Chapter 7: Periodic Properties of the Elements.

7.1 Development of the Periodic Table

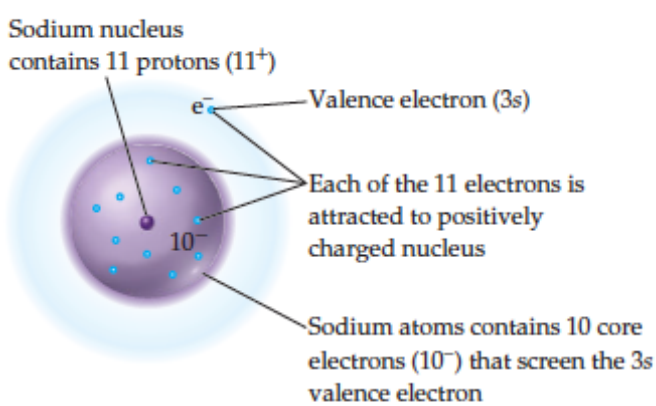
The periodic table is the most significant tool that chemists use for organizing and recalling chemical facts.
Elements in the same column contain the same number of outer-shell electrons or **valence electrons.**
The majority of the elements were discovered between 1735 and 1843.
In the first attempt Mendeleev and Meyer arranged the elements in order of increasing atomic weight.
Modern periodic table: Elements are arranged in order of *increasing atomic number*.

7.2 Effective Nuclear Charge

Effective nuclear charge is the net positive charge experienced by an electron on a many-electron atom.
The effective nuclear charge is not the same as the charge on the nucleus because of the effect of the inner electrons.
The electrons is attracted to the nucleus, but repelled by the inner-shell electrons that shield or screen it from the full nuclear charge.
This shielding is called the screening effect;
The nuclear charge experienced by an electron depends on its distance from the nucleus and the number of electron in the spherical volume out the electron in question.
As the average number of screening electrons (S) increases, the effective nuclear charge (Z_{eff}) decreases

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

As the distance from the nucleus increases, S increases and Z_{eff} decreases.
The value of S is usually close to the number of core electrons in an atom.
the number of protons in the nucleus Z
$Z_{eff} = 11 - 10 = 1+$



7.3 Size of Atoms and Ions

Periodic Trends in Atomic Radii
Atomic size varies consistently through the periodic table.

As we move down a group the atoms become larger.

As we move across a period atoms become smaller.

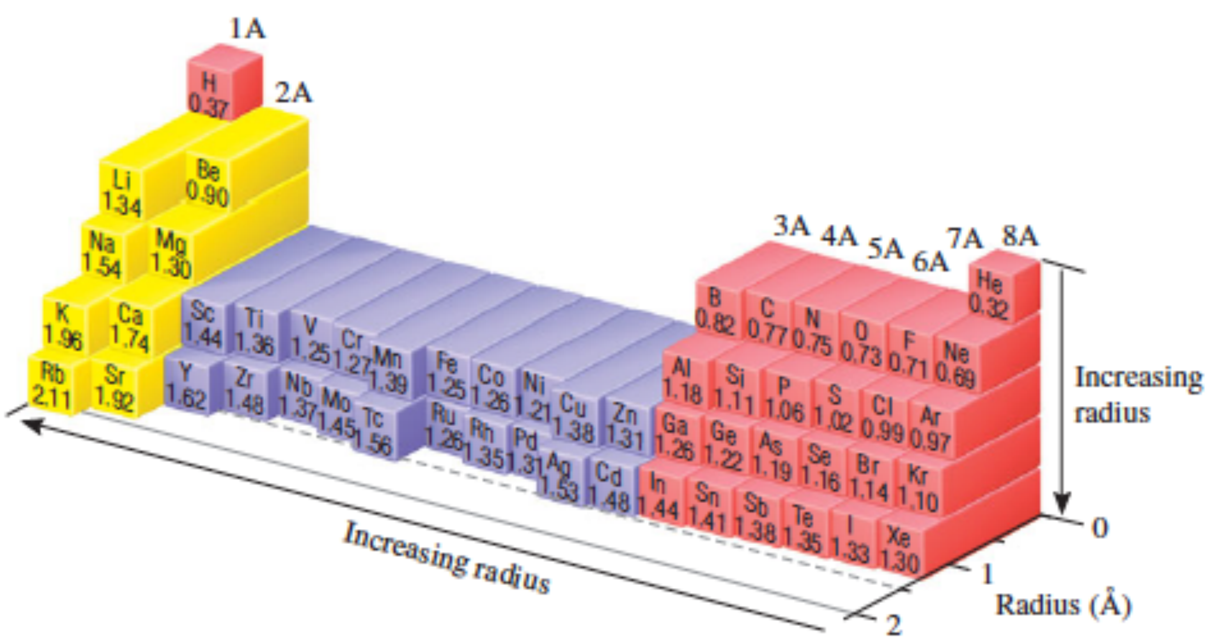
There are two factors at work:

The principal quantum number, *n* and

The effective nuclear charge, Z_{eff}

As the principal quantum number increases (i.e, we move down a group), the distance of the outermost electron from the nucleus becomes larger. Hence the atomic radius increases.

As we move across the periodic table, the number of core electrons remains constant, however, the nuclear charge increases. Therefore, there is an increased attraction between the nucleus and the outermost electrons. This attraction causes the atomic radius to decrease.



Trends in the Size of Ions

Just as the atomic size is periodic, ionic size is also periodic

In general:

Cations are smaller than their parent atoms.

Electrons have been removed from the most spatially extended orbital.

The effective nuclear charge has increased.

Therefore, the cation is smaller than the parent atom.

Anions are larger than their parent atoms.

Electrons have been added to the most spatially extended orbital.

This means total electron-electron repulsion has increased.

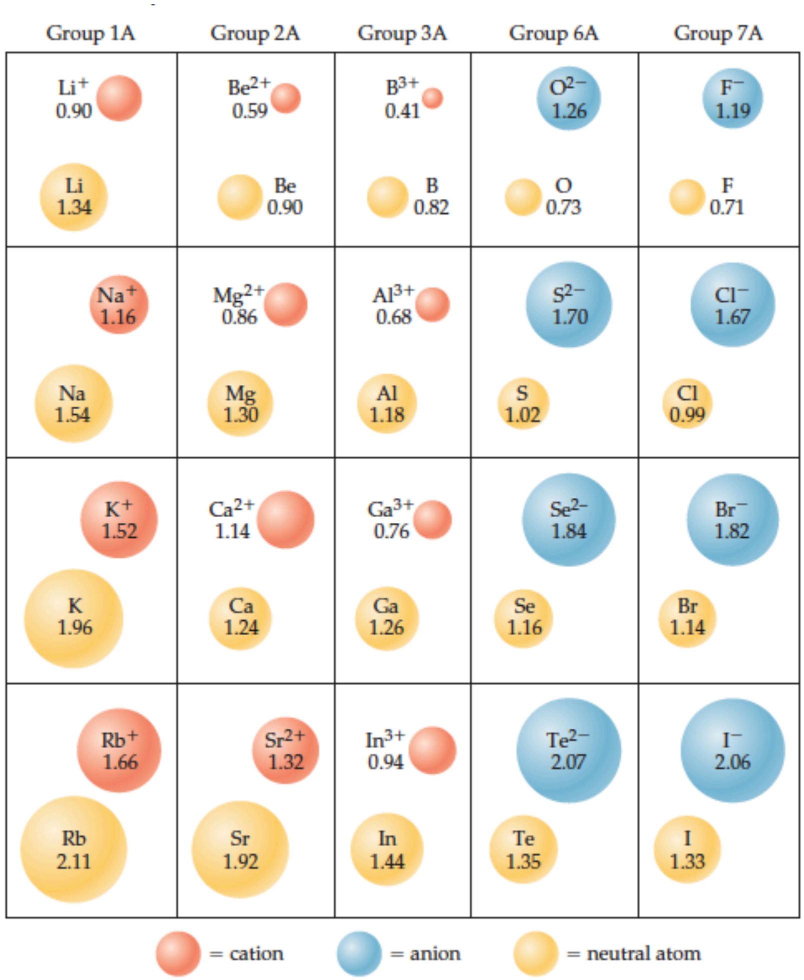
Therefore, anions are larger than the parent atoms.

For ion with the same charge, ionic size increases down a group

All the members of an **isoelectronic series** have the same number of electrons

As the nuclear charge increases in an isoelectronic series the ions become smaller

O^{2-} F^{-} Na^{+} Mg^{2+} Al^{3+}



7.4 Ionization Energy

the ionization energy of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atoms or ion.
The first ionization energy, I_1, is the amount of energy required to remove an electron from a gaseous ion:

$$Na\,(g) \quad Na^{+}\,(g) + e^{-}$$

The second ionization energy, I_2, is the amount of energy required to remove a second electron from a gaseous ion:

$$Na^{+}(g) \quad Na^{2+}\,(g) + e^{-}$$

The larger the ionization energy, the more difficult it is to remove the electrons.
There is a sharp increase in ionization energy when a core electron is removed.

$I_1 < I_2 < I_3$

$$I_1 < I_2 < I_3,$$

TABLE 7.2 • Successive Values of Ionization Energies, *I*, for the Elements Sodium through Argon (kJ/mol)

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	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

Variation in Successive Ionization Energies.
Ionization energies for an element increase in magnitude as successive electrons are removed .

As each successive electron is removed, more energy is required to pull an electron away from an increasingly more positive ion.
A sharp increase ionization energy occurs when an inner-shell electron is removed.

Periodic Trends in First ionization Energies.
Ionization energy decreases down a group.

This means that the outermost electron is more readily removed as we go down a group.

As the atom gets bigger, it become easier to remove an electron from the most spatially extended orbital.

Example: for the noble gases the ionization energies follow the order

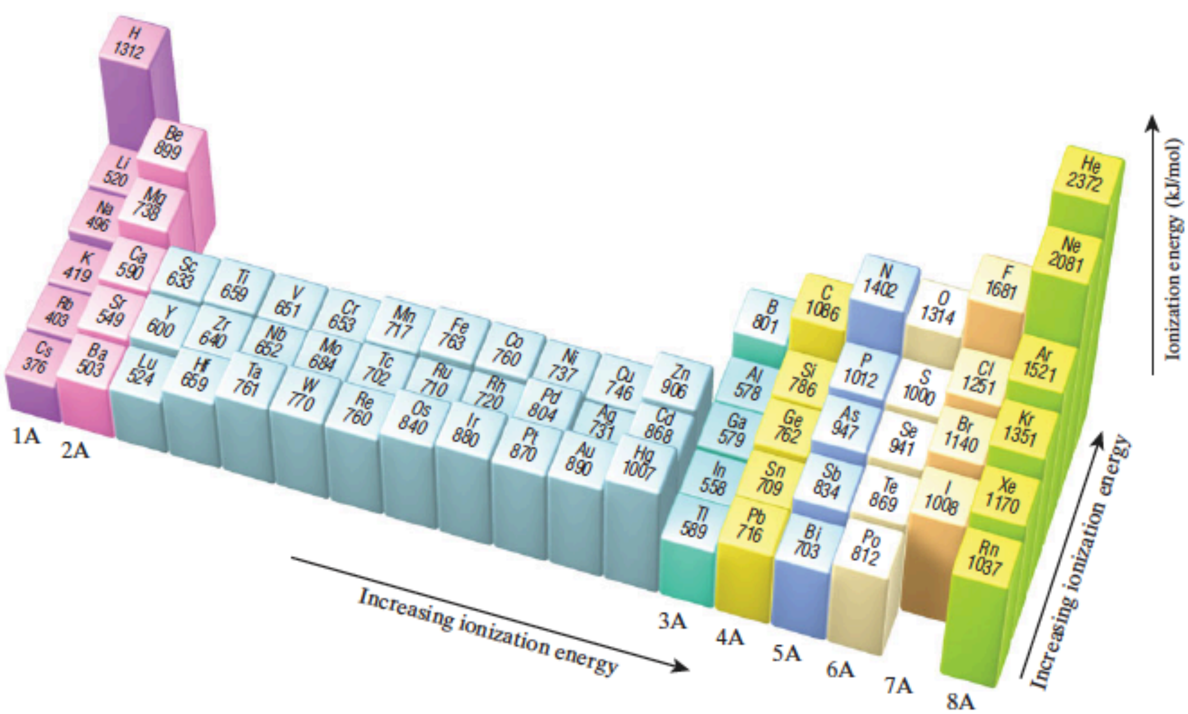
He Ne Ar kr Xe

Ionization energy generally increases across a period.
As we move across a period Z_{eff} increases, making it more difficult to remove an electron.

[[Two exceptions: removing the first *p* electron and removing the fourth *p* electron.

The *s* electrons are more effective at shielding than *p* electrons. So, forming the s^2 p^0 configuration is more favorable.

When a second electron is placed in a *p* orbital, the electron-electron repulsion increases. When this electron is removed, the resulting s^2 p^3 configuration is more stable than the starting s^2 p^4 configuration. Therefore, there is a decrease in ionization energy.]]



Electron Configurations of Ions.

These are derived from the electron configurations of elements with the required number of electrons added or removed from the most accessible orbital.

Li: [He] $2s^1$ becomes Li^+: [He]

F: [he] $2s^2\ 2p^5$ becomes F^-: [He] $2s^2\ 2p^6$ = [Ar]

Transition metals tend to lose the valence shell electrons first and then as many *d* electrons as are required to reach the desired charge on the ion.

Thus electrons are removed from 4*s* **before** the 3*d*, etc.

7.5 Electron Affinities.

Electron affinity is the energy change when a gaseous atom gains an electron to form a gaseous ion. the negative sign indicating that energy is released during the process

Electron affinity: $Cl\,(g) + e^- \longrightarrow Cl^-\,(g)$ E = -349 kJ/mol

$[Ne]3s^23p^5$ $[Ne]3s^23p^6$

Ionization energy: $Cl\,(g) \longrightarrow Cl^+\,(g) + e^-$ E = 1251 kJ/mol

$[Ne]3s^23p^5$ $[Ne]3s^23p^4$

The positive ionization energy means that energy must be put into the atom to remove the electron.

Electron affinity can either be exothermic (as above example) or endothermic:

$Ar\,(g) + e^- \longrightarrow Ar^-\,(g)$ $E > 0$

$[Ne]3s^23p^6$ $[Ne]3s^23p^64s^1$

Electron configuration helps to determine whether electron affinity is positive or negative.

Electron affinity in kJ/mol for selected s- and p-block elements.

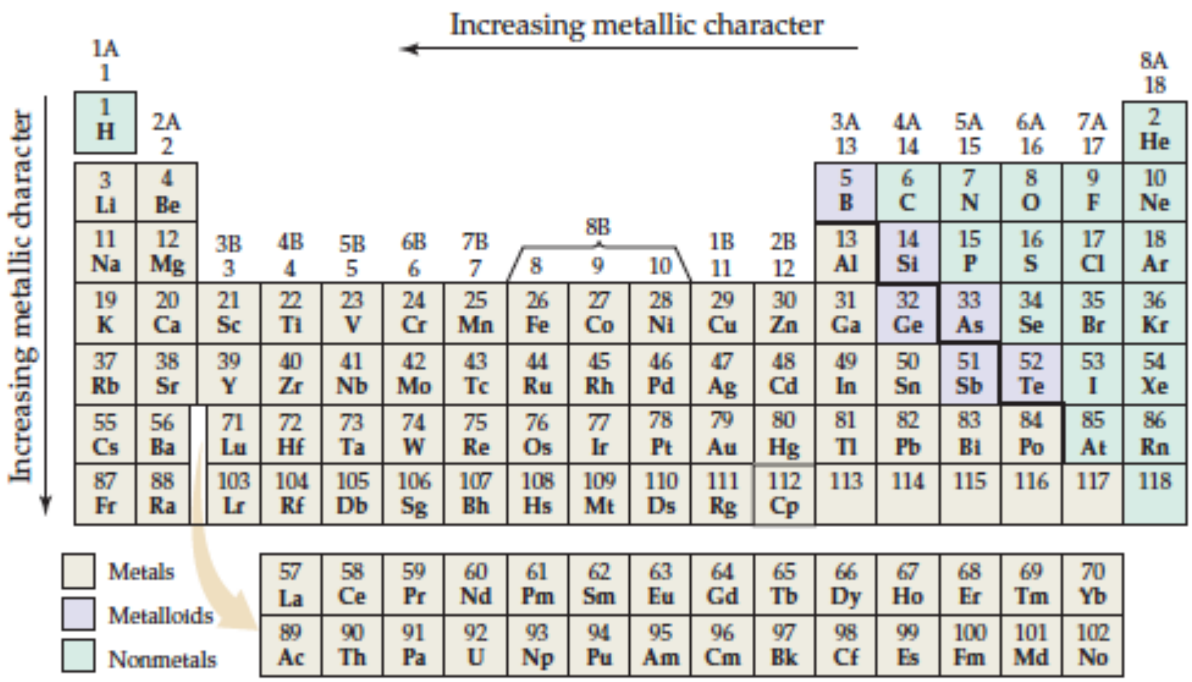
1A	2A	3A	4A	5A	6A	7A	8A
H −73							He > 0
Li −60	Be > 0	B −27	C −122	N > 0	O −141	F −328	Ne > 0
Na −53	Mg > 0	Al −43	Si −134	P −72	S −200	Cl −349	Ar > 0
K −48	Ca −2	Ga −30	Ge −119	As −78	Se −195	Br −325	Kr > 0
Rb −47	Sr −5	In −30	Sn −107	Sb −103	Te −190	I −295	Xe > 0

7.6 Metal, Nonmetals and Metalloids

Metallic character refers to the extent to which the element exhibits the physical and chemical properties of metals.

Metallic character increases down a group.

Metallic character decreases from left to right across a period.



Metals

Metals are shiny and lustrous, malleable and ductile.

Metal are solids at room temperature (exception; mercury is liquid at room temperature, gallium and cesium melt just above room temperature) and have very high melting temperature.

Metal tend to have low ionization energies and tend to form cations easily

Metals tend to be oxidized when they react.

Compounds of metals with nonmetals tend to be ionic substances.

Most metal oxides are basic:

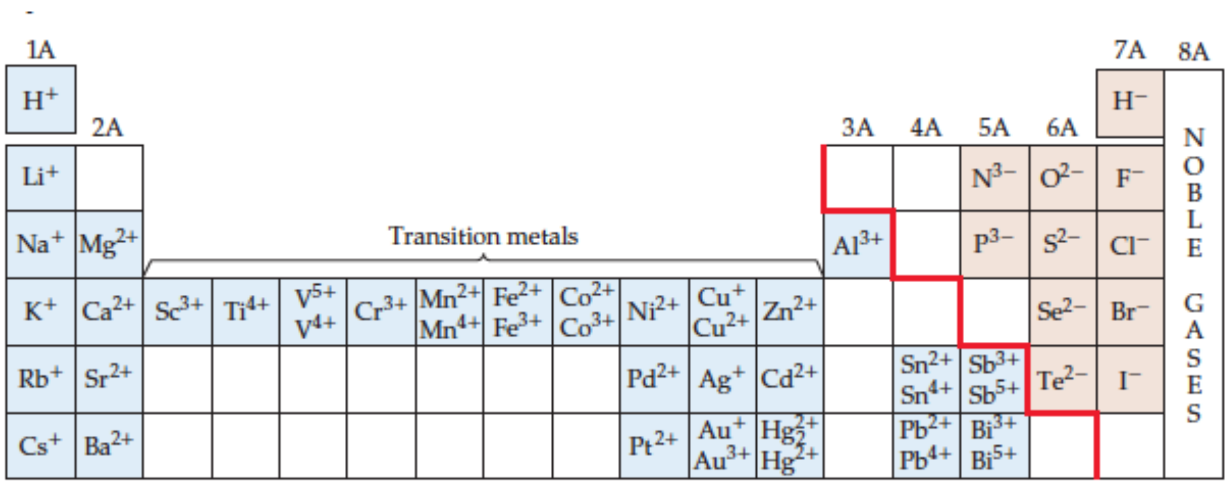
Metal oxide + water   metal hydroxide

$Na_2O\ (s) + H_2O\ (l)\quad 2\ NaOH\ (aq)$

Metal oxides are able to react with acids to form salts and water.

Metal oxide + acid   salt + water

MgO (*s*) + 2 HCl (*aq*) $MgCl_2$ (*aq*) +H_2O (*l*).



Representative oxidation states of the elements. Note that hydrogen has both positive and negative oxidation numbers, 1 and 1.

Nonmetals

Nonmetals are more diverse in their behavior than metals.

In general, nonmetals are nonlustrous, are poor conductors of heat and electricity, and exhibit lower melting point than metals.

Seven nonmetallic elements exist as diatomic molecules under ordinary conditions.

H_2 (*g*), N_2 (*g*), O_2 (*g*), F_2 (*g*), Cl_2 (*g*), Br_2 (*l*), I_2 (*s*)

When nonmetals react with metals, nonmetals tend to gain electrons:

Metal + nonmetal salt

Al (*s*) + 3 Br_2 (*l*) 2 $AlBr_3$ (*s*)

Compounds entirely of nonmetals are molecular substances.

Most nonmetal oxides are acidic:

Nonmetal oxide + water acid

P_4O_{10} (*s*) + 6 H_2O (*l*) 4 H_3PO_4 (*aq*)

CO_2 (*g*) + H_2O (*l*) H_2CO_3 (*aq*)

Nonmetal oxides react with bases to form salts and water:

Nonmetal oxide + base salt + water

CO_2 (*g*) + 2 NaOH (*aq*) Na_2CO_3 (*aq*) + H_2O (*l*)

Metalloids

Metalloids have properties that are intermediate between those of metals and nonmetals (Si)

Metalloids have found fame in the semiconductor industry

7.7 Group Trends for the Active Metals

the alkali metals (group 1A) and the alkaline earth metals (group 2A) are often called the active metals.

Group 1A: The Alkali Metals.

The alkali metals are in Group 1A

Alkali metals are all soft.

Their chemistry is dominated by the loss of their single s electron

M M^+ + e^-

Ractivity increases as we move down a group

Alkali metals react with hydrogen to form hydrides.

In hydrides, the hydrogen present as H-, called the **hydride ion**.

M (*s*) + H_2 (*s*) 2 MH (*s*)

Alkali metals react with water to form MOH and hydrogen gas:

2M (*s*) + 2 H_2O (*l*) 2 MOH (*aq*) + H_2 (*g*)

Alkali metals produce different oxides when reacting with O_2:

4 Li (*s*) + O_2 (*g*) 2 Li_2O (*s*) (*oxide*)

2 Na (*s*) + O_2 (*g*) Na_2O_2 (*s*) (per*oxide*)

K (*s*) + O_2 (*g*) KO_2 (*s*) (super*oxide*)

Alkali metals emit characteristic colors when placed in a high-temperature flame.

The *s* electron is excited by the flame and emits energy when it returns to the ground state.

The Na line occurs at 589 nm (yellow), characteristic of the 3*P* 3*s* transition.

The Ni line is crimson red (2*P* 2*s*)

The K line is lilac (4*P* 4*s*)

the alkali metals have low densities and melting points, and these properties vary in a fairly regular way with increasing atomic number.

TABLE 7.4 • Some Properties of the Alkali Metals

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

Group 2A: The Alkaline Earth Metals

Alkaline earth metals are harder and denser than the alkali metals

Their chemistry is dominated by the loss of two *s* electrons:

$M \quad M^{2+} + 2\ e^{-}$

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

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

Reactivity increases down the group

Be does not react with water

Mg will only react with steam

Ca and the elements below it react with water at room temperature as follows:

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

Compared with the alkali metals, the alkaline earth metals are harder and more dense and melt at higher temperatures.

TABLE 7.5 • Some Properties of the 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

7.8 Group Trends for Selected Nonmetals

Hydrogen

Hydrogen is a unique element.

It most often occurs as a colorless diatomic gas, H_2.

It can either gain another electron to form the hydride ion, H^-, or lose its electron to become H^+:

$$2\ Na\ (s) + H_2\ (g) \quad 2\ NaH\ (s)$$

$$H_2\ (g) + O_2\ (g) \quad 2\ H_2O\ (l).$$

H^+ is a proton

The aqueous chemistry of hydrogen is dominated by H^+ (aq).

Group 6A: The Oxygen Group

As we move down the group the metallic character increases.

O_2 is a gas, Te is a metalloid, Po is a metal

There are two important forms of oxygen; O_2 and **ozone**, O_3.

O_2 and O_3 are allotropes

Allotropes are different forms of the same element in the same state (in this case, gaseous)

Ozone can be prepared from oxygen:

$$3\ O_2\ (g) \quad 2\ O_3\ (g) \qquad\qquad H = +284.6\ \text{kJ}$$

Ozone is pungent and toxic

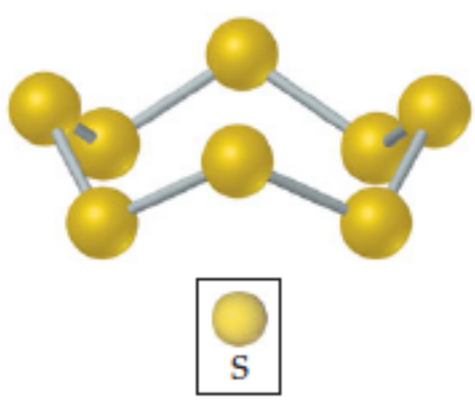
Oxygen (or dioxygen, O_2) is a potent oxidizing agent since the O^{2-} ion has a noble gas configuration.

There are two oxidation states for oxygen (e.g., H_2O) and –1 (e.g., H_2O_2)

Sulfur is another important member of this group.

The most common form of sulfur is yellow S_8.

Sulfur tends to form S^{2-} in compounds (sulfides).



Oxygen is a colorless gas at room temperature; all of the other members of group 6A are solids

TABLE 7.6 • Some Properties of the Group 6A Elements

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	$[Ne]3s^2 3p^4$	115	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

Group 7A: The halogens

Group 7A elements are known as the **halogens** (‘salt formers’).

The chemistry of the halogens is dominated by gaining an electron to form an anion:

$$X_2 + 2\ e^- \quad 2\ X^-$$

Fluorine is one of the most reactive substances known;

$$F_2\ (g) + 2\ H_2O\ (l) \quad 4\ HF\ (aq) + O_2\ (g) \qquad\qquad H = -758.9\ \text{kJ}$$

All halogens consist of diatomic molecules, X_2.

Chlorine is the most industrially useful halogen

The reaction between chlorine and water produces hypochlorous caic (HOCl), which is used to disinfect swimming pool water:

$$Cl_2\ (g) + H_2O\ (l) \quad HCl\ (aq) + HOCl\ (aq)$$

Halogens react with hydrogen to form gaseous hydrogen halide compounds.

$$H_2\ (g) + X_2 \quad 2\ HX\ (g)$$

Hydrogen compounds of the halogens are all strong acids with the exception of HF.

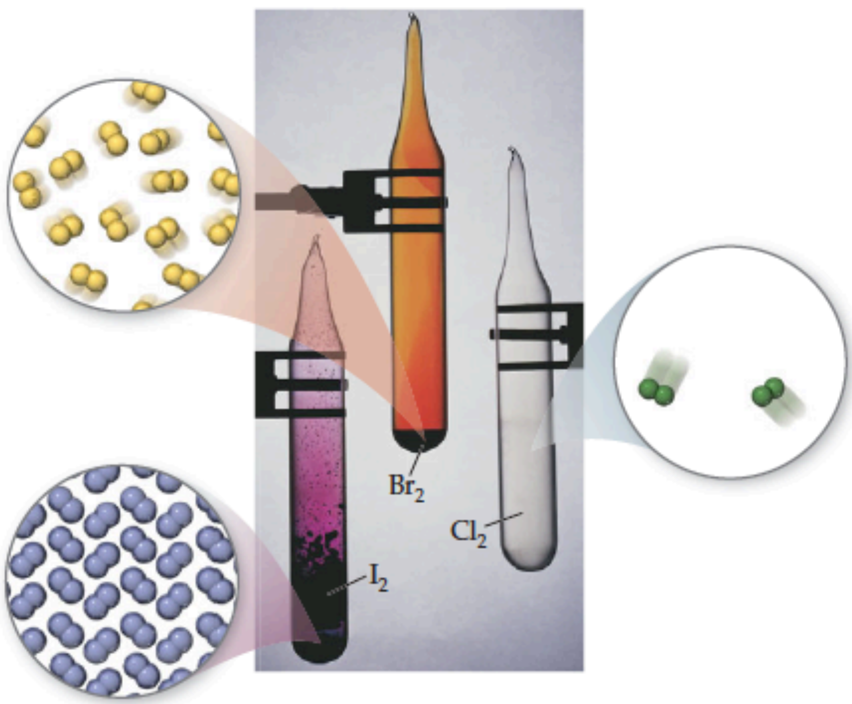


TABLE 7.7 • Some Properties of the Halogens

Element	Electron Configuration	Melting Point (°C)	Density	Atomic Radius (Å)	I_1 (kJ/mol)
Fluorine	$[He]2s^22p^5$	−220	1.69 g/L	0.71	1681
Chlorine	$[Ne]3s^23p^5$	−102	3.12 g/L	0.99	1251
Bromine	$[Ar]3d^{10}4s^24p^5$	−7.3	3.12 g/cm^3	1.14	1140
Iodine	$[Kr]4d^{10}5s^25p^5$	114	4.94 g/cm^3	1.33	1008

Group 8A; The Noble Gases

The group 8A elements are known as the **noble gases.**

These are all nonmetals and monoatomic.

They are notoriously unreactive because they have completely filled *s* and *p* subshells.

In 1962 the first compounds of the noble gases were prepared: XeF_2, XeF_4 and XeF_6 .

The high radioactivity of radon (Rn, atomic number 86) has limited the study of its reaction chemistry and some of its properties.

TABLE 7.8 • Some Properties of the 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