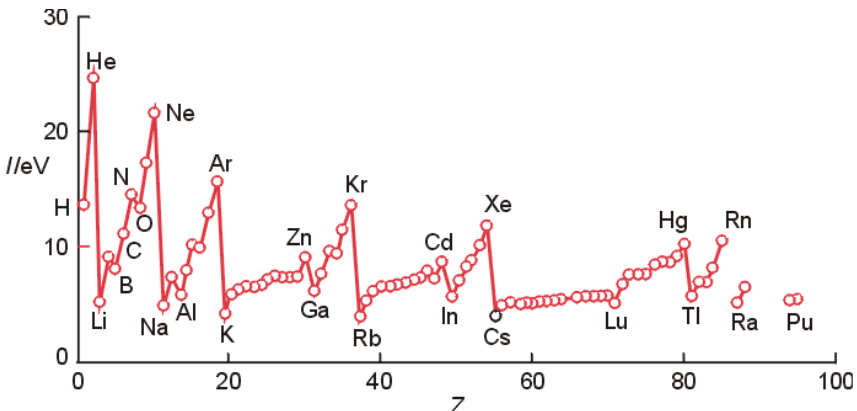
$E_{(g)} \rightarrow E^+_{(g)} + e^-$ $\Delta H°_{ie}$ "First ionization potential"

$E^+_{(g)} \rightarrow E^{2+}_{(g)} + e^-$ $\Delta H°_{ie}$ "Second ionization potential" > first

$E^{2+}_{(g)} \rightarrow E^{3+}_{(g)} + e^-$ $\Delta H°_{ie}$ "Third ionization potential" > second

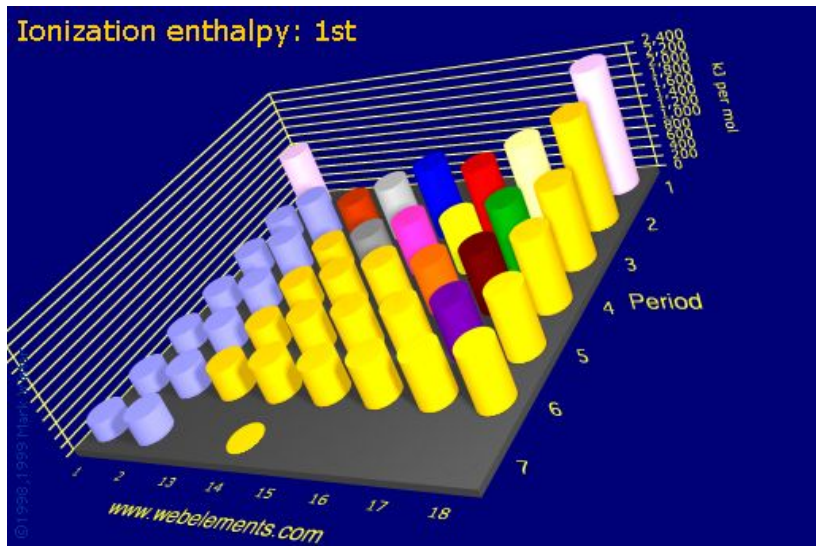
… …





$\Delta H°_{ie}$ increases

$\Delta H°_{ie}$ decreases



Ionization Enthalpy, $\Delta H°_{ie}$

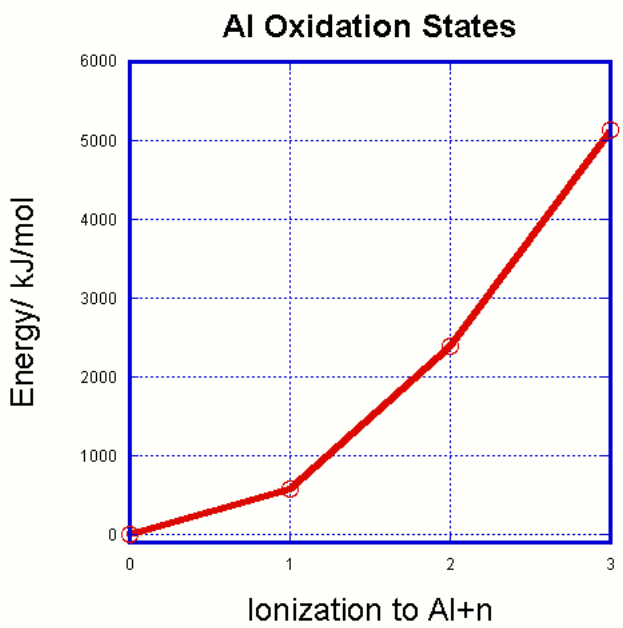
Some examples:

$Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-} \quad \Delta H°_{ie} = 502$ kJ/mol

$Al_{(g)} \rightarrow Al^{+}_{(g)} + e^{-} \quad \Delta H°_{ie} = 578$ kJ/mol

$Al^{+}_{(g)} \rightarrow Al^{2+}_{(g)} + e^{-} \quad \Delta H°_{ie} = 1817$ kJ/mol

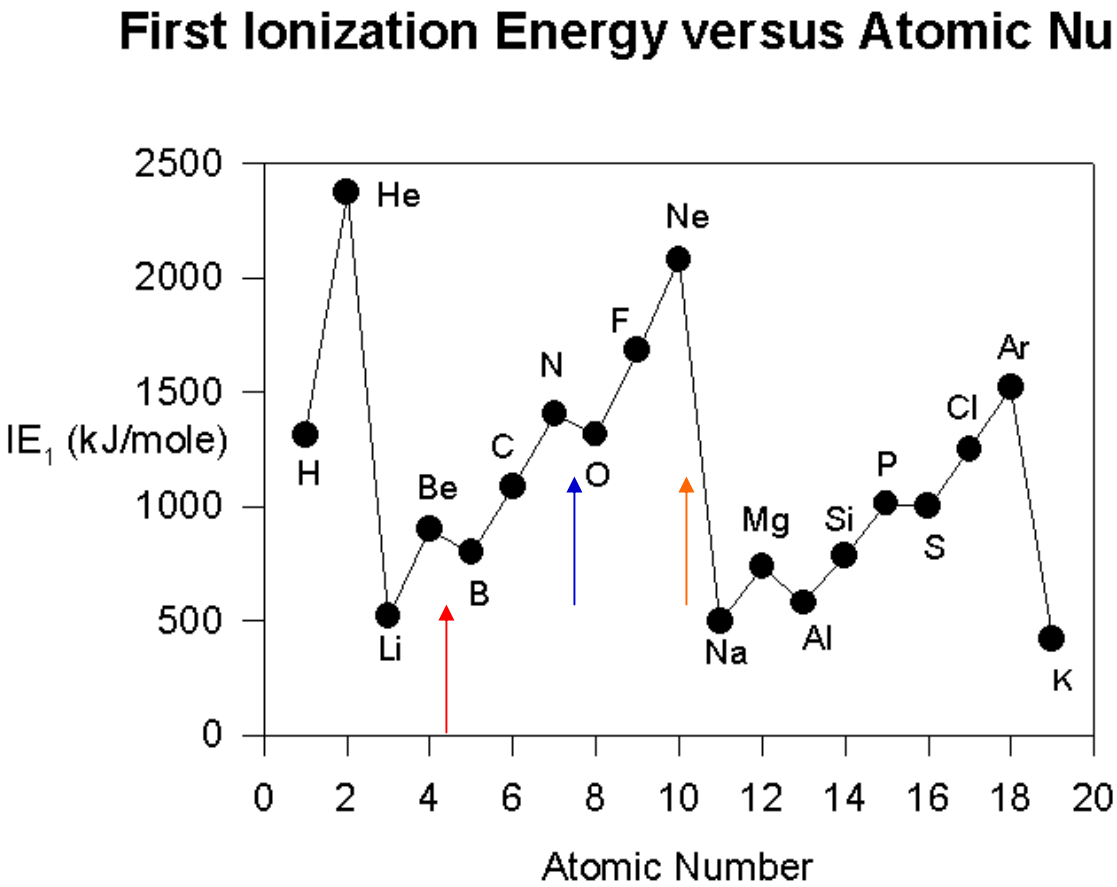
$Al^{2+}_{(g)} \rightarrow Al^{3+}_{(g)} + e^{-} \quad \Delta H°_{ie} = 2745$ kJ/mol



Thus:

$Al_{(g)} \rightarrow Al^{3+}_{(g)} + 3e^{-} \quad \Delta H°_{ie} = 5140$ kJ/mol

Features and anomalies in the trend of first ionization energies

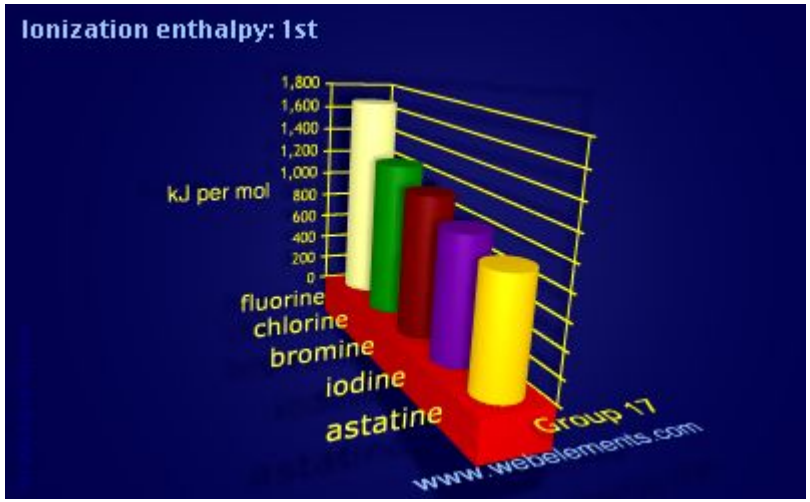


→ B: [He]$2s^2\ 2p^1$ – p orbitals are more effectively sheilded than s orbitals so smaller Z^* and lower $\Delta H°_{ie}$. (also [He]$2s^2$ is a full subshell)

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

→ Na: [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



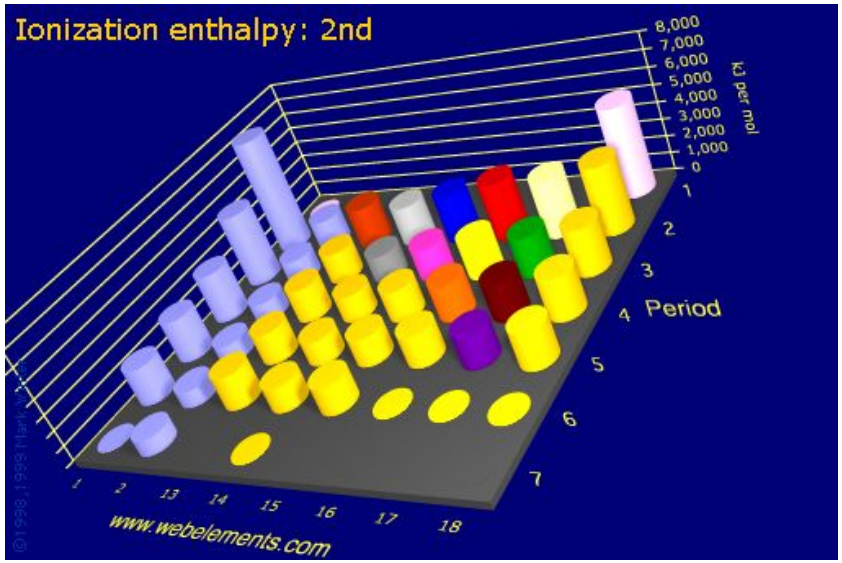
Group 17 is "normal" – $\Delta H°_{ie}$ decreases down the group as one would expect based on the increasing distance of the electrons from the nucleus.

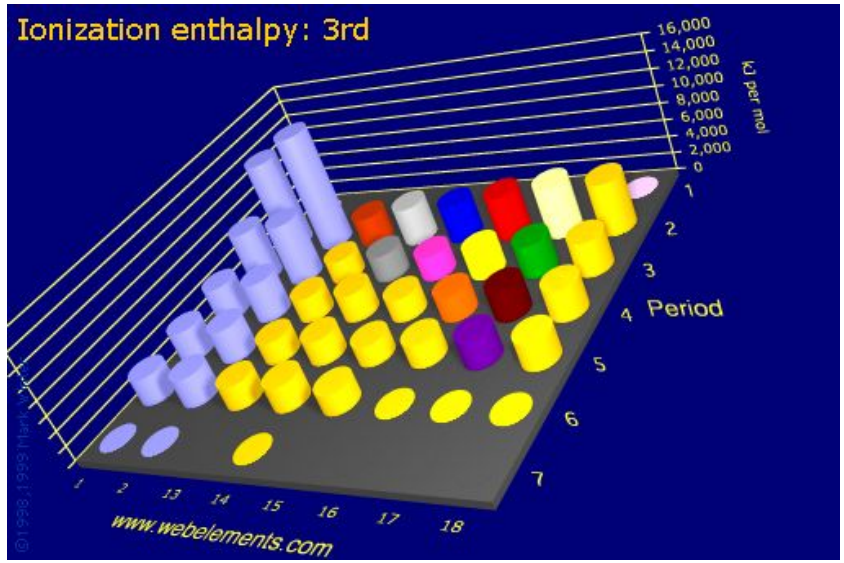
Group 13 has unusual features – $\Delta H°_{ie}$ does not decrease down the group (and is higher for Tl than for Al, Ga or In.

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

$\Delta H°_{ie}$ is greater than expected for Tl because of the "greater *Z**" caused by relativistic effects.

The trends are “shifted” for higher ionization enthalpies





Just consider the new electron configurations of the ions and the same arguments apply. The one new feature is the very high $\Delta H°_{ie}$ for early groups.

Ca: $[Ne]3s^2\ 3p^6\ 4s^2 \rightarrow Ca^+$: $[Ne]3s^2\ 3p^6\ 4s^1$ $\quad \Delta H°_{ie} = 6.1$ eV

Ca^+: $[Ne]3s^2\ 3p^6\ 4s^1 \rightarrow Ca^{2+}$: $[Ne]3s^2\ 3p^6$ $\quad \Delta H°_{ie} = 11.9$ eV

Ca^{2+}: $[Ne]3s^2\ 3p^6 \rightarrow Ca^{3+}$: $[Ne]3s^2\ 3p^5$ $\quad \Delta H°_{ie} = 50.9$ eV

- core electrons are much more stable and require much more energy to remove