CH-110 Advanced General Chemistry I

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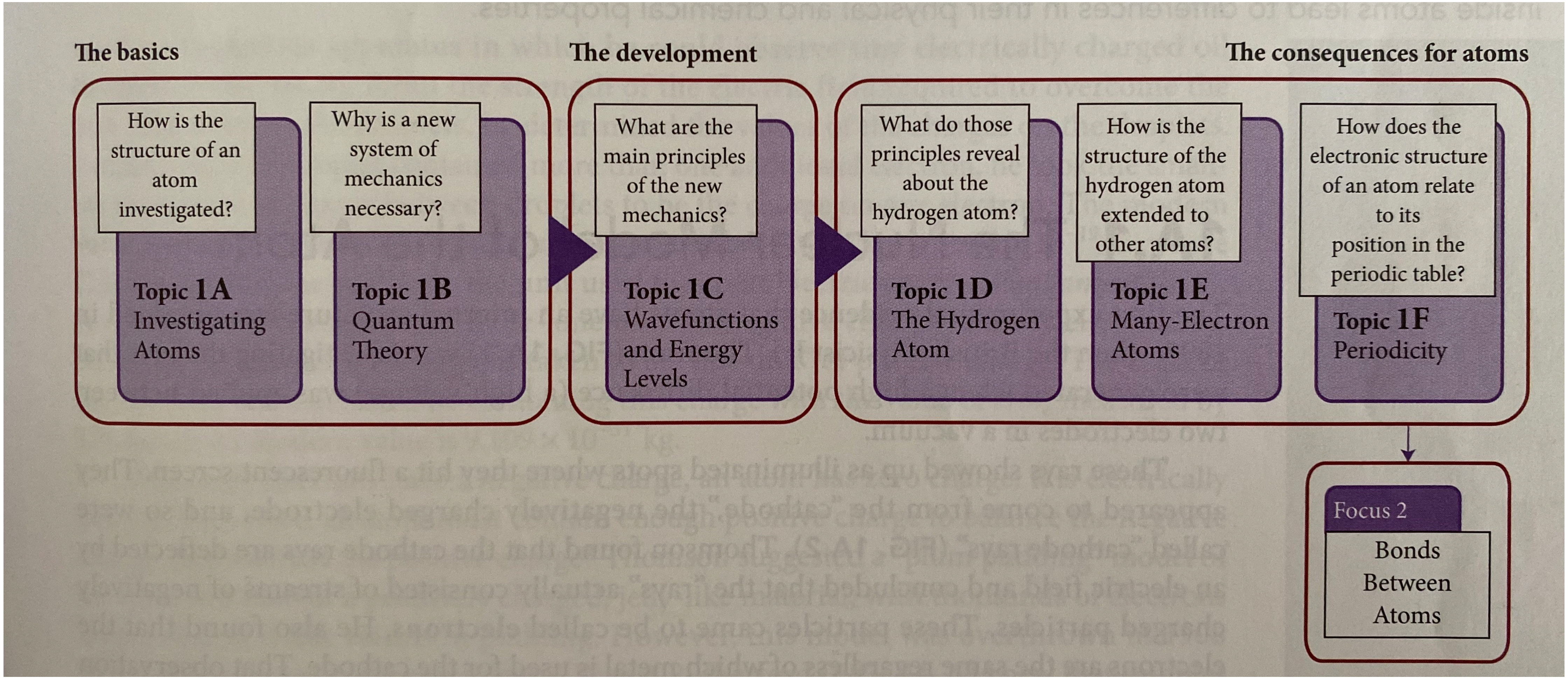
Overview Chapter 1 (Focus 1: Atoms)



Periodicity

Topic 1F

Topic 1F.1 Atomic radius
Topic 1F.2 Ionic radius
Topic 1F.3 Ionization energy
Topic 1F.4 Electron affinity
Topic 1F.5 Electronegativity
Topic 1F.6 The general properties of the elements

WHY DO YOU NEED TO KNOW THIS MATERIAL?

- The periodic table summarizes trends in the properties of the elements. The ability to **predict the properties of an element from its location** in the periodic table is a central skill of a chemist.

WHAT DO YOU NEED TO KNOW ALREADY?

- The structure of the **periodic table**, the **building-up principle** (Topic 1E)
- **Oxidation state** (Fundamentals K)
- Definition of **ionization energy** (Topic 1D)

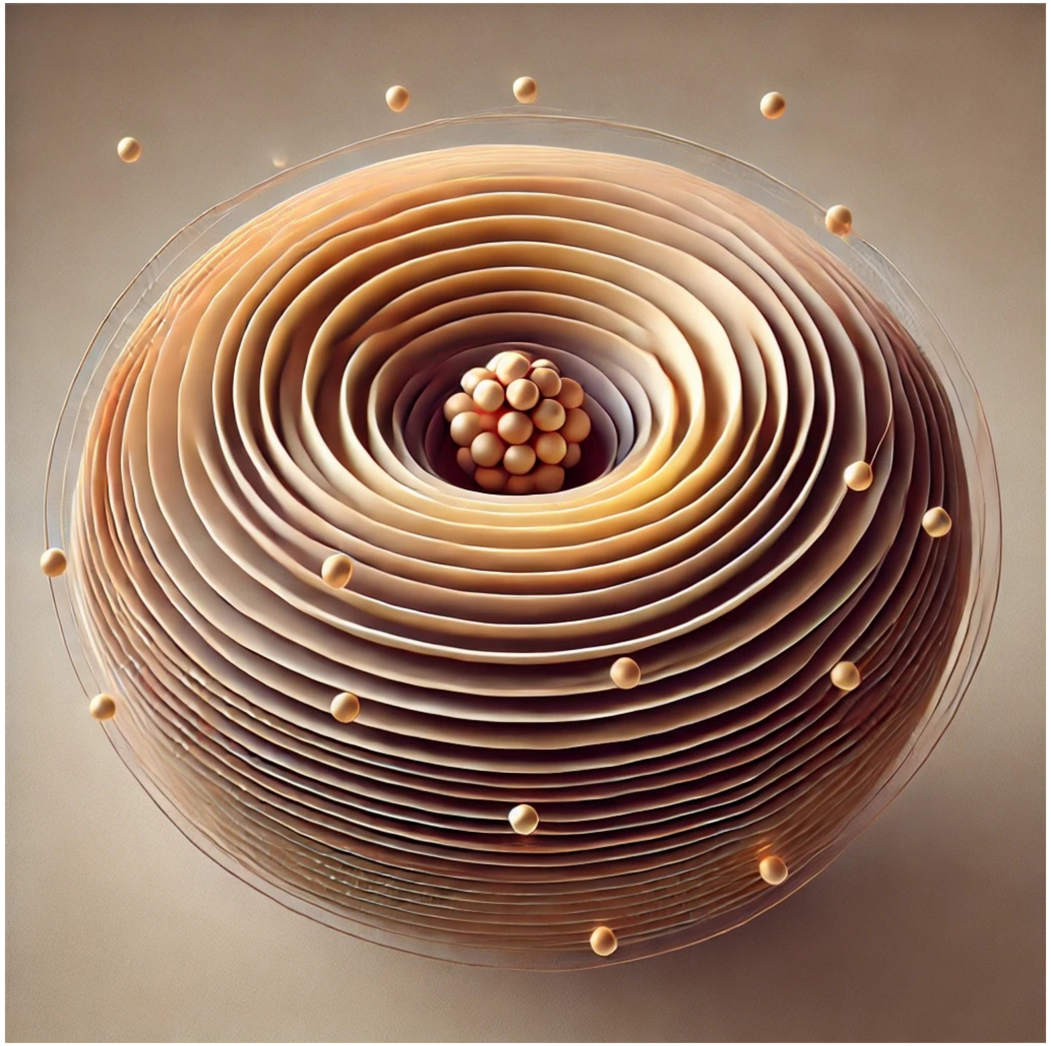
Atomic Radius

Topic 1F.1

1F.1 Atomic radius

Effective nuclear charge, Z_{eff} and Shielding

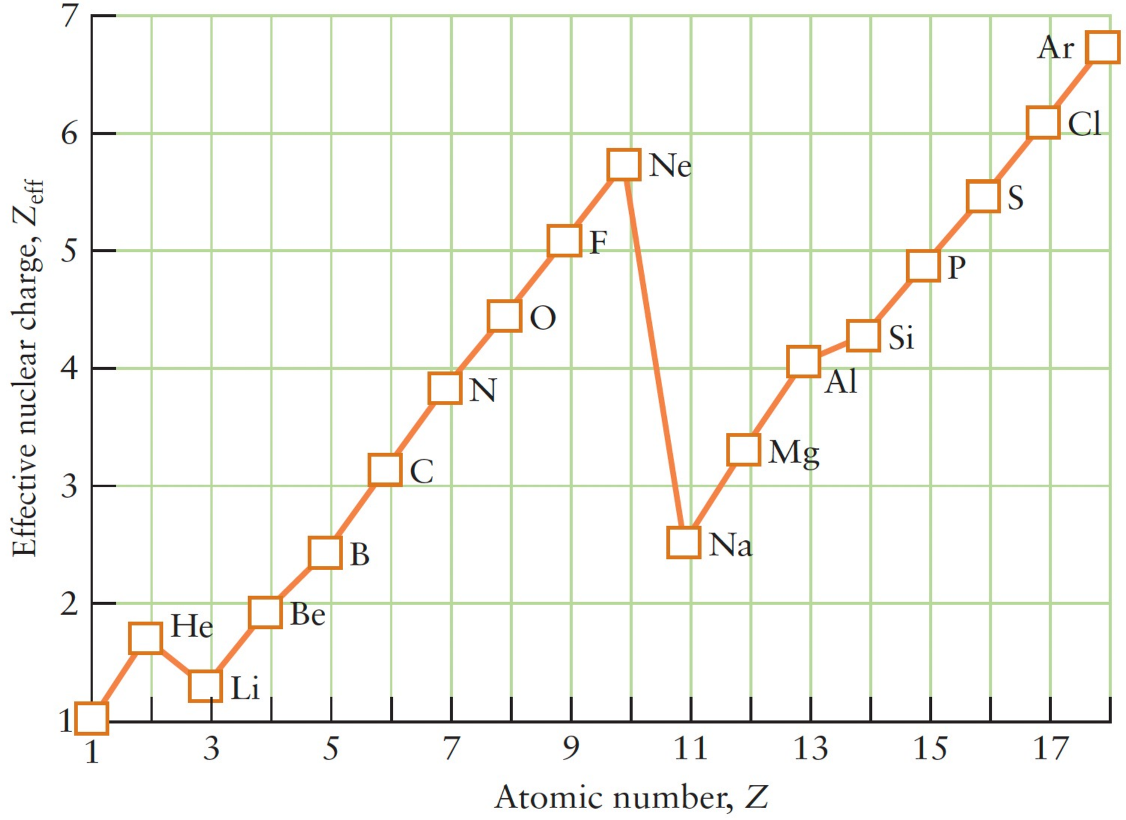
The **effective nuclear charge** is the net positive charge that a valence electron feels after accounting for the shielding effect of inner electrons.



Effective nuclear charge, Z_{eff}

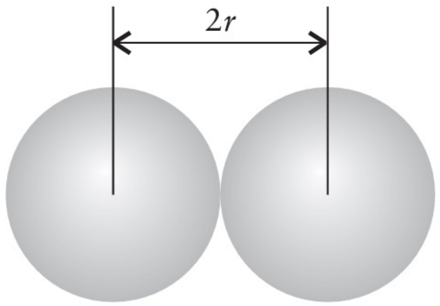
- The **effective nuclear charge** is the net positive charge that a valence electron feels after accounting for the shielding effect of inner electrons.
- The **effective nuclear charge**, $Z_{eff}e$, is always smaller than Ze.

Figure 1F.1



Different types of radii

- Electron clouds have no sharp boundaries → exact radius is technically undefined
- Atomic radius: half the distance between centers of neighbouring atoms
- **For metals:** defined as half of the distance between neighbouring nuclei in the solid sample
- Example: Cu–Cu distance = 256 pm → atomic radius = 128 pm



Atomic radius

Different types of radii

- **For nonmetals/metalloids:** covalent radius = half the bond length of atoms joined together (see Topic 2D)

  Example: Cl_2 bond = 198 pm → radius(Cl) = 99 pm.

- **Noble gases**: van der Waals radius = half the distance between neighbouring atoms in solidified gas

  Larger than covalent radius; not included in discussion of periodic trends

1F.1 Atomic radius

Atomic radii of main-group elements

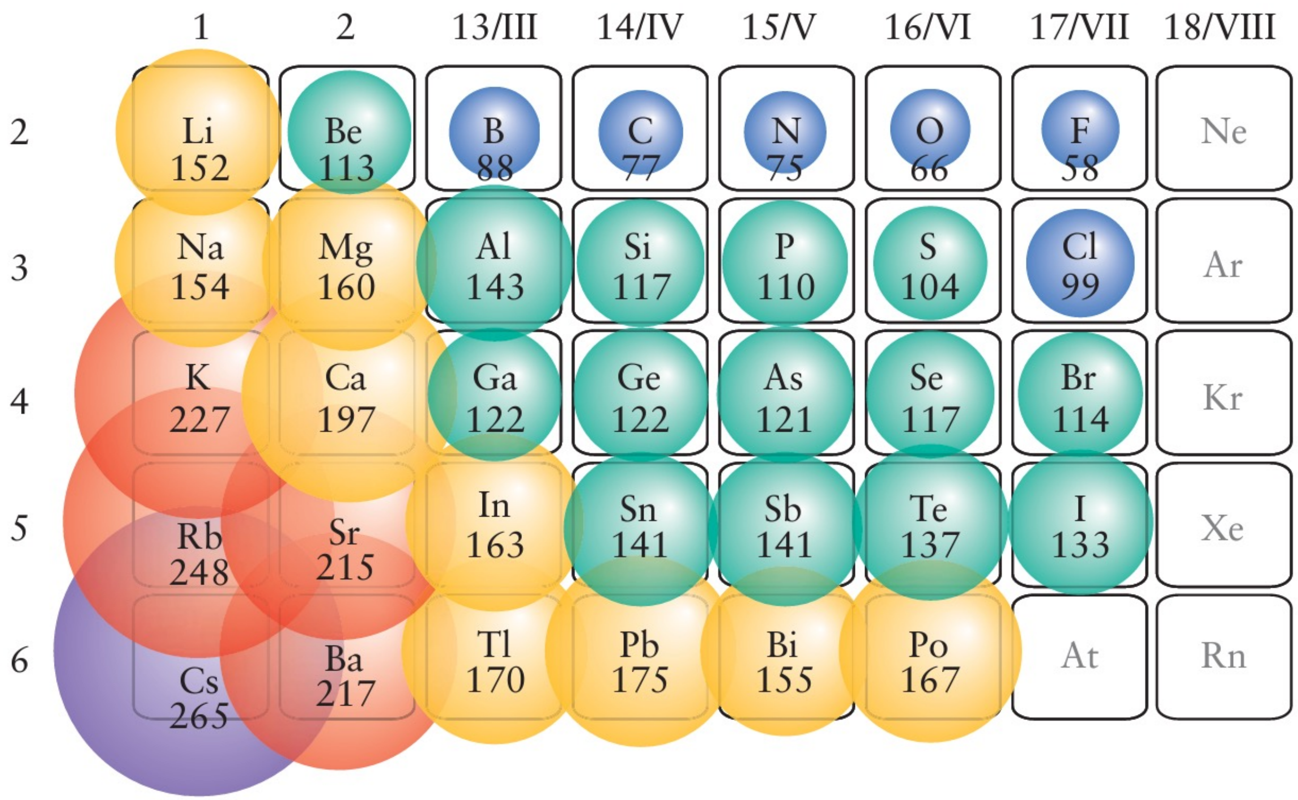


Figure 1F.2

TREND: Atomic radius generally decreases from left to right across a period and increases down a group.

Summary: Atomic radii of main-group elements

TREND: Atomic radius generally decreases from left to right across a period and increases down a group.

↓ **Group (Li → Cs):** radius ↑

- Electrons added to higher shells (larger *n*) → farther from nucleus

→ **Period (Li → Ne):** radius ↓

- Electrons added to same shell.
- Poor shielding → effective nuclear charge ↑
- Stronger attraction pulls electrons closer → atom more compact

Ionic Radius

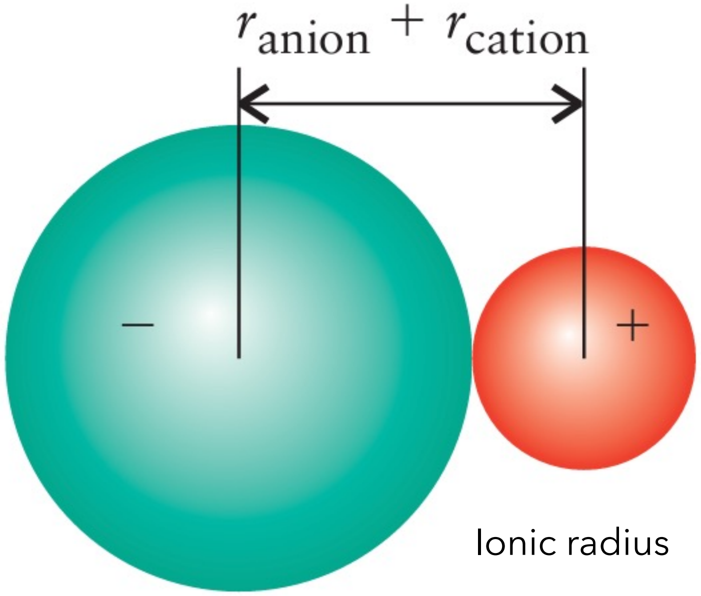
Topic 1F.2

Another type of radius: ionic radius

- The radii of ions are **very different** to the radii of their parent atoms.

How is it measured:

- Each ion in an ionic solid is surrounded by ions of opposite charge.
- The ionic radius of an element is its share of the distance between neighboring ions in an ionic solid.
- In practice, the radius of the oxide ion is taken to be 140 pm, and the radii of other atoms are then calculated on the basis of that value.
- For example, the distance of Mg^{2+} and O^{2-} ions in magnesium oxide is 212 pm, the radius of the Mg^{2+} ion is reported as 212 - 140 pm = 72 pm.



Ionic radius

Ionic radii of the ions of the main-group elements

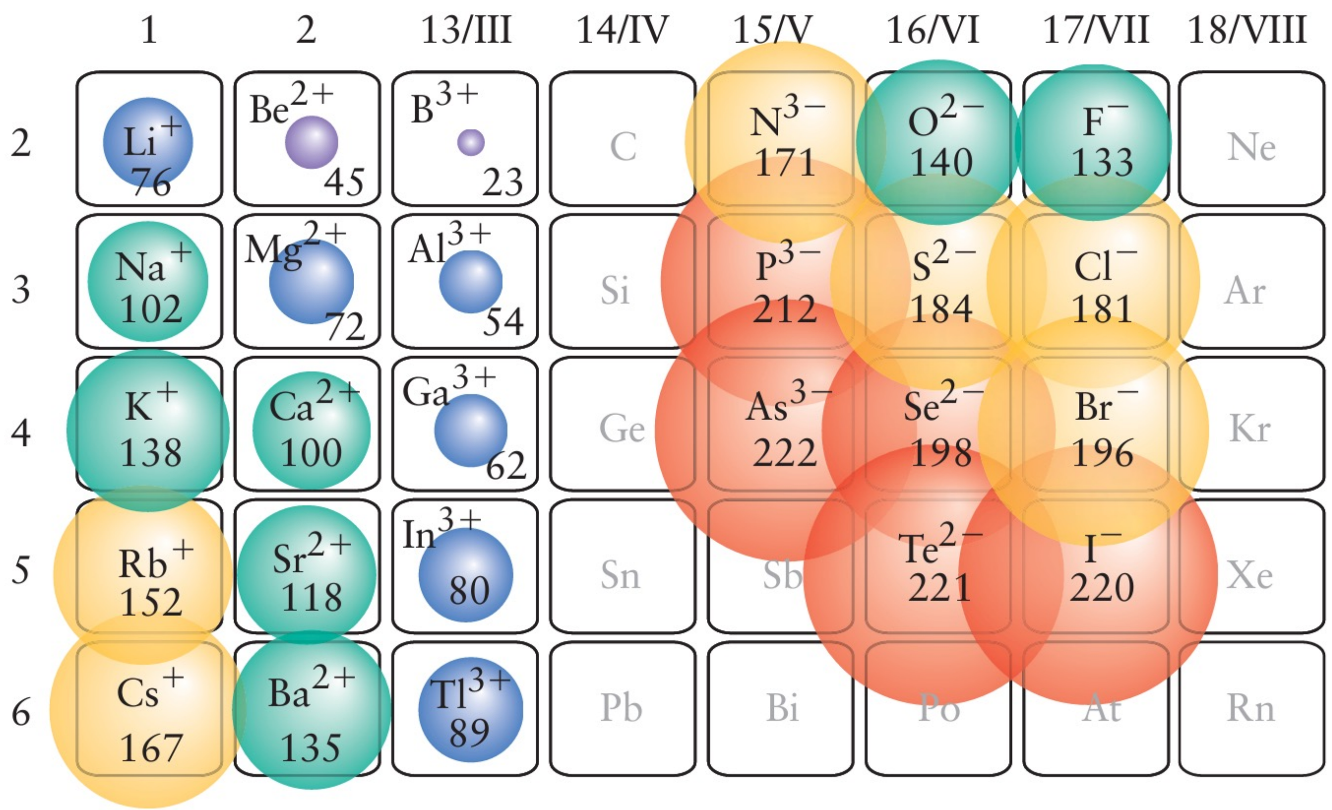


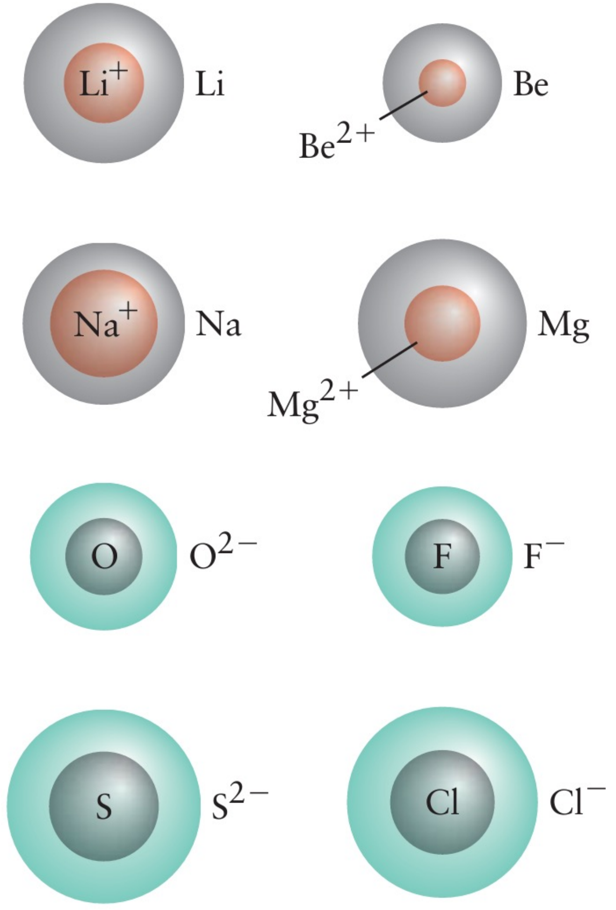
Figure 1F.4

TREND: Cations are smaller than their parent atoms, whereas anions are larger.

Ionic radii of the ions of the main-group elements

- **Anions are larger than their parent atom**: increased number of electrons in the valence shell → repulsive effects exerted by electrons on one another.
- **Isoelectronic:** atoms and ions with the same number of electrons.
- Na^+, F^-, and Mg^{2+} are isoelectronic with their electronic configuration $[He]2s^22p^6$. Radii differ, because of different nuclear charge.

Figure 1F.5



TREND: Cations are smaller than their parent atoms, whereas anions are larger.

Example 1F.1 Predicting the relative sizes of ions

- Arrange each of the following pairs of ions in order of increasing ionic radius

(a) Mg^{2+} and Ca^{2+}

(b) O^{2-} and F^{-}

Example 1F.1 Predicting the relative sizes of ions

EXAMPLE 1.11 **Deciding the relative sizes of ions**

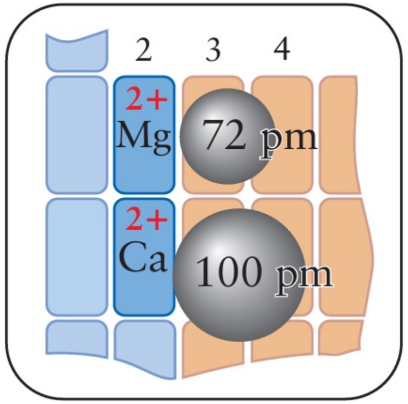
Arrange each of the following pairs of ions in order of increasing ionic radius: (a) Mg^{2+} and Ca^{2+}; (b) O^{2-} and F^{-}.

PLAN The smaller member of a pair of isoelectronic ions in the same period will be an ion of an element that lies farther to the right in a period, because that ion has the greater effective nuclear charge. If the two ions are in the same group, the smaller ion will be the one that lies higher in the group, because its outermost electrons are closer to the nucleus.

SOLVE

(a) Mg lies above Ca in Group 2.

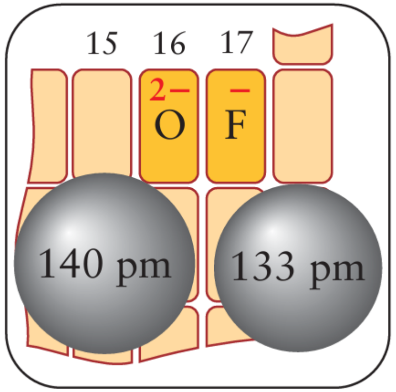
Mg^{2+} has the smaller ionic radius.



Example 1F.1 Predicting the relative sizes of ions

(b) F^- lies to the right of O in Period 2.

F^- has the smaller ionic radius.



Evaluate Appendix 2C shows that the actual values are (a) 72 pm for Mg^{2+} and 100 pm for Ca^{2+}; (b) 133 pm for F^- and 140 pm for O^{2-}.

Self-Test 1.13A Arrange each of the following pairs of ions in order of increasing ionic radius: (a) Mg^{2+} and Al^{3+}; (b) O^{2-} and S^{2-}.

[***Answer:*** (a) $r(Al^{3+}) < r(Mg^{2+})$; (b) $r(O^{2-}) < r(S^{2-})$]

Self-Test 1.13B Arrange each of the following pairs of ions in order of increasing ionic radius: (a) Ca^{2+} and K^+; (b) S^{2-} and Cl^-.

1F.2 Ionic radius

Summary

TREND: Ionic radii generally increase down a group and decrease from left to right across a period. Cations are smaller than their parent atoms, and anions are larger.

1F.3 Ionization energy

- The formation of an **ionic compound** depends on the **removal of one or more electrons from one atom** (Na to Na^+) and the transfer of those electrons to another atom (Cl to Cl^-).
- The **ionization energy**, I, is the miminum energy needed to remove an electron from an atom in the gas phase:

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

$$I = E(X^+) - E(X)$$

- Where $E(X)$ is the energy of species X.
- And $E(X^+) - E(X)$ is the energy difference between the ionized and the neutral atom.
- Reported as molar quantities in kilojoules per mole (kJ/mol) or in electronvols (eV).

1F.3 Ionization energy

- **First ionization energy I_1**: minimum energy needed to remove an electron from a neutral atom in the gas phase

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

$$energy\ required = I_1(746\,\frac{kJ}{mol}, 7.73\ eV)$$

- Ionization energy is a measure of how difficult it is to remove an electron:
  - *Elements with **low ionization energies** can be expected to form cations readily, conduct electricity (requires movement of free electrons)*
  - *Elements with **high ionization energies** are unlikely to form cations and are unlikely to conduct electricity*

1F.3 Ionization energy

Figure 1F.7

	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				H 1310				He 2370
2	Li 519	Be 900	B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
3	Na 494	Mg 736	Al 577	Si 786	P 1011	S 1000	Cl 1255	Ar 1520
4	K 418	Ca 590	Ga 577	Ge 784	As 947	Se 941	Br 1140	Kr 1350
5	Rb 402	Sr 548	In 556	Sn 707	Sb 834	Te 870	I 1008	Xe 1170
6	Cs 376	Ba 502	Tl 590	Pb 716	Bi 703	Po 812	At 1037	Rn 1036

- **Decrease down group:** outermost electrons are farther and farther away from nucleus, experiencing less nuclear charge.

TREND: First ionization energies typically decrease down a group.

First ionization energies generally increase across a period.

1F.3 Ionization energy

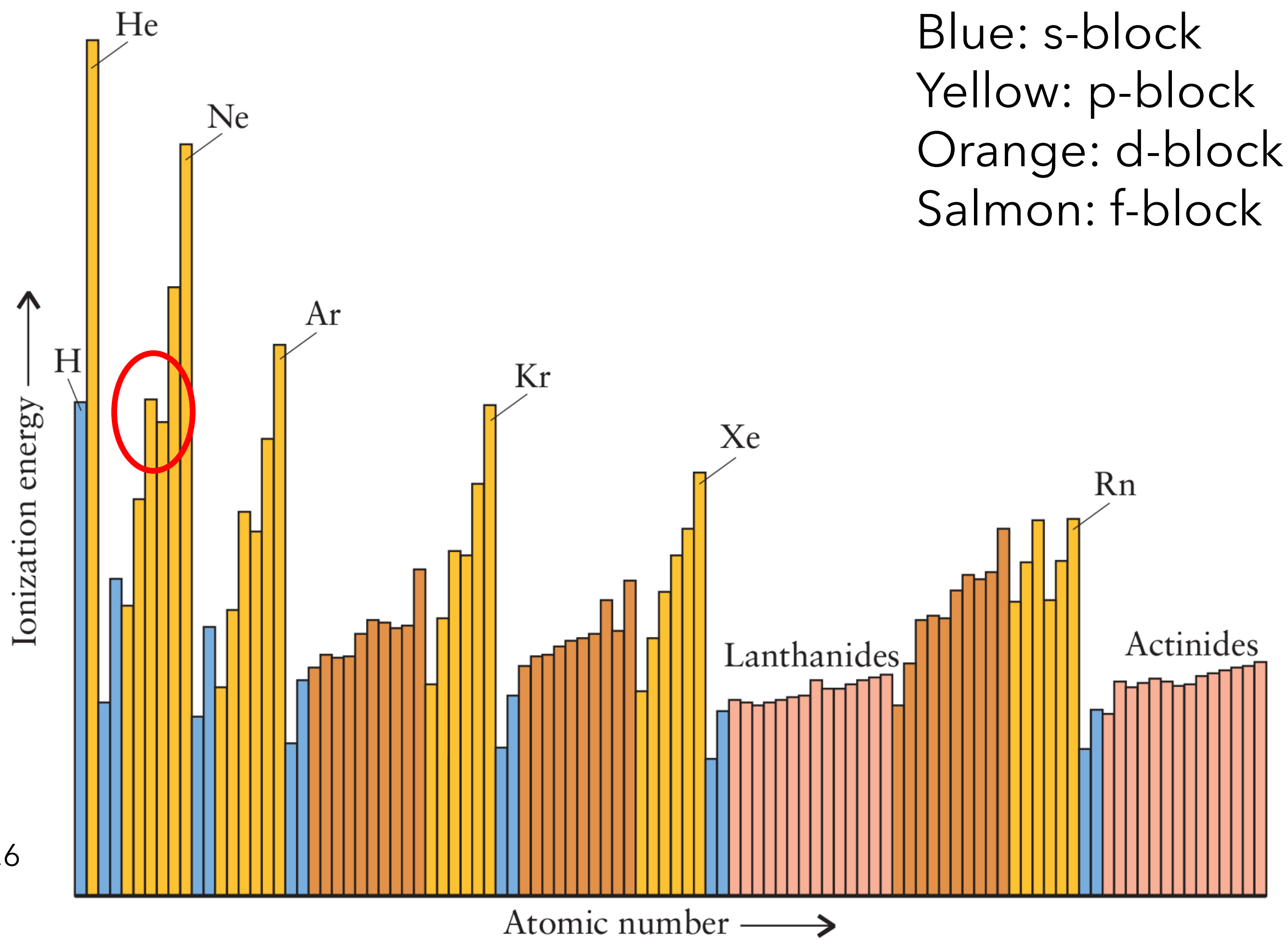


Figure 1F.6

Blue: s-block
Yellow: p-block
Orange: d-block
Salmon: f-block

- First ionization energies **increase across period**: increase in effective nuclear charge across period.
- **Ionization energy of oxygen < nitrogen:** nitrogen has one electron per p-orbital, oxygen is pairing up the 8th electron with other p-electrons, energy goes up

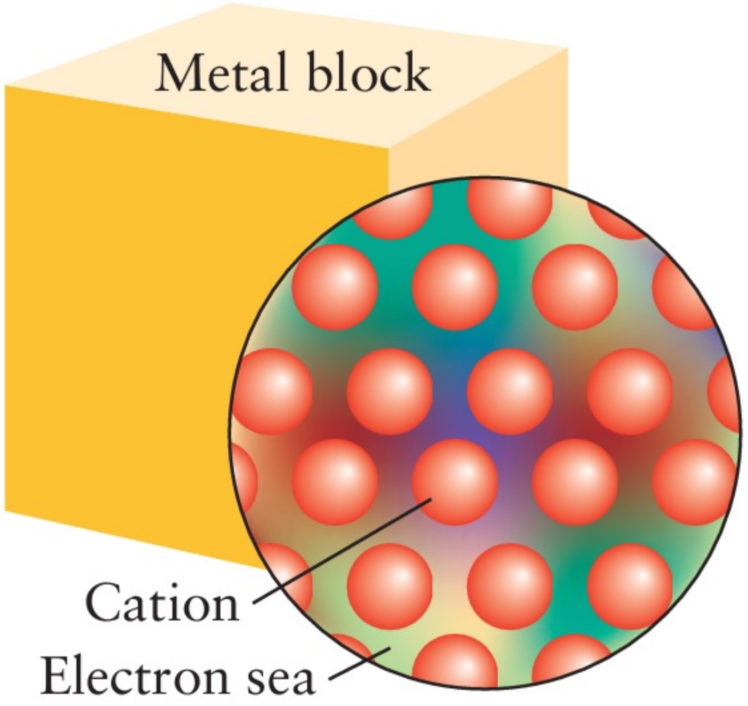
TRENDs: First ionization energies typically decrease down a group.

First ionization energies generally increase across a period.

Metallic character

- **Low ionization energies**
- Lower left of periodic table
- A block of metal: **collection of cations of the element surrounded by a sea of valence electrons that the atoms have lost**
- s-block, d-block, f-block, lower left of the p-block can form metallic solids because they can lose electrons easily.
- Elements with high ionization energies are on the upper right of the periodic table

Figure 1F.8



1F.3 Ionization energy

The second ionization energy, I_2

- The minimum energy needed to remove an electron from a singly charged gas-phase cation.

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

$$energy\ required = I_2\ \left(1958\,\frac{kJ}{mol}, 20.29\ eV\right)$$

- The second ionization energy is **always higher than the first** → it takes more energy to remove an electron from a positively charged atom than from a neutral one
- Group 1: $I_2 >> I_1$
- Group 2: $I_2 > I_1$

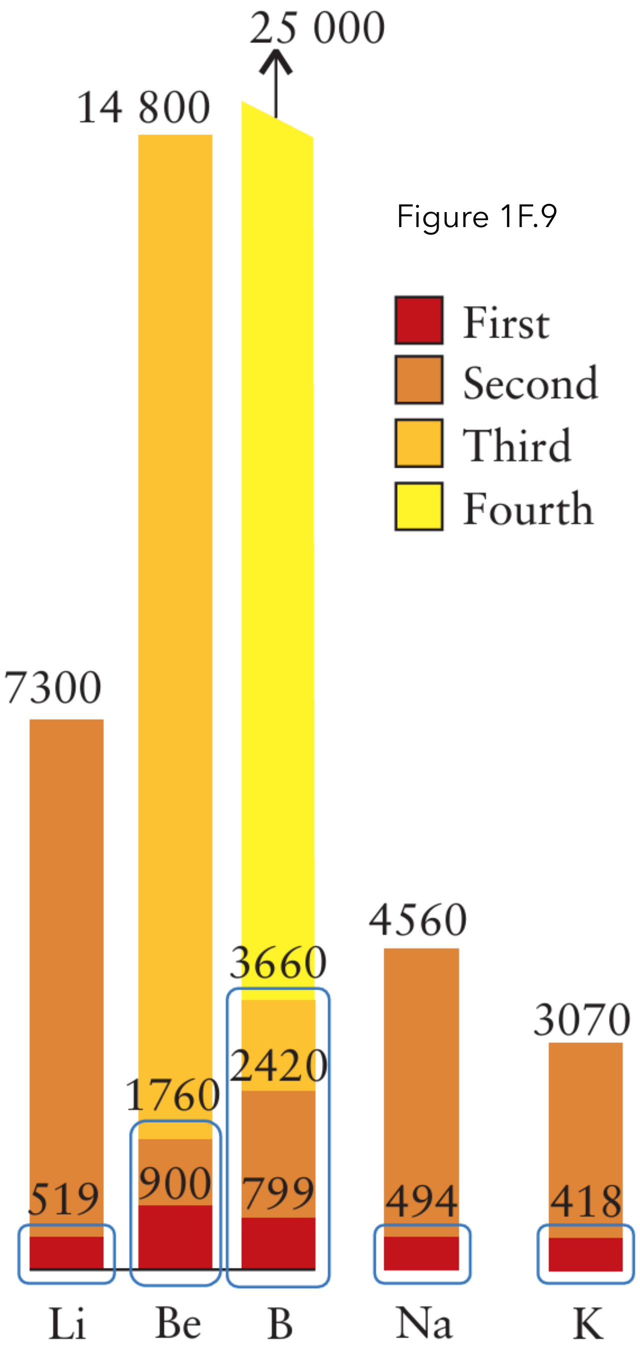
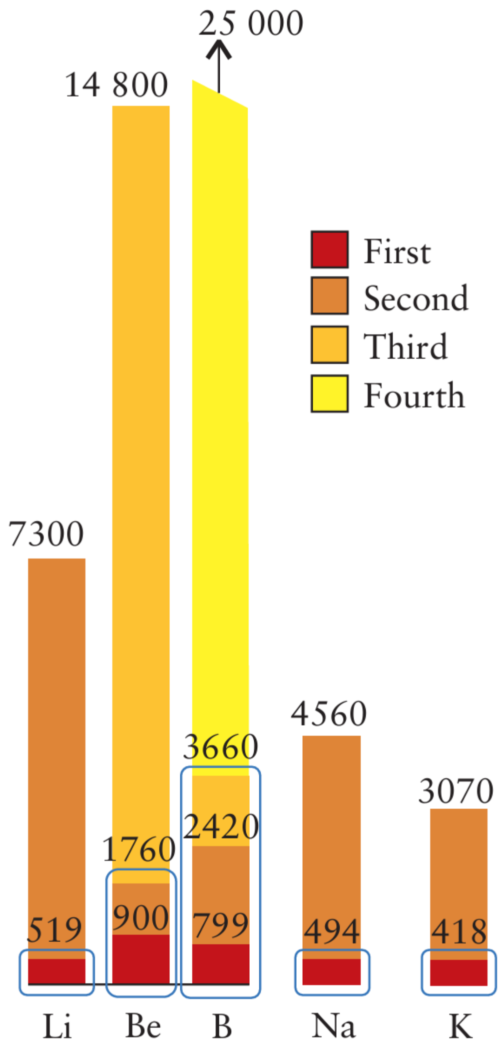


Figure 1F.9

Why is there a large decrease in third ionization energy between beryllium and boron?

There is a large decrease in third ionization energy between beryllium and boron because, after removing two electrons from beryllium, the third ionization involves removing an electron from a stable, fully-filled noble gas core, which requires significantly more energy, while boron's third electron is from a higher-energy p-orbital, making it easier to remove.



Summary

TRENDS:

The **first ionization energy** is highest for elements close to helium and is lowest for elements close to cesium.

Second ionization energies are higher than first ionization energies (of the same element) and very much higher if the electron is to be removed from a closed shell.

Metals are found toward the lower left of the periodic table because these elements have low ionization energies and can readily lose their electrons.

Electron Affinity

Topic 1F.4

Ionization energy vs. electron affinity

- Ionization energy indicates how difficult it is to **remove** an electron from an atom.
- How does the energy change when an electron **attaches** to an atom to form a negative ion (Cl to Cl^-)?
- **The electron affinity, E_{ea}, of an element is the energy released when an electron is added to a gas-phase atom.**
- **Pos. E_{ea}:** energy released when an electron attaches to atom
- **Neg. E_{ea}:** energy must be supplied to push an electron onto an atom

Ionization energy vs. electron affinity

The electron affinity of an element X is defined as

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

$$E_{ea}(X) = E(X) - E(X^{-})$$

Where $E(X)$ is the energy of a gas-phase atom X and $E(X^{-})$ is the energy of the gas-phase anion.

For instance, the electron affinity of chlorine is the energy released in the process

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

$$energy\ released = E_{ea}\left(349\frac{kJ}{mol}, 3.63\ eV\right)$$

Because the electron has a lower energy when it occupies one of the atom’s orbitals, the difference $E(Cl) - E(Cl^{-})$ is positive, and the electron affinity of chlorine is positive.

1F.4 Electron affinity

Variation in electron affinity in kJ/mol of main-group elements

Period	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
1	H +73							He <0
2	Li +60	Be ≤0	B +27	C +122	N −7	O +141 −844	F +328	Ne <0
3	Na +53	Mg ≤0	Al +43	Si +134	P +72	S +200, −532	Cl +349	Ar <0
4	K +48	Ca +2	Ga +29	Ge +116	As +78	Se +195	Br +325	Kr <0
5	Rb +47	Sr +5	In +29	Sn +116	Sb +103	Te +190	I +295	Xe <0
6	Cs +46	Ba +14	Tl +19	Pb +35	Bi +91	Po +174	At +270	Rn <0

Figure 1F.10

TREND: Electron affinities are highest toward the right of the periodic table.

Pos. E_{ea}: energy released when an electron attaches to atom

Neg. E_{ea}: energy must be supplied to push an electron onto an atom

1F.4 Electron affinity

TRENDs

TREND: Elements with the highest electron affinities are those in Groups 16 and 17.

- Particularly true in the upper right of the periodic table: **oxygen, sulfur, halogens**
- **Noble gases have negative electron affinities** because any electron added to them must occupy an orbital outside a closed shell and far from the nucleus: this process requires energy, the electron affinity is negative
- **Halide (group 17) plus electron builds a closed shell** (noble-gas configuration). Second electron affinity for halides is strongly negative.
- Group 16 (O or S): two vacancies in its valence shell p-orbitals, can accommodate two additional electrons. First electron affinity positive.

Electronegativity

Topic 1F.5

A combination of ionization energy and electron affinity

- Introduced by American chemist Robert Mulliken in 1934:
- Electronegativity, Χ (Greek letter chi)
- **“The power of an atom to attract electrons to itself when part of a compound.”** (see Topic 2D)

Definition:

$$\mathrm{X} = \frac{1}{2}(I + E_a)/eV$$

With the ionization energy and the electron affinity expressed in electronvolts (so electronegativity is **unitless**).

Variation in the electronegativities of the main-group elements

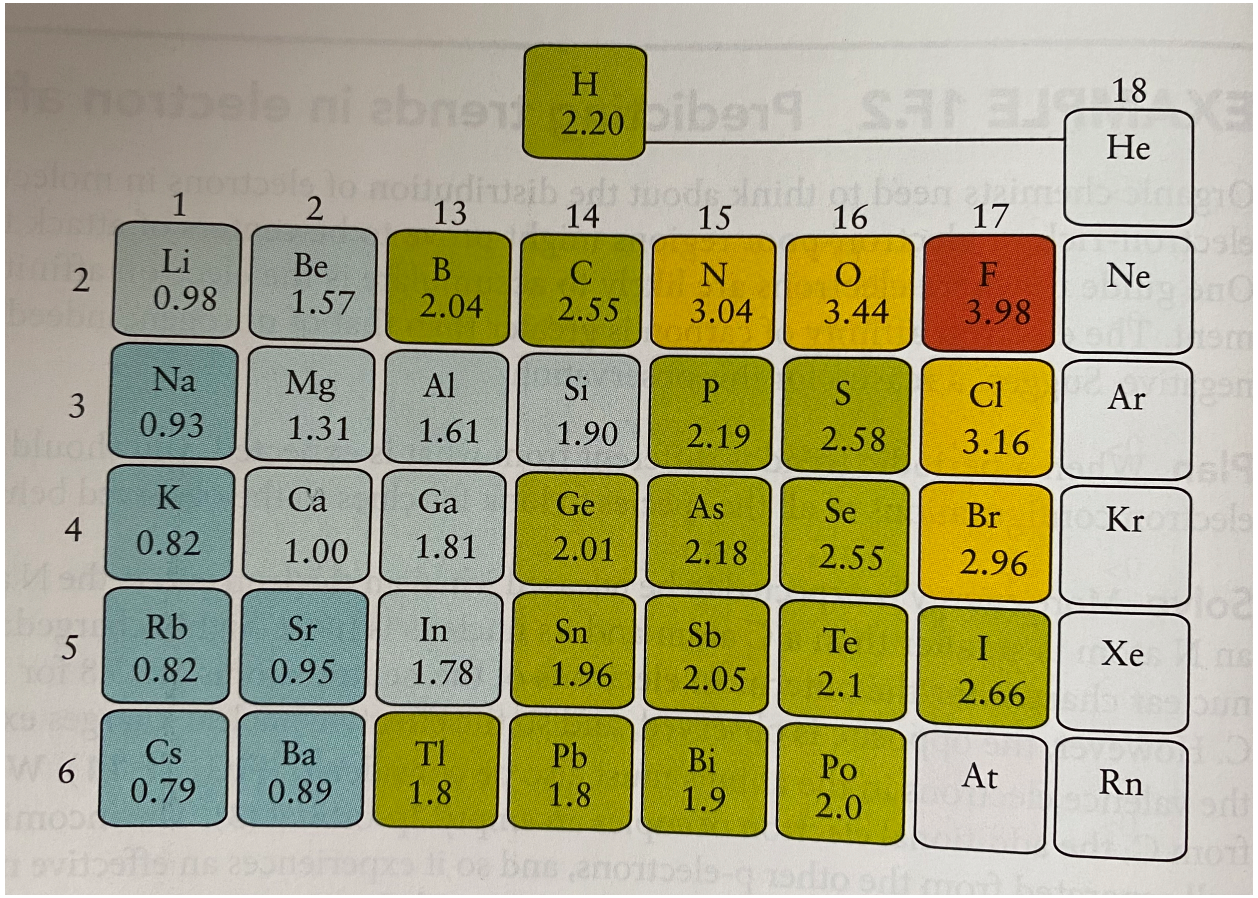


Figure 1F.12

- Elements with **high ionization energies and high electron affinities**: highly electronegative
- Elements **with low ionization energies and low electron affinities**: low electronegativity.
- Careful: electropositive is used for a different concept and is NOT the opposite of electronegative.

1F.5 Electronegativity

Summary

TREND: The electronegativity of an element, its power of an atom to attract electros to itself when part of a compound, is highest close to the top right of the periodic table.

F > O > Cl > N > Br > I > S > C/Se > H >…

The General Properties of the Elements

Topic 1F.6

1F.6 The general properties of the elements

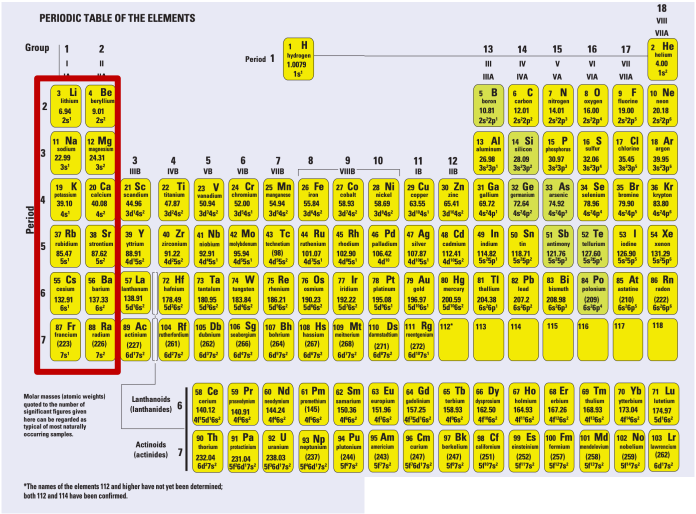
TABLE 1F.1 Characteristics of Metallic and Nonmetallic Elements

Metallic	Nonmetallic
Physical properties	
good conductors of electricity	poor conductors of electricity
malleable	not malleable
ductile	not ductile
lustrous	not lustrous
typically: solid; high melting point; good conductors of heat	typically: solid, liquid, or gas; low melting point; poor conductors of heat
Chemical properties	
react with acids	do not react with acids
form basic oxides	form acidic oxides
form cations	form anions
form ionic halides	form covalent halides

Figure 1F.13- 1F.16

1F.6 The general properties of the elements

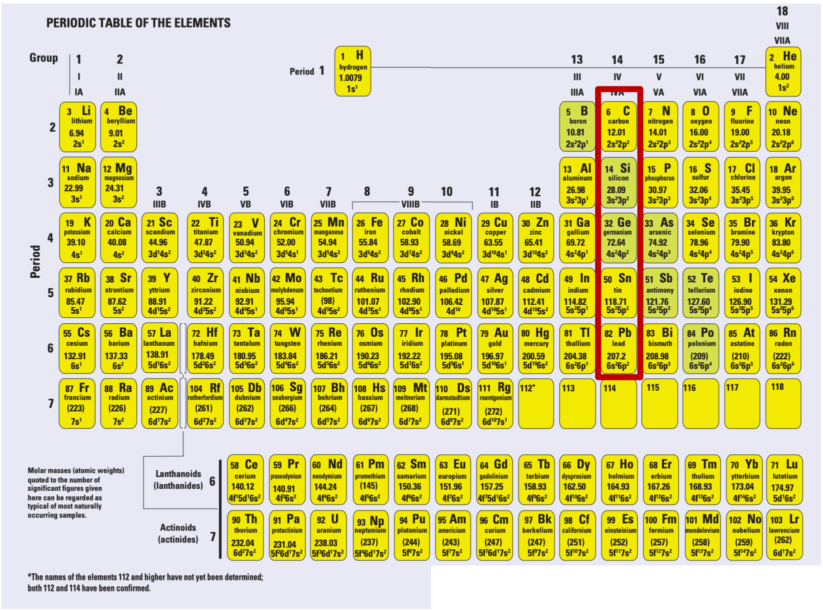
Alkali metals (Group 1)



- **s-block** elements
- Low ionization energy: valence electrons easily lost
- Soft, silvery, reactive metals
- Low melting points
- Produce hydrogen when they come in contact with water.
- Sodium is kept under mineral oil to protect it from air (**Fig. 1F.13**)
- A freshly cut surface becomes quickly covered with oxide.

Figure 1F.13

1F.6 The general properties of the elements



Group 14 elements

- Elements on the left of the **p-block**
- As you move down the group, they have low enough ionization energies to have metallic character.
- From left to right (**Fig. 1F.14**): carbon (as graphite), silicon germanium, tin, and lead

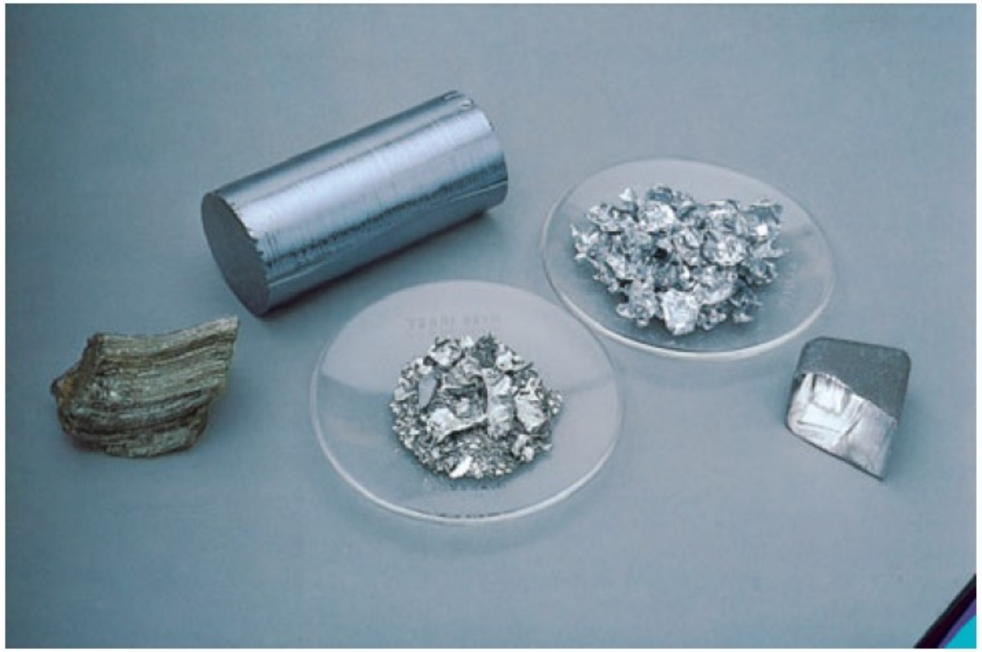
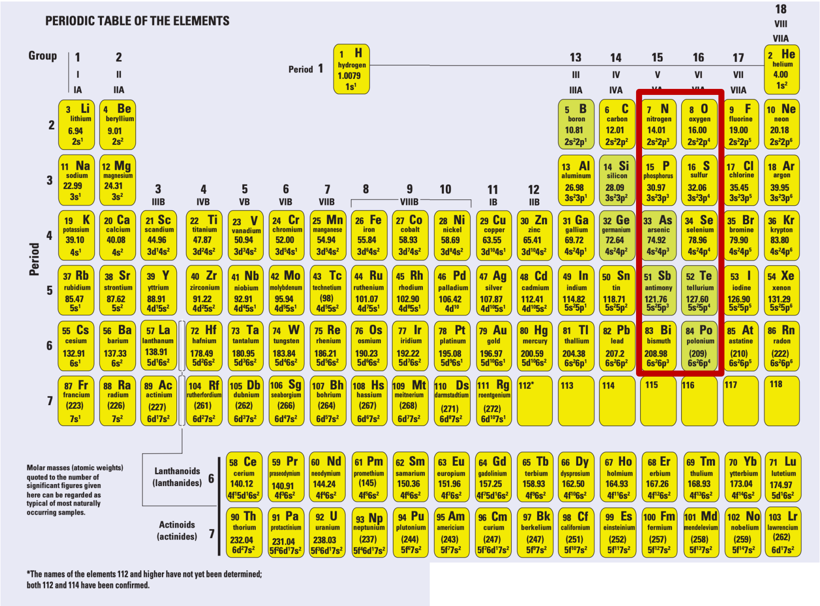


Figure 1F.14

1F.6 The general properties of the elements

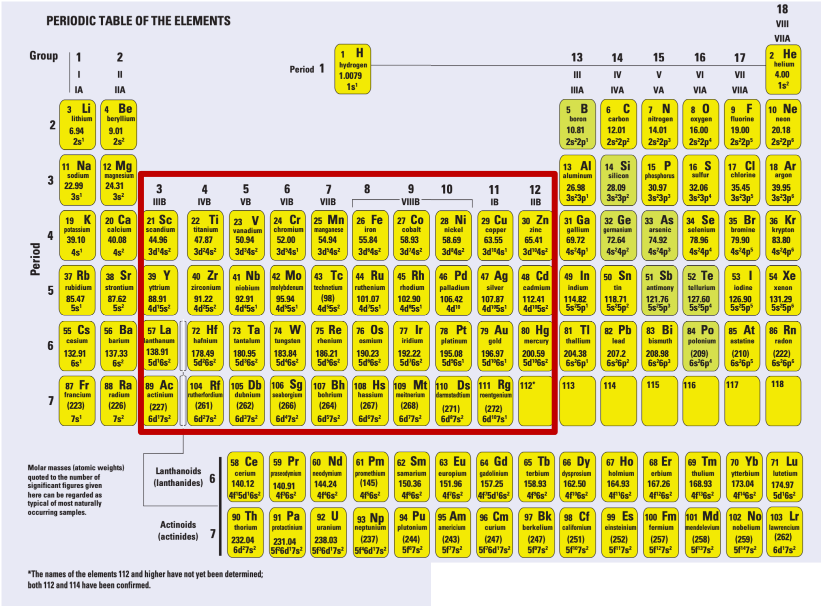


Group 16 to 18 elements

- Elements at the right of the **p-block**
- **High electron affinities**: they tend to gain electrons to complete shells.
- Except for the metalloids tellurium and polonium, the members of group 16 and 17 are **non-metals**.
- They typically form molecular **compounds** with one another.
- From left to right (**Fig. 1F.15**): oxygen, sulfur, selenium, and tellurium (Group 16). Note the trend from nonmetal to metalloid moving down the group.
- Group 18: Noble gases, completed shells, unreactive (inert gases).

Figure 1F.15

1F.6 The general properties of the elements



d-block elements

- All **d-block** elements are metals: d-metals or **transition metals**
- Their properties are transitional between the s- and the p-block elements (except group 12)
- **When a d-block element loses electrons to form a cation, it first loses its s-electrons.**
- From left to right (**Fig. 1F.16**). Top row: scandium, titanium, vanadium, chromium, and manganese. Bottom row: iron, cobalt, nickel, copper, and zinc.

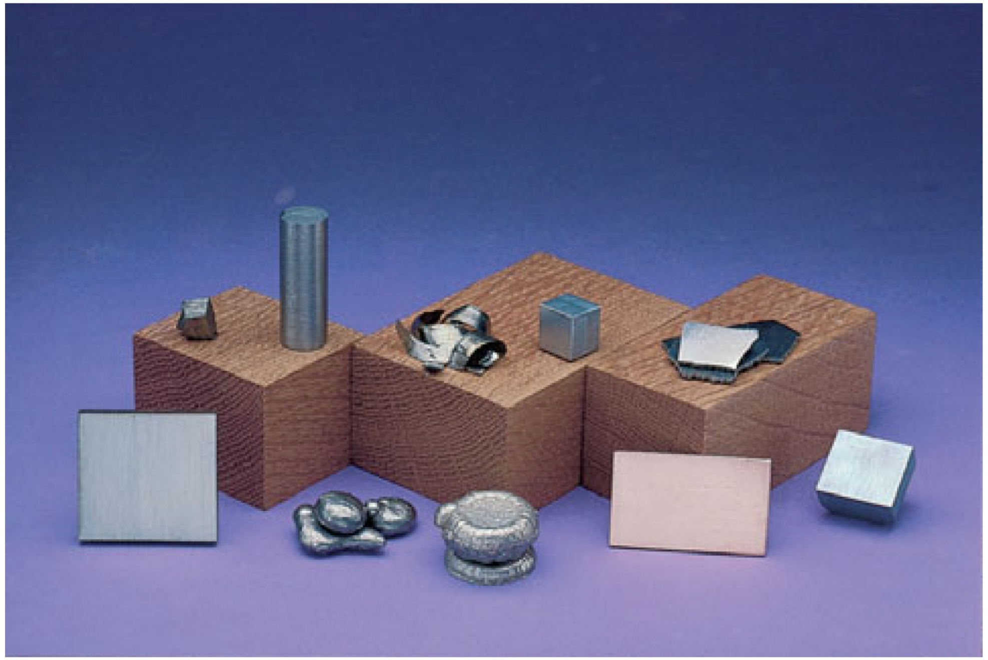


Figure 1F.16

d-block elements are (bio-)catalysts

- Availability of d-orbitals and the similarity of atomic radii of the d-block elements are important for many areas:
- They can accelerate reactions as **catalysts** in industry.

  Catalyst: a substance that accelerates a reaction but is not itself consumed
- Ability to form ions with different charges is important **in nature**

f-block elements

- f-block elements of same period **have very similar radii** and chemical properties
- Studied intensely for **superconducting** materials
- Actinoids ("actinides") are radioactive
- None of the elements following plutonium occurs naturally on earth in any significant amount

1F.6 The general properties of the elements

Summary

All elements in the s-block are reactive metals.

The p-block elements tend to gain electrons to complete closed shells; they range from metals through metalloids to nonmetals.

All d-block elements are metals with properties between those of s-block and p-block metals. Many d-block elements are capable of forming cations with several different charges.

The skills you have mastered are the ability to

- ❑ Account for periodic trends in atomic radii, ionization energies, electron affinities, and electronegativities.
- ❑ Summarize in a general way the properties of the elements in relation to their location in the periodic table.

Summary: Many properties of the elements, especially their periodic variation, can be predicted through the periodic table and the concept of effective nuclear charge.