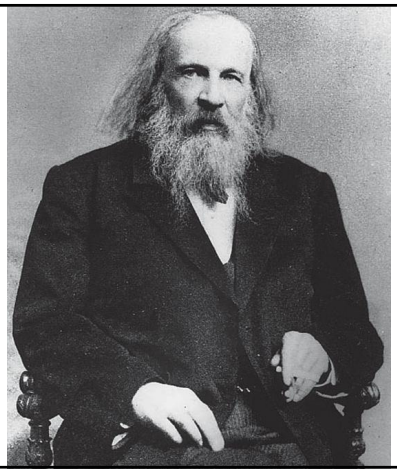


Electron Configuration and Chemical Periodicity

The Periodic Table

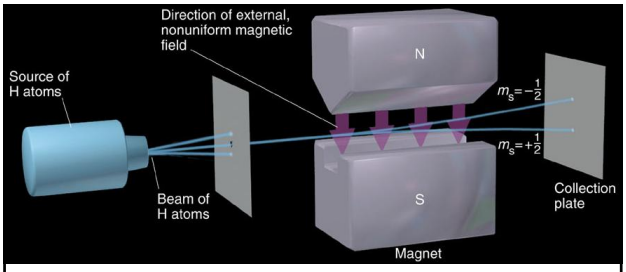
- **Periodic law** (**Mendeleev**, **Meyer**, 1870) – periodic reoccurrence of similar physical and chemical properties of the elements arranged by increasing **atomic mass**
  - Periodic table included the 65 known elements
  - Mendeleev left blank spaces for the undiscovered elements and was able to predict their properties
  - The true basis of periodicity is the **atomic number** not the atomic mass (Mosley, 1913)

8.1 Many-Electron Atoms

- Only approximate solutions of the Schrödinger equation are available
- Electron-electron interactions are important
- The same tree quantum numbers (***n, l*** and m_l) are used to describe the solutions (the orbitals are hydrogen-like)

The Electron Spin

- The electron can be viewed as a ball of spinning charge – has a magnetic moment
- The magnetic moment is quantized – only two orientations of the spin are allowed in a magnetic field



⇒**Spin quantum number (m_s) –** two possible values of m_s **(+1/2 and -1/2)**

- Each electron in an atom is described by four quantum numbers – ***n***, ***l***, m_l, m_s

- **The Pauli exclusion principle** – no two electrons in an atom can have the same set of four quantum numbers

  ⇒**Each orbital can hold no more than two electrons and they must have opposite spins** (paired spins, ↑↓)

Orbital Energies

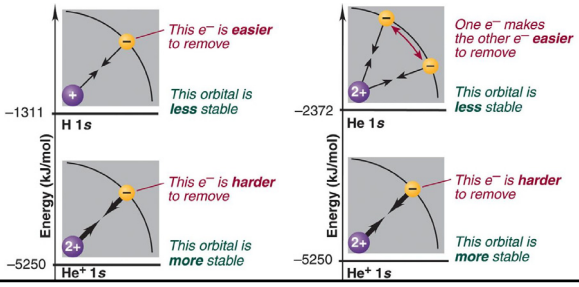
- Orbital energies depend on both ***n*** and ***l***

$$n\uparrow \rightarrow E\uparrow \qquad l\uparrow \rightarrow E\uparrow$$

  ⇒ **Orbitals in different subshells of a given principal shell have different energies**

  – Evidence – many-electron atoms have more complex atomic spectra (splitting of *E*-levels)

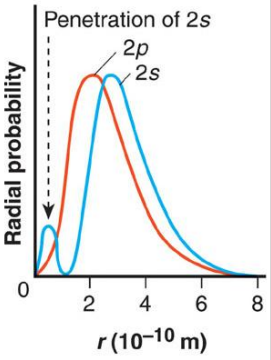
- Electrons are attracted by the nucleus and repelled by each other
  - **The effect of nuclear charge** (***Z***) – higher ***Z*** lowers the orbital energy
  - **The effect of electron repulsion** – an additional **e**$^-$ in the same orbital raises the orbital energy



- **Electron shielding** – electrons shield each other from the nuclear charge
  - **Inner electrons** shield **outer electrons** more effectively than electrons in the same orbital or subshell
- **Effective nuclear charge** (Z_{eff}) – smaller than the actual nuclear charge (Z) due to electron shielding
- **Penetration** – electrons on orbitals in different subshells of a given shell are shielded to a different extent depending on their penetration (closeness) to the nucleus

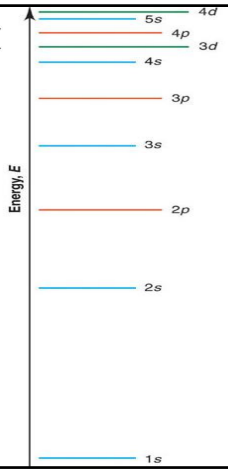
More penetration → less shielding → higher Z_{eff}

- The ***s*-orbitals** have the greatest penetration to the nucleus
  - Least shielded → highest Z_{eff} → lowest energy
- The ***p*-orbitals** have a node at the nucleus and lower penetration than the ***s*-orbitals**
  - More effectively shielded → lower Z_{eff} → higher energy



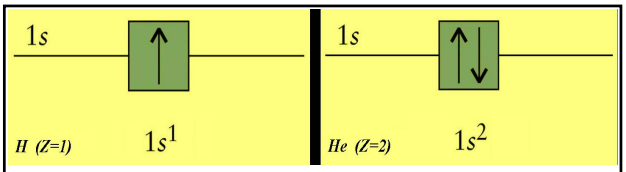
- Penetration decreases with increasing ***l***
  - More effective shielding → lower Z_{eff} → higher energy
  - Energy order of the subshells in a given shell:

    s < p < d < f < g ...
  - This leads two much greater number of energy levels compared to one-electron species like H

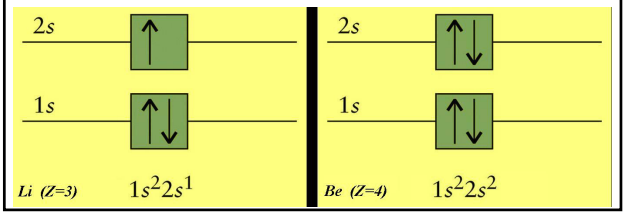


8.2 Electron Configurations

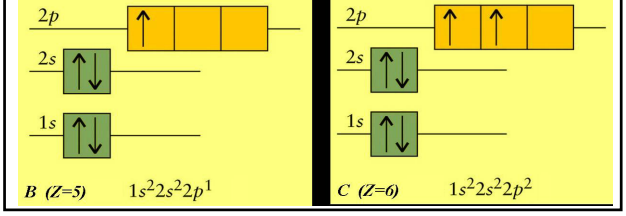
- **Building-up (aufbau) principle** – as new electrons are added to the atom, they are placed in the lowest energy available orbital (minimization of the total energy of the atom)
  - **Electron configuration** – a list of the occupied subshells and the number of electrons on them
  - **Orbital diagrams** – each orbital is represented by a box; the electrons are shown as up or down arrows depending on the spin quantum number (+1/2 or -1/2)

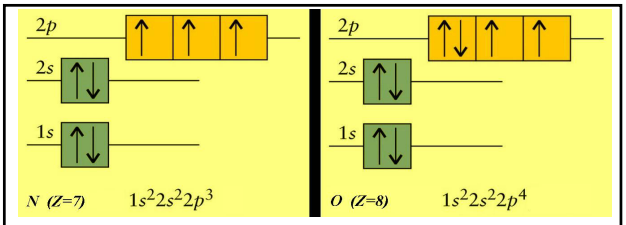


- **Closed shell** configuration represents a completely filled principal shell **(He → $1s^2$)**



- **Degenerate orbitals** – orbitals with equal energies
  - All orbitals in a subshell are degenerate (same ***n*** and ***l***) → the three **2*p***-orbitals are degenerate
- **Hund's rule** – in filling degenerate orbitals, electrons enter the empty orbitals having identical spins before pairing in one of them (minimization of the repulsion between the electrons)





- **Outer electrons** – electrons in the outermost occupied principal shell
- **Inner (core) electrons** – inner shells
- **Condensed e⁻ configurations** – inner shells (or part of them) can be abbreviated with the symbol of the previous noble gas in brackets

  $1s^2$ → abbreviated as [He]

Example: Predict the electron configurations of **F** and **Ne**.

orbital order: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, …

F (Z = 9, 9 e⁻) → $1s^2 2s^2 2p^5$ → [He]$2s^2 2p^5$

Ne (Z = 10, 10 e⁻) → $1s^2 2s^2 2p^6$ → [He]$2s^2 2p^6$

[He]$2s^2 2p^6$ → closed shell → abbreviated as [Ne]

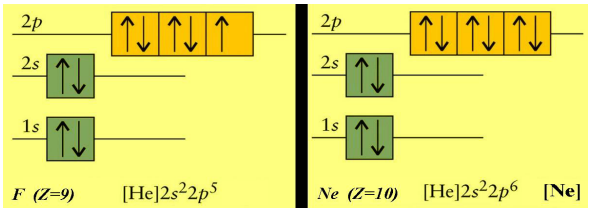


Table 8.3 Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 3

Atomic Number/ Element	Partial Orbital Diagram (3*s* and 3*p* Sublevels Only)	Full Electron Configuration	Condensed Electron Configuration
	3*s* 3*p*		
11/Na	↑	[$1s^2 2s^2 2p^6$] $3s^1$	[Ne] $3s^1$
12/Mg	↑↓	[$1s^2 2s^2 2p^6$] $3s^2$	[Ne] $3s^2$
13/Al	↑↓ ↑	[$1s^2 2s^2 2p^6$] $3s^2 3p^1$	[Ne] $3s^2 3p^1$
14/Si	↑↓ ↑ ↑	[$1s^2 2s^2 2p^6$] $3s^2 3p^2$	[Ne] $3s^2 3p^2$
15/P	↑↓ ↑ ↑ ↑	[$1s^2 2s^2 2p^6$] $3s^2 3p^3$	[Ne] $3s^2 3p^3$
16/S	↑↓ ↑↓ ↑ ↑	[$1s^2 2s^2 2p^6$] $3s^2 3p^4$	[Ne] $3s^2 3p^4$
17/Cl	↑↓ ↑↓ ↑↓ ↑	[$1s^2 2s^2 2p^6$] $3s^2 3p^5$	[Ne] $3s^2 3p^5$
18/Ar	↑↓ ↑↓ ↑↓ ↑↓	[$1s^2 2s^2 2p^6$] $3s^2 3p^6$	[Ne] $3s^2 3p^6$

- How to remember the energy order of the orbitals:

  $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p$

Note:

4*s* is filled before 3*d*

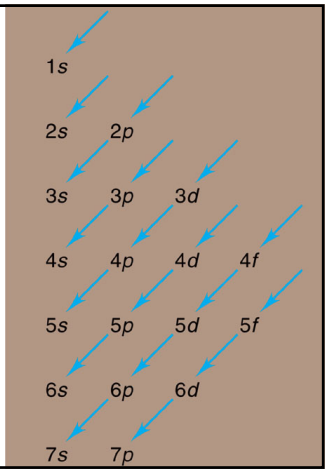


Table 8.4 Partial Orbital Diagrams and Electron Configurations* for Period 4

Atomic Number	Element	Partial Orbital Diagram (4*s*, 3*d*, and 4*p* Sublevels Only)	Condensed El. Configuration
		4*s* 3*d* 4*p*	
19	K	↑	[Ar] $4s^1$
20	Ca	↑↓	[Ar] $4s^2$
21	Sc	↑↓ ↑	[Ar] $4s^2 3d^1$
22	Ti	↑↓ ↑ ↑	[Ar] $4s^2 3d^2$
23	V	↑↓ ↑ ↑ ↑	[Ar] $4s^2 3d^3$

- Exceptions to the building-up principle
  - **Half-filled subshells** have exceptional stability

    Cr → [Ar]$4s^1 3d^5$ instead of **[Ar]$4s^2 3d^4$**

Table 8.4 Partial Orbital Diagrams and Electron Configurations* for Period 4

Atomic Number	Element	Partial Orbital Diagram (4*s*, 3*d*, and 4*p* Sublevels Only)	Condensed El. Configuration
		4*s* 3*d* 4*p*	
24	Cr	↑ ↑ ↑ ↑ ↑ ↑	[Ar] $4s^1 3d^5$
25	Mn	↑↓ ↑ ↑ ↑ ↑ ↑	[Ar] $4s^2 3d^5$
26	Fe	↑↓ ↑↓ ↑ ↑ ↑ ↑	[Ar] $4s^2 3d^6$
27	Co	↑↓ ↑↓ ↑↓ ↑ ↑ ↑	[Ar] $4s^2 3d^7$
28	Ni	↑↓ ↑↓ ↑↓ ↑↓ ↑ ↑	[Ar] $4s^2 3d^8$
29	Cu	↑ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	[Ar] $4s^1 3d^{10}$
30	Zn	↑↓ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓	[Ar] $4s^2 3d^{10}$

  - **Completely filled subshells** have exceptional stability

    Cu → [Ar]$4s^1 3d^{10}$ instead of **[Ar]$4s^2 3d^9$**

Table 8.4 Partial Orbital Diagrams and Electron Configurations* for Period 4

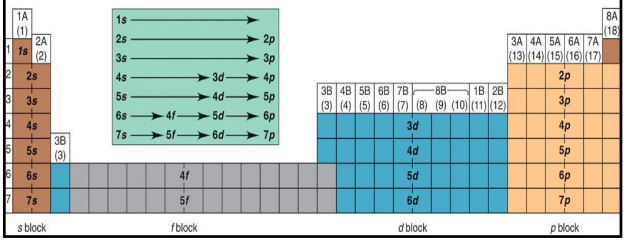
Atomic Number	Element	Partial Orbital Diagram (4s, 3d, and 4p Sublevels Only)	Condensed El. Configuration
		4s 3d 4p	
31	Ga	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	[Ar] $4s^2 3d^{10} 4p^1$
32	Ge	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	[Ar] $4s^2 3d^{10} 4p^2$
33	As	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	[Ar] $4s^2 3d^{10} 4p^3$
34	Se	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	[Ar] $4s^2 3d^{10} 4p^4$
35	Br	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	[Ar] $4s^2 3d^{10} 4p^5$
36	Kr	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	[Ar] $4s^2 3d^{10} 4p^6$

– Similarly, the building-up principle is used to obtain the electron configurations for periods 5, 6 and 7 (similar and even more drastic exceptions are observed)

Electronic Structure and the Periodic Table

- The table is divided into ***s***, ***p***, ***d***, and ***f*** blocks named by the last occupied subshell being filled
- Electron configurations can be deduced from the positions of elements in the periodic table
  - Outer shell principal quantum numbers equal period numbers (F → 2nd period, n=2)
  - All elements in a period have the same noble-gas core configurations ([He], [Ne], [Ar], …)

- The filling order of the orbitals can be obtained from the periodic table:
  - The ***ns***, ***np***, ***(n-1)d*** **and** ***(n-2)f*** orbitals are filled in the ***n*th** period from left to right
  - The filling order is ***ns*** **<** ***(n-2)f*** **<** ***(n-1)d*** **<** ***np***



Examples:

Write the full and condensed electron configurations of galium, **Ga**.

(H, He) $1s^2$ → (Li, Be) $2s^2$ → (B-Ne) $2p^6$ → (Na, Mg) $3s^2$ → (Al-Ar) $3p^6$ → (K, Ca) $4s^2$ → (Sc-Zn) $3d^{10}$ → (Ga) $4p^1$

⇒Ga → $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^1$

⇒Ga → [Ar]$4s^2 3d^{10} 4p^1$

Write the electron configuration of osmium, **Os**.

Os is in the 6th period → outer shell n=6

Previous noble gas is Xe → noble-gas core is [Xe]

After Xe → 2 *ns*, 14 *(n-2)*f, and 6 *(n-1)*d elements

⇒ [Xe]$6s^2 4f^{14} 5d^6$

- **Valence electrons** – the electrons in the outermost occupied principal shell and in partially filled subshells of lower principal shells (important in chemical reactions)
  - The number of valence electrons equals the "new" group # or (group # - 10 for ***p***-elements)
  - All elements in a group have analogous **valence shell electron configurations** (**F → [He]$2s^2 2p^5$; Cl → [Ne]$3s^2 3p^5$; all halogens → $ns^2 np^5$**)

➢**s** and **p** elements → group 1 ns^1, group 2 ns^2, group 13 ns^2np^1, ..., group 18 ns^2np^6

➢**d** elements → group 3 $(n-1)d^1ns^2$, …, group 12 $(n-1)d^{10}ns^2$

Example:

Write the electron configuration and the valence shell orbital diagram of lead, **Pb**.

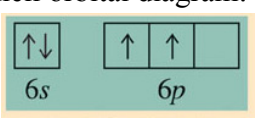
outer shell n=6 noble-gas core [Xe]

After Xe → 2 *6s*, 14 *4f*, 10 *5d*, and 2 *6p* elements

⇒[Xe] $6s^2 4f^{14} 5d^{10} 6p^2$

⇒Valence shell configuration → $6s^2 6p^2$

⇒Valence shell orbital diagram:

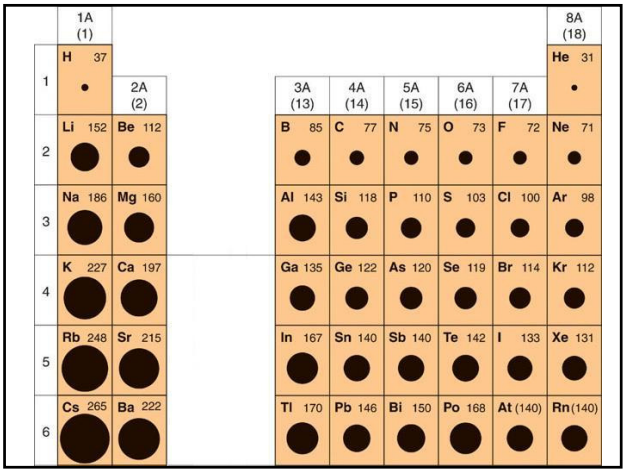


8.3 Periodic Trends in Atomic Properties

– Periodicity is based on the electron configuration which depends on the # of electrons which in turn depends on the number of protons (atomic #)

Trends in Atomic Size

- **Atomic radius** – half of the distance between the centers of two adjacent identical atoms
  - **Metallic radius** – for metals in the solid phase
  - **Covalent radius** – for nonmetals in molecules
- Atomic radii **increase down a group** and **decrease** from left to right **across a period** (for main group elements)



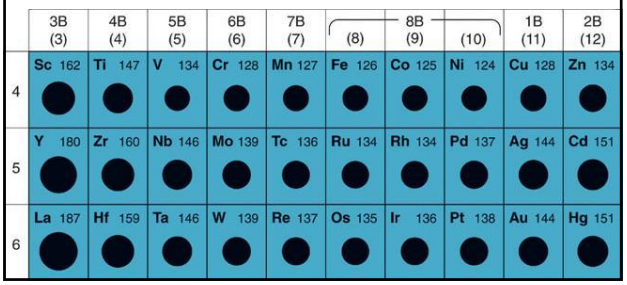
- **Down a group** – the valence shell **principal quantum number (*n*) increases** ⇒ orbitals and electron clouds become larger
- **Across a period** – the nuclear charge increases while the new electrons enter the same principal shell (do not shield each other effectively) ⇒ the **effective nuclear charge (Z_{eff}) increases** and draws the electrons closer to the nucleus

Example: Compare the sizes of **Ge**, **Sn** and **Se**.

Sn is below Ge ⇒ Sn>Ge

Ge is to the left of Se ⇒ Ge>Se

- For the **transition elements**, the size trend **across a period** is not as pronounced because electrons are added to inner shells which provides better shielding of the outer electrons, so Z_{eff} does not increase as much



Trends in Ionization Energy

- **Ionization energy (*I*)** – energy required to remove an electron from a gas-phase atom
  - **First** ionization energy (I_1) – to remove the 1st e^-

$$X(g) \rightarrow X^+(g) + e^-$$

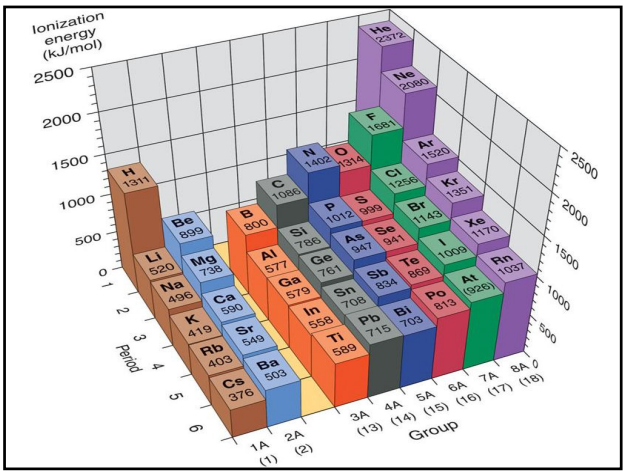
  - **Second** ionization energy (I_2) – to remove a 2nd e^-

$$X^+(g) \rightarrow X^{2+}(g) + e^-$$

- Ionization energies are positive (endothermic) and become larger with every subsequent ionization

$$0 < I_1 < I_2 < I_3 < I_4 \ldots$$

  - It's harder to remove an e^- from a positive ion



- First ionization energies **decrease down a group** and **increase** from left to right **across a period** (with some exceptions)
  - **Down a group** electrons are removed from shells that are farther from the nucleus (less tightly bound)
  - **Across a period** Z_{eff} increases (valence electrons are more tightly bound to the nucleus)
- Low ionization energy accounts for the metallic character of elements in the lower left corner of the table (***s***, ***d***, ***f*** and some of the ***p*** block) – easy removal of e^- provides better conductivity and tendency to form cations

- Irregularities in the ionization energy trends
  - Decrease in I_1 between groups 2(2A) and 13(3A) elements

    group 2A → ns^2 **group 3A →** ns^2np^1
    - The ***n*p** electron is easier to remove than the ***n*s** electron – ***p***-subshells have higher energy and are less tightly bound
  - Decrease in I_1 between groups 15 and 16 elements

    group 15(5A) → $ns^2np_x^1np_y^1np_z^1$

    group 16(6A) → $ns^2np_x^2np_y^1np_z^1$
    - It's easier to remove the paired electron on the p_x-orbital – paired electrons repel each other stronger than unpaired electrons

- Considerable **jump** in the successive ionization energies occurs after removal of all valence electrons – core electrons are much more difficult to remove than valence electrons
  - explains the charges of stable metal cations

Na → $[Ne]3s^1$

I_1 **= 496 kJ/mol,** I_2**=4562 kJ/mol**

Stable cation → Na^+

Mg → $[Ne]3s^2$

I_1 **= 738 kJ/mol,** I_2 **= 1450 kJ/mol,** I_3 **= 7734 kJ/mol**

Stable cation → Mg^{2+}

Trends in Electron Affinity

- **Electron affinity (*A*)** – energy associated with the addition of an electron to a gas-phase atom
  - **First** electron affinity (A_1) – to add the 1st e^-

    $X(g) + e^- \rightarrow X^-(g)$
  - **Second** electron affinity (A_2) – to add a 2nd e^-

    $X^-(g) + e^- \rightarrow X^{2-}(g)$
- Electron affinities can be either exothermic (-) or endothermic (+)
  - A_1 is typically (-) (exceptions: group 2A, 8A, …)
  - A_2, A_3 … are always positive
  - By convention, "larger" ***A*** is more exothermic (-)

1A (1)							8A (18)
H −72.8	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	He (0.0)
Li −59.6	Be (+18)	B −26.7	C −122	N +7	O −141	F −328	Ne (+29)
Na −52.9	Mg (+21)	Al −42.5	Si −134	P −72.0	S −200	Cl −349	Ar (+35)
K −48.4	Ca (+186)	Ga −28.9	Ge −119	As −78.2	Se −195	Br −325	Kr (+39)
Rb −46.9	Sr (+146)	In −28.9	Sn −107	Sb −103	Te −190	I −295	Xe (+41)
Cs −45.5	Ba (+46)	Tl −19.3	Pb −35.1	Bi −91.3	Po −183	At −270	Rn (+41)

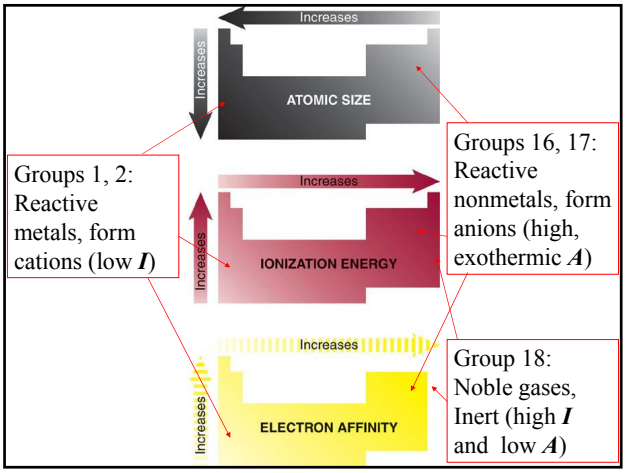
- First electron affinities tend to be **larger (more exothermic) in the upper right corner** of the table similarly to the first ionization energies
- Successive electron affinities are smaller and smaller – more endothermic ($A_1 > A_2 > A_3$ **...**)
  - It's harder to add an e^- to a negative ion
- Considerable **drop** in the successive electron affinities occurs after achieving a noble gas configuration – the new electrons are added to a higher principal shell
  - Explains the charges of the stable anions of groups 15, 16 and 17 (N^{3-}, O^{2-}, F^- …)

- Irregularities in the electron affinity trends
  - Decrease in A_1 between groups 1 and 2 elements

    group 1 → ns^1 **group 2 → ns^2**
    - For group 2 the new electron is added to the higher energy ***np*** subshell
  - Decrease in A_1 between groups 14 and 15 element

    group 14 → $ns^2np_x^1np_y^1$

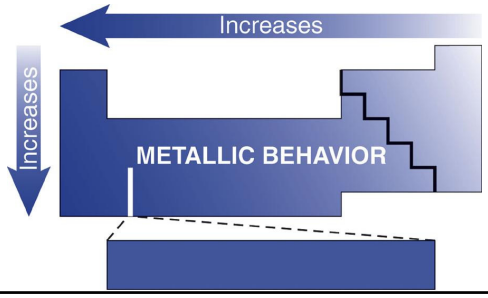
    group 15 → $ns^2np_x^1np_y^1np_z^1$
    - For group 15 the new electron is added to an already occupied ***np*** orbital – pairing of electrons is energetically unfavorable (stronger repulsion)



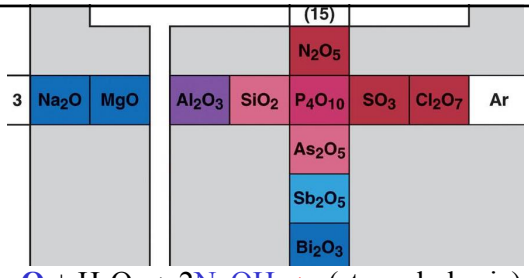
8.4 Atomic Structure and Chemical Behavior

Trends in Metallic Behavior

- Related to the trends in the size, ***I*** and ***A***



- Relative tendency to lose or gain electrons
  - The tendency to form cations increases to the left and toward the bottom (***I*** decreases)
  - The tendency to form anions increases to the right and toward the top (***A*** increases)
- Elemental oxides
  - **Metals** tend to form ionic oxides that act as bases in water → **basic oxides** (Na_2O, CaO, BaO, …)
  - **Nonmetals** tend to form covalent oxides that act as acids in water → **acidic oxides** (CO_2, SO_3, …)
  - Most **metalloids** and **some metals** form **amphoteric oxides** → can act as acids or bases in water (Al_2O_3, GeO_2, …)



$Na_2O + H_2O \rightarrow 2NaOH$ ← (strongly basic)

$P_4O_{10} + H_2O \rightarrow H_3PO_4$ ← (weakly acidic)

$SO_3 + H_2O \rightarrow H_2SO_4$ ← (strongly acidic)

$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$ ← (amphoteric)

$Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2Al(OH)_4^-$ ↵

Properties of Monatomic Ions

- Electron configurations of **cations**
  - For ***s*-** and ***p*-elements**, electrons are lost first from the ***np*** subshell followed by the ***ns*** subshell
  - All valence electrons are lost until a **noble gas** (or a **pseudo-noble gas**) **configuration** is achieved (high stability)

Example: Write the electron configurations of the stable cations of **Sr** and **Ga**.

Sr → [Kr]$5s^2$ **Sr^{2+} → [Kr]**

Ga → [Ar]$4s^2 3d^{10} 4p^1$ **Ga^{3+} → [Ar]$3d^{10}$**

Pseudo-noble gas configuration → [Noble]$(n\text{-}1)d^{10}$

– **Inert pair** effect – the ***np***-electrons have higher energy than the ***ns***-electrons and are lost first, so the two ***ns***-electrons may or may not be lost (for the heavier metals in the ***p***-block → In, Tl, Sn, Pb, and Bi)

Example: Write the electron configurations of the two common cations of **Pb**.

Pb → [Xe]$6s^2 4f^{14} 5d^{10} 6p^2$

Pb^{2+} → [Xe]$6s^2 4f^{14} 5d^{10}$ **Pb^{4+} → [Xe]$4f^{14} 5d^{10}$**

Inert pair

Pseudo-noble gas config. → [Noble]$(n\text{-}2)f^{14}(n\text{-}1)d^{10}$

– For ***d*-elements**, electrons are lost first from the ***ns*** subshell followed by the ***(n-1)d*** subshell

– In general, not all valence electrons are lost and more than one cations are possible

Example: Write the electron configuration of **Co^{3+}**.

Co → [Ar]$4s^2 3d^7$ **Co^{3+} → [Ar]$3d^6$**

- Electron configurations of **anions**
  - Electrons are added until a noble-gas configuration is reached

Example: Write the electron configuration of the **nitride** ion.

N → [He]$2s^2 2p^3$ **N^{3-} → [He]$2s^2 2p^6$ → [Ne]**

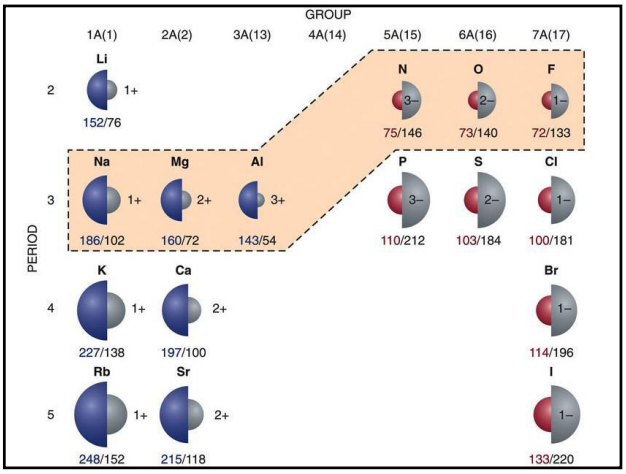
- **Magnetic properties** of atoms and ions
  - Species with unpaired electrons are **paramagnetic** (attracted by magnetic fields)
  - Species having all electrons paired are **diamagnetic** (not attracted by magnetic fields)

Example: Write the electron configurations of **V** and **V^{3+}** and determine which species is more paramagnetic.

V → [Ar]$4s^2 3d^3$ **V^{3+} → [Ar]$3d^2$**

More paramagnetic (more unpaired e^-)

- **Ionic sizes** (ionic radii)
  - Part of the distance between the centers of two neighboring ions in an ionic solid (**O^{2-}** is used as a standard with radius 140 pm)
- **Cations** are smaller than their parent atoms
  - Cation size decreases as charge increases for the different cations of an element
- **Anions** are larger then their parent atoms
- Ionic sizes of cations as well as anions follow the same trends in the periodic table as the sizes of atoms (increase down and to the left)
  - In a given period, the anions are larger than the cations



- **Isoelectronic species** – atoms and ions with the same number of electrons (have the same electron configuration)
  - Size decreases with increasing the atomic number of the element (nuclear charge increases)

Example: Compare the sizes of **Cl^-**, **Ca^{2+}** and **Sc^{3+}**

Isoelectronic, electron configuration of argon **[Ar]**

⇒ $Sc^{3+} < Ca^{2+} < Cl^-$ (atomic number ↓)

Example: Compare the sizes of **Ca**, **Ca^{2+}** and **Mg^{2+}**

$Ca^{2+} <$ Ca (cation is smaller)

$Mg^{2+} < Ca^{2+}$ (Mg is above Ca) ⇒ $Mg^{2+} < Ca^{2+} <$ Ca