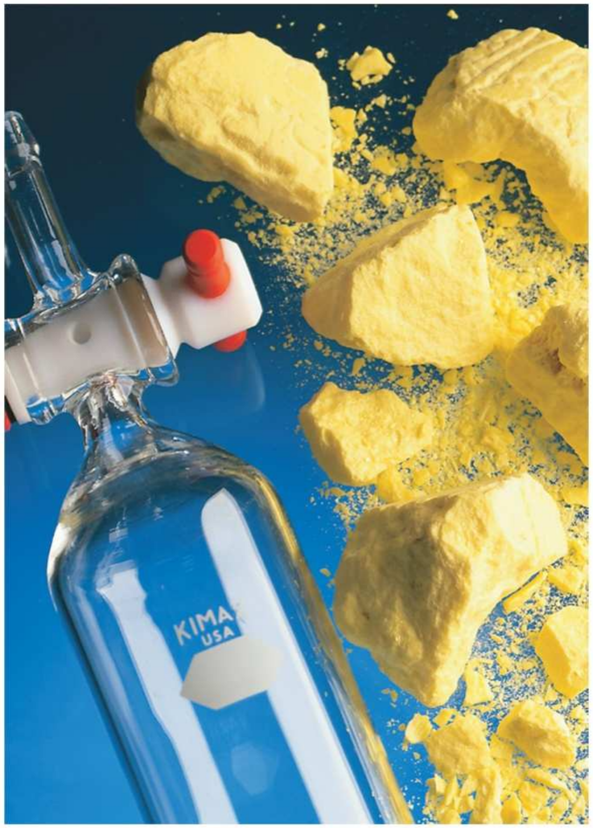
Chemistry, The Central Science, 10th edition
Theodore L. Brown; H. Eugene LeMay, Jr.; and Bruce E. Bursten

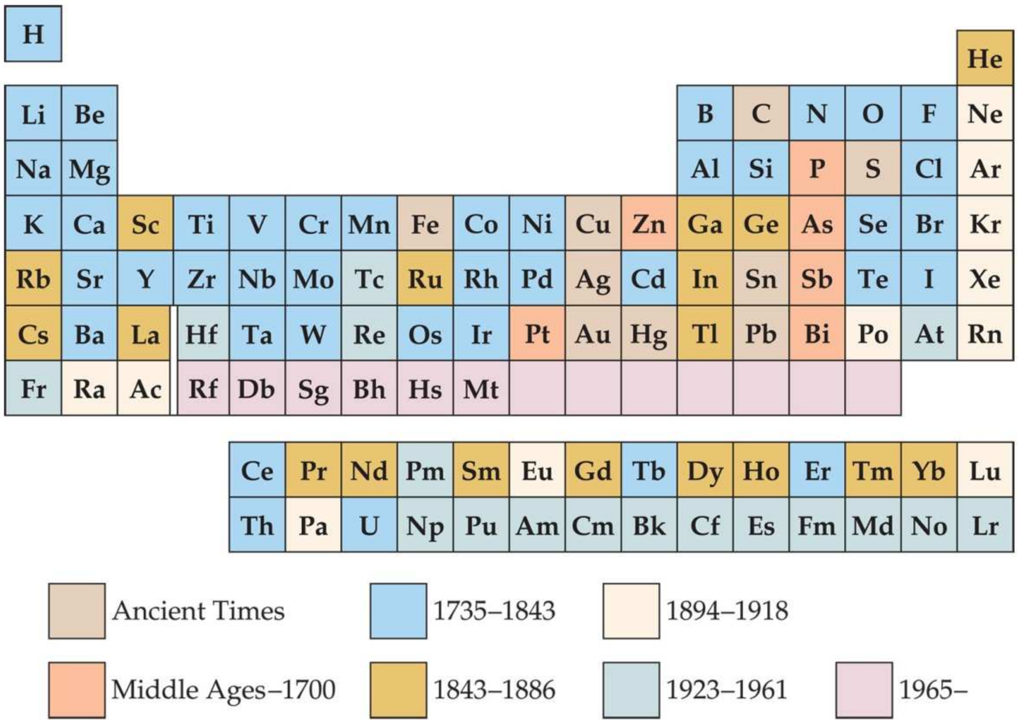
Chapter 7
Periodic Properties of the Elements

Development of Periodic Table

- Elements in the same group generally have similar chemical properties.
- 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.

Periodic Properties of the Elements

Development of Periodic Table

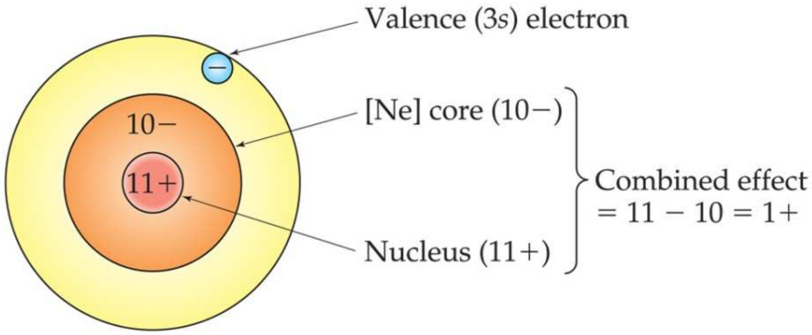
Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat (J/g-k)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide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

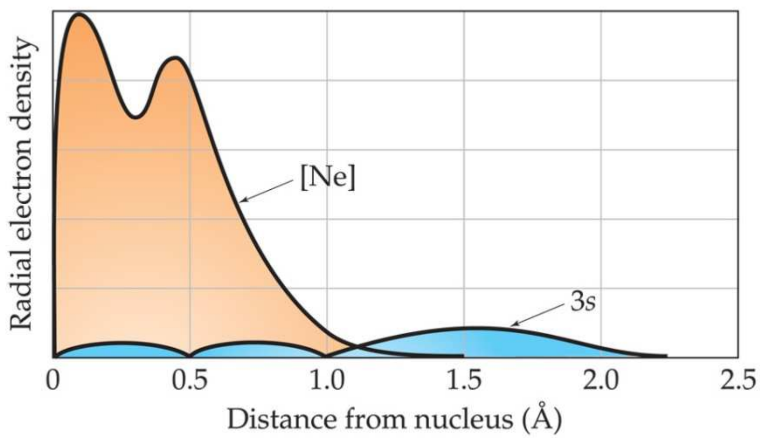
Periodic Trends

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

Effective Nuclear Charge

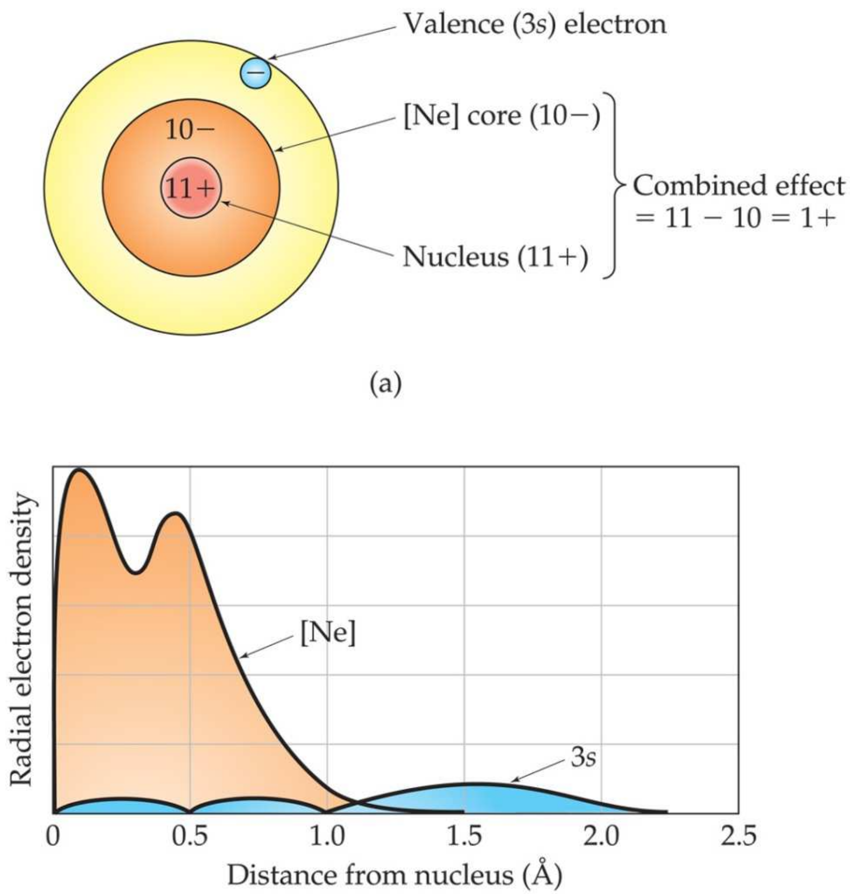


(a)



- 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:

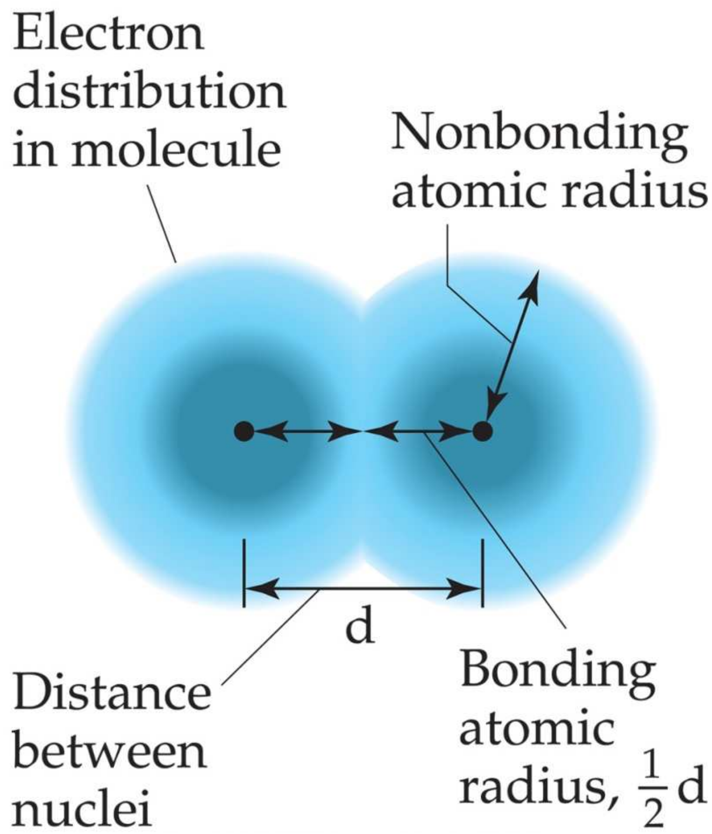
$$Z_{eff} = Z - S$$

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

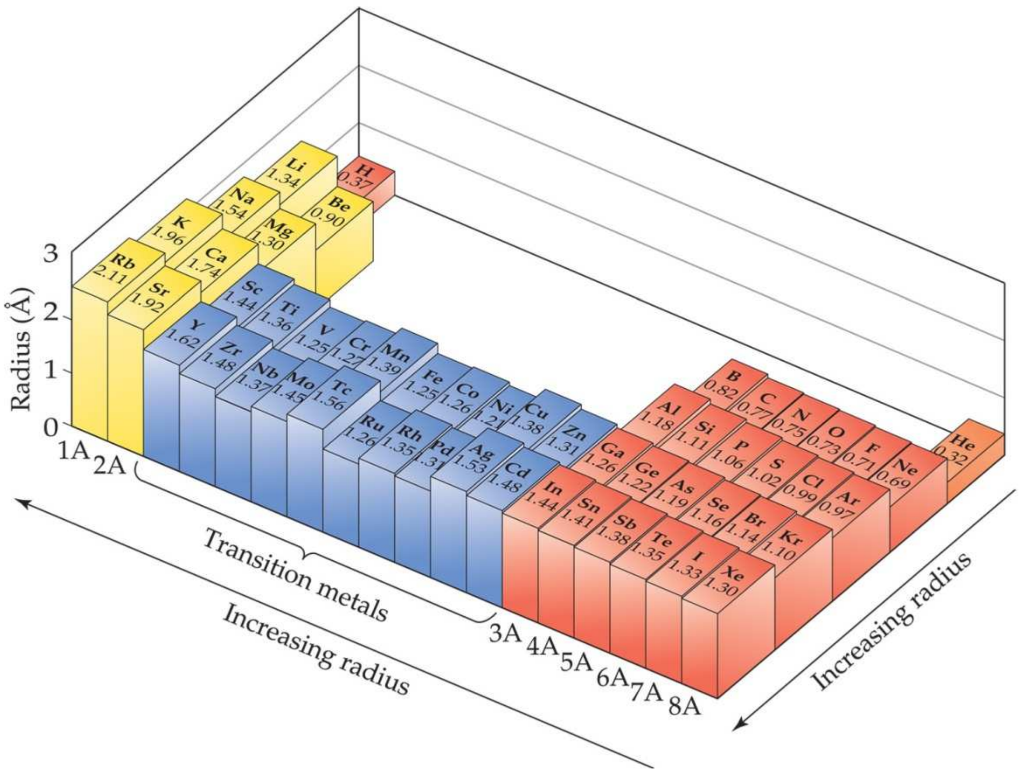
Periodic Properties of the Elements

Sizes of Atoms

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



Sizes of Atoms

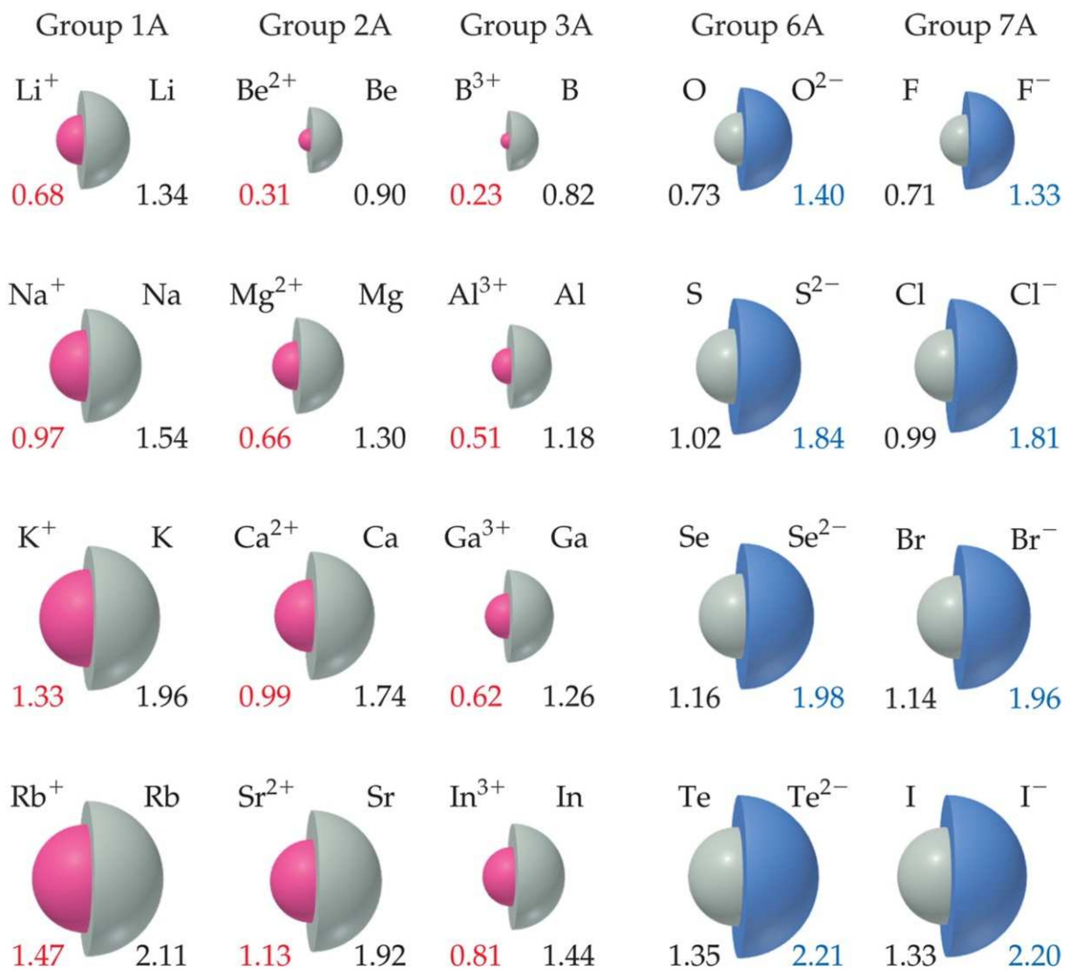


Bonding atomic radius tends to…

- …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*

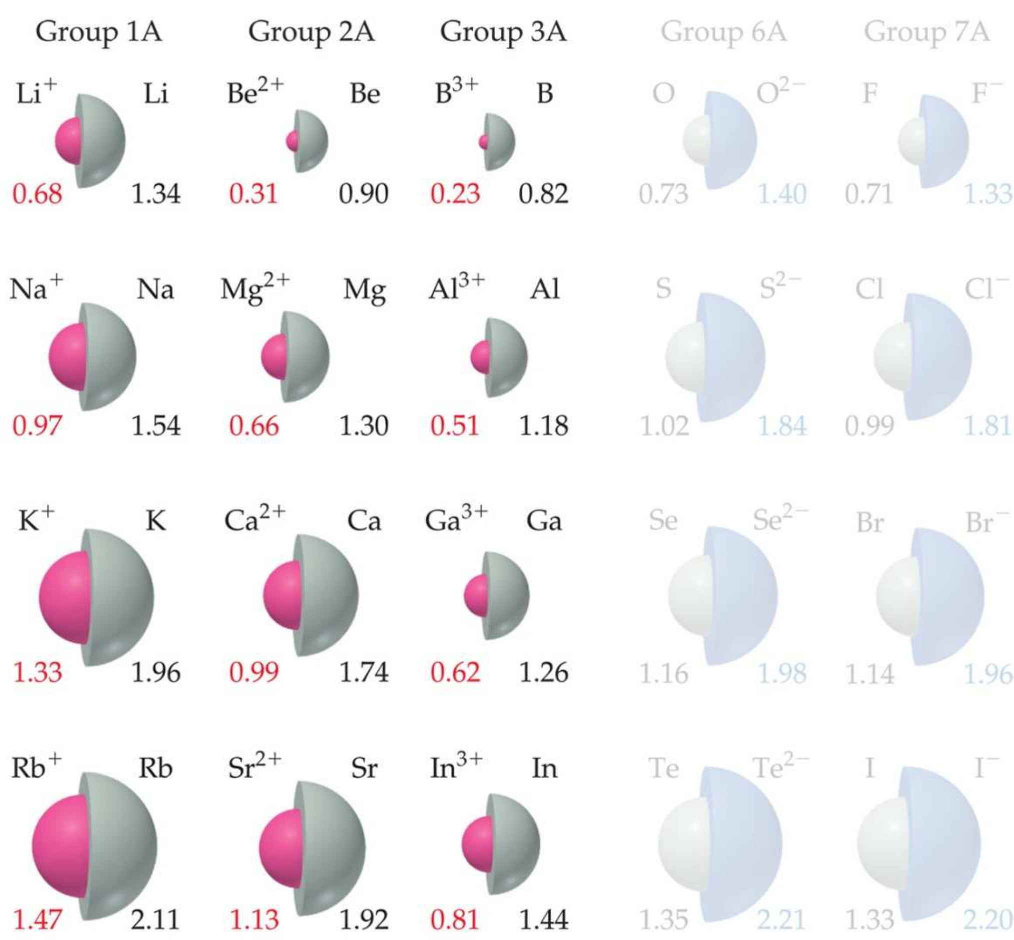
Periodic Properties of the Elements

Sizes of Ions



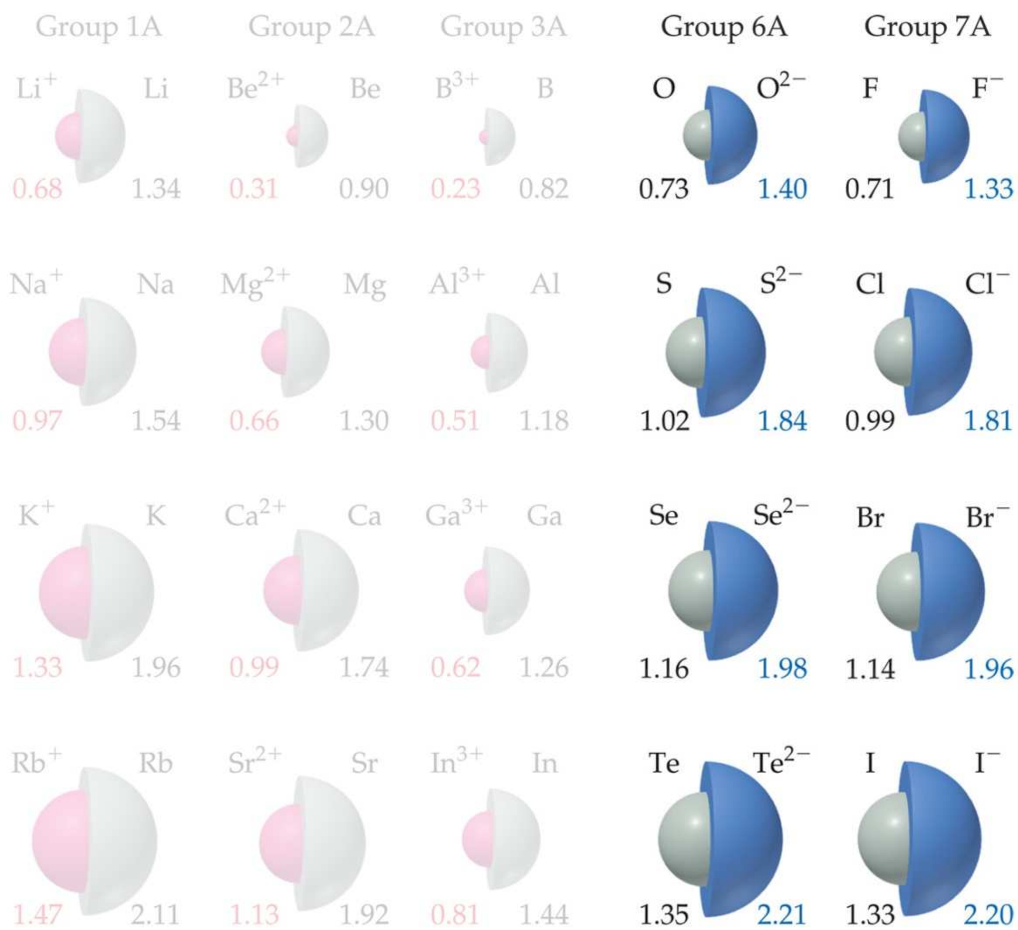
- Ionic size depends upon:
  - Nuclear charge.
  - Number of electrons.
  - Orbitals in which electrons reside.

Sizes of Ions



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

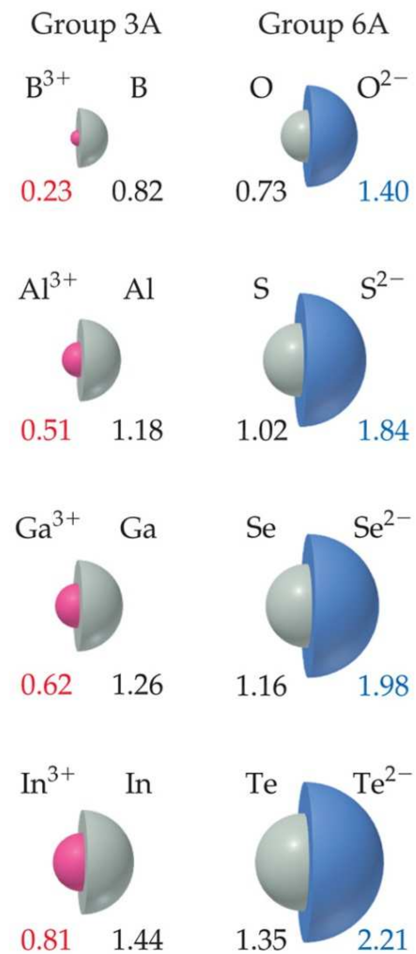
Sizes of Ions



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

Sizes of Ions

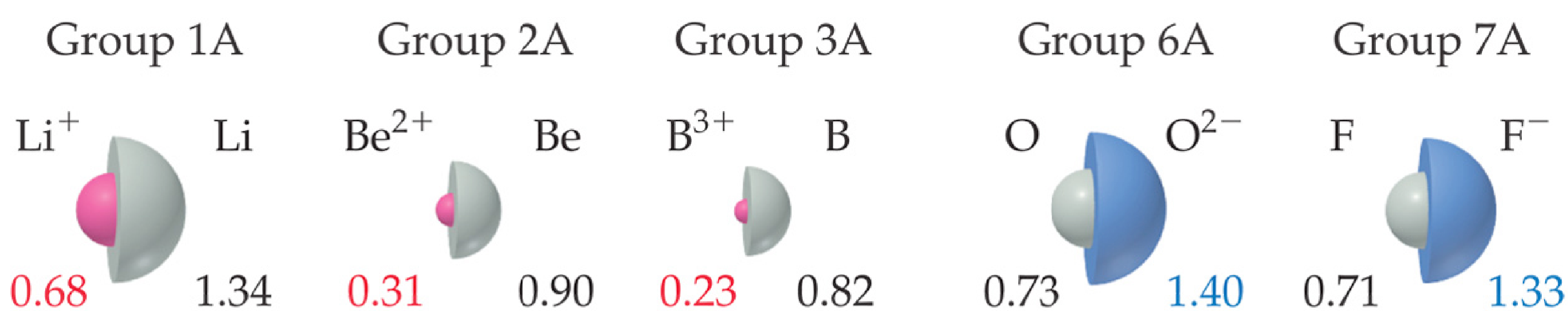
- Ions increase in size as you go down a column.
  - Due to increasing value of *n*.



Periodic Properties of the Elements

Sizes of Ions

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



Ionization Energy

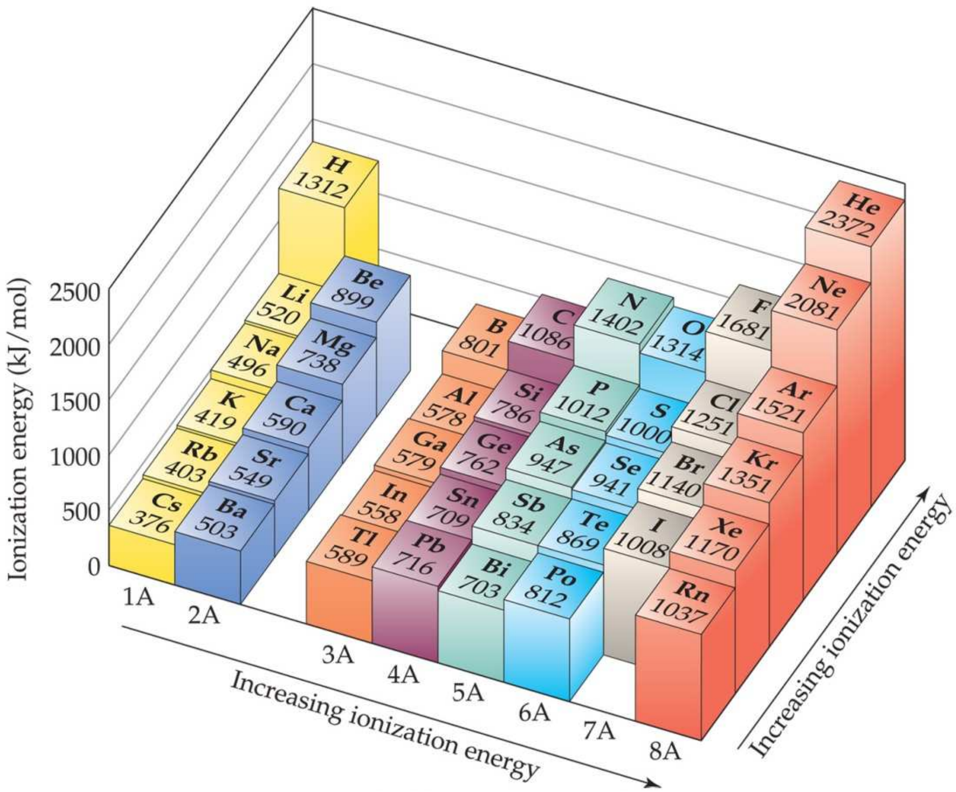
- Amount of energy required to remove an electron from the ground state of a gaseous atom or ion.
  - First ionization energy is that energy required to remove first electron.
  - Second ionization energy is that energy required to remove second electron, etc.

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

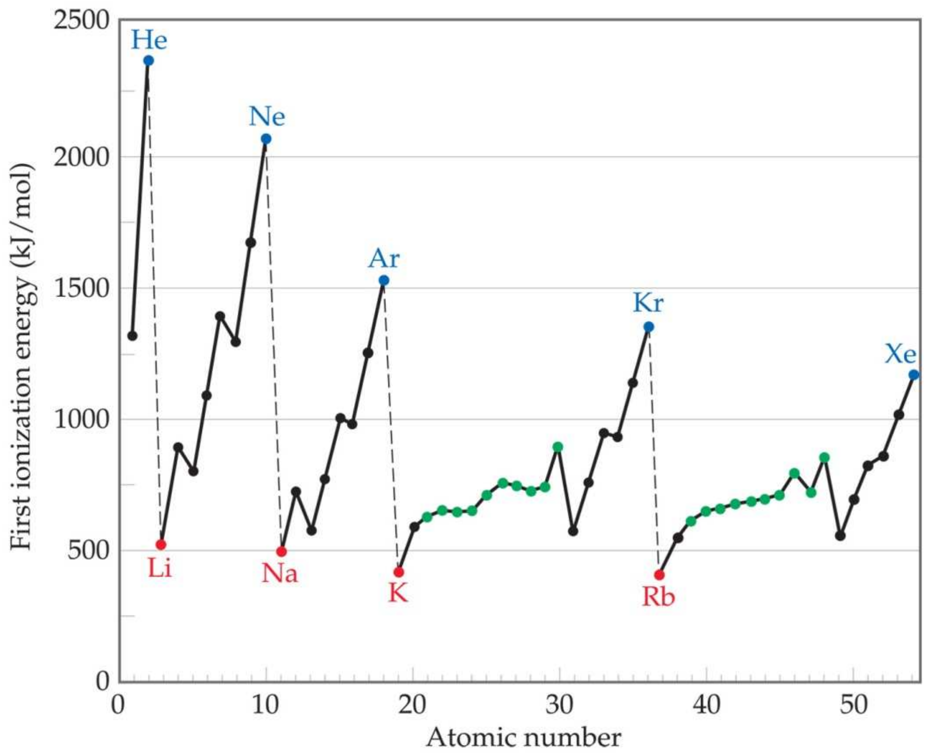


- As one goes down a column, less energy is required to remove the first electron.
  - For atoms in the same group, Z_{eff} is essentially the same, but the valence electrons are farther from the nucleus.

Periodic Properties of the Elements

Trends in First Ionization Energies

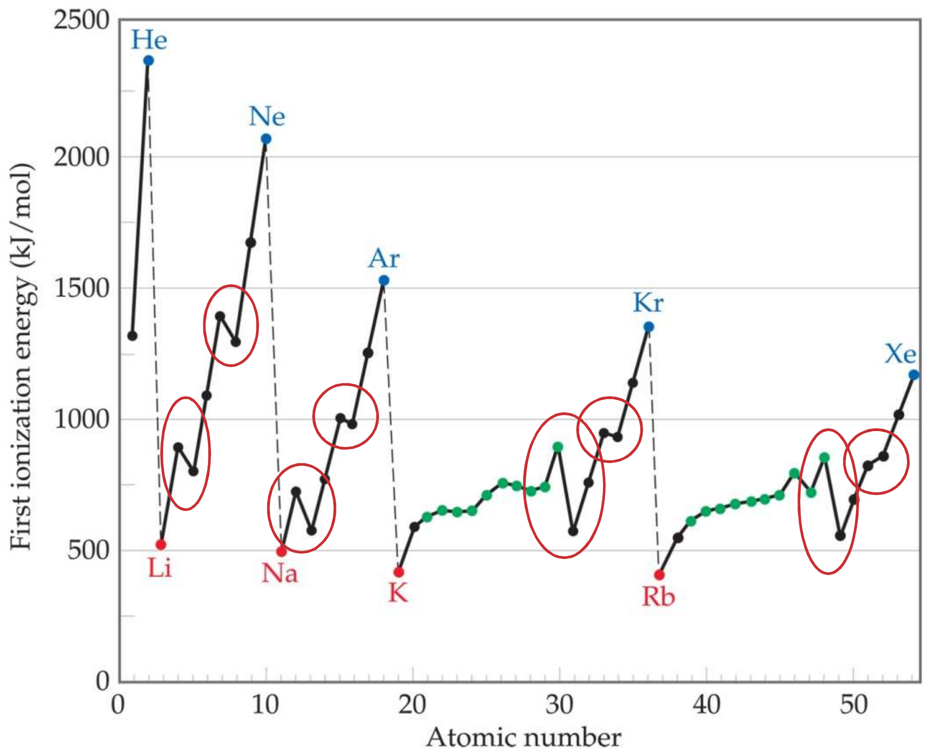
- Generally, as one goes across a row, it gets harder to remove an electron.
  - As you go from left to right, Z_{eff} increases.
  - Within each group the ionization energy decreases due to the increase in atomic radii.
  - The representative elements show a larger range in values than the transition metals.



Periodic Properties of the Elements

Trends in First Ionization Energies

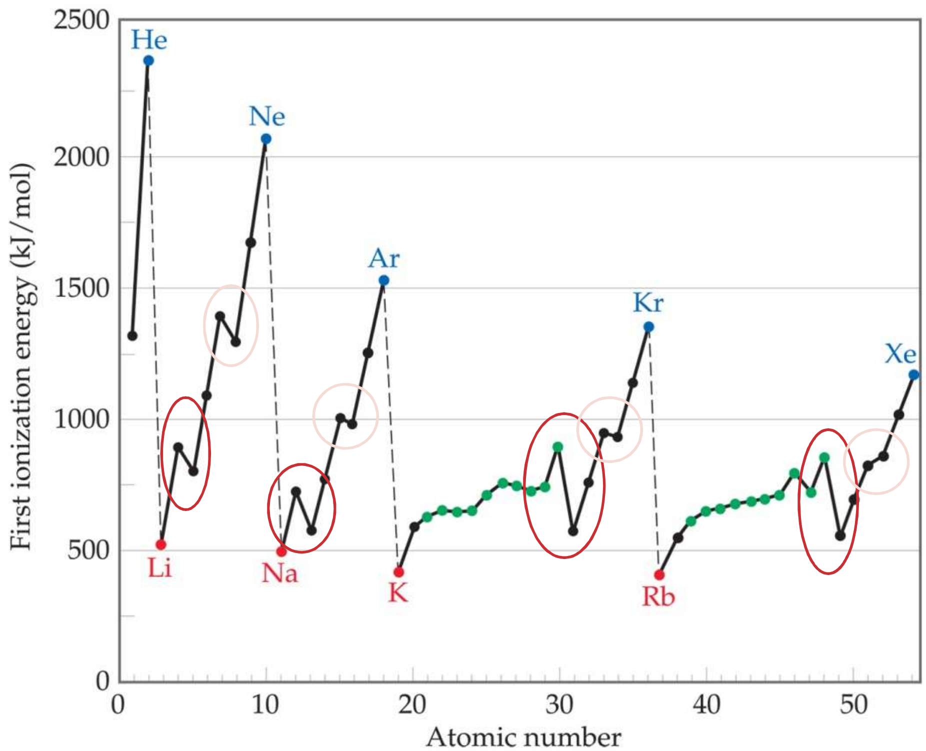
However, there are two apparent discontinuities in this trend.



Periodic Properties of the Elements

Trends in First Ionization Energies

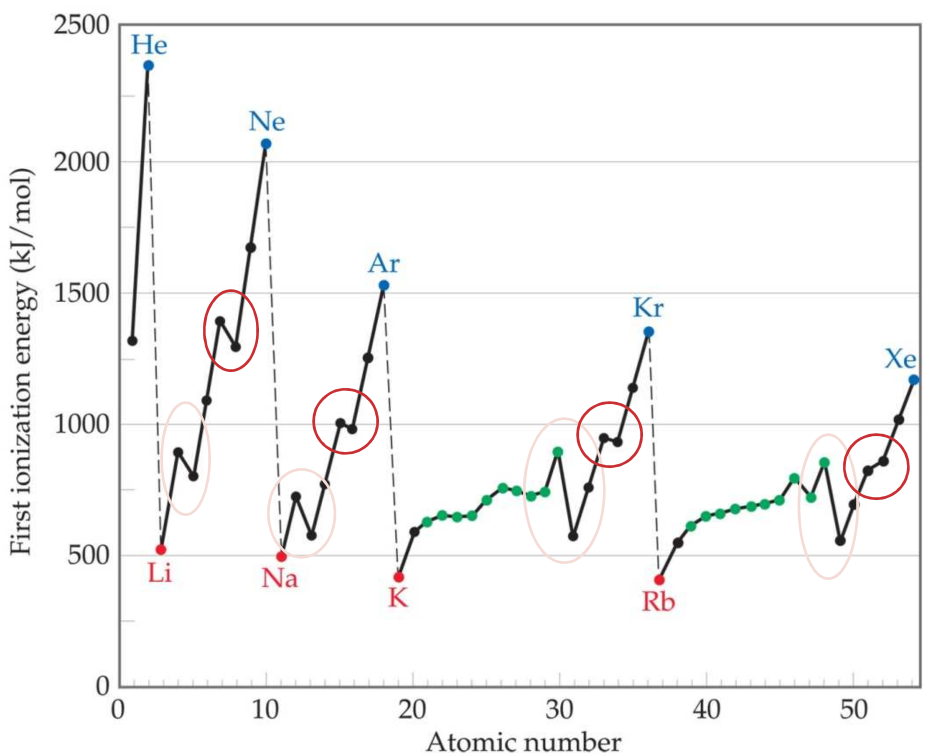
- The first occurs between Groups IIA and IIIA.
- Electron removed from *p*-orbital rather than *s*-orbital
  - Electron farther from nucleus
  - Small amount of repulsion by *s* electrons.



Periodic Properties of the Elements

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.



Electron Affinity

Energy change accompanying addition of electron to gaseous atom:

$$Cl + e^{-} \longrightarrow Cl^{-}$$

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.

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

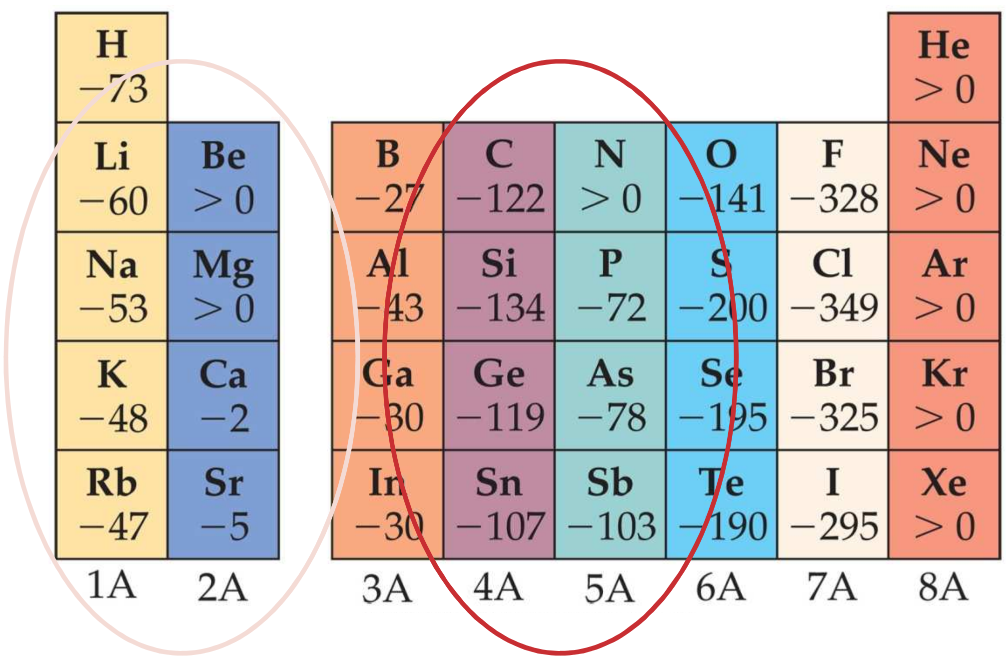
There are again, however, two discontinuities in this trend.

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

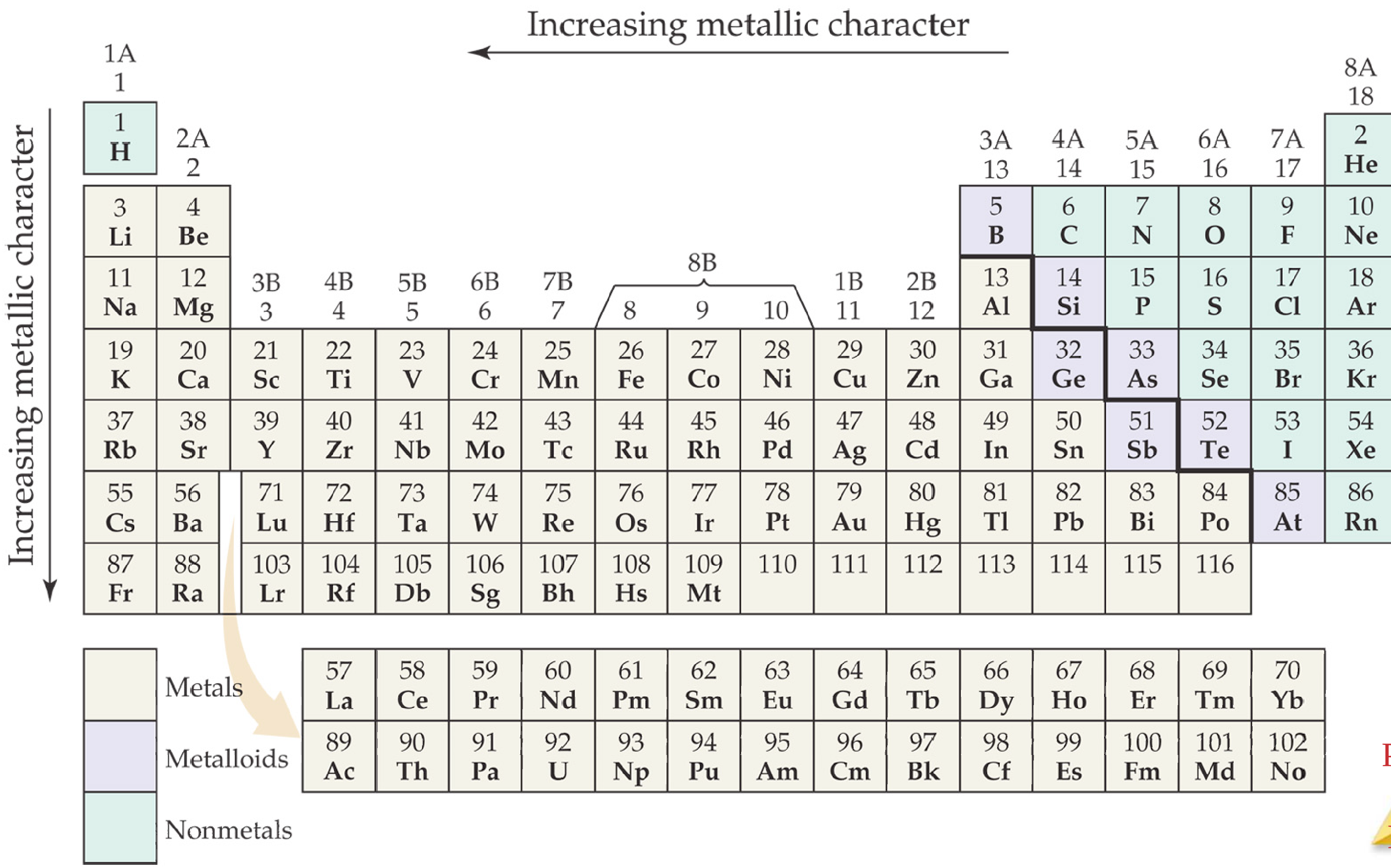
- The first occurs between Groups IA and IIA.
  - Added electron must go in *p*-orbital, not *s*-orbital.
  - Electron is farther from nucleus and feels repulsion from *s*-electrons.

Trends in Electron Affinity



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

Properties of Metal, Nonmetals, and Metalloids



Periodic Properties of the Elements

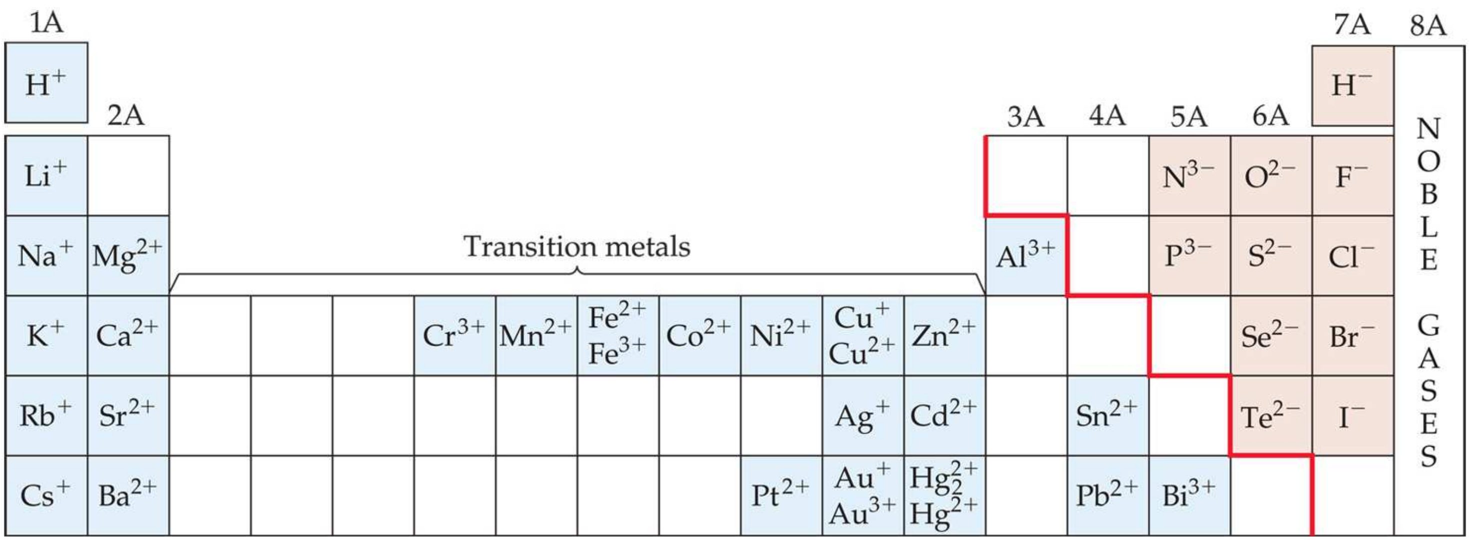
Metals versus Nonmetals

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.



Periodic Properties of the Elements

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.
- Metal oxides tend to be basic.

$$Na_2O_{(s)} + H_2O(l) \longrightarrow 2NaOH(aq)$$

$$CaO(s) + H_2O(l) \longrightarrow 2Ca(OH)_2(aq)$$

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.

Metal oxides also demonstrate their basicity by reacting with acids

Metal oxide + acid $\longrightarrow$ Salt + water

$NiO(s) + 2HCl(aq) \longrightarrow NiCl_2(aq) + H_2O(l)$

Nonmetals

- Substances containing only nonmetals are molecular compounds.
- Most nonmetal oxides are acidic.

- Most nonmetal oxides are acidic.
- Those that dissolve in water react to form acid

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

$$P_4H_{10}(s) + 6\,H_2O(l) \rightarrow 4\,H_3PO_4(aq)$$

acidity of carbonated drinks & rain water.

SO_2 & SO_3 from oil & coal
Contributes towards acid rain

Like acids most nonmetal oxides dissolve in basic solutions to give salt + water

$$CO_2(g) + 2NaOH \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

Periodic Properties of the Elements

Metalloids

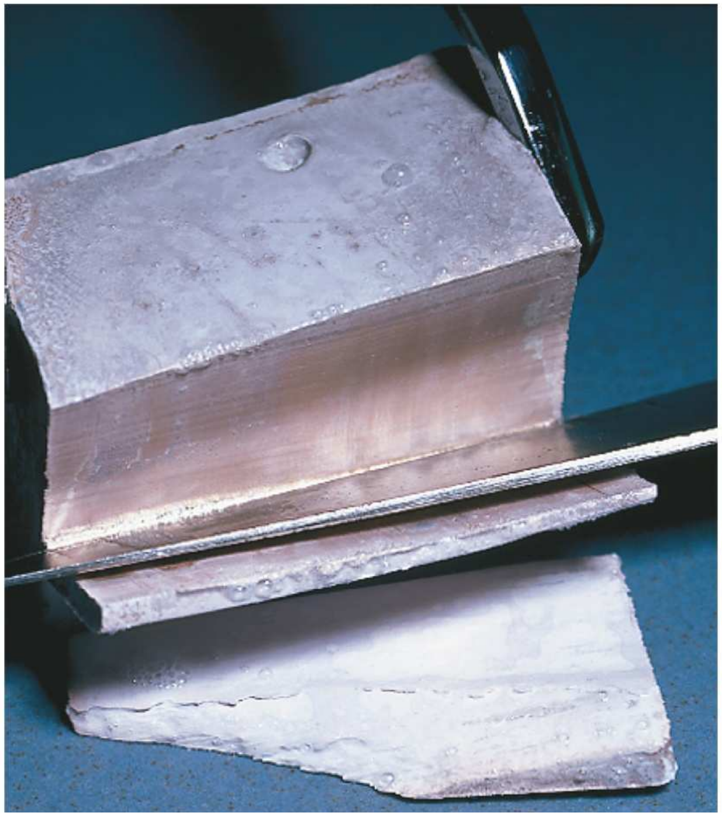
- Have some characteristics of metals, some of nonmetals.
- For instance, silicon looks shiny, but is brittle and fairly poor conductor.

Group Trends

Periodic Properties of the Elements

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 react directly with nonmetals to form ionic compounds.

$$2M(s) + H_2(g) \rightarrow 2MH(s) \quad \text{(Metal hydride)} \quad H^-$$

$$2M(s) + S(s) \rightarrow M_2S(s)$$

Alkali Metals

$$2M(s) + H_2O(l) \longrightarrow 2MOH(aq) + H_2(g)$$

These reactions are very exothermic.

This reactions are more violent for heavier members.

Their reactions with water are famously exothermic.

The reactions between alkali metals and oxygen are more complex

1) Metal oxides are formed

$$4Li_{(s)} + O_{2(g)} \longrightarrow 2Li_2O_{(s)}$$ lithium oxide.

$$Na + O_2 \longrightarrow Na_2O$$

$$K + O_2 \longrightarrow K_2O$$

etc - - .

These oxides react with water to give hydroxide

$$Li_2O + H_2O \longrightarrow 2LiOH$$

Other than Lithium <u>all other</u> alkali metals react with oxygen to give peroxide

$$2Na_{(s)} + O_2(g) \longrightarrow Na_2O_2$$

sodium peroxide

K Rb + Cs also react with O_2 to give superoxide

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

potassium superoxide

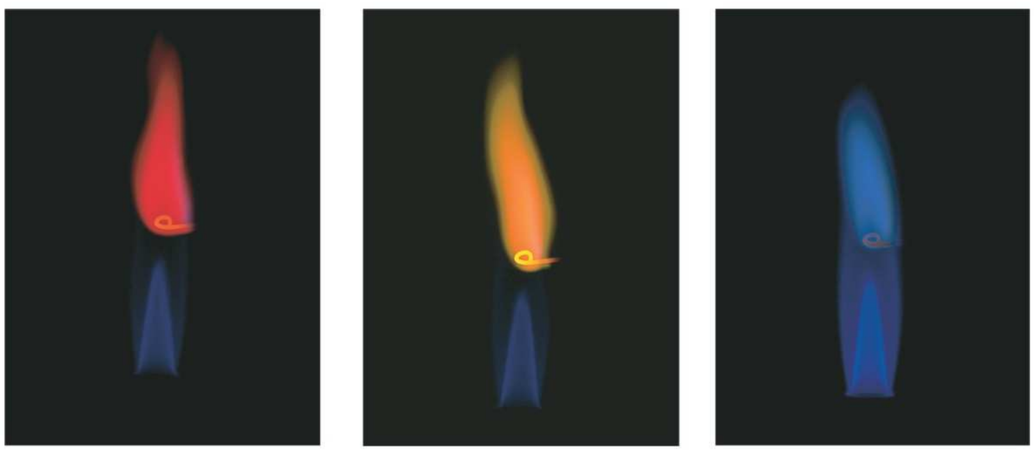
peroxide + superoxide are unusual products
the normal metal + oxygen products are oxides

Periodic Properties of the Elements

- Due to the high reactivity of alkali metals with water and oxygen they are stored under mineral oil or kerosene

Alkali Metals

- Produce bright colors when placed in flame.



- The high temperature of the flame excites the valence electron to a higher energy orbital. When this electron comes back to its lower energy orbital it emits the energy in the form of visible light.

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 even when red hot, Mg reacts only with steam, but others react readily with water.
- Reactivity tends to increase as go down group.

$$Mg(s) + \underline{\underline{H_2O(g)}} \rightarrow MgO(s) + H_2(g)$$

Periodic Properties of the Elements

- Calcium and elements below it react readily with water at room temperature, though not as vigorously as the alkali metals

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

- The alkali metals show the pattern of reaction where they lose two outer s electrons to give 2+ ions.

$$Mg(s) + Cl_2(g) \longrightarrow MgCl_2(s)$$

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$

These also give off characteristic colors when strongly heated on a fame.

Magnesium and Calcium are essential for living organisms.

Hydrogen

- Hydrogen is a diatomic gas under ordinary conditions.
- Under extreme conditions it can exist in a metallic state. It is understood to exist in this state on the planets Jupiter and Saturn.
- It has a much higher ionization energy than the IA elements

- Unlike the alkali metals that lose their electron to form cations, hydrogen forms mostly covalent compounds with nonmetals.
- Its reaction with oxygen is very exothermic.

Hydrogen also reacts with active metals to form solid metal hydrides H^- (LiH, NaH etc).

This property of hydrogen resembles the halogens.

Hydrogen does lose its electron to g=fom H^+ ion.

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.

Group IIIA

- Group IA and IIA show only an increase in the metallic character as we go down.
- Group IIIA shows a very significant increase.
- Boron is a metalloid, rest are all metals and form oxides of the general formula R_2O_3.

- Boron oxide is acidic, Al and Ga oxides are amphoteric and the rest are basic.
- This is indicative of the increase in metallic character of the elements.
- Amphoteric: species that can react both with an acid and a base.

Group IV A Elements

- Stars with a nonmetal C, followed by the metalloid Si and Germanium then metals Sn and Pb.
- All make oxides with the general formula RO_2

Group VA Elements

- Group VA follow the nonmetal to metalloid to metals trend.

These form oxides with general formula R_2O_3 and R_2O_5.

(2) In some cases the molecular formulas are twice these formulas R_4O_6 & R_4O_{10}.

(3) Nitrogen has an oxide NO besides N_2O_3 & N_2O_5.

(4) P has P_4O_6 & P_4O_{10}

(5) As has As_2O_3 + As_2O_5

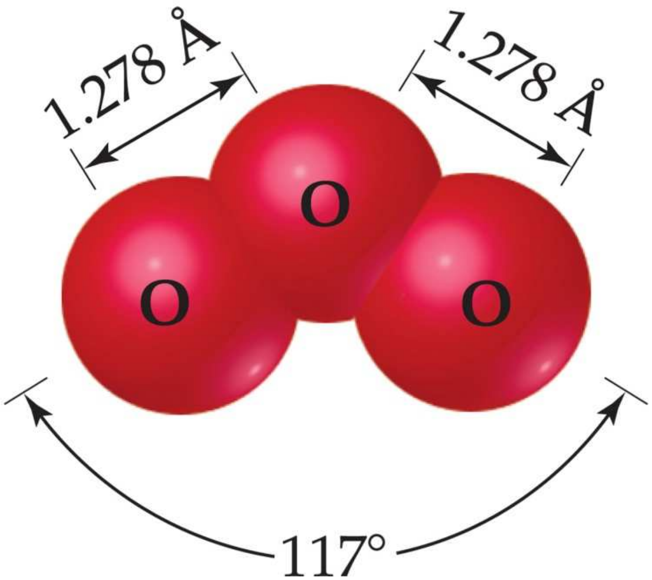
Antimony has amphoteric oxide

Sb_2O_3 & Sb_2O_5

Bismuth has basic oxide Bi_2O_3

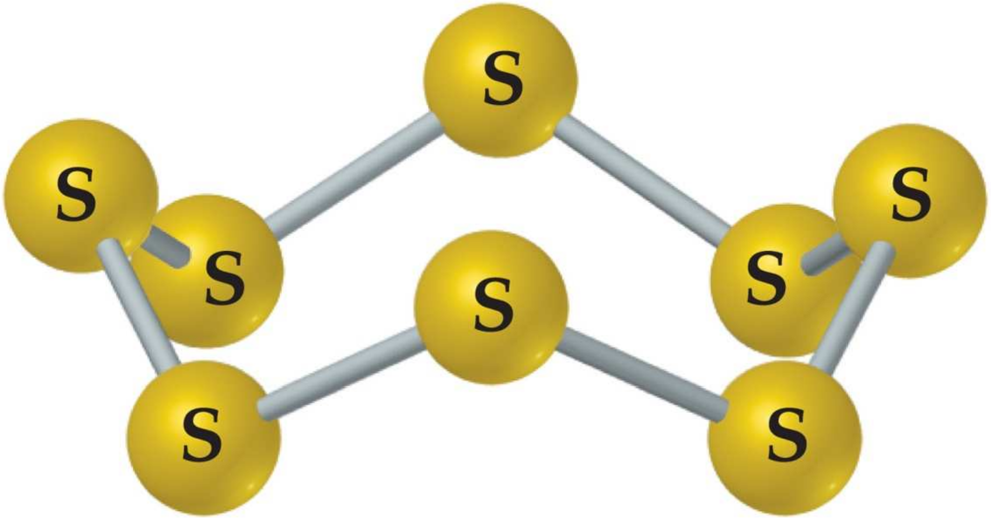
Periodic Properties of the Elements

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



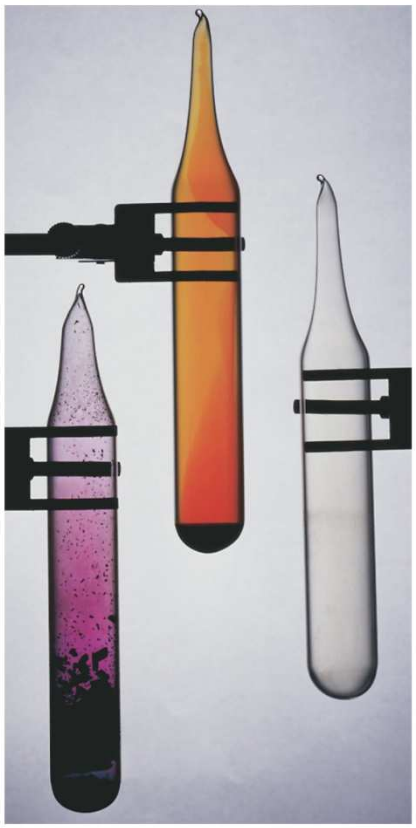
- Weaker oxidizing agent than oxygen.
- Most stable allotrope is S_8, a ringed molecule.

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	$[He]2s^22p^6$	27.1	0.90	0.69	2081
Argon	$[Ne]3s^23p^6$	87.3	1.78	0.97	1521
Krypton	$[Ar]3d^{10}4s^24p^6$	120	3.75	1.10	1351
Xenon	$[Kr]4d^{10}5s^25p^6$	165	5.90	1.30	1170
Radon	$[Xe]4f^{14}5d^{10}6s^26p^6$	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.