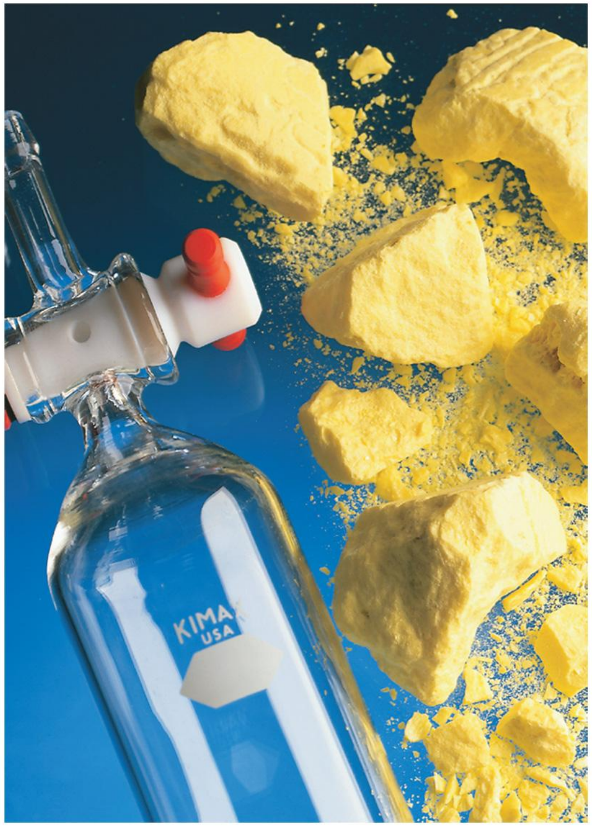
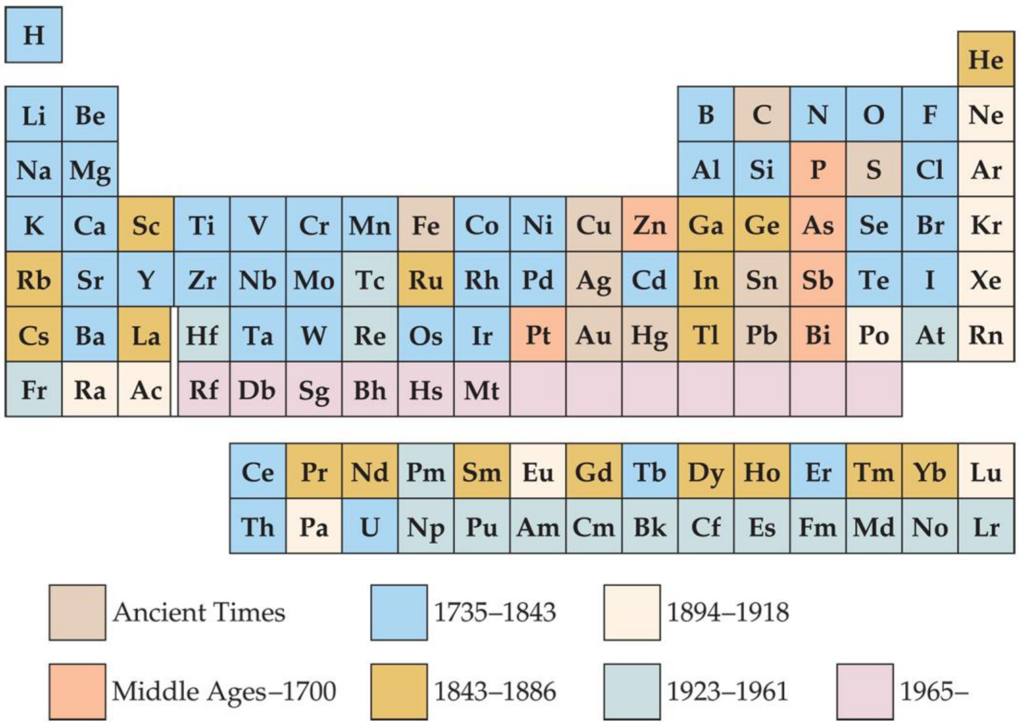
Chapter 7
Periodic Properties of the Elements

7.1 Development of Periodic Table

- Elements in the same group generally have similar chemical properties.
- Physical Properties are not identical, however.



Development of Periodic Table



Dmitri Mendeleev and Lothar Meyer independently came to the same conclusion about how elements should be grouped.

Development of Periodic Table

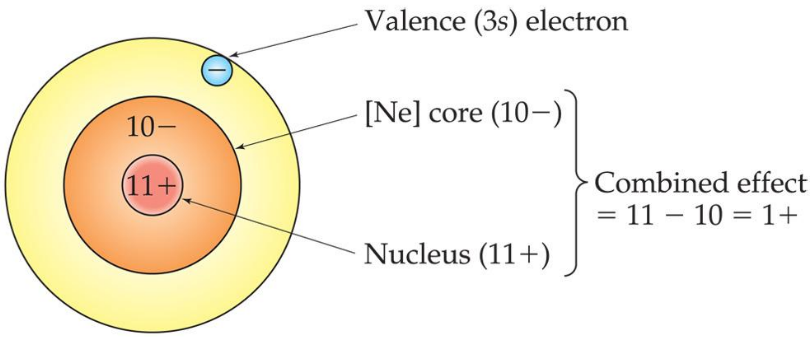
Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat (J/g-k)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride (°C)	A little under 100	84

Mendeleev, for instance, predicted the discovery of germanium (which he called eka-silicon) as an element with an atomic weight between that of zinc and arsenic, but with chemical properties similar to those of silicon.

Periodic Trends

- In this chapter, we will rationalize observed trends in
  - Sizes of atoms and ions.
  - Ionization energy.
  - Electron affinity.

7.2 Effective Nuclear Charge



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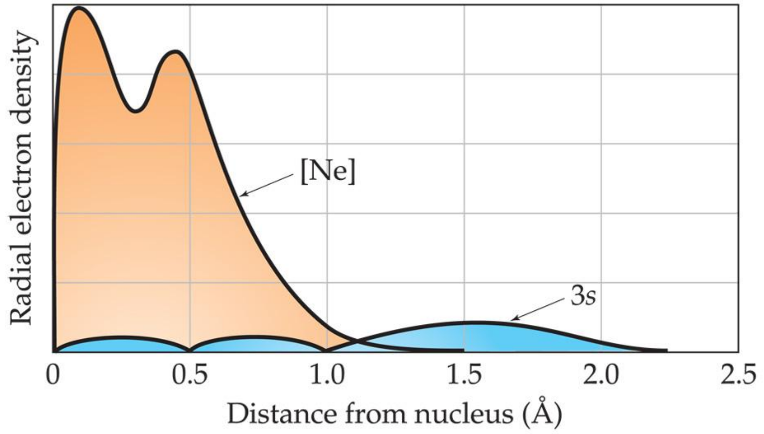
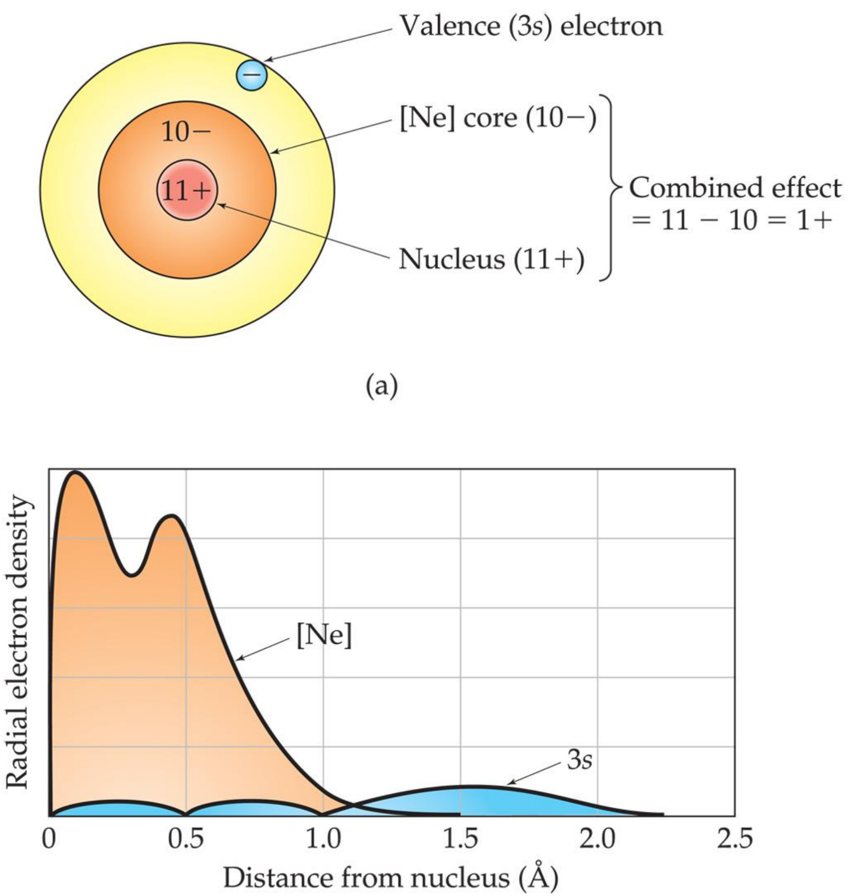


- In a many-electron atom, electrons are both attracted to the nucleus and repelled by other electrons.
- The nuclear charge that an electron experiences depends on both factors.

Effective Nuclear Charge



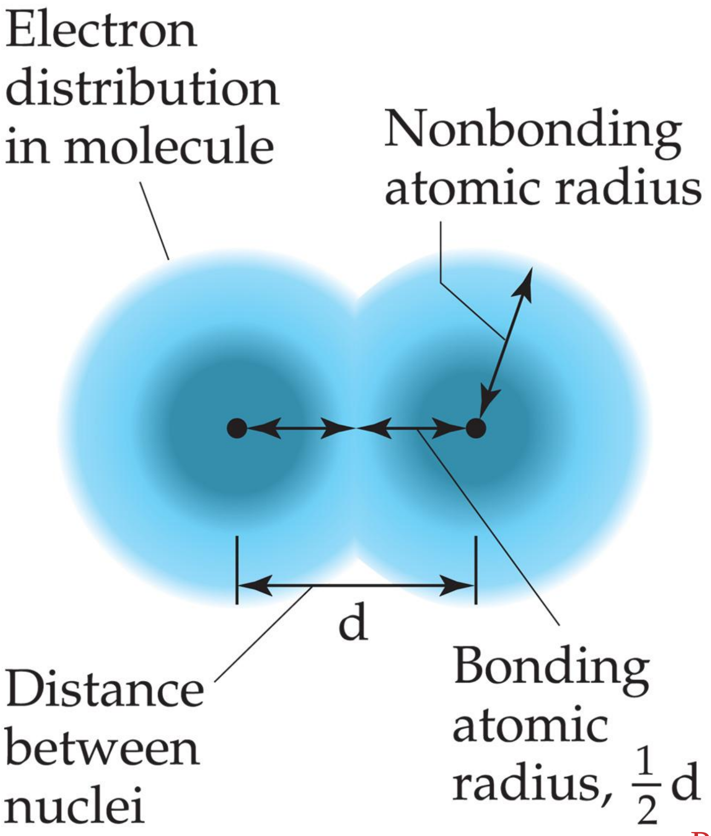
The effective nuclear charge, Z_{eff}, is found this way:

$$Z_{eff} = Z - S$$

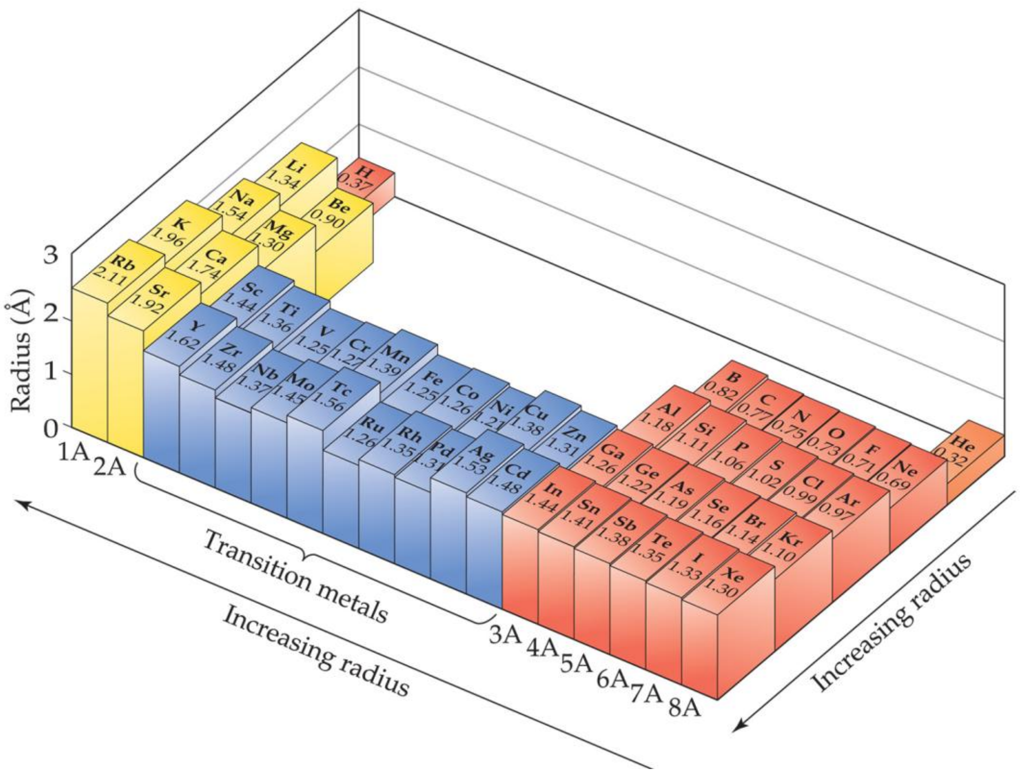
where Z is the atomic number and S is a screening constant, usually close to the number of inner electrons.

7.3 Sizes of Atoms

The bonding atomic radius is defined as one-half of the distance between covalently bonded nuclei.



Sizes of Atoms



Bonding atomic radius tends 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

Sizes of Atoms Example

- Page 266: Use Figure 7.6 to determine the length of the C-S, C-H and S-H bond.
  - C-S Bond = radius of C + radius of S
  - C-H bond = radius of C + radius of H
  - S-H bond = radius of S + radius of H

Sizes of Atoms

- C-S bond = 1.79 Angstroms
- C-H bond = 1.14 Angstroms
- S-H bond = 1.39 Angstroms

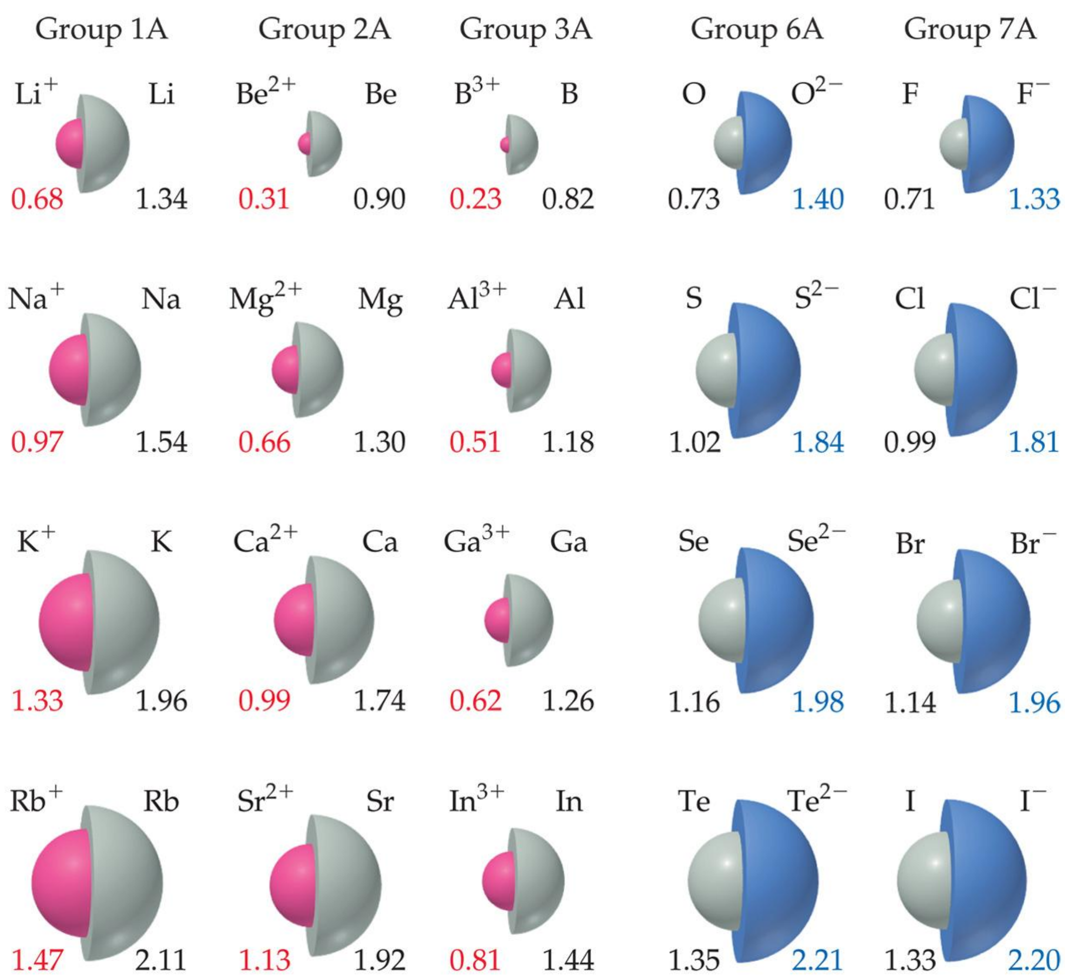
Sizes of Atoms

- Referring to a periodic table, arrange (as much as possible)the following atoms in order of increasing size:
  - Na, Be, Mg

Sizes of Atoms

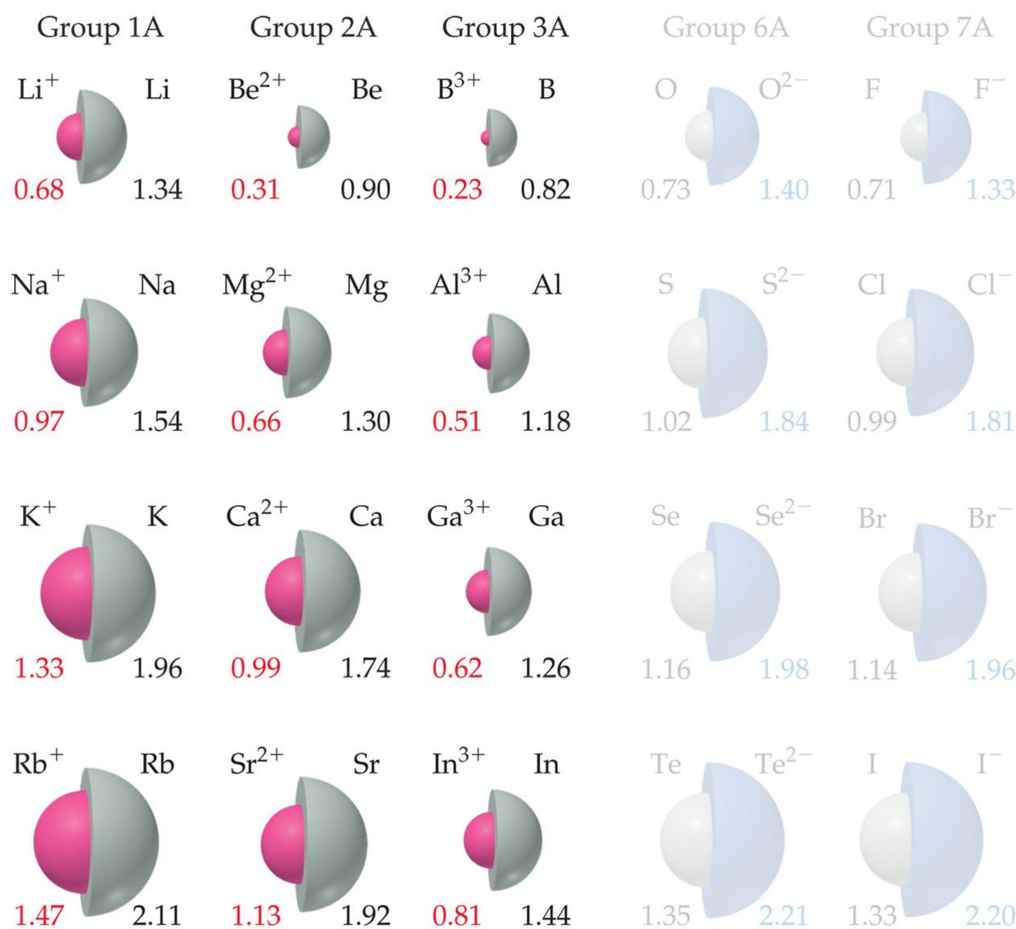
- Answer: Be < Mg < Na

Sizes of Ions



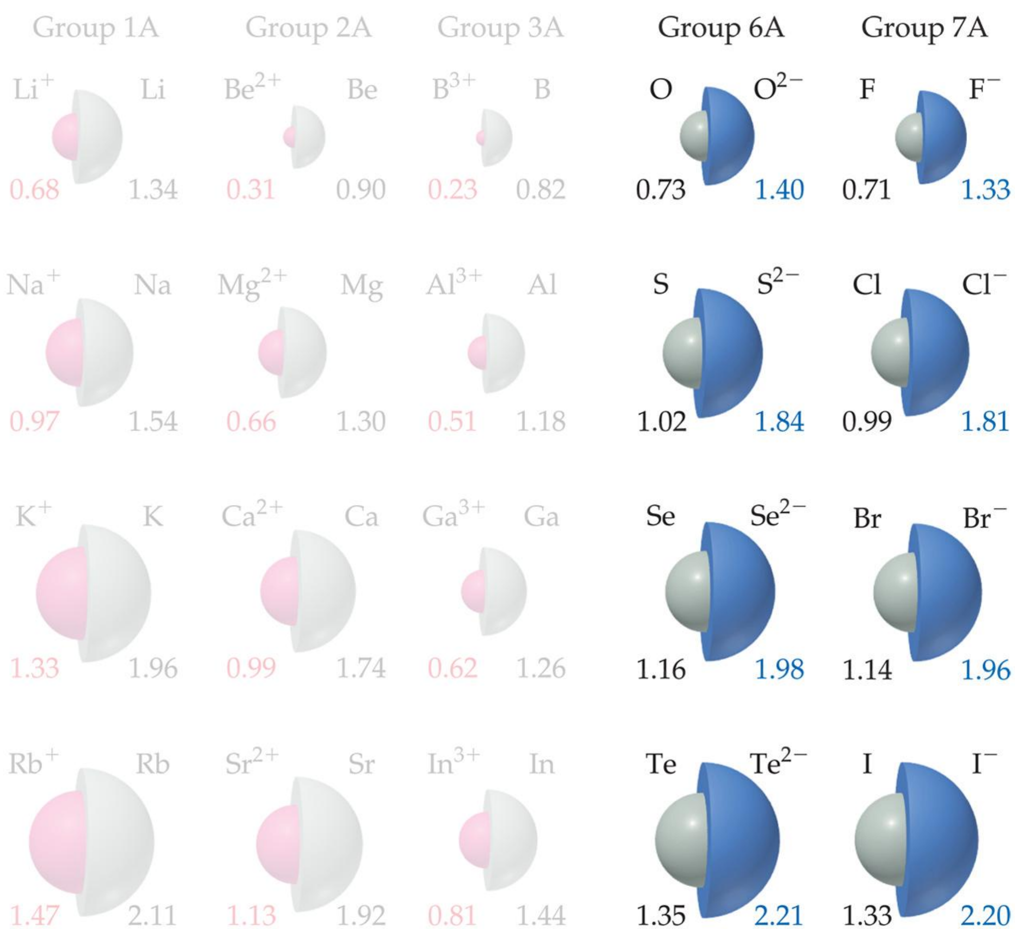
- Ionic size depends upon:
  - Nuclear charge.
  - Number of electrons.
  - Orbitals in which electrons reside.
- Neutral atoms in gray, cations in red, anions in blue.

Sizes of Ions



- Cations are smaller than their parent atoms.
  - The outermost electron is removed and repulsions are reduced.

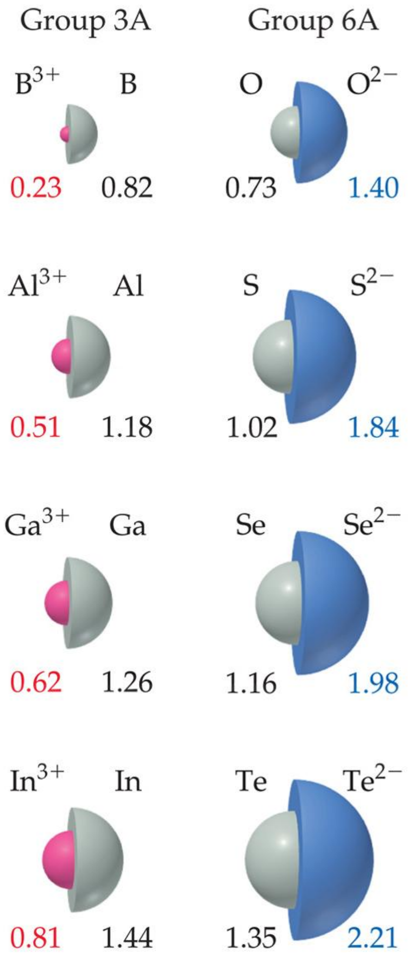
Sizes of Ions



- Anions are larger than their parent atoms.
  - Electrons are added and repulsions are increased.

Sizes of Ions

- Ions increase in size as you go down a column.
  - Due to increasing value of *n*.



Practice

- Arrange these atoms and ions in order of decreasing size: Mg^{+2}, Ca^{+2}, and Ca.

Answer

- Cations are smaller than their parent atoms, and so the Ca^{+2} is smaller than Ca atom. Because Ca is below Mg in group 2A, Ca^{+2} is larger than Mg^{+2}.
- $Ca > Ca^{+2} > Mg^{+2}$

Practice

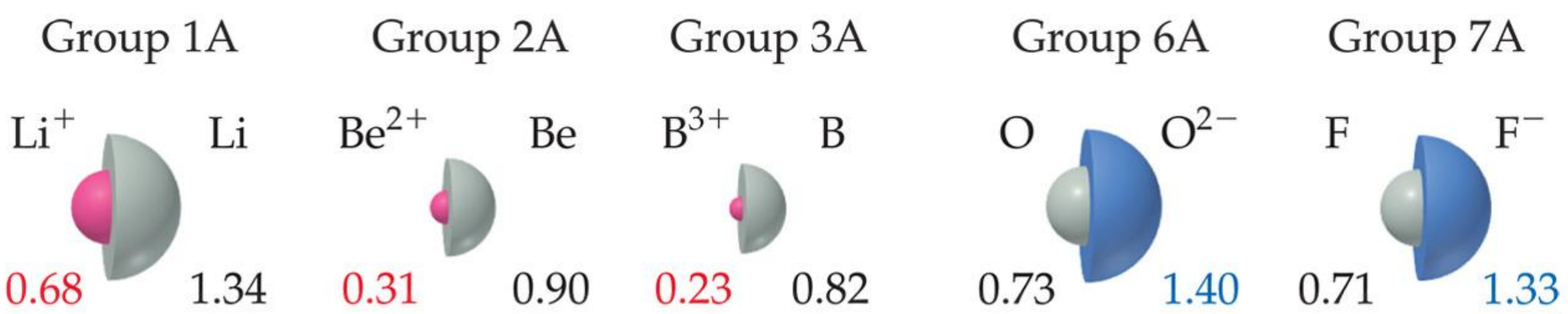
- Which of the following atoms and ions is largest?
  - Sulfide ion, Sulfur atom, or oxide ion?

Answer

- Sulfide Ion
- Increase size as you down a column, and anions are larger than their parent atoms.

Sizes of Ions

- In an isoelectronic series, ions have the same number of electrons.
- Ionic size decreases with an increasing nuclear charge.



Practice

- Arrange the ions K^{+}, Cl^{-}, Ca^{+2}, and S^{-2} in order of decreasing size.

Answer

- Isoelectronic series of ions – they all have 18 electrons.
- In such a series, size decreases as the nuclear charge (atomic number) of the ion increases. The atomic numbers of the ions are
  - S = 16, Cl = 17, K = 19, Ca = 20.
  - Thus, the ions decrease in size in the order
  - Sulfide Ion > Chloride Ion > Potassium Ion > Calcium Ion

7.4 Ionization Energy

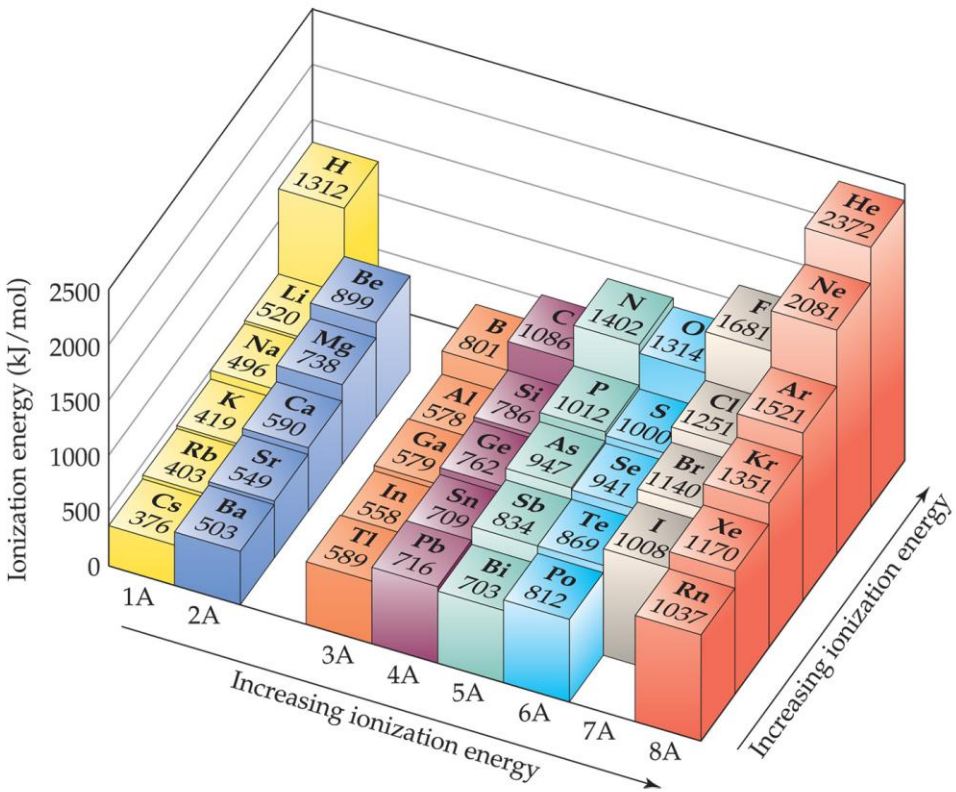
- Amount of energy required to remove an electron from the ground state of a gaseous atom or ion.
  - First ionization energy is that energy required to remove first electron.
  - Second ionization energy is that energy required to remove second electron, etc.

Ionization Energy

- It requires more energy to remove each successive electron.
- When all valence electrons have been removed, the ionization energy takes a quantum leap.

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

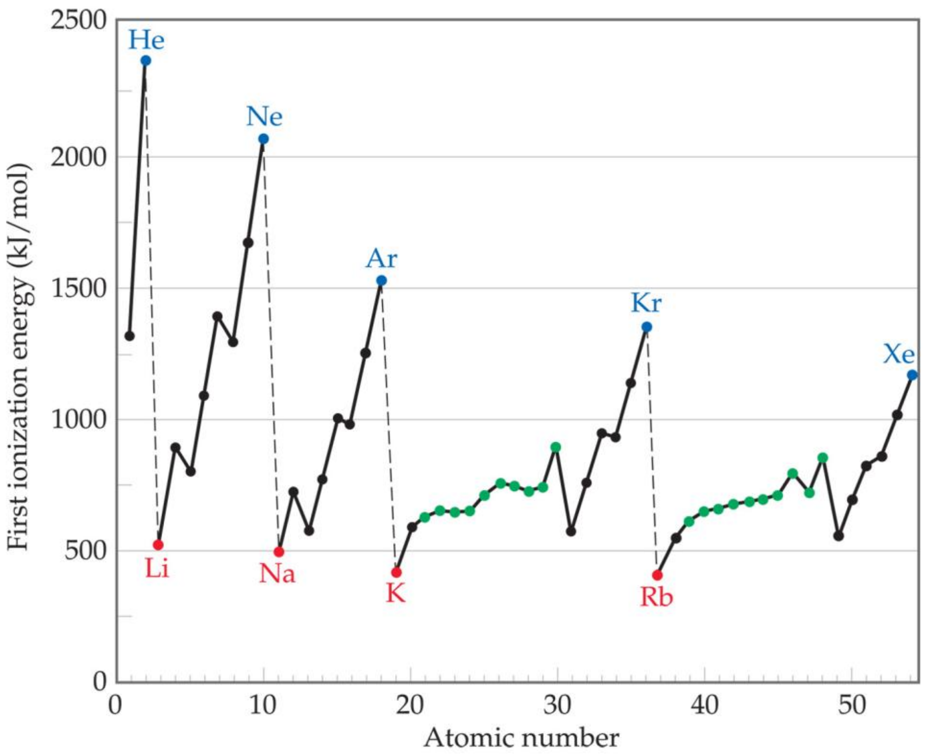
Trends in First Ionization Energies



- As one goes down a column, 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 the nucleus.

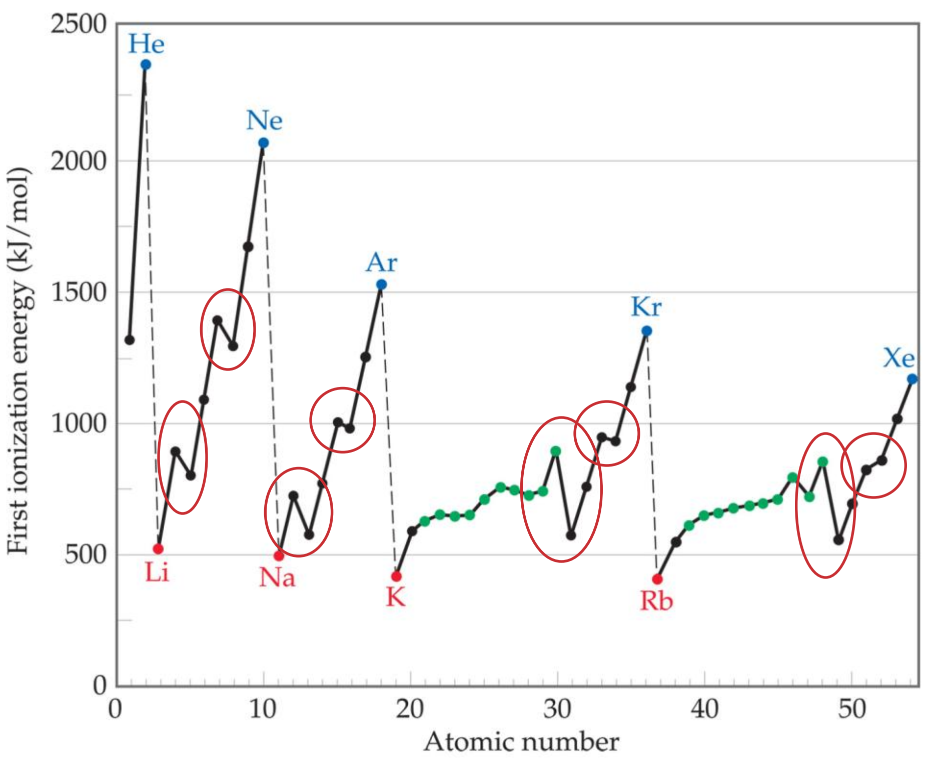
Trends in First Ionization Energies

- Generally, as one goes across a row, it gets harder to remove an electron.
  - As you go from left to right, Z_{eff} increases.



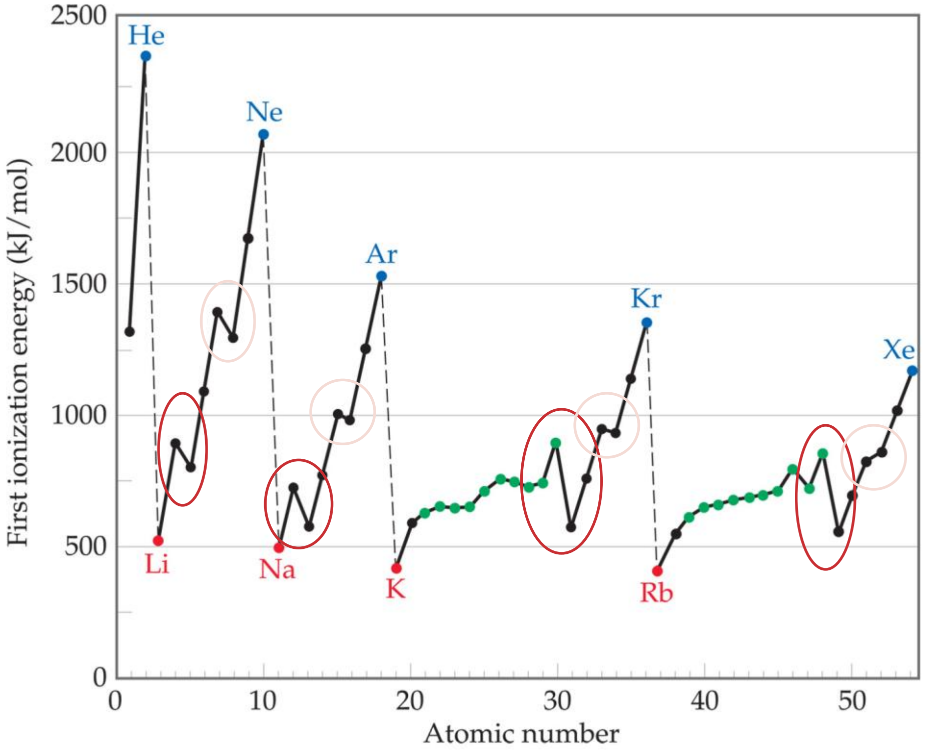
Trends in First Ionization Energies

However, there are two apparent discontinuities in this trend.



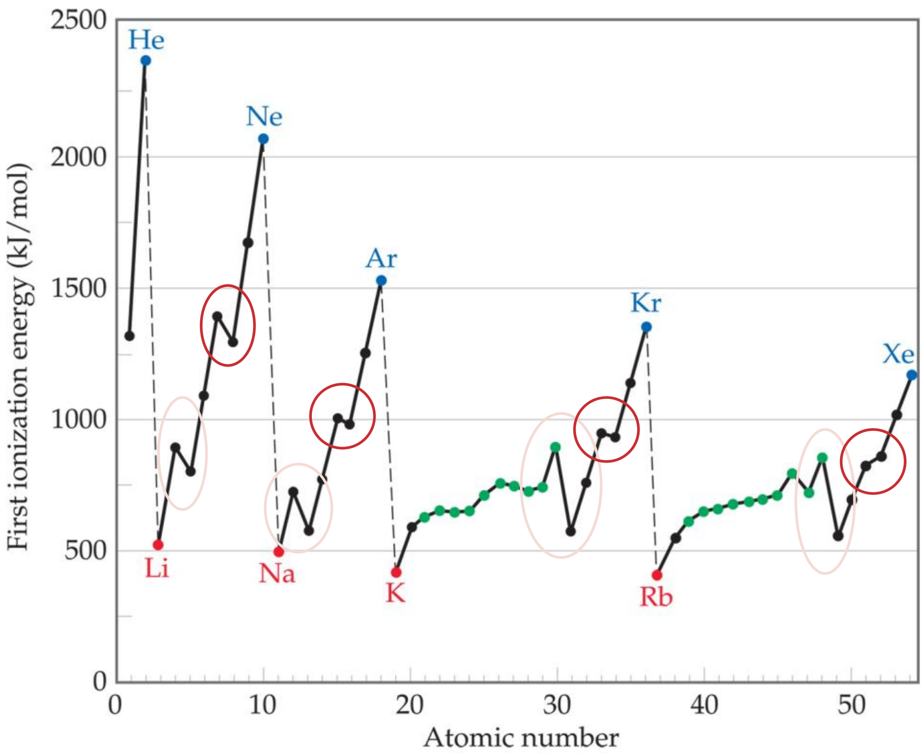
Trends in First Ionization Energies

- The first occurs between Groups IIA and IIIA.
- Electron removed from *p*-orbital rather than *s*-orbital
  - ➢ Electron farther from nucleus
  - ➢ Small amount of repulsion by *s* electrons.



Trends in First Ionization Energies

- The second occurs between Groups VA and VIA.
  - Electron removed comes from doubly occupied orbital.
  - Repulsion from other electron in orbital helps in its removal.



Periodic Properties of the Elements

Practice

- Referring to a periodic table, arrange the following atoms in order of increasing first ionization energy:
  - Ne, Na, P, Ar, K

Answer

- Ionizations energy increases as we move left to right across a row.
- It decreases as we move from the top of a group to the bottom.
- Na, P and Ar are in the same row, we expect I_1 to vary in the order Na < P < Ar.
- Because Ne is above Ar in group 8A, we expect Ne to have a greater I_1: Ar < Ne. Similarly K is below Na so K < Na
- K < Na < P < Ar < Ne

Practice

- Which has the lowest first ionization energy?
    - B, Al, C or Si?
- Which has the highest first ionization energy?
    - B, Al, C or Si?

Answer

- Al has the lowest, C has the highest.

Electron Configurations of Ions

- Write the electron configuration for
  - Calcium ion
  - Cobalt III ion
  - Sulfide Ion

Answer

- Ca Atom
  - [Ar] $4s^2$
- Ca Ion
  - [Ar]
- Co Atom
  - [Ar] $3d^7$ $4s^2$
- Cobalt III Ion
  - [Ar] $3d^6$
- Sulfur Atom
  - [Ne] $3s^2$ $3p^4$
- Sulfide Ion
  - [Ne] $3s^2$ $3p^6$ = [Ar]

7.5 Electron Affinity

Energy change accompanying addition of electron to gaseous atom:

$$Cl + e^{-} \longrightarrow Cl^{-} \quad \Delta E = -349 \text{ kJ/mol}$$

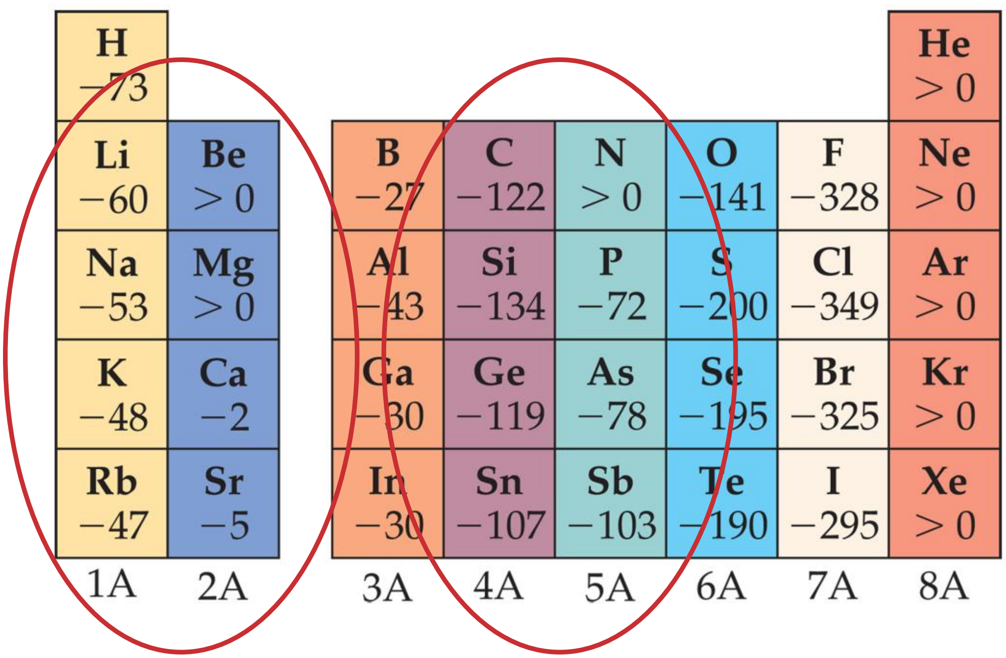
Trends in Electron Affinity

1A	2A	3A	4A	5A	6A	7A	8A
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

In general, electron affinity becomes more exothermic as you go from left to right across a row.

The more negative the electron affinity, the greater the attraction of the atom for an electron.

Trends in Electron Affinity



There are again, however, two discontinuities in this trend.

Trends in Electron Affinity

1A	2A	3A	4A	5A	6A	7A	8A
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

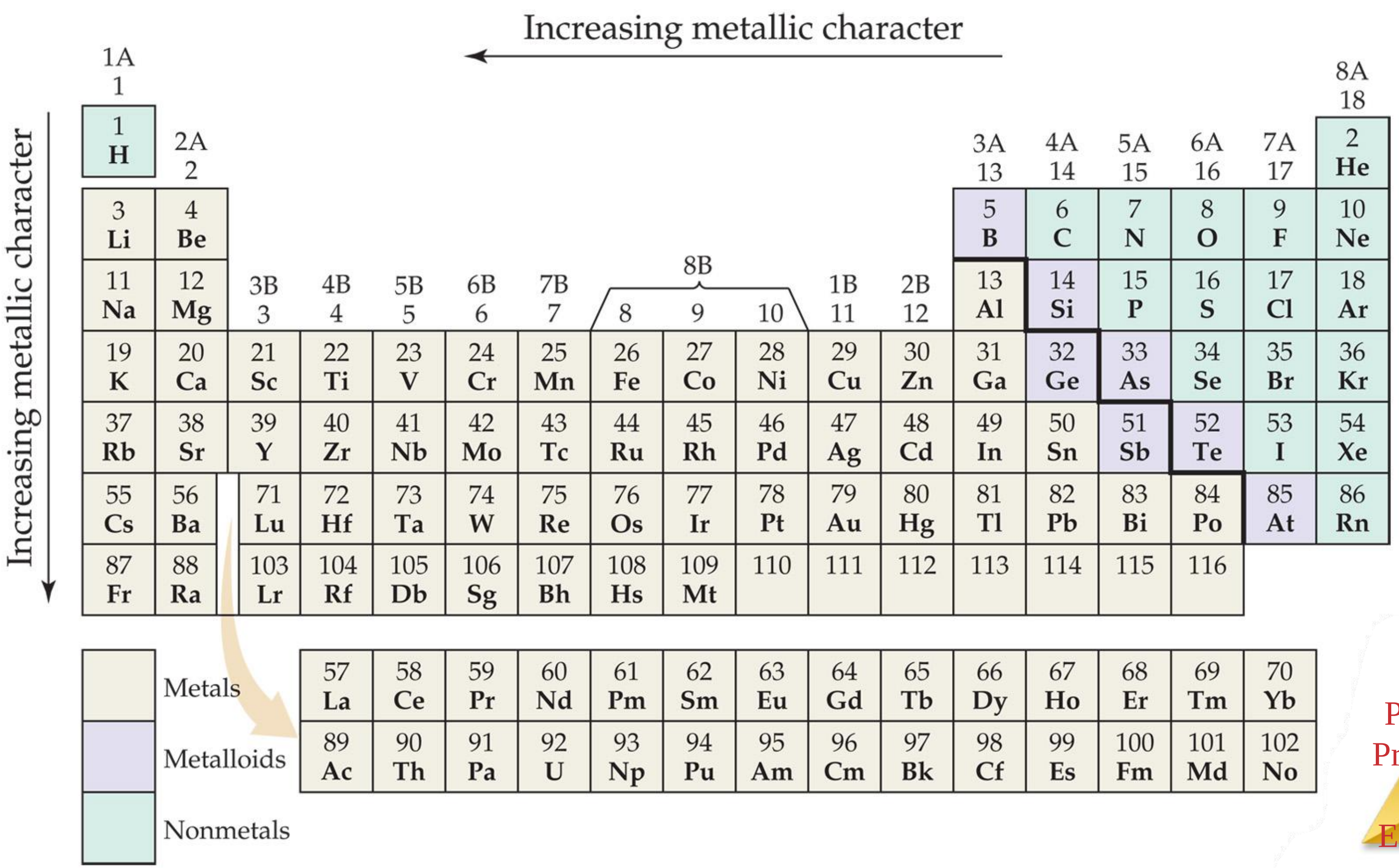
- The first occurs between Groups <u>IA and IIA.</u>
  - Added electron must go in *p*-orbital, not *s*-orbital.
  - Electron is farther from nucleus and feels repulsion from *s*-electrons.

Trends in Electron Affinity

1A	2A	3A	4A	5A	6A	7A	8A
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

- The second occurs between Groups IVA and VA.
  - Group VA has no empty orbitals.
  - Extra electron must go into occupied orbital, creating repulsion.

7.6 Properties of Metal, Nonmetals, and Metalloids



Periodic Properties of the Elements

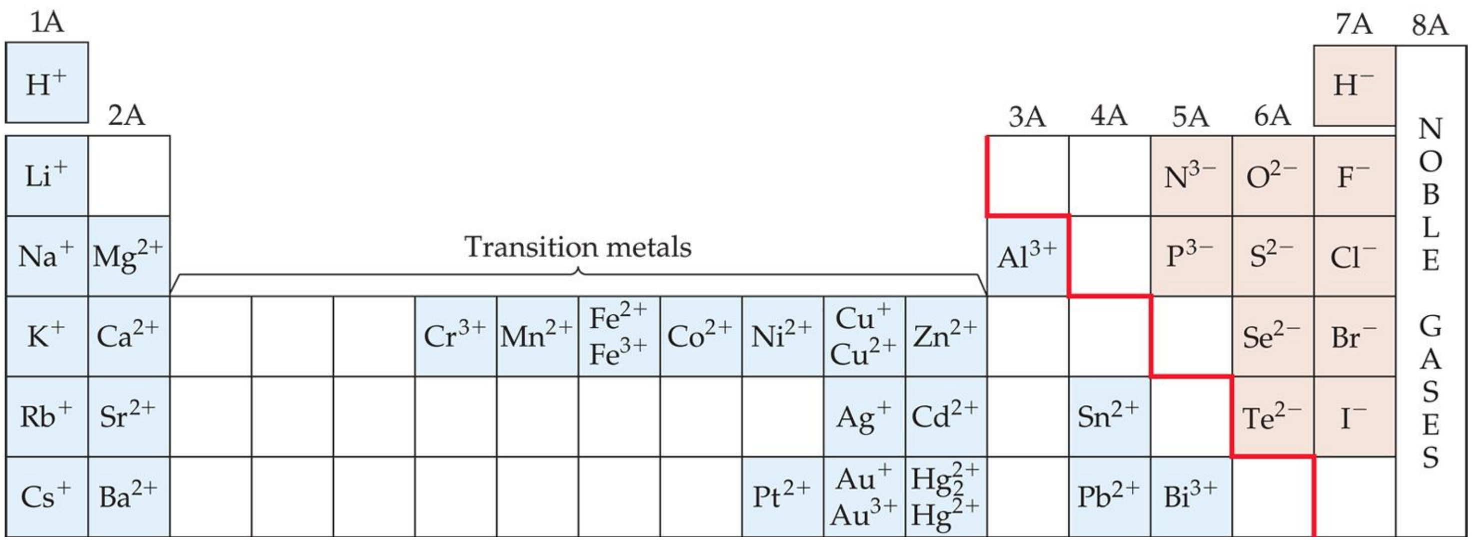
Metals versus Nonmetals

Metals	Nonmetals
Have a shiny luster; various colors, although most are silvery	Do not have a luster; various colors
Solids are malleable and ductile	Solids are usually brittle; some are hard, some are soft
Good conductors of heat and electricity	Poor conductors of heat and electricity
Most metal oxides are ionic solids that are basic	Most nonmetal oxides are molecular substances that form acidic solutions
Tend to form cations in aqueous solution	Tend to form anions or oxyanions in aqueous solution

Differences between metals and nonmetals tend to revolve around these properties.

Metals versus Nonmetals

- Metals tend to form cations.
- Nonmetals tend to form anions.

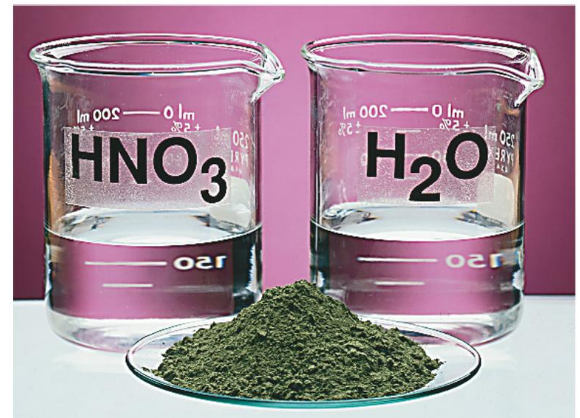


Metals

Tend to be lustrous, malleable, ductile, and good conductors of heat and electricity.

Metals

- Compounds formed between metals and nonmetals tend to be ionic.
- Example: NaCl
- Metal oxides tend to be basic.
- Example:
  - $Na_2O + H_2O \rightarrow 2\ NaOH$



Nonmetals

- Dull, brittle substances that are poor conductors of heat and electricity.
- Tend to gain electrons in reactions with metals to acquire noble gas configuration.

Nonmetals

- Substances containing only nonmetals are molecular compounds.
  - Example: CO_2
- Most nonmetal oxides are acidic.
  - Example: $CO_2 + H_2O \rightarrow H_2CO_3$

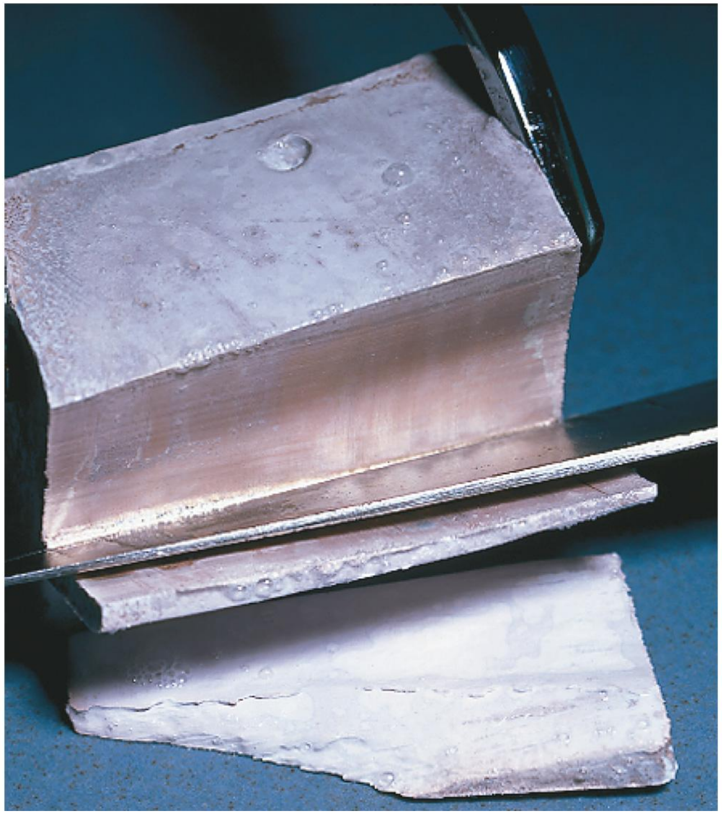
Metalloids

- Have some characteristics of metals, some of nonmetals.
- For instance, silicon looks shiny, but is brittle and fairly poor conductor.

7.7 Group Trends

Alkali Metals

- Soft, metallic solids.
- Name comes from Arabic word for ashes.



Alkali Metals

- Found only as compounds in nature.
- Have low densities and melting points.
- Also have low ionization energies.

Element	Electron Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius (Å)	I_1 (kJ/mol)
Lithium	[He]$2s^1$	181	0.53	1.34	520
Sodium	[Ne]$3s^1$	98	0.97	1.54	496
Potassium	[Ar]$4s^1$	63	0.86	1.96	419
Rubidium	[Kr]$5s^1$	39	1.53	2.11	403
Cesium	[Xe]$6s^1$	28	1.88	2.25	376

Alkali Metals

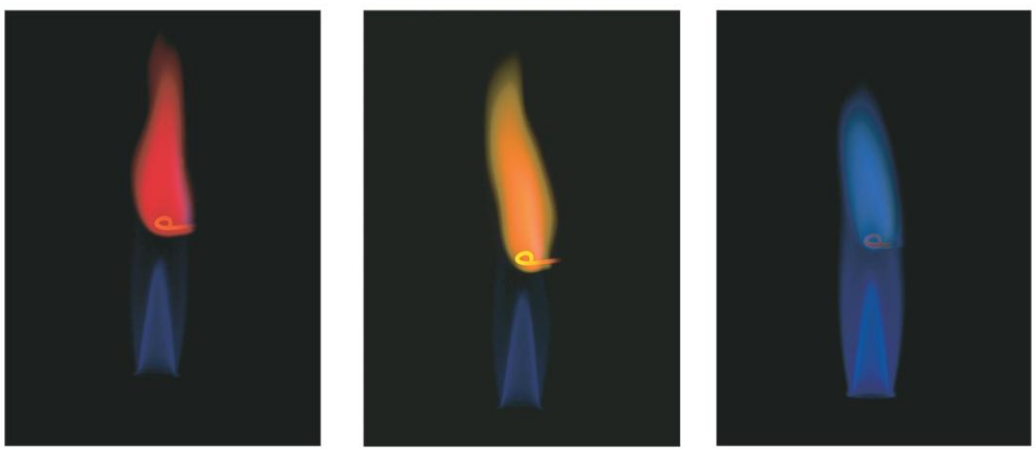
Their reactions with water are famously exothermic.

Alkali Metals

- Alkali metals (except Li) react with oxygen to form peroxides.
- K, Rb, and Cs also form superoxides:

$$K + O_2 \longrightarrow KO_2$$

- Produce bright colors when placed in flame.



Alkaline Earth Metals

Element	Electron Configuration	Melting Point (°C)	Density (g/cm^3)	Atomic Radius (Å)	I_1 (kJ/mol)
Beryllium	[He]$2s^2$	1287	1.85	0.90	899
Magnesium	[Ne]$3s^2$	650	1.74	1.30	738
Calcium	[Ar]$4s^2$	842	1.55	1.74	590
Strontium	[Kr]$5s^2$	777	2.63	1.92	549
Barium	[Xe]$6s^2$	727	3.51	1.98	503

- Have higher densities and melting points than alkali metals.
- Have low ionization energies, but not as low as alkali metals.

Alkaline Earth Metals

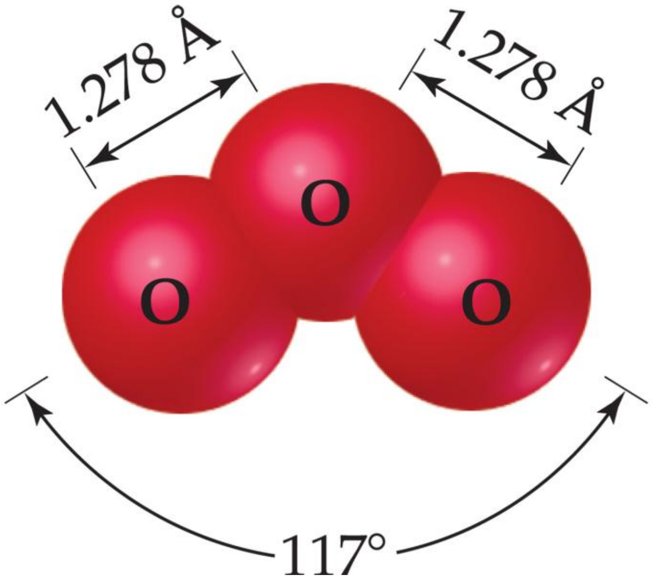
- Be does not react with water, Mg reacts only with steam, but others react readily with water.
- Example: $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2$
- Reactivity tends to increase as go down group.

Group 6A

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ/mol)
Oxygen	$[He]2s^2 2p^4$	−218	1.43 g/L	0.73	1314
Sulfur	$[Ne]3s^2 3p^4$	15	1.96 g/cm^3	1.02	1000
Selenium	$[Ar]3d^{10} 4s^2 4p^4$	221	4.82 g/cm^3	1.16	941
Tellurium	$[Kr]4d^{10} 5s^2 5p^4$	450	6.24 g/cm^3	1.35	869
Polonium	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$	254	9.20 g/cm^3	—	812

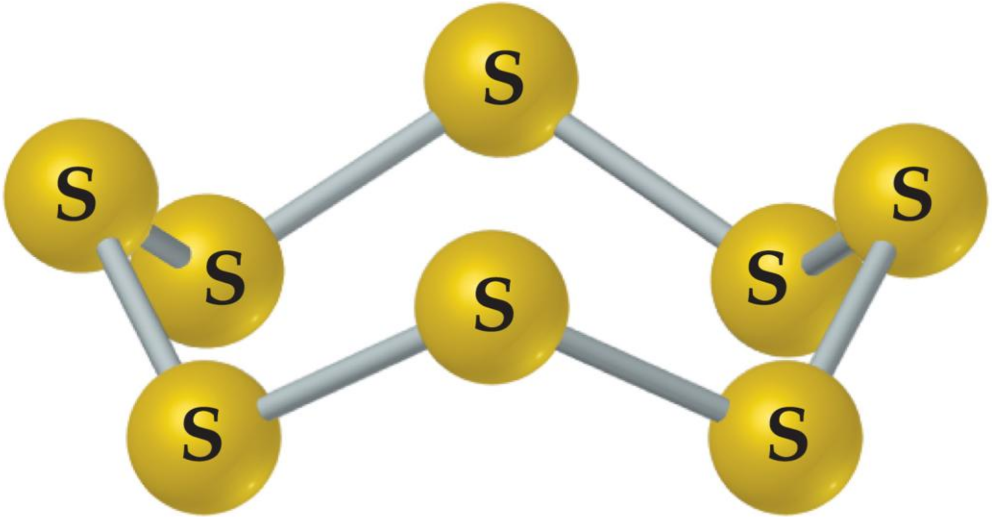
- Oxygen, sulfur, and selenium are nonmetals.
- Tellurium is a metalloid.
- The radioactive polonium is a metal.

Oxygen



- Two allotropes:
  - O_2
  - O_3, ozone
- Three anions:
  - O^{2-}, oxide
  - O_2^{2-}, peroxide
  - O_2^{1-}, superoxide
- Tends to take electrons from other elements (oxidation)

Sulfur



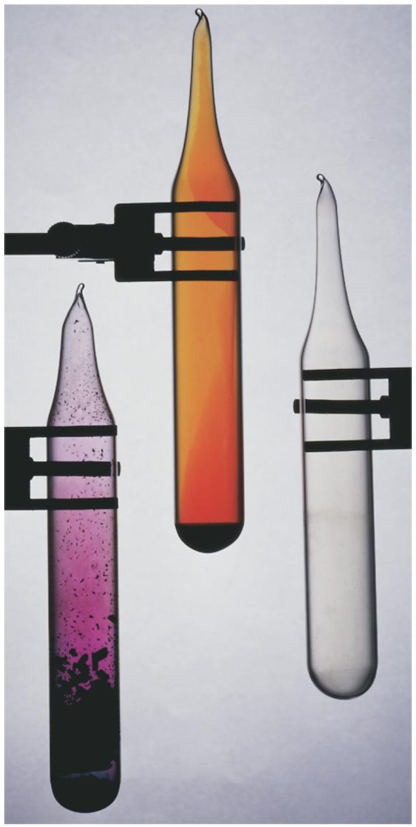
- Weaker oxidizing agent than oxygen.
- Most stable allotrope is S_8, a ringed molecule.

Group VIIA: Halogens

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ/mol)
Fluorine	$[He]2s^2 2p^5$	−220	1.69 g/L	0.71	1681
Chlorine	$[Ne]3s^2 3p^5$	−102	3.21 g/L	0.99	1251
Bromine	$[Ar]3d^{10} 4s^2 4p^5$	−7.3	3.12 g/cm^3	1.14	1140
Iodine	$[Kr]4d^{10} 5s^2 5p^5$	114	4.94 g/cm^3	1.33	1008

- Prototypical nonmetals
- Name comes from the Greek *halos* and *gennao*: “salt formers”

Group VIIA: Halogens



- Large, negative electron affinities
  - Therefore, tend to oxidize other elements easily
- React directly with metals to form metal halides
- Chlorine added to water supplies to serve as disinfectant

Group VIIIA: Noble Gases

Element	Electron Configuration	Boiling Point (K)	Density (g/L)	Atomic Radius* (Å)	I_1 (kJ/mol)
Helium	$1s^2$	4.2	0.18	0.32	2372
Neon	$[He]2s^2 2p^6$	27.1	0.90	0.69	2081
Argon	$[Ne]3s^2 3p^6$	87.3	1.78	0.97	1521
Krypton	$[Ar]3d^{10} 4s^2 4p^6$	120	3.75	1.10	1351
Xenon	$[Kr]4d^{10} 5s^2 5p^6$	165	5.90	1.30	1170
Radon	$[Xe]4f^{14} 5d^{10} 6s^2 6p^6$	211	9.73	1.45	1037

*Only the heaviest of the noble-gas elements form chemical compounds. Thus, the atomic radii for the lighter noble-gas elements are estimated values.

- Astronomical ionization energies
- Positive electron affinities
  - Therefore, relatively unreactive
- Monatomic gases

Group VIIIA: Noble Gases

- Xe forms three compounds:
  - XeF_2
  - XeF_4 (at right)
  - XeF_6
- Kr forms only one stable compound:
  - KrF_2
- The unstable HArF was synthesized in 2000.

Periodic Properties of the Elements