

Chapter 8

Periodic Properties of the Elements

8.1 Outline

- History of the periodic table
- Effective nuclear charge
- Sizes of atoms and ions
- Trends in ionization energies
- Trends in electron affinities

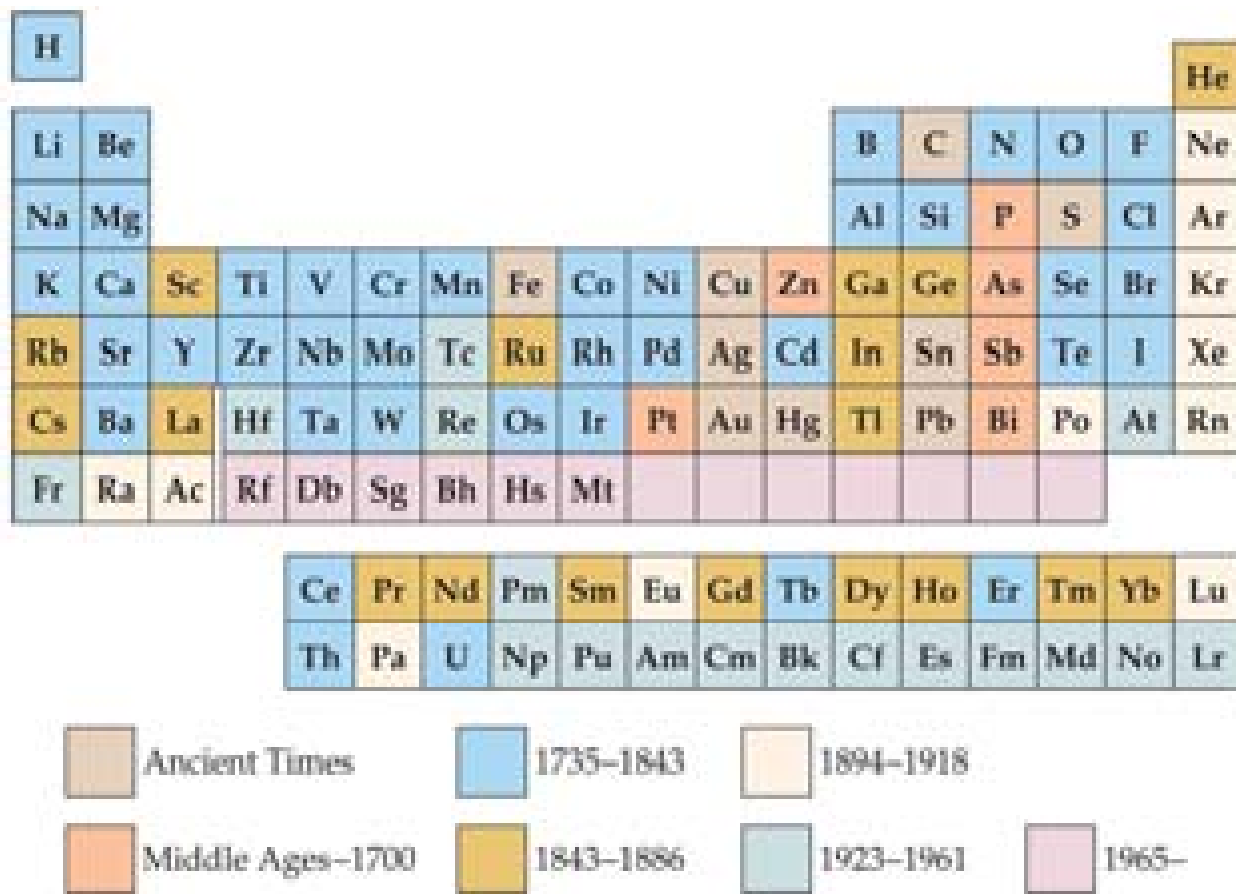


Figure 8.1: Discovery Dates of the Elements

8.2 Development of the Periodic Table

- Mendeleev's insistence that elements with similar properties be listed in the same group lead him to leave several blanks in the periodic table.
- For example, Mendeleev predicted some properties of now what is called Germanium based on the fact that it is in the same group as Silicon. Silicon was discovered almost 100 years before that of Germanium!
- Once germanium was discovered, its observed properties matched exceptionally well with Mendeleev's predictions (see the table on the next slide).

Table 8.1: Comparison of the Properties of Eka-Silicon (“under” silicon) Predicted by Mendeleev with the Observed Properties of Germanium

Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm ³)	5.5	5.35
Specific heat (J/g×K)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO ₂	GeO ₂
Density of oxide (g/cm ³)	4.7	4.70
Formula of chloride	XCl ₄	GeCl ₄
Boiling point of chloride (°C)	A little under 100	84

Periodic law 1860–1870's (Mendeleev and Meyer) – A periodic repetition of physical and chemical properties occurs when the elements are arranged in order of increasing atomic weight [*number*]

The diagram illustrates the periodic table with the following structure:

- Main groups:** Groups I, II, III, IV, V, VI, VII, and VIII (labeled 18) are indicated at the top.
- Representative elements:** Groups I, II, and groups III through VII are highlighted in yellow.
- Transition metals:** Groups III through VII are highlighted in blue.
- Alkali metals:** Group I is highlighted in light blue.
- Alkaline earth metals:** Group II is highlighted in light blue.
- Chalcogens:** Group VI is highlighted in light blue.
- Halogens:** Group VII is highlighted in light blue.
- Noble gases:** Group VIII (18) is highlighted in light blue.
- s block:** Groups I and II.
- d block:** Groups III through VII.
- p block:** Groups VIII (18) through VII.
- f block:** Lanthanoids and Actinoids are shown below the main table.

Figure 8.2

8.3 Ordering by Atomic Weight

Inconsistencies in ordering by atomic weight:

- Co (58.93 amu; $Z = 27$) and Ni (58.69 amu; $Z = 28$)
- Ar (39.95 amu; $Z = 18$) and K (39.10 amu; $Z = 19$)
- Te (127.60 amu; $Z = 52$) and I (126.90 amu; $Z = 53$)

However, all of the above are correctly ordered by atomic number, Z (i.e., the number of protons).

8.4 Development of Periodic Table

- Elements in the same group generally have similar chemical properties.
- However, physical properties are not necessarily similar.
- For example, even though Oxygen and Sulfur are in the same group (6A), Oxygen is a colorless gas, while Sulfur is a yellow solid under normal conditions.

8.5 But why do elements in the same group have similar properties?

- Underlying valence electronic structure is the same (almost) for elements of a group:
 - e.g., alkaline earth metals (Group 2) metals are all

[Noble Gas] ns^2

- halogens (Group 17) are all

[Noble Gas] ns^2np^5

- So, broadly speaking, elements in the same group *should* have similar chemistry
- But why do properties like **atomic size**, **ionization energies** and **electron affinity** vary from group to group?.

8.6 Effective Nuclear Charge

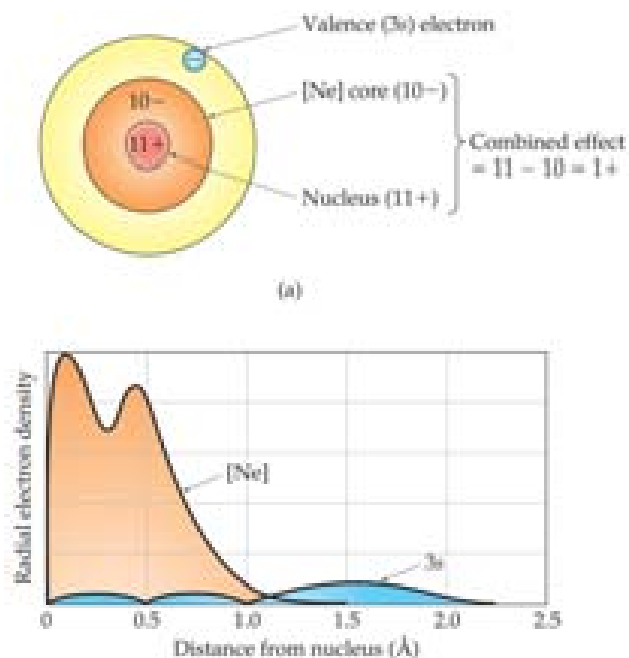


Figure 8.3: Effective Nuclear Charge

- In a many-electron atom, electrons are both attracted to the nucleus and repelled by other electrons.
- The nuclear charge that an electron experiences depends on both factors.
- The effective nuclear charge, Z_{eff} , is found this way:

$$Z_{eff} = Z - \sigma \quad (8.1)$$

where Z is the atomic number and σ is the screening constant, usually close to the number of inner/core electrons.

- Z_{eff} is always less than Z (atomic number) due to shielding!
- Electrons in the same shell don't screen one another very well.

8.7 What is the Size of an Atom?

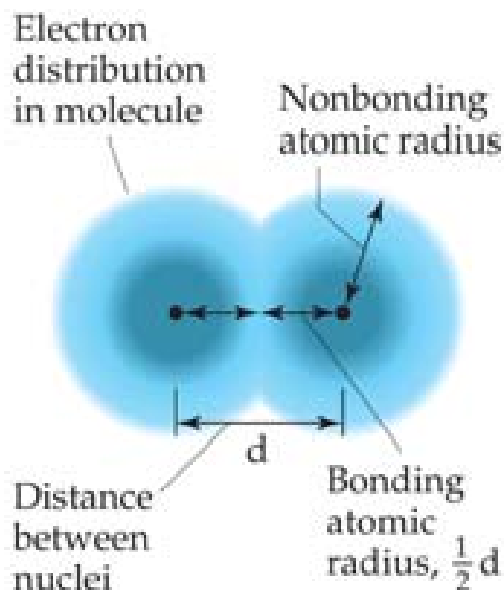


Figure 8.4: Atom Size

- The bonding atomic radius is defined as $\frac{1}{2}$ of the distance between covalently bonded nuclei.

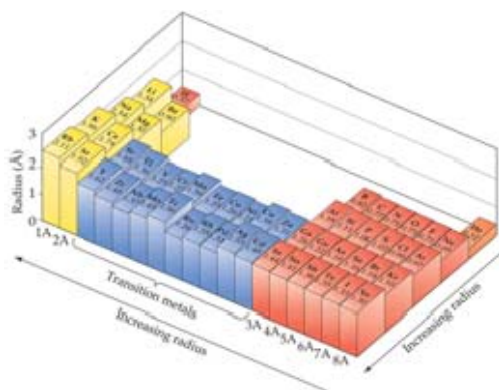


Figure 8.5: Sizes of Atoms

- Bonding atomic radii tend to:
 - decrease from left to right across a row (due to increasing Z_{eff}).
 - increase from top to bottom of a column (due to increasing value of n).

8.8 Estimating Bond Lengths

- Atomic radii allows one to estimate bond lengths.
- Example, estimate the carbon-chlorine bond length in carbon tetrachloride, CCl_4 .
 Atomic radius of C: 0.77 \AA
 Atomic radius of Cl: 0.99 \AA
 Internuclear bond length = $0.77 \text{ \AA} + 0.99 \text{ \AA} = 1.76 \text{ \AA}$
- The experimentally determined carbon-chlorine bond length in carbon tetrachloride is actually 1.77 \AA .

8.9 Radii of Cations and Anions

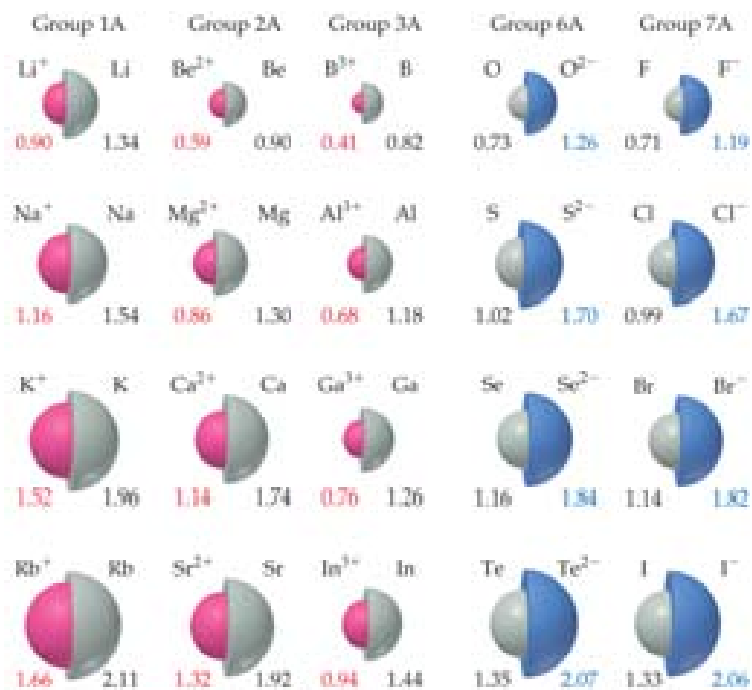


Figure 8.6: Radii of Cations and Anions

- Cations are smaller than parent neutral atoms (e.g., Li⁺ is smaller than Li.) **Why?**
- Increased Z_{eff} upon electron removal.
- Anions are larger than parent neutral atoms (e.g., I⁻ is larger than I.) **Why?**
- Increased electron-electron repulsions upon electron addition, causing electrons to spread out more in space.
- Ions with the same charge – ion size increases going down a group **due to increasing values of n .**
- For example, a Sr²⁺ ion (radius = 1.32 Å) is larger than a Ca²⁺ ion (radius = 1.14 Å).

8.10 Sizes of Isoelectronic Ions

- In an **isoelectronic series**, ions have the same number of electrons.
- Ionic size decreases with an increasing nuclear charge (Z_{eff}).

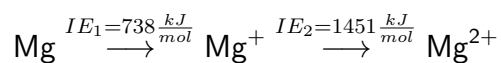


Figure 8.7: Sizes of Isoelectronic Ions

8.11 Ionization Energy

- **Ionization energy** – energy required to remove an electron from a gaseous species.

- The first ionization energy is the energy required to remove the first electron.
- The second ionization energy is the energy required to remove the second electron, etc.

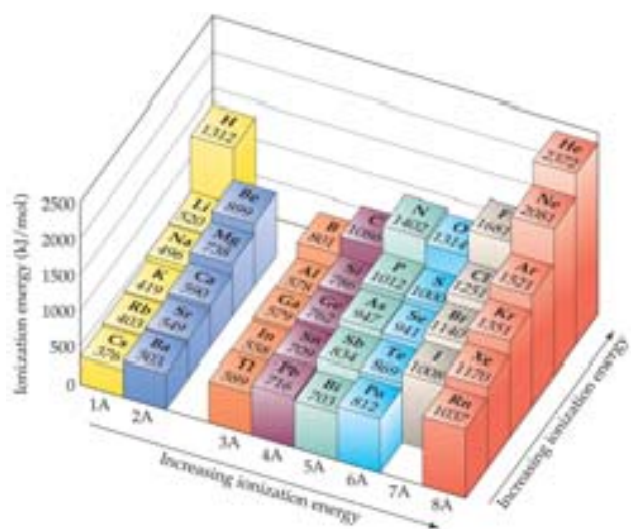


- It requires more energy to remove each successive electron.
- When all valence electrons have been removed, the ionization energy takes a large leap.
- Ionization energies for all elements can be found at: <https://www.webelements.com>

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4562	(inner-shell electrons)				
Mg	738	1451	7733				
Al	578	1817	2745	11,577			
Si	786	1577	3232	4356	16,091		
P	1012	1907	2914	4964	6274	21,267	
S	1000	2252	3357	4556	7004	8496	27,107
Cl	1251	2298	3822	5159	6542	9362	11,018
Ar	1521	2666	3931	5771	7238	8781	11,995

Figure 8.8: Ionization Energy

8.12 Trends in First Ionization Energies



- As one goes down a group, less energy is required to remove the first electron.
 - For atoms in the same group, Z_{eff} is essentially the same, but the valence electrons are farther from than nucleus (i.e., increasing value of n).

Figure 8.9: Periodic Table Ionization Energies

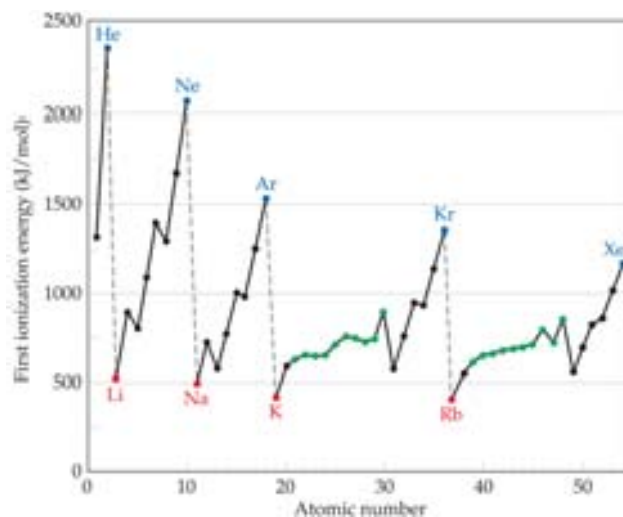


Figure 8.10: Trends in Ionization Energy

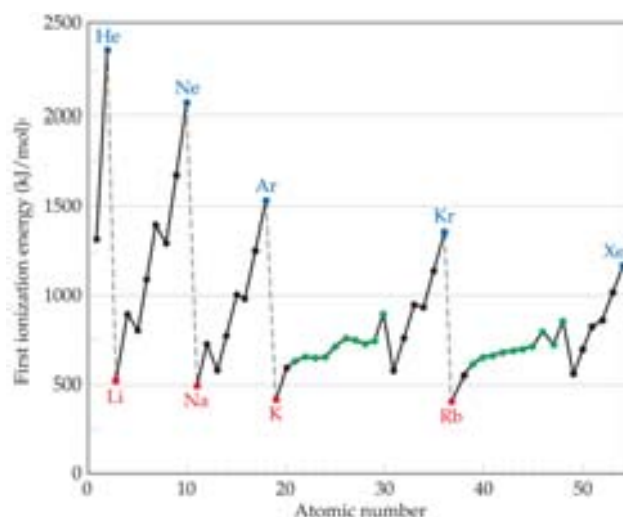


Figure 8.11: Discontinuities in Trends in Ionization Energy

- Generally, as one goes across a row/period, it becomes more difficult to remove an electron.

- As you go from left to right $\Rightarrow Z_{eff}$ increases!

- However, there are two apparent discontinuities in this trend.

- The first occurs between Groups IIA (2) and IIIA (13).

- In this case, the electron is removed from a p -orbital rather than an s -orbital.

- The electron removed is further from the nucleus.

- There is also a small amount of repulsion by the s electrons.

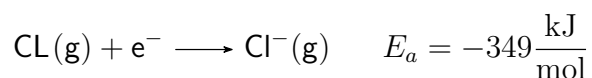
- The second occurs between Groups VA (15) and VIA (16).

- The electron removed comes from a doubly occupied orbital.

- Repulsion from the other electron in the orbital aids in the removal.

8.13 Electron Affinity

Electron affinity is the energy change accompanying the addition of an electron to a gaseous atom:



Energy is typically released when an electron is added to a gaseous atom. The process is said to be **exothermic**, so the energy has a negative sign associated with it.

The electron affinity of lithium is a negative value, whereas the electron affinity of Beryllium is a positive value. Use electron configuration to account for this observation.

8.14 Trends in Electron Affinity

H -73							He > 0
Li -60	Be > 0	B -27	C -122	N > 0	O -141	F -328	Ne > 0
Na -53	Mg > 0	Al -43	Si -134	P -72	S -200	Cl -349	Ar > 0
K -48	Ca -2	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr > 0
Rb -47	Sr -5	In -30	Sn -107	Sb -103	Te -190	I -295	Xe > 0
1A	2A	3A	4A	5A	6A	7A	8A

- In general, electron affinities become more exothermic/more negative as you go from left to right across a period.

Figure 8.12: Trends in Electron Affinity

H -73							He > 0
Li -60	Be > 0	B -27	C -122	N > 0	O -141	F -328	Ne > 0
Na -53	Mg > 0	Al -43	Si -134	P -72	S -200	Cl -349	Ar > 0
K -48	Ca -2	Ga -30	Ge -119	As -78	Se -195	Br -325	Kr > 0
Rb -47	Sr -5	In -30	Sn -107	Sb -103	Te -190	I -295	Xe > 0
1A	2A	3A	4A	5A	6A	7A	8A

- However, there are two discontinuities in this trend.

Figure 8.13: Discontinuities in Trends in Electron Affinity

- This first occurs between Groups IA and IIA.
 - The added electron must go in a *p*-orbital, not an *s*-orbital.
 - The electron is farther from nucleus and feels repulsion from the *s*-electrons.
- The second occurs between Groups IVA and VA.
 - Group VA has no empty orbitals.
 - The extra electron must go into an already occupied orbital, creating repulsion.