CH-110 Advanced General Chemistry I

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Housekeeping notes

- You are allowed to write your answers **in French on the exam**.
- Exercises marked with **“requires calculus”** are not part of the material tested at the exam.
- **SESSION ID: 161855**

Student questions

Radial distribution function vs. Radial wavefunction?

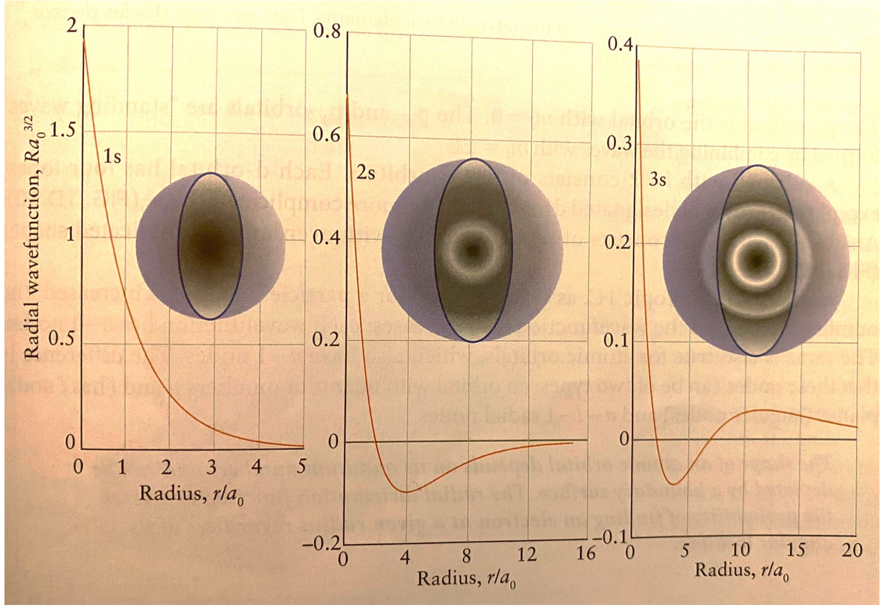
(1) Radial Wavefunction

1. **Definition**: The radial wavefunction, often denoted as $R(r)$, is a part of the overall wavefunction $\psi(r,\theta,\varphi)$ for an electron in an atom, specifically in spherical coordinates. It describes how the **probability amplitude** of finding an electron varies with distance r from the nucleus.
2. **Mathematical Form**: The radial wavefunction is derived from the solution of the Schrödinger equation for the hydrogen atom (or hydrogen-like atoms). For example, for s-orbital, it is:

$$\psi(r,\theta,\varphi) = \left(\frac{1}{\pi a_0^3}\right)^{\frac{1}{2}} e^{-\frac{r}{a_0}} \text{ where } a_0 \text{ is the Bohr radius}$$

1. **Interpretation**: The radial wavefunction itself does not directly give probabilities. It provides the **amplitude of the wavefunction** that varies with distance from the nucleus.

Figure 1D.7



$Ra_0^{\frac{3}{2}}$: **dimensionless** radial wavefunction

Student questions

Radial distribution function vs. Radial wavefunction?

(2) Radial Distribution Function

1. **Definition**: The radial distribution function, often denoted as $P(r)$, represents the **probability of finding an electron within a thin spherical shell** between r and r + δr from the nucleus, accounting for the volume of that shell.

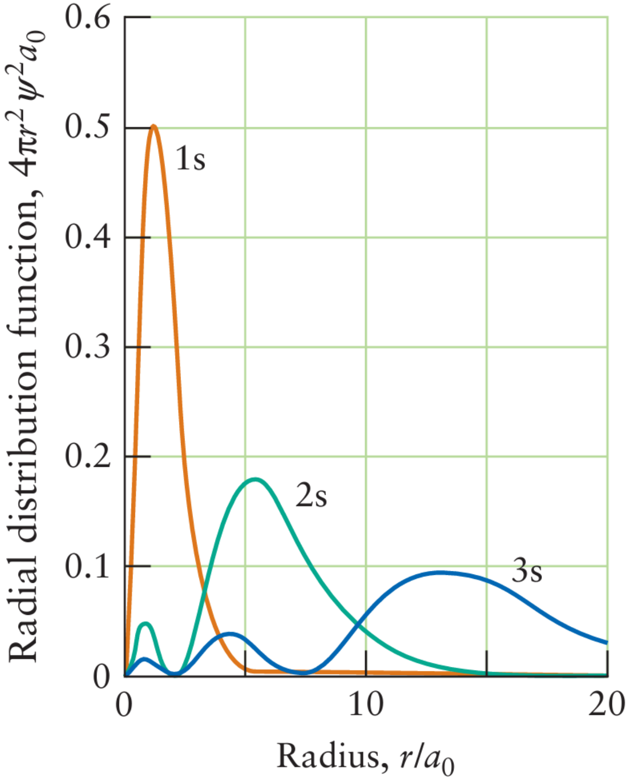
2. **Mathematical Form**: The radial distribution function is given by:

$$P(r) = r^2 R^2(r)$$

Here, $R^2(r)$ is the probability density associated with the radial wavefunction, and r^2 accounts for the volume of the spherical shell, which grows with the square of the radius.

1. **Interpretation**: The radial distribution function provides a clearer picture of where electrons are likely to be found in space. It indicates the probability of locating an electron at a certain distance r from the nucleus, integrating the radial wavefunction's contributions over all angles.

Figure 1D.5



Student questions

Radial distribution function vs. Radial wavefunction?

The relationship between the **radial wavefunction** R(r) and the **radial distribution function** P(r) is analogous to the relationship between the **wavefunction** $\psi(x)$ and the **probability density** $\psi(x)^{2.}$ Both pairs relate a more abstract, non-physical quantity (the wavefunction) to a physically meaningful probability (the distribution function or probability density).

Student questions

Is there a way to deduce the shapes of the x^2-y^2 and z^2 orbital logically?

Yes, if you solve the Schrödinger equation and look at the individual wavefunctions. However, this is beyond the scope of this class. What you should know that helps you deduce the shapes:

Each d-orbital has **two angular nodes (either nodal planes or nodal cones)**

- $\boldsymbol{d_{xy}}$, $\boldsymbol{d_{xz}}$, and $\boldsymbol{d_{yz}}$ have two nodal planes:
- For $\boldsymbol{d_{xy}}$, the nodal planes are the x- and y-axes.
- For $\boldsymbol{d_{xz}}$, the nodal planes are the x- and z-axes.
- For $\boldsymbol{d_{yz}}$, the nodal planes are the y- and z-axes.
- $\boldsymbol{d_{x^2-y^2}}$ has two angular nodes that are aligned along the diagonal planes y=x and y=−x.
- $\boldsymbol{d_{z^2}}$ has two **conical nodes**, which are cone-shaped regions around the z-axis.

1D.4 The shapes of orbitals

d-orbitals

- Subshell l = 2 consists of **five d-orbitals**
- Each d-orbital has four lobes, except d_{z^2}

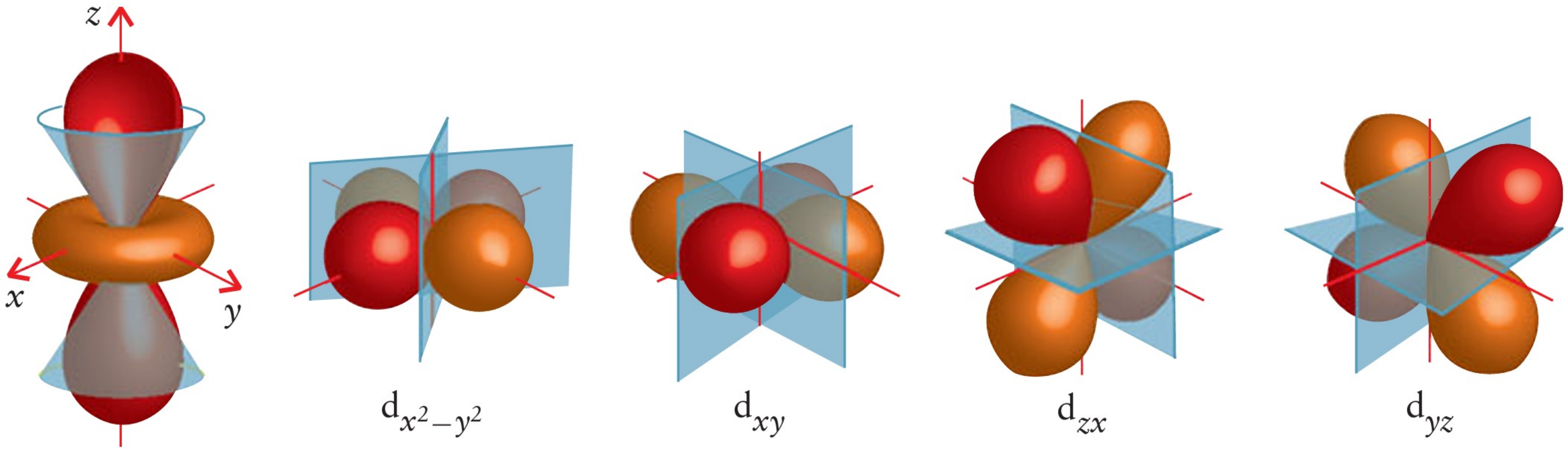
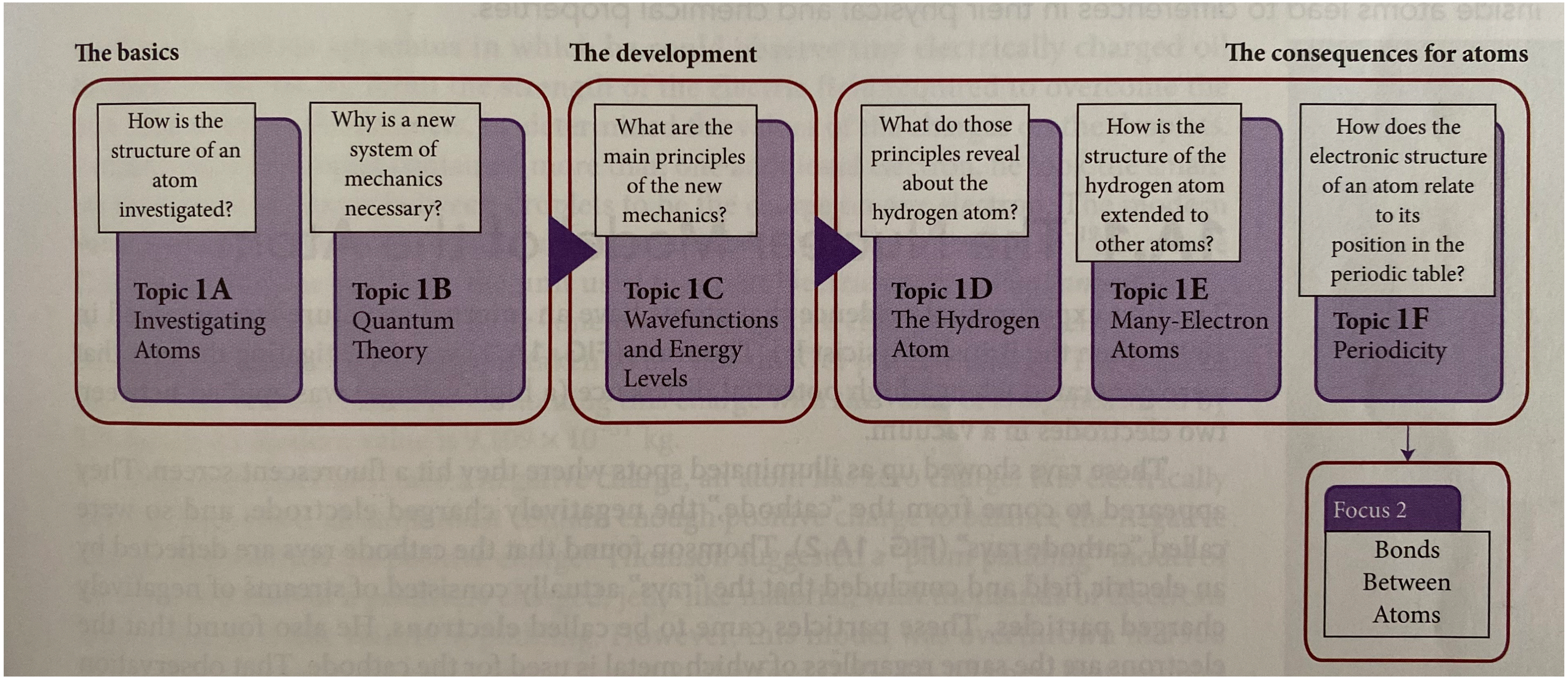


Figure 1D.10

Overview Chapter 1 (Focus 1: Atoms)



The basics

How is the structure of an atom investigated?

Topic 1A Investigating Atoms

Why is a new system of mechanics necessary?

Topic 1B Quantum Theory

The development

What are the main principles of the new mechanics?

Topic 1C Wavefunctions and Energy Levels

The consequences for atoms

What do those principles reveal about the hydrogen atom?

Topic 1D The Hydrogen Atom

How is the structure of the hydrogen atom extended to other atoms?

Topic 1E Many-Electron Atoms

How does the electronic structure of an atom relate to its position in the periodic table?

Topic 1F Periodicity

Focus 2

Bonds Between Atoms

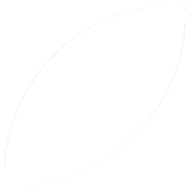
1E.2 The building-up principle

Example 1E.1 Predicting the ground-state electron configuration of a heavy atom

- (a) vanadium
- (b) lead

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?

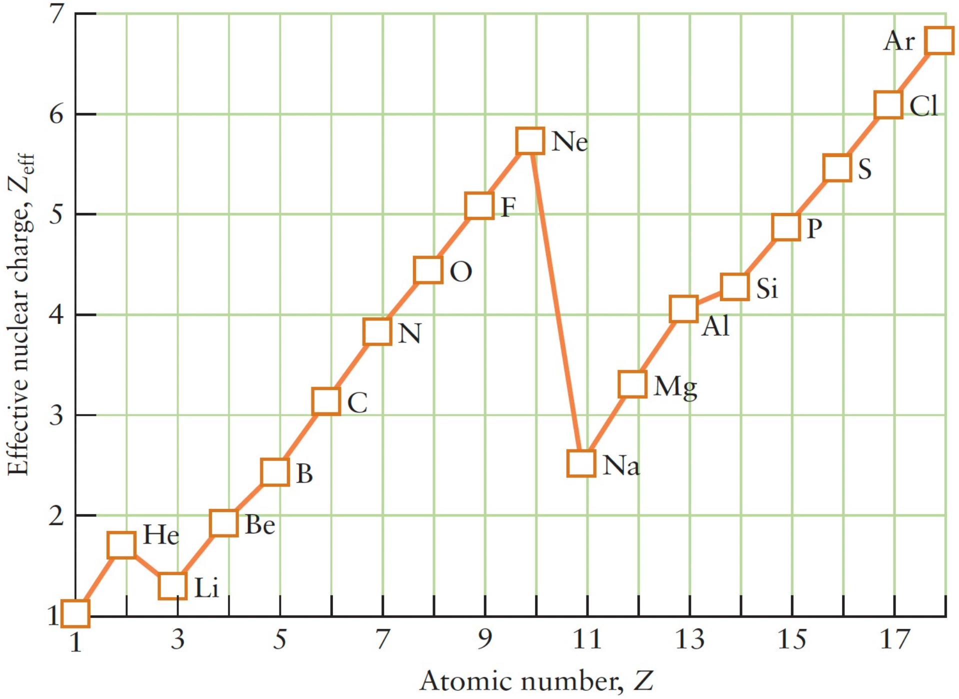
- The structure of the **periodic table**, the **building-up principle** (Topic 1E)
- **Oxidation state** (Fundamentals K)
- Definition of **ionization energy** (Topic 1D)

1F.1 Atomic radius

Effective nuclear charge, Z_{eff}

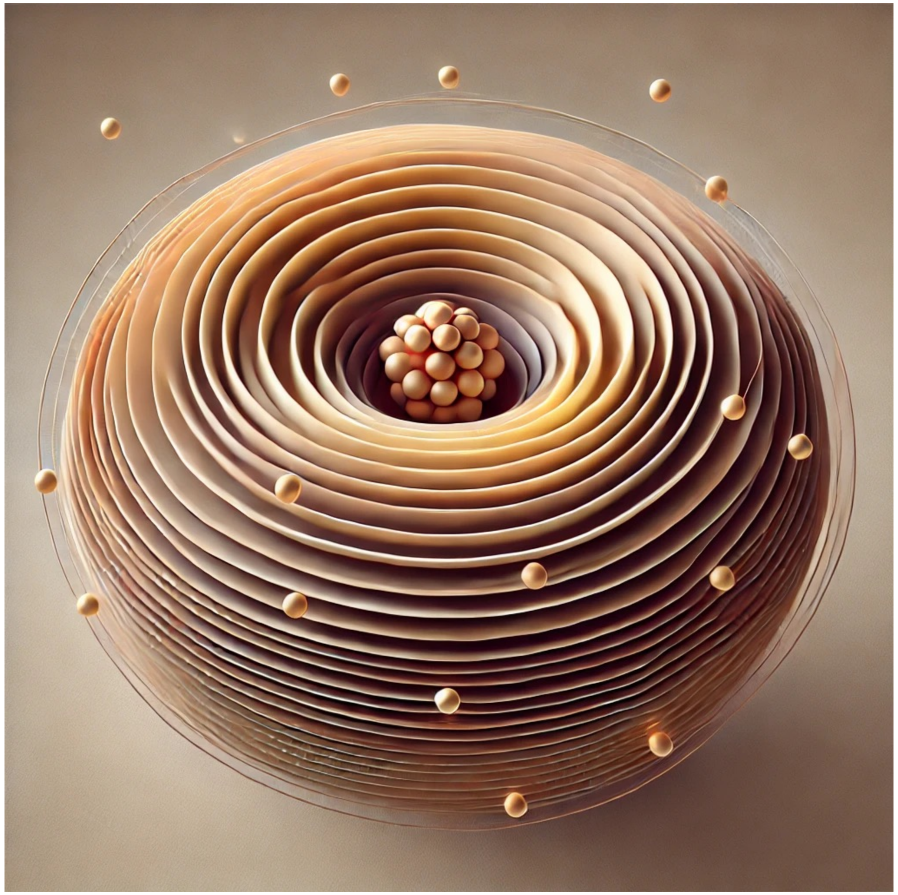
- The **effective nuclear charge** is the net positive charge that a valence electron actually feels after accounting for the shielding effect of inner electrons.
- The **effective nuclear charge**, $Z_{eff}e$, is always smaller than Ze.
- $Z_{eff}e$: To convert Z_{eff} into a **physical force** or **potential energy** that the electron experiences, you multiply Z_{eff} by the elementary charge e.

Figure 1F.1



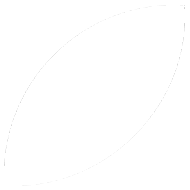
1F.1 Atomic radius

Shielding



Atomic Radius

Topic 1F.1

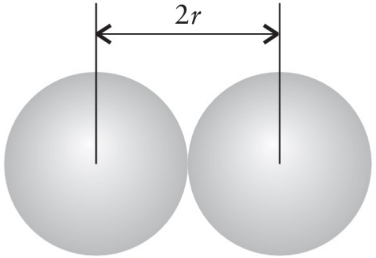


1F.1 Atomic radius

Different types of radii

- Electron clouds don’t have sharp boundaries → exact radius of an atom unknown
- **Edge of atom**: when electron density of atom falls off sharply = atomic radius
- The atomic radius of an element is defined as the distance between the centers of neighbouring atoms.
- If the element is a **metal**, its **atomic radius** is taken to be half the distance between the centers of neighbouring atoms in a solid sample

E.g. the distance between two neighbouring nuclei in solid copper is 256 pm, the atomic radius of copper is 128 pm



Atomic radius

1F.1 Atomic radius

Different types of radii

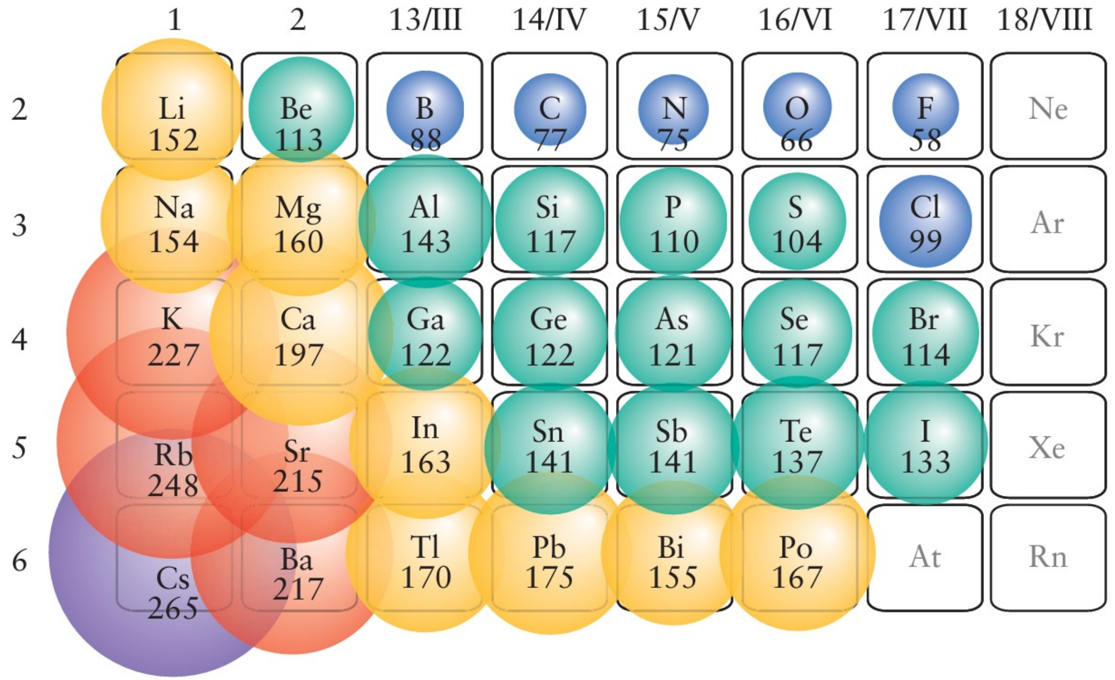
- If the element is a **nonmetal** or a **metalloid**, half the distance between the nuclei of atoms joined by a chemical bond is used; this radius is also called the **covalent radius** of the elements for reasons explained in Topic 2D.

E.g. the distance between the nuclei in Cl_2 is 198 pm, and so the covalent radius of chlorine is 99 pm.

- If the element is a noble gas, the **van der Waals radius** is used, which is half the distance between the centers of neighbouring atoms in a sample of the gas that has been solidified.
- Atoms are not bonded together in a noble gas, van der Waals radii are generally much larger than covalent radii → **not included in discussion of trends**

1F.1 Atomic radius

Atomic radii of main-group elements



	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
2	Li 152	Be 113	B 88	C 77	N 75	O 66	F 58	Ne
3	Na 154	Mg 160	Al 143	Si 117	P 110	S 104	Cl 99	Ar
4	K 227	Ca 197	Ga 122	Ge 122	As 121	Se 117	Br 114	Kr
5	Rb 248	Sr 215	In 163	Sn 141	Sb 141	Te 137	I 133	Xe
6	Cs 265	Ba 217	Tl 170	Pb 175	Bi 155	Po 167	At	Rn

Figure 1F.2

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

1F.1 Atomic radius

The periodic variation of the atomic radii of the elements

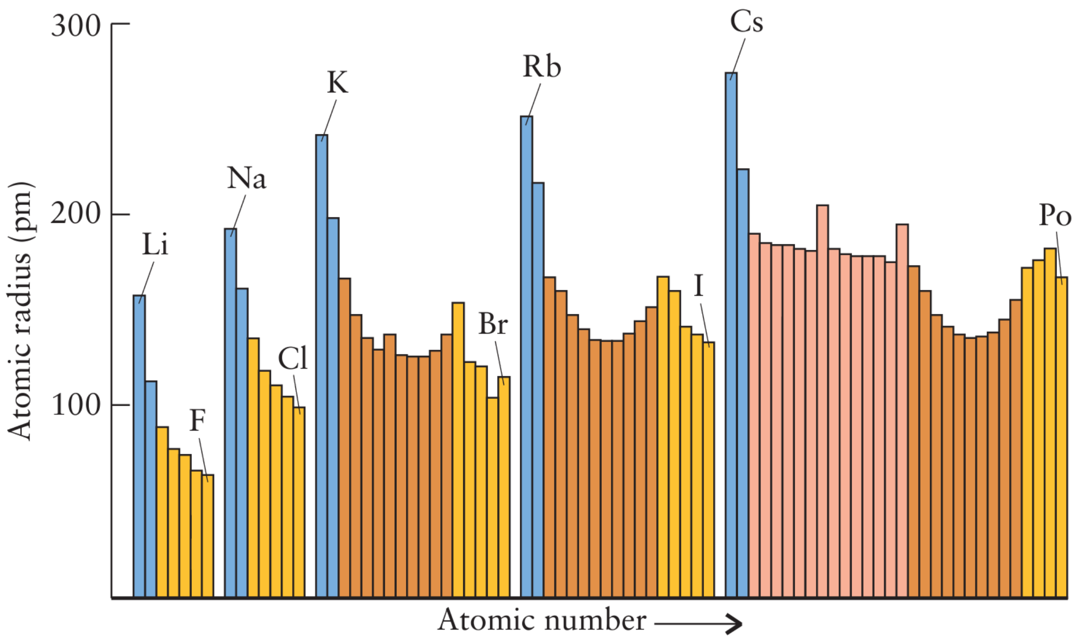


Figure 1F.3

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

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

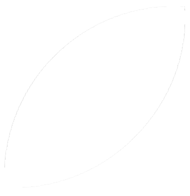
1F.1 Atomic radius

Summary

TREND: Atomic radii generally decrease from left to right across a period as the effective nuclear charge increases, and they increase down a group as successive shells are occupied.

Ionic Radius

Topic 1F.2



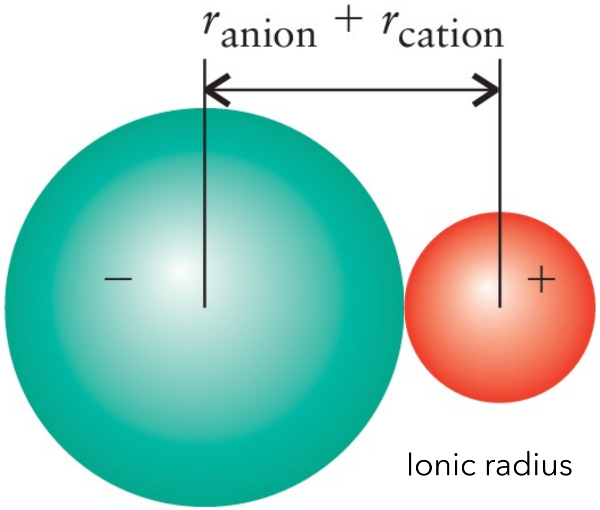
1F.2 Ionic radius

Another type of radius: ionic radius

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

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 calculated on the basis of that value.
- For example, Mg^{2+} and O^{2-} ions in magnesium is 212 pm, the radius of the $Mg^{2}+$ ion is reported as 212 - 140. pm = 72 pm.



Ionic radius

1F.2 Ionic radius

Ionic radii of the ions of the main-group elements

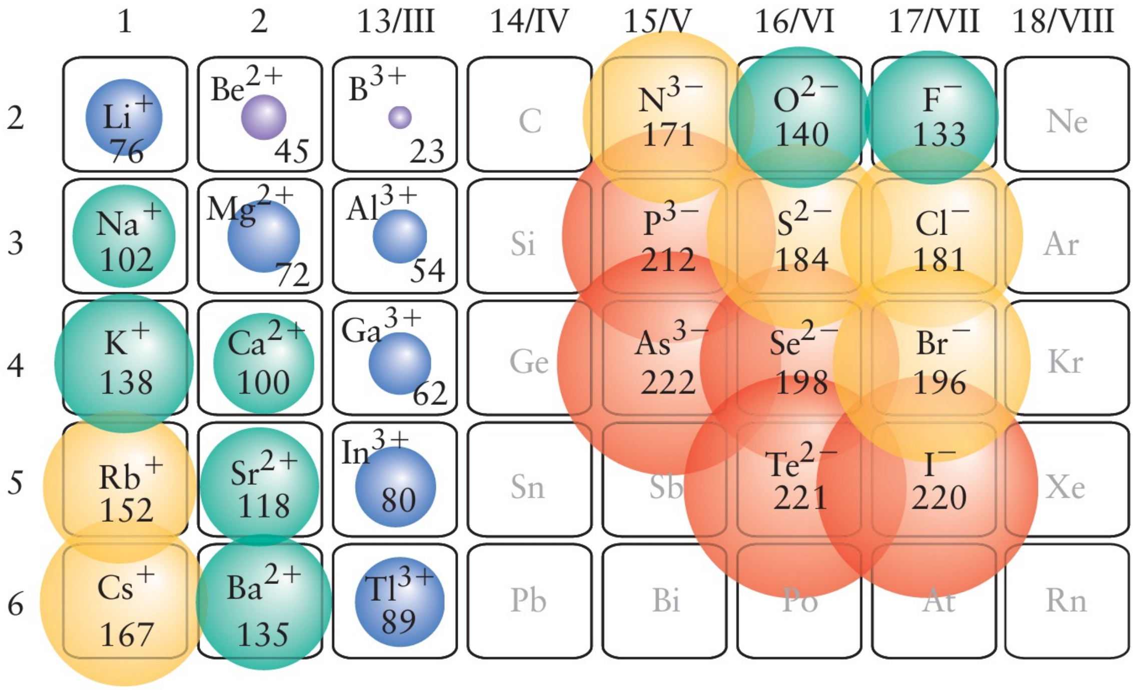


Figure 1F.4

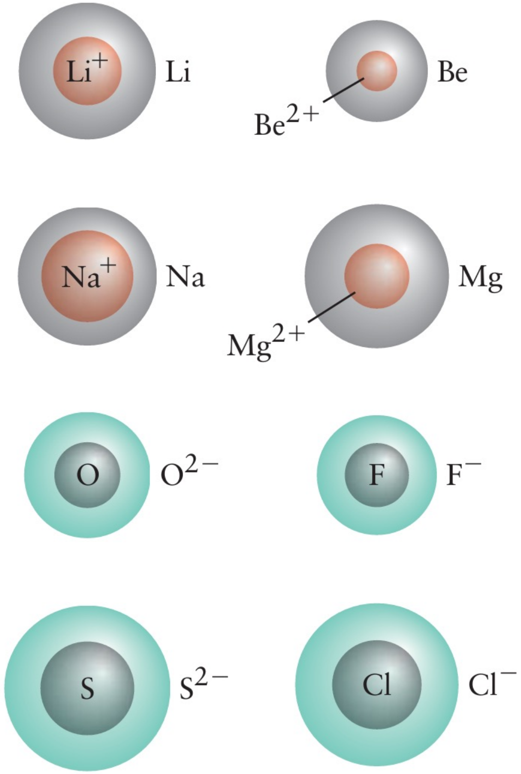
TREND: Cations are smaller than their parent atoms, whereas anions are larger.

1F.2 Ionic radius

Ionic radii of the ions of the main-group elements

- **Anions are larger than their parent ions**: increased number of electrons in the valence shell plus repulsive effects 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!

Figure 1F.5



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

1F.2 Ionic radius

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^{-}

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.

Ionization Energy

Topic 1F.3

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.
- Reported as molar quantities (kJ/mol) or in electronvols (eV)

1F.3 Ionization energy

- **First ionization energy $\boldsymbol{I_1}$**: 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

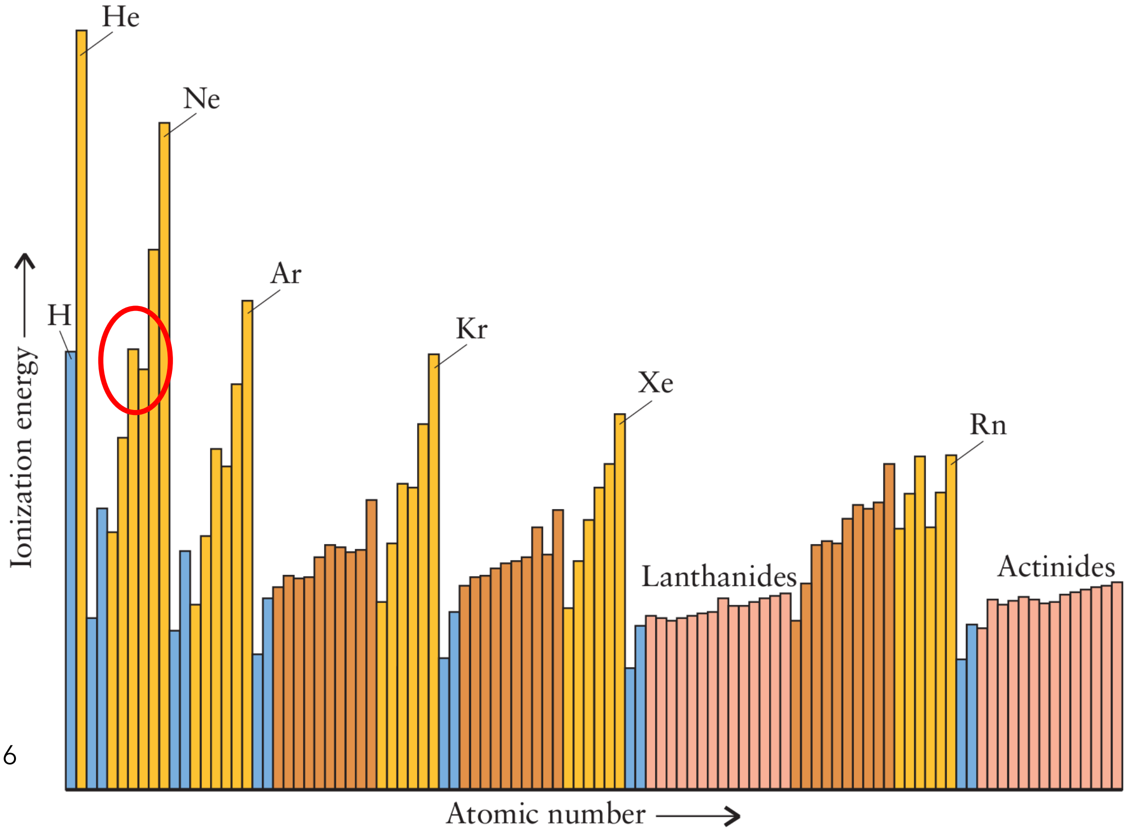


Figure 1F.6

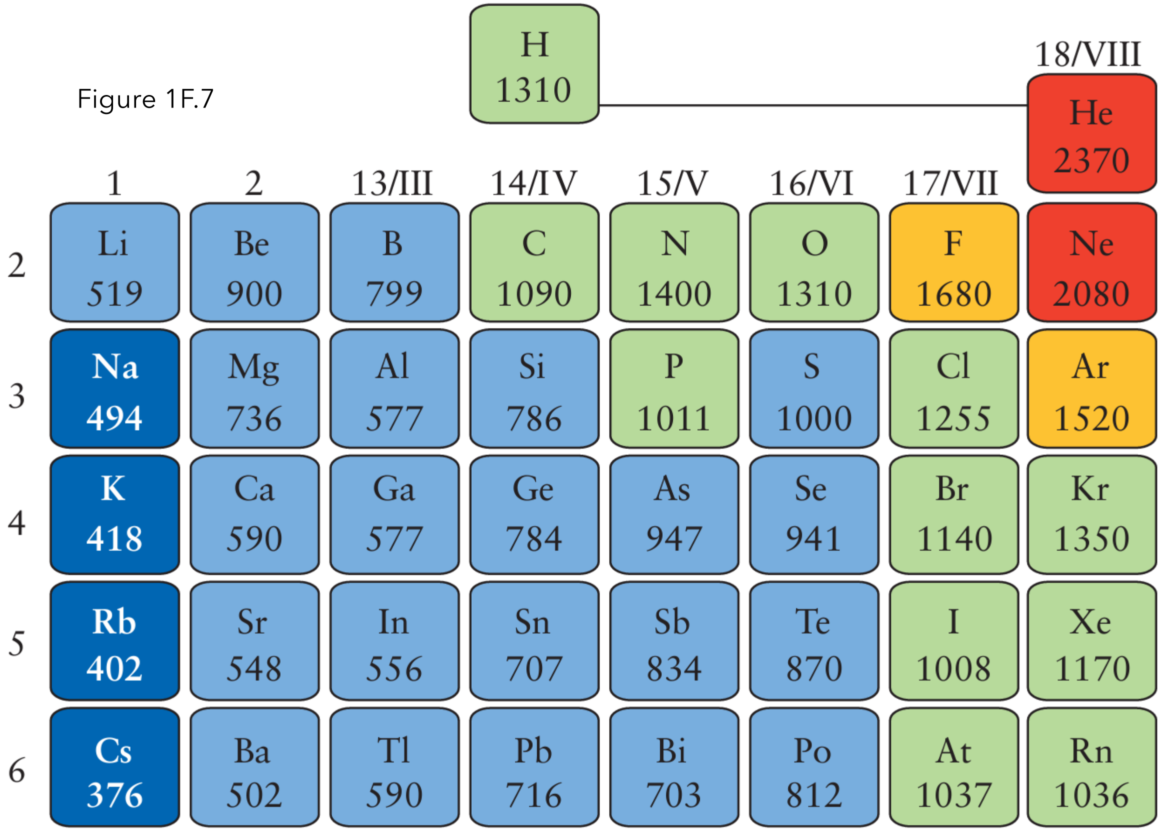
TREND: First ionization energies typically decrease down a group.

First ionization energies generally increase across a period.

- 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 8th electron with other p-electrons, energy goes up

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.

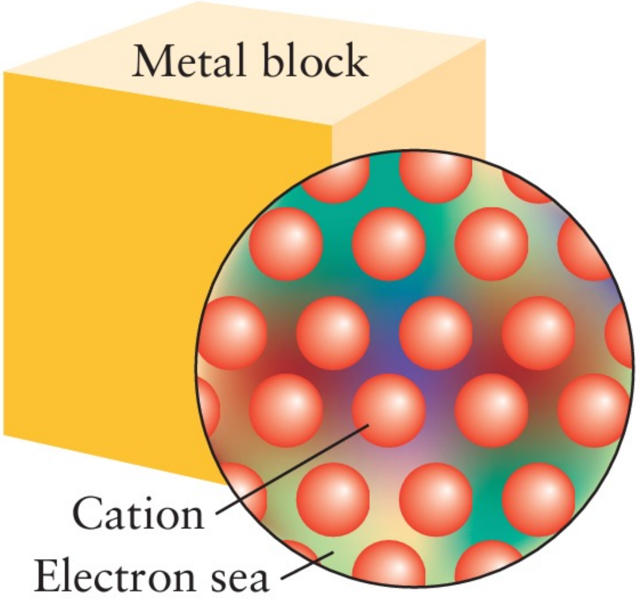
First ionization energies generally increase across a period.

1F.3 Ionization energy

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: $I_2 = I_1$

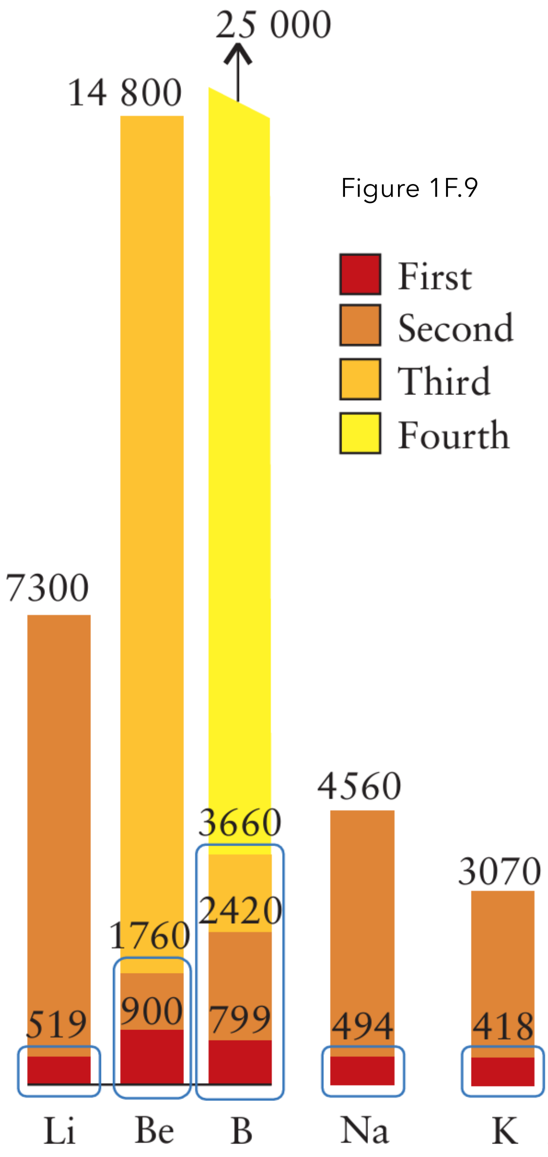


Figure 1F.9

1F.3 Ionization energy

Summary

TRENDS:

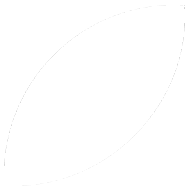
The **first ionization energy** is highest for elements close to helium and is lowest for elements close to cesium.

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



1F.4 Electron affinity

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

1F.4 Electron affinity

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 X atom 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

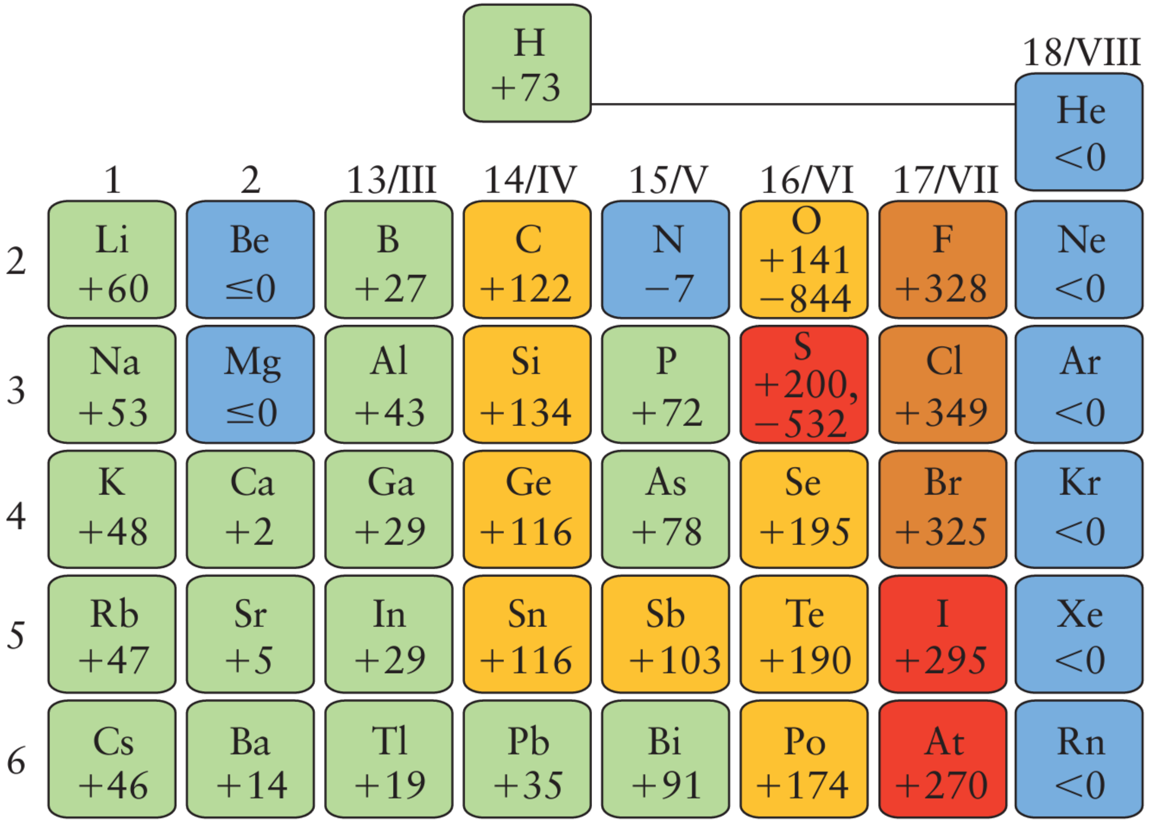
$$Cl(g) + e^-(g) \rightarrow Cl^-(g)$$

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

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



	1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
				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.

1F.4 Electron affinity

TRENDs

- **TREND:** Electron affinities are highest toward the right of the periodic table.
- Particularly true in the upper right of the periodic table: oxygen, sulfur, halogens
- In these atoms, an incoming electron occupies a p-orbital close to a nucleus with a high effective charge and can experience its attraction quite strongly
- 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

1F.4 Electron affinity

Summary

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