EPFL

General Chemistry – Week 8
Materials

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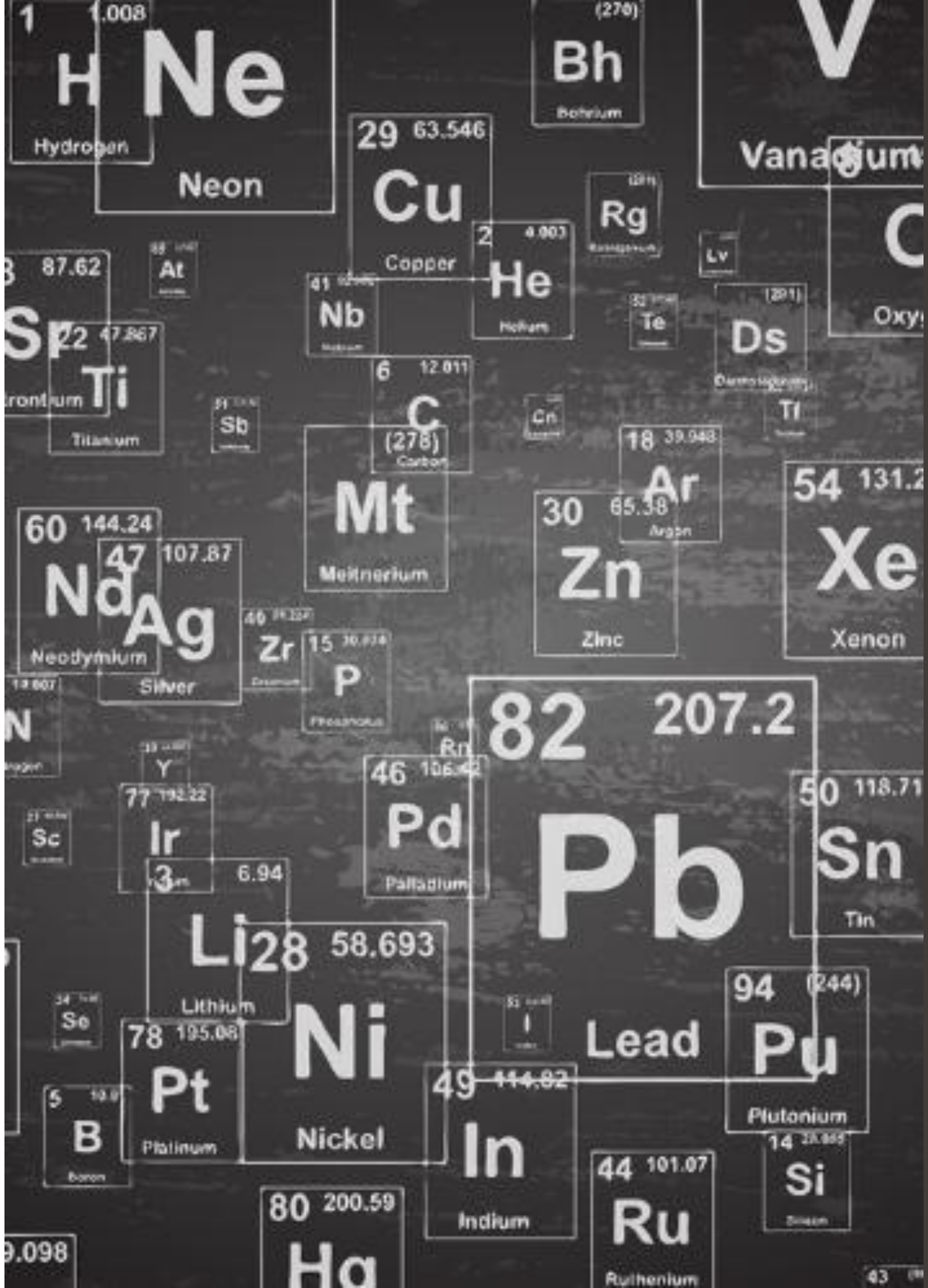

Trends in Atomic properties

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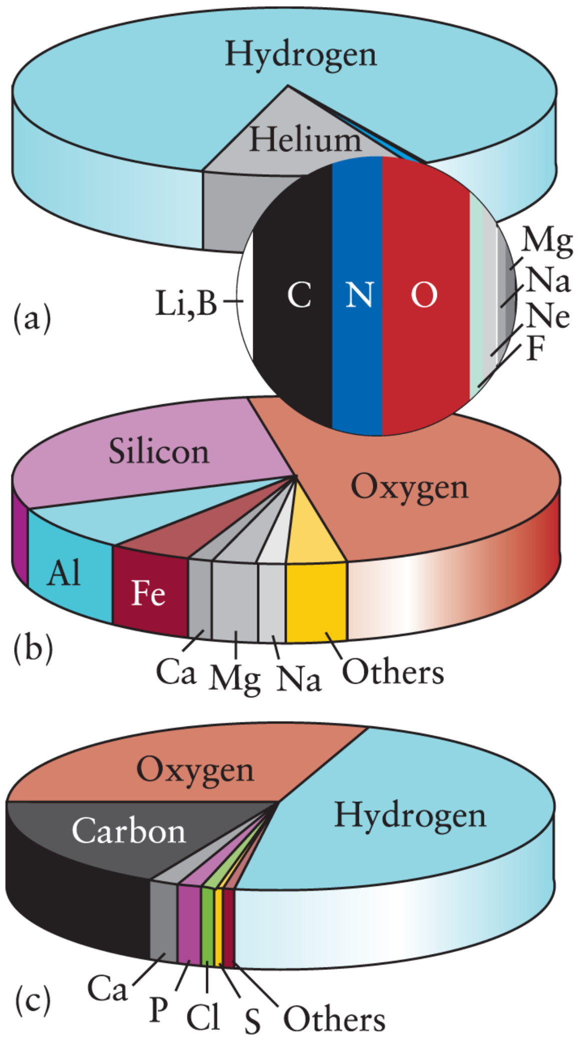
Hydrogen

Relative Abundance of Principal Elements

- The relative abundance of principal elements in (a) **the universe**, (b) the **crust of the earth**, and (c) the **human body** are quite different.

- Mainly elements located in periods 1, 2 and 3 and groups 1, 14, 16.



Hydrogen

- Hydrogen is widely considered to be the fuel of our future.
- Hydrogen has the same valence configuration as Group 1 elements and forms +1 ions, but has few other similarities with alkali metals.
- Hydrogen is a nonmetal and is similar to the halogens, in that it needs one electron to fill its valence shell and exists as diatomic molecules (H_2). But hydrogen is very different from the halogens chemically.
- Therefore, we do not assign a group number to hydrogen.

Hydrogen

- Hydrogen is the most abundant element in the universe: it accounts for 89% of all atoms.
- However, there is little free hydrogen on earth because H_2 molecules are light and move at high average speeds and escape from the Earth’s gravity.
- Most hydrogen atoms on Earth are present in water, either in the oceans or trapped inside minerals or clays. Hydrogen is also found in the hydrocarbons that make up fossil fuels.

Properties of Hydrogen

- Liquid hydrogen has a very low mass density which makes liquid hydrogen a lightweight fuel.
- Hydrogen has the highest specific enthalpy of any known fuel (the highest enthalpy of combustion per gram), and so liquid hydrogen is used with liquid oxygen to power some space vehicles.
- Each year, about half the 3 × 108 kg of hydrogen used in industry is converted into ammonia by the Haber process.

Processes involving Hydrogen

- The only product in the combustion of hydrogen is water, so it does not pollute the air. Hydrogen is highly sought after as a fuel, because the oceans have enough hydrogen for all of our energy needs.
- Hydrogen may be obtained from the electrolysis of water, but the process requires electricity.
- Hydrogen may also be obtained by using sunlight to drive the water-splitting reaction, the photochemical decomposition of water into its elements.

$$2\ H_2O\ (l) \xrightarrow{\text{sunlight}} 2\ H_2(g) + O_2(g) \quad \Delta G° = +474\ \text{kJ}$$

Hydrogen Production

- Most commercial hydrogen is produced as a by-product of petroleum refining in two-reaction sequence. First, a reforming reaction using a nickel catalyst produces a mixture of gases called synthesis gas.

$$CH_4(g) + H_2O\ (l) \xrightarrow{\text{Ni}} 3\ H_2(g) + CO\ (g)$$

- Second, in the shift reaction the CO in the synthesis gas reacts with more water over an iron or copper catalyst.

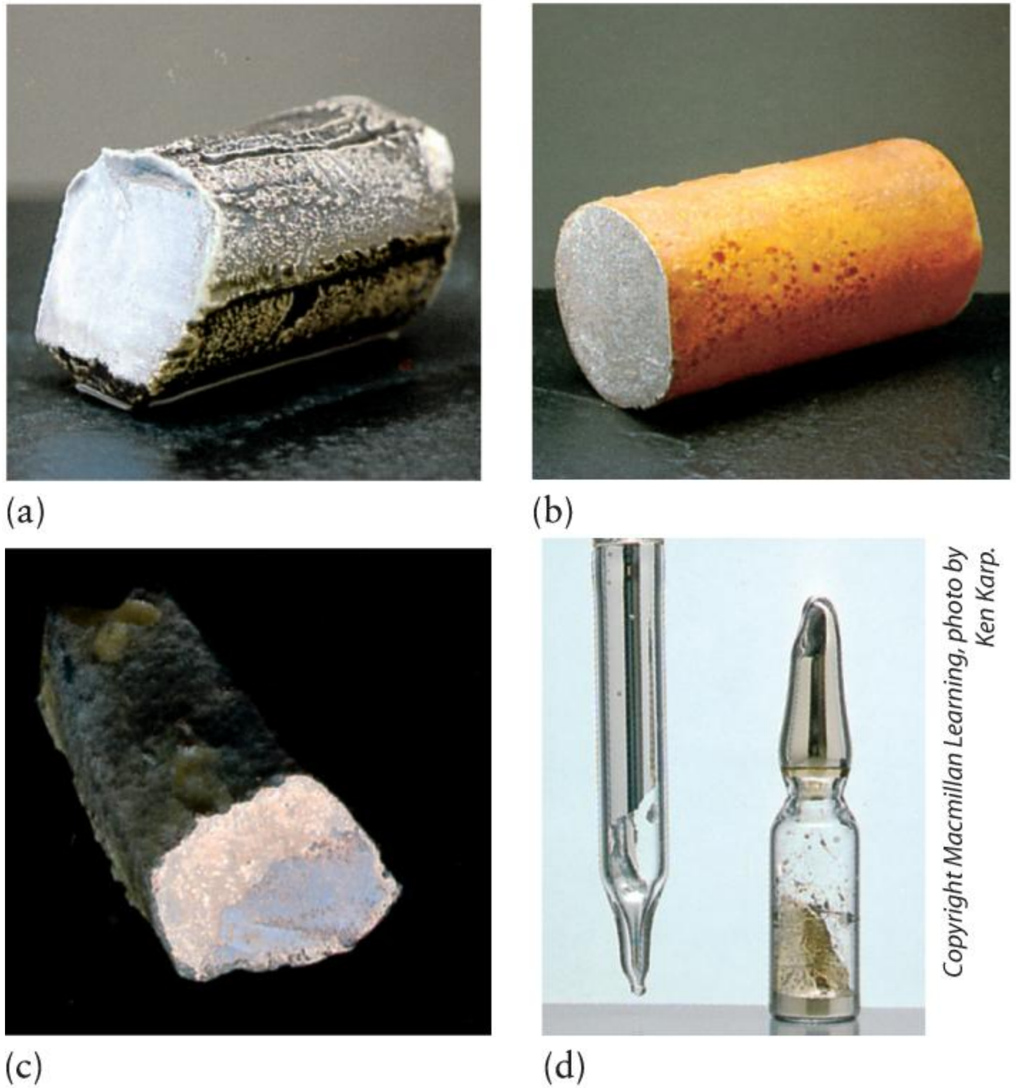
$$CO\ (g) + H_2O\ (l) \xrightarrow{\text{Fe/Cu}} 3\ H_2(g) + CO_2(g)$$

- In the lab, pure hydrogen gas is produced with an acid and metal.

$$Zn\ (s) + 2\ H^+\ (aq) \longrightarrow 2\ H_2(g) + Zn^{2+}(g)$$

Compounds of Hydrogen

- Hydrogen forms both H^- and H^+. Hydrogen has an intermediate electronegativity of 2.2 on the Pauling scale and typically forms covalent bonds with nonmetals and metalloids.
- The hydride ion, H^-, has a large radius, 154 pm, and the single proton has a hard time holding both electrons, so the second electron is easily lost. Because of this, ionic hydrides are powerful reducing agents.
- A hydrogen atom can participate in hydrogen bonding with N−H, O−H, or F−H bonds. A hydrogen bond is about 5% as strong as a covalent bond, but ten times stronger than other intermolecular forces.



Group 1: The Alkali Metals

- The chemical properties of alkali metals are striking similar.
- Sodium and potassium are used to transmit electrical signals throughout our brain and nervous system.
- The valence electron configuration of the alkali metals is ns^1, where n is the period number. One valence electron dominates their chemical and physical properties.

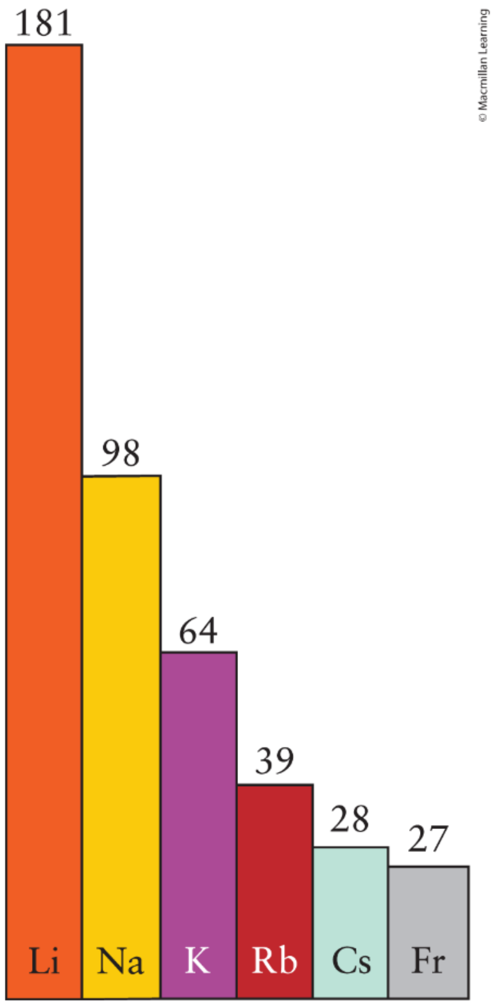
Group 1: The Alkali Metals

- Common name: alkali metals
- Valence configuration: ns1
- Normal form*: soft, silver-gray metals

Z	Name	Symbol	Molar mass/ ($g \cdot mol^{-1}$)	Melting point/°C	Boiling point/°C	Density/ ($g \cdot cm^{-3}$)
3	lithium	Li	6.94	181	1347	0.53
11	sodium	Na	22.99	98	883	0.97
19	potassium	K	39.10	64	774	0.86
37	rubidium	Rb	85.47	39	688	1.53
55	cesium	Cs	132.91	28	678	1.87
87	francium	Fr	(223)	27	677	–

Properties of Group 1 Elements

- Group 1 elements are low-density metals. Since the valence only has one electron, bonding in the metals is weak, resulting in low melting and boiling points. The graph shows the melting points of group 1 elements in degrees Celsius.
- Francium is intensely radioactive and very difficult to study.
- The alkali metals react most violently of all metals.



Properties of Group 1 Elements

- To make pure metal, oxygen is completely removed and molten salts are electrolytic exposed to sodium vapor in the Downs process:

$$\mathrm{KCI\ (l) + Na\ (g) \xrightarrow{750\ ℃} NaCI\ (s) + K\ (g)}$$

- Lithium had few uses until the development of thermonuclear weapons, which use lithium-6. Lithium is also used in rechargeable lithium-ion batteries.
- The first ionization energies of alkali metals are negative, meaning they are strong reducing agents.

$$2\, Na\ (s) +\ 2\, H_2O\ (l) \rightarrow\ H_2\, (g)\ +\ 2\, NaOH\ (aq)$$

Lithium

- Lithium differs from its congeners (other members of the group). The Li^+ cation is small, resulting in strong polarizing power and strong ion–dipole interactions.
- Lithium is used in ceramics, lubricants, and medicine. Small daily doses of lithium carbonate are an effective treatment for bipolar (manic depressive) disorder. Lithium is found in soaps, as thickener in lubricating greases for high-temperature applications.

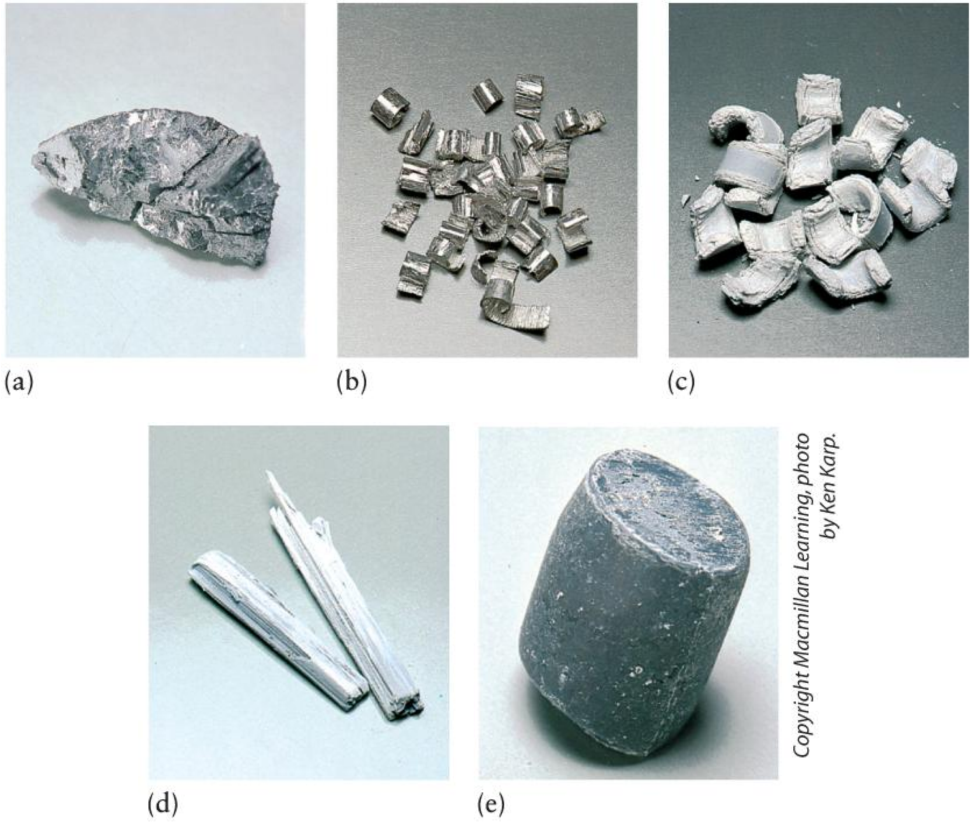
Sodium Compounds

- Sodium hydrogen carbonate, $NaHCO_3$ (sodium bicarbonate), is commonly called bicarbonate of soda or baking soda. The rising action of baking soda in batter depends on the reaction of a weak acid with the hydrogen carbonate ions.

$$Ca^{2+}\,(aq) + CO_3{}^{2-}\,(aq) \rightarrow CaCO_3\,(s)$$

- Sodium carbonate decahydrate, $Na_2CO_3 \cdot 10\ H_2O$, was once widely used as washing soda. Sometimes it is added to water to precipitate Mg^{2+} and Ca^{2+} ions.

$$HCO_3{}^{-}\,(aq) + HA\,(aq) \rightarrow A^{-}\,(aq) + H_2O\,(l) + CO_2\,(g)$$



Group 2:
The Alkaline Earth Metals

- The Group 2 elements are called the alkaline earth metals, because their “earths”—the old name for oxides—are basic (alkaline).
- The valence electron configuration of the alkaline earth metals Is ns^2, where n is the period number. Group 2 elements have an oxidation number of +2 as the M^{2+} cation in their compounds.

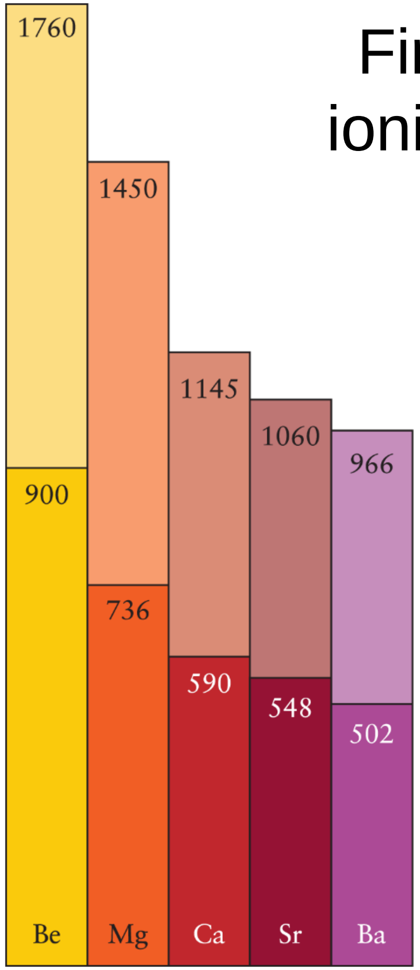
Group 2: The Alkaline Earth Metals

- Common name: alkaline earth metals (Ca, Sr, Ba)
- Valence configuration: ns2
- Normal form*: soft, silver-gray metals

Z	Name	Symbol	Molar mass/ ($g \cdot mol^{-1}$)	Melting point/°C	Boiling point/°C	Density/ ($g \cdot cm^{-3}$)
4	beryllium	Be	9.01	1285	2470	1.85
12	magnesium	Mg	24.21	650	1100	1.74
20	calcium	Ca	40.08	840	1490	1.53
38	strontium	Sr	87.62	770	1380	2.58
56	barium	Ba	137.33	710	1640	3.59
88	radium	Ra	(226)	700	1500	5.00

Group 2: Alkaline Earth Metals

- The Group 2 elements share many characteristics with Group 1 metals. Group 1 and Group 2 elements are both too reactive to occur in the free state in nature. Group 2 elements are generally found as doubly charged cations in compounds.
- The second ionization energy of Group 2 elements is low enough for both valence electrons to be lost.



First and second ionization energies

Occurrence of Group 2 Elements

- Beryllium is found mainly as the mineral *beryl*, 3 $BeO \cdot Al_2O_3 \cdot 6\ SiO_2$. These crystals can weigh several tons. Emeralds are a form of beryl with the green color caused by Cr^{3+} impurities.
- Magnesium occurs in seawater and as the mineral dolomite, $CaCO_3 \cdot MgCO_3$.
- Calcium also occurs as $CaCO_3$ in compressed deposits of the sea shells including limestone, calcite, and chalk.


M. Claye/Science Source.

The Group 2 Elements

- Beryllium is used as windows for X-ray tubes, because Be atoms have so few electrons, thin sheets of the metal are transparent to X-rays and allow the rays to escape.
- Beryllium is added in small amounts to copper to form a beryllium–copper mixture that is hard and able to conduct electricity. They are used to make nonsparking tools and tiny nonmagnetic parts.
- Magnesium has 1/3 the density of aluminum and is very soft. It is used as an alloy for building aircraft.
- Magnesium burns vigorously in air as a brilliant white flame.

The Group 2 Elements

- Calcium, strontium, and barium are obtained either by electrolysis or by reduction with aluminum in a version of the thermite process.

$$3\ BaO\ (s) + 2\ Al\ (s) \xrightarrow{\Delta} Al_2O_3(s) + 3\ Ba\ (s)$$

- Except beryllium, all Group 2 metals react with water to make a basic solution.

$$Ca\ (s) + 2\ H_2O\ (l) \rightarrow Ca^{2+}\ (aq) + 2\ OH^-\ (aq) + H_2\ (g)$$

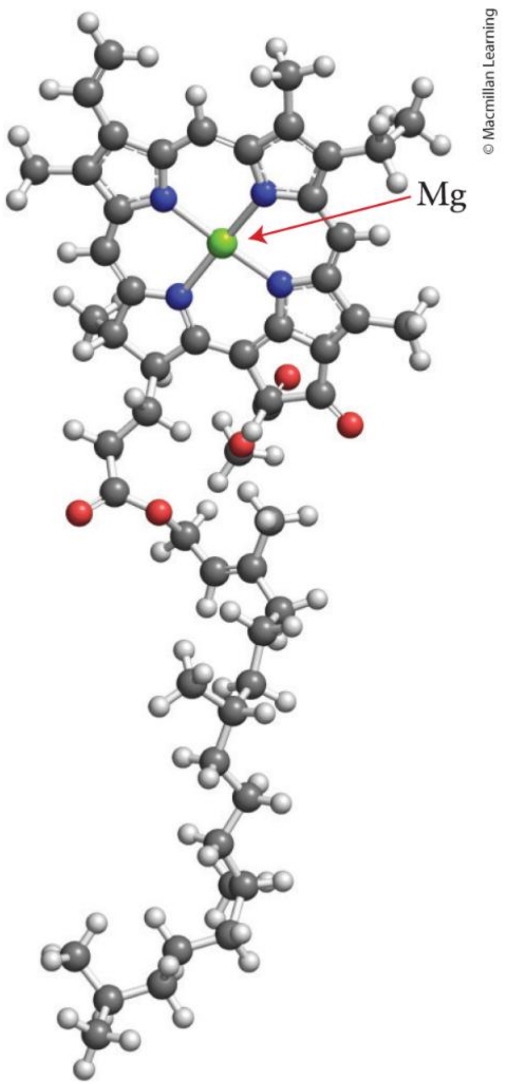
- Alkaline earth metals can be detected by the colors they give to flames, and their salts are often used to make fireworks.

Compounds of Magnesium

- Magnesium oxide, MgO, is formed when magnesium burns in air. Magnesium oxide is refractory, meaning that it is able to withstand high temperatures.
- Magnesium hydroxide, $Mg(OH)_2$, is a base. It is not very soluble in water, but forms a white colloidal suspension. This suspension is known as milk of magnesia and is used as a stomach antacid.
- Magnesium sulfate, $MgSO_4 \cdot 7\ H_2O$, also known as Epsom salt, is a common laxative.

Compounds of Magnesium

- Perhaps the most important compound of magnesium is chlorophyll. This green organic compound captures light from the Sun for photosynthesis.
- The Mg2+ ion, lies just above the plane and appears to keep the ring rigid to minimize vibrational energy which would otherwise be lost as heat.
- Mg plays a role in muscle contraction.



3 Chlorophyll

Compounds of Calcium

- Calcium carbonate, $CaCO_3$, decomposes to make calcium oxide, CaO, or quicklime, when heated.

$$CaCO_3(s) \xrightarrow{\Delta} CaO\ (s) + CO_2(g)$$

- Calcium oxide (“thirsts” for water) is called quicklime because it reacts so exothermically and rapidly with water.

$$CaCO_3(s) \xrightarrow{\Delta} CaO\ (s) + CO_2(g)$$

- Calcium hydroxide, $Ca(OH)_2$, is commonly known as slaked lime because the thirst of quicklime for water has been quenched (slaked).

$$Ca(OH)2\ (aq)\ +\ CO_2\ (g) \qquad CaCO_3\ (s)\ + H_2O\ (l)$$

Group 13: The Boron Family

- The Group 13 elements have subtle properties because neither gaining nor losing electrons is energetically favorable.
- The valence electron configuration of the Group 13 elements is ns2np1, where n is the period number. Group 13 elements have a maximum oxidation number of +3. The oxidation numbers of B and Al are +3 in most cases, but the heavier elements are more likely to keep s-electrons and have an oxidation number of +1.

Group 13: The Boron Family

- Valence configuration: ns2np1

Z	Name	Symbol	Molar mass/ $(g{\cdot}mol^{-1})$	Melting point/°C	Boiling point/°C	Density/ $(g{\cdot}cm^{-3})$	Normal form*
5	boron	B	10.81	2300	3931	2.47	powdery brown metalloid
13	aluminum	Al	26.98	660	2467	2.70	silver-white metal
31	gallium	Ga	69.72	30	2403	5.91	silver metal
49	indium	In	114.82	156	2080	7.29	silver-white metal
81	thallium	Tl	204.38	304	1457	11.87	soft metal

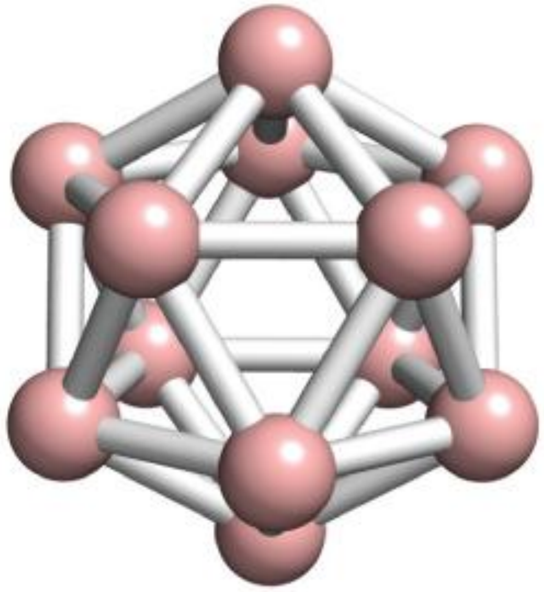
Boron

- Boron forms perhaps the most extraordinary structures of all the elements.
- With only three valence electrons and a small atomic radii, it tends to form only three covalent bonds with an incomplete octet.
- Boron is mined in the Mojave Desert region of California as borax and kernite, $Na_2B_4O_7 \cdot x\, H_2O$, with $x = 10$ and 4.
- It is converted to an amorphous boron using magnesium

$$B_2O_3(s) + 3\,Mg\,(s) \xrightarrow{\Delta} 2\,B\,(s) + 3\,MgO\,(s)$$

Boron

- Boron has many allotropes. The most common an icosahedral (20-faced) clusters of 12 atoms.
- Elemental boron is very hard and is chemically unreactive.
- Boron fibers are tough, so they are incorporated into plastics. They are stiffer than steel yet lighter than aluminum so are found in aircrafts, missiles, and body armor.



1 B_{12}

Obtaining Aluminum from Bauxite

- Aluminum is the most abundant metal in the Earth's crust after oxygen and silicon.
- The commercial source of aluminum is bauxite, a hydrated oxide, $Al_2O_3 \cdot x\ H_2O$, where x can range from 1 to 3.
- Bauxite ore is processed into alumina, Al_2O_3, by the Bayer process. Ore is dissolved in NaOH, forming aluminate, $Al(OH)_4^-$ (aq). CO_2 (g) is bubbled in to remove OH^- as HCO_3^- forming insoluble $Al(OH)_3$ (s). When heated to 1200 °C to dehydrate it, it forms aluminum oxide.

Properties of Aluminum

- Aluminum has a low density, and it is a strong metal and an excellent electrical conductor.
- Aluminum is also resistant to corrosion because its surface is passivate in air by a stable oxide film. The thickness of the oxide layer can be increased producing anodized aluminum.
- Aluminum is more metallic and can react with either an acid or base, and so is amphoteric.

$$2\ Al\ (s) + 6\ H^{+}\ (aq) \rightarrow\ 2\ Al^{3+}\ (aq) + 3\ H_2\ (g)$$

$$2\ Al\ (s) + 2\ OH^{-}\ (aq) + 6\ H_2O\ (l) \rightarrow 2\ Al(OH)4-\ (aq) +\ 3\ H_2\ (g)$$

Gallium, Indium, and Thallium

- Gallium is produced as a by-product of the Bayer process. It is a common doping agent for semiconductors, and some of its compounds are used in light-emitting diodes.
- Indium is also used in semiconductor applications.
- Thallium is a dangerously poisonous heavy metal.

Aluminum Oxides

- Aluminum oxide, Al_2O_3, is known as *alumina*. Alumina exists in a variety of forms such as α-alumina, and γ-alumina.

- Forms of α-alumina include (a) ruby (alumina with Cr^{3+} instead of some Al^{3+} ions); (b) sapphire (alumina with Fe^{3+} and Ti^{4+} impurities); and (c) topaz (alumina with Fe^{3+} impurities).

- γ-Alumina is less dense and used in the stationary phase in chromatography.


(a) (b) (c)

Applications of Group 13 Elements

- Aluminum is widely used in the construction and aerospace industries because of its low density, wide availability, and corrosion resistance.
- Boron oxide is commonly used in fiberglass and borosilicate glass, such as Pyrex, with very low thermal expansion. Boron nitride is used in the electronics industry. Under high pressure, boron nitride is converted into a very hard form called Borazon (proprietary name).
- Gallium and indium are widely used as dopants in semiconductors.

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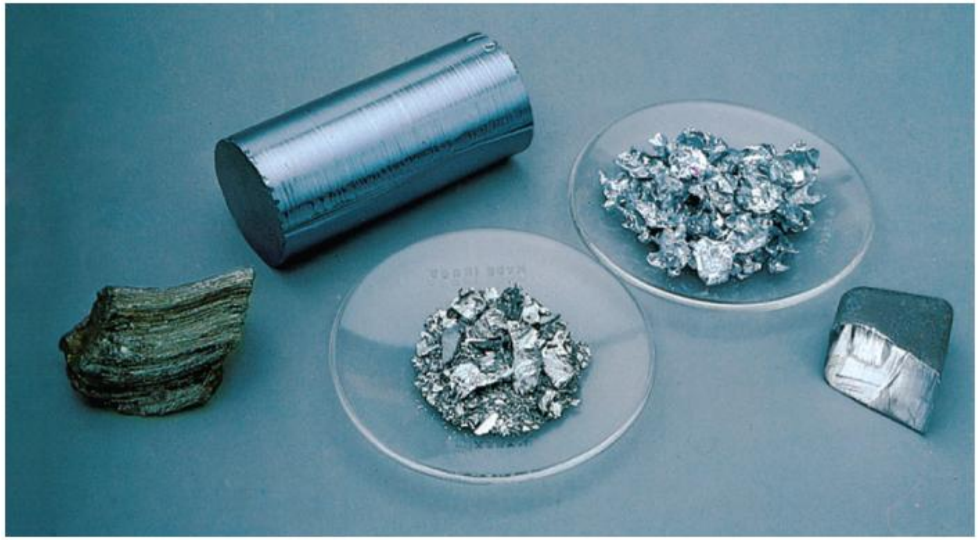


Group 14: The Carbon Family

- The valence electron configuration of the Group 14 elements is ns2np2, where n is the period number. The valence electron configuration explains why carbon and silicon form four covalent bonds.
- The inert-pair effect is common for the heavier elements and why lead is commonly in a +2 oxidation state.

Group 14: The Carbon Family

- Valence configuration: ns2np2

Z	Name	Symbo l	Molar mass/ (g·mol^{-1})	Melting point/°C	Boiling point/°C	Density/ (g·cm^{-3})	Normal form*
6	carbon	C	12.01	3370s	–	1.9-2.3 3.2-3.5	black nonmetal (graphite) transparent nonmetal (diamond) brown nonmetal (fullerite)
14	silicon	Si	28.09	1410	2620	2.33	gray metalloid
32	germanium	Ge	72.61	937	2830	5.32	gray-white metalloid
50	tin	Sn	118.71	232	2720	7.29	whit lustrous metal
82	lead	Pb	207.2	328	1760	11.34	blue-white lustrous metal

Metallic Character of Group 14 Elements

- The metallic character of the elements increases down the group.
- Carbon has nonmetallic properties, forming covalent compounds. Carbon and silicon oxides are acidic.
- Germanium is a metalloid, exhibiting metallic or nonmetallic properties depending on the other elements present in the compound.
- Tin and lead have definite metallic properties. Tin has some amphoteric properties.

$$Sn\,(s) + 2\,H_3O^+\,(aq) \rightarrow Sn^{2+}\,(aq) + H_2\,(g) + 2\,H_2O\,(l)$$

$$Sn\,(s) + 2\,OH^-\,(aq) + 2\,H_2O\,(l) \rightarrow Sn(OH)22-\,(aq) + H_2\,(g)$$

Comparing Carbon and Silicon

- Carbon has a smaller radius than silicon, so carbon's p-orbitals get closer together forming π-bonds like C=C and C=O, whereas silicon double bonds are rare.
- Carbon forms discrete molecules, O=C=O. Silicon dioxide (silica) forms networks of -O-Si-O- groups.
- Silicon compounds can act as Lewis acids, whereas carbon compounds usually cannot. Silicon is bigger than carbon and can expand its valence shell by using d-orbitals, accommodating the lone pair from a Lewis base, whereas carbon cannot.

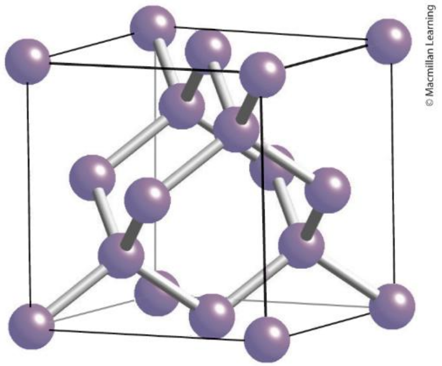
The Different Forms of Carbon

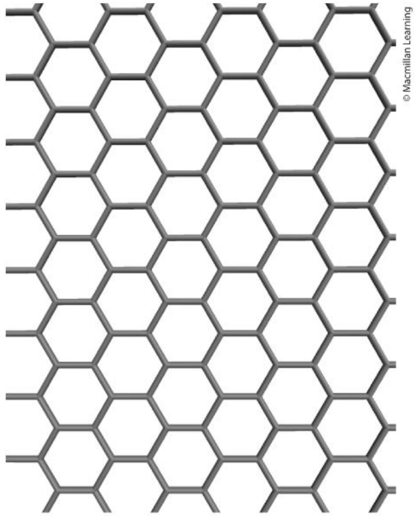
- Coke is an impure form of carbon used in steel production. Soot and carbon black contain small crystals of graphite and carbon forms. Carbon black, produced by heating hydrocarbons to nearly 1000 °C in the absence of air, is used for reinforcing rubber, for pigments, and for printing inks.
- Activated carbon is produced by heating waste organic matter in the absence of air. The very high specific surface area (2000 $m^2 \cdot g^{-1}$) enables it to remove organic impurities from liquids and gases in air purifiers, gas masks, and aquarium water filters as well as water purification plants.

The Different Forms of Carbon: Diamond and Graphite

- In diamond, sp3 hybridized carbon atoms are linked tetrahedrally with four neighbors. All C—C are σ-bonded.

- Graphite has planar sheets of sp2 hybridized carbon atoms in a hexagonal network. Pure graphite is obtained by passing a high electric current through rods of coke.

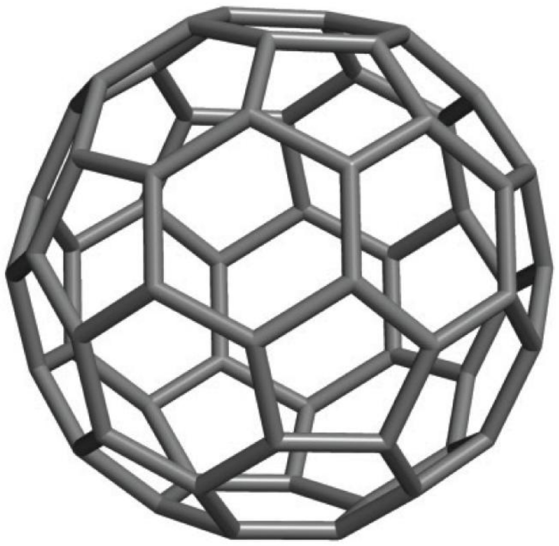




4 Graphene

The Different Forms of Carbon: Fullerenes

- First identified in 1985, C_{60} might be more abundant than graphite and diamond. The C_{60} molecule is named after the American architect R. Buckminster Fuller's geodesic dome resemblance.
- Crystals of C_{60} are called fullerite. The discovery of C_{60} and other structures like it, such as C_{70}, opened up the prospect of a whole new field of chemistry.
- The family of molecules resembling C_{60} are called fullerenes.



2 Buckminsterfullerene, C_{60}

Silicon

- Silicon is the second most abundant element in the Earth's crust and occurs in as silicates. Pure silicon is obtained from quartzite, which is a granular form of quartz (a type of solid of SiO_2).
- Silicon is used in semiconductors. In one process, a large crystal is grown by pulling a solid rod of the element slowly away from the melt. Then, the silicon is purified using zone refining, in which a hot, molten zone is dragged from one end of the rod to the other, removing impurities.

Germanium, Tin, and Lead

- Germanium was predicted by Mendeleev prior to its discovery in 1886. It is mainly used as a semiconductor.
- Tin and lead are obtained easily from their ores and have been known since antiquity. Tin primarily occurs as the mineral cassiterite, SnO_2 , and is obtained by the reduction of it with carbon at 1200 °C.

$$\mathrm{SnO_2(s) + \ C\ (s) \xrightarrow{\Delta} Sn\ (l) + CO_2(g)}$$

- Lead ore is called galena, PbS, and converted to the oxide first, then to the metal.

$$\mathrm{2\ PbS\ (s) + 3\ O_2(g) \xrightarrow{\Delta} 2\ PbO\ (s) + 2\ SO_2(g)}$$

$$PbO(s) + CO\ (g) \longrightarrow \mathrm{2PbO(s)} + 2\ SO_2$$

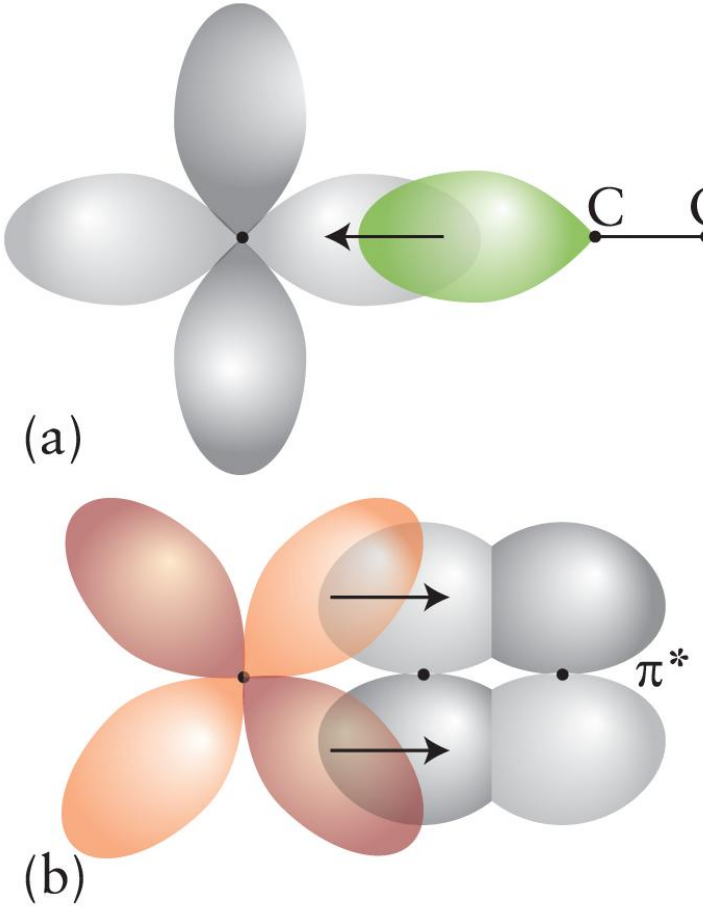
Oxides of Carbon

- Carbon dioxide, CO_2, comes from burning organic matter and animal respiration. There is evidence and concern that an increase in CO_2 due to the combustion of fossil fuels contributes to global warming.
- Carbon dioxide is the acid anhydride of carbonic acid, H_2CO_3 , and forms an equilibrium mixture of CO_2, H_2CO_3, HCO_3^-, and a very small amount of CO_3^{2-} in water.
- Carbonated beverages are made by injecting high partial pressures of CO_2 into water.

$$H_2CO_3\,(aq) \rightleftharpoons CO_2\,(g) + H_2O\,(l)$$

Oxides of Carbon

- Carbon monoxide, CO, is produced when carbon or organic compounds burn in a limited supply of air. It is a colorless, odorless, flammable, almost insoluble, and very toxic gas.
- CO is a Lewis base. The lone pair on the carbon atom forms covalent bonds with d-block atoms and ions.
- CO is also a Lewis acid because its empty antibonding π-orbitals can accept electron density from a metal.



Silicates

- Silica, SiO_2, is a hard, rigid network solid, that is insoluble in water and occurs naturally in quartz.
- There are three common forms of silica: (a) quartz, (b) quartzite, and (c) cristobalite. Sand consists mostly of small pieces of impure quartz.

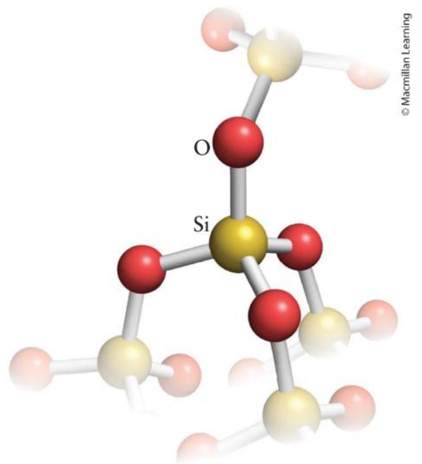
(a) (b) (c)

Field Museum Library/Getty Images.

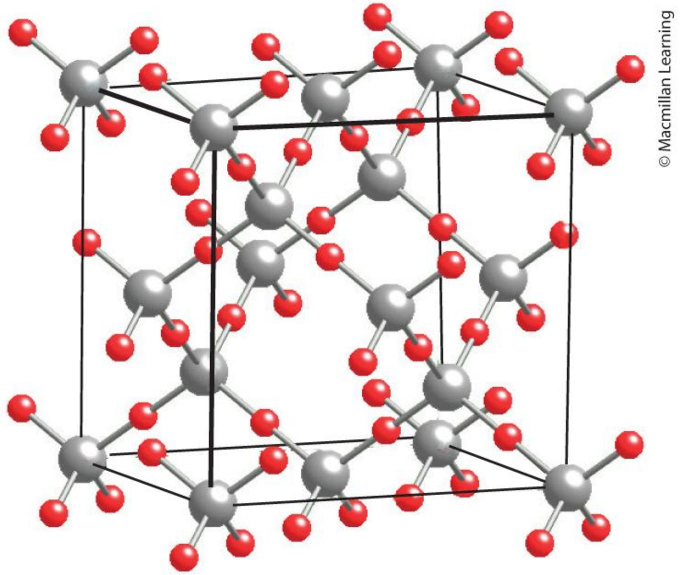
Arrangements of Silicon

- Silica gets its strength from its covalently bonded network structure.
- Each tetrahedron contributes
- one Si atom and 4 × ½ = 2 O atoms to the unit cell; SiO_2 is the empirical formula.

- When heated to 1500 °C, the atoms rearrange into the mineral cristobalite, a structure similar to C's diamond, except with -O-Si-O-.



3 An SiO_4 unit



Types of Silicates

- Orthosilicates, are the simplest silicates and are built from SiO_4^{4-} ions.
- Pyroxenes consist of chains of SiO_4 units and include the gemstone jade. Chains of silicate units can link together forming ladderlike structures such as tremolite. Asbestos is a tremolite.
- Aluminosilicates are complex structures that form when some of the silicon(IV) is replaced by aluminum(III).

Types of Silicates

- Pyroxenes are chains of SiO_4 units. Asbestos, which was once used to insulate buildings, is a pyroxene. Asbestos can become lodged in lungs and cause issues in the lungs.
- Aluminosilicate mica is used for windows in furnaces because it cleaves into thin transparent sheets with high melting points.

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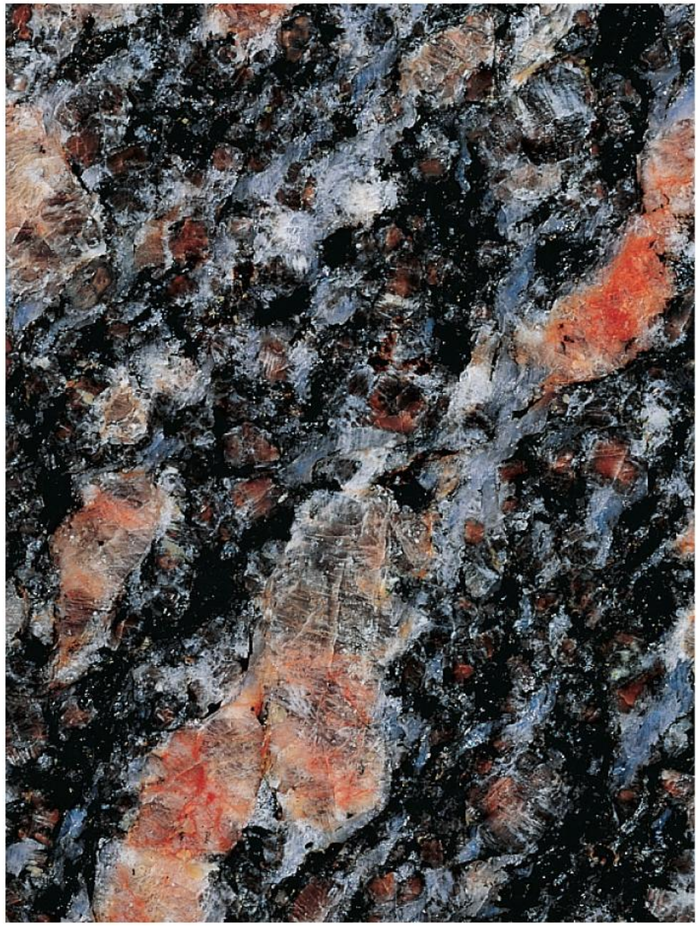
Chip Clark/Fundamental Photographs.

Types of Silicates

- Feldspars are aluminosilicates where up to half of the silicon(IV) has been replaced by aluminum(III). A typical feldspar has the formula $KAlSi_3O_8$.
- Granite is a compressed mixture of mica, quartz, and feldspar.



Phillip Hayson/Science Source.

Carbides

- Carbon is the only Group 14 element that forms both monatomic and polyatomic anions. There are three classes of carbides: saline, covalent, and interstitial.
- Saline carbides are most common with Groups 1, 2, Al, and a few other elements.

$$Al_4C_3 + 12\,H_2O\,(l) \longrightarrow 4\,Al(OH)_3\,(s) + 3\,CH_4\,(g)$$

- Covalent carbides include silicon carbide, SiC, which is sold as carborundum, which is an excellent abrasive.

$$\mathrm{SiO_2(s) + 3\,C\,(s) \xrightarrow{2000\,°C} SiC\,(s) + 2\,CO\,(g)}$$

Carbides

- Interstitial carbides are compounds with a d-block metal and carbon formed above 2000 °C.
- Like in steel, the C atoms pin the metal atoms together into a rigid structure, resulting in very hard substances with melting points above 3000 °C.
- Tungsten carbide, WC, is used for the cutting surfaces of drills.

Silanes

- Carbon easily forms bonds with itself and hydrogen, and there are huge numbers of hydrocarbons (Organic Chemistry).
- Silicon forms a much smaller number of compounds with hydrogen, called silanes. The simplest silane is silane itself, SiH_4, is the analog of methane.
- Silane is much more reactive than methane and bursts into flame on contact with air. Although silane survives in pure water, it forms SiO_2 when a trace of alkali is present.

$$SiH_4(g) + 2\,H_2O\,(l) \xrightarrow{\text{base}} SiO_2(s) + 4\,H_2(g)$$

Group 15: The Nitrogen Family

- The valence electron configuration of the Group 15 elements is ns2np3, where n is the period number.
- The chemical and physical properties vary sharply in this group. Nitrogen gas, N2, is inert in air, phosphorus ignites in air, and arsenic, antimony, and bismuth are used in semiconductors.

Group 15: The Nitrogen Family

- Valence configuration: ns2np3

Z	Name	Symbol	Molar mass/ $(g \cdot mol^{-1})$	Melting point/°C	Boiling point/°C	Density/ $(g \cdot cm^{-3})$	Normal form*
7	nitrogen	N	14.01	−210	−196	1.04†	colorless gas
15	phosphorus	P	30.97	44	280	1.82	white or red nonmetal
33	arsenic	As	74.92	613s‡	–	5.78	gray metalloid
51	antimony	Sb	121.76	631	1750	6.69	blue-white lustrous metalloid
83	bismuth	Bi	208.98	271	1650	8.90	white-pink metal

Properties of Group 15 Elements

- The metallic character of Group 15 elements increases down the group. However, only bismuth is considered to be metallic.
- The oxidation number of Group 15 elements range from −3 to +5. However, only nitrogen and phosphorus display the full range.

Nitrogen

- Nitrogen, N, is rare in the Earth's crust, but elemental nitrogen is 76% by mass in our atmosphere.
- Pure nitrogen gas (N_2) is obtained by the fractional distillation of liquid air. Air is cooled to below −196 °C by repeated expansion and compression in a refrigerator. The liquid is then warmed, and the nitrogen (b.p. −196 °C) boils off.
- Plants need nitrogen to grow, but they cannot use N_2 directly because the N≡N bond is strong (944 $kJ \cdot mol^{-1}$), making nitrogen gas almost as inert as the noble gases. Nitrogen must be “fixed” or combined with other elements into more useful compounds.

Nitrogen

- Nitrogen differs in many ways from its congeners. Because nitrogen is highly electronegative, (χ = 3.0, about the same as chlorine) it is the only Group 15 element that forms hydrides capable of hydrogen bonding.
- Nitrogen is capable of forming multiple bonds with other Period 2 elements by using its p-orbitals because of its small size.
- Nitrogen has wide range of oxidation numbers from –3 (in NH_3) to +5 (in nitric acid and nitrates). It also has fractional oxidation numbers, –1/3 in the azide ion, N^{3-}.

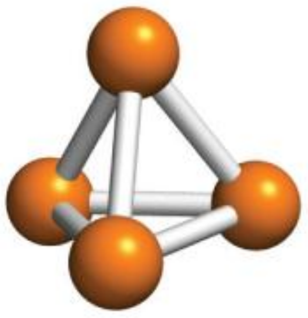
Phosphorus

- Phosphorus is significantly different from nitrogen. It is nearly 50% larger than nitrogen, too big for π-bonding. Nitrogen can form multiple bonded structures like N_2O_3, but phosphorus forms additional single bonds as in P_4O_6. The large size of phosphorus and availability of d-orbitals means it can form as many as six bonds (PCl_6^-). Nitrogen forms four.
- Phosphorus is obtained from apatites, mineral forms of calcium phosphate, $Ca_3(PO_4)_2$. The rocks are heated in an electric furnace with carbon and sand.

$$2\ Ca_3(PO_4)_2(s) + 6\ SiO_2(s) + 10\ C\ (s) \xrightarrow{\Delta} P_4(g) + 6\ CaSiO_3(l) + 10\ CO\ (g)$$

Phosphorus

- White phosphorus is a soft, white, poisonous molecular solid consisting of tetrahedral P_4 molecules. This allotrope is highly reactive with strained 60° bond angles. It is normally stored in water because it bursts into flame on contact with air.
- White phosphorus changes into red phosphorus when it is heated in the absence of air. It is a less reactive allotrope and is only ignited by friction, It is used on the surfaces of matchbooks. It is thought to consist of linked P_4-chains.
- The name phosphorus means “light bringer.” It comes from the observation that white phosphorus gas glows yellow-green in moist air in a process called chemiluminescence.



3 Phosphorus, P_4

Compounds with Hydrogen and Nitrogen

- The most important hydrogen compound of Group 15 elements is ammonia, NH_3, which is prepared using the Haber process. Ammonia is a toxic gas that condenses to a colorless liquid at –33 °C.
- It has a dipole moment of 1.47 D (slightly lower than H_2O, 1.85 D). Salts with strong ionic character like KCl cannot dissolve in liquid ammonia. However, salts with polarizable anions tend to be more soluble than salts with greater ionic character.
- Liquid ammonia undergoes much less extensive autoprotolysis than water.

$$2\,NH_3\,(am) \rightleftharpoons NH_4^{+}\,(am) + NH_2^{-}\,(am); \qquad K_{am} = [NH_4^{+}][NH_2^{-}] = 1 \times 10^{-33}$$

Compounds with Hydrogen and Nitrogen

- Temperature-dependent reactions can be violently explosive, e.g., dynamite.

$$NH_4NO_3(s) \xrightarrow{250\ ℃} N_2O\ (g) + H_2O\ (g)$$

$$NH_4NO_3(s) \xrightarrow{>300\ ℃} 2\ N_2(g) + O_2(g) + 4\ H_2O\ (g)$$

- Hydrazine, NH_2NH_2, is prepared by the gentle oxidation of ammonia with alkaline hypochlorite solution.

$$2\ NH_3\ (aq) + ClO^-\ (aq) \rightarrow NH_2NH_2\ (aq) + Cl^-\ (aq) + H_2O\ (l)$$

- The physical properties of hydrazine are similar to water, but its chemical properties are not. It is dangerously explosive and is stored and used in aqueous solution.

Compounds of Phosphorous and Hydrogen

- Hydrogen compounds decrease in stability down the group.
- Phosphine, PH_3, is a poisonous gas that smells faintly of garlic and bursts into flame in air if it is slightly impure. PH_3 is much less soluble in water than NH_3, because it cannot form hydrogen bonds.
- P^{3-} is a strong Brønsted base and is easily protonated by water to make PH_3.
  $2\ P^{3-}\ (s) + 6\ H_2O\ (l) \rightarrow 2PH_3\ (g) + 6OH^-\ (aq)$

Nitrogen Oxides and Oxoacids

- Nitrogen forms several oxides, with oxidation numbers ranging from +1 to +5.
- Nitrogen oxides in the atmosphere are both a pollutant but also helpful in removing them, and are referred to as NOx (read "nox").
- Dinitrogen oxide, N_2O (oxidation number +1), is commonly called nitrous oxide. Because it is tasteless, unreactive, nontoxic in small amounts, and soluble in fats, it is used as a foaming agent and propellant for whipped cream.

Nitrogen Oxides and Oxoacids

- Nitrogen oxide (or nitrogen monoxide), NO, is commonly called nitric oxide and rapidly oxidizes to nitrogen dioxide in air, contributing to acid rain.

  $$2\ NO\ (g) + O_2\ (g) \rightarrow 2\ NO_2\ (g)$$

- Nitrogen oxide is both harmful and beneficial.
- Combustion engines produce NO, which contributes to acid rain, smog, and the destruction of the ozone layer.
- Yet our bodies use small amounts as a neurotransmitter to dilate blood vessels, and for other physiological changes.

Nitrogen Oxides and Oxoacids

- Nitrogen dioxide, NO2 (oxidation number +4), is a choking, poisonous, brown gas that contributes to the color and odor of smog. When it dissolves in water, it makes nitric acid.

$$3\ NO_2 + H_2O\ (l) \rightarrow 2\ HNO_3\ (aq) + NO\ (g)$$

- The same atmospheric reaction that makes acid rain.
- Aqueous blue gas dinitrogen trioxide, N2O3, forms nitrous acid, HNO2(aq), though it has never been isolated.
- Nitrites are made when reducing metals and are toxic.

$$KNO_3\ (s) + Pb\ (s) \rightarrow KNO_2\ (s) + PbO\ (s)$$

Phosphorus Oxides and Oxoacids

- Phosphate fertilizer production consumes two-thirds of all the sulfuric acid produced in the United States.
- Phosphorus oxides are based on the tetrahedral PO_4 unit. In a limiting oxygen environment:

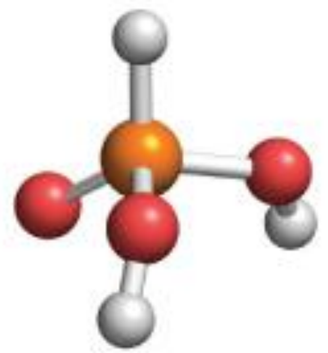
$$P_4\,(s,white) + 3\,O_2\,(g) \rightarrow P_4O_6\,(s)$$

- In an excess oxygen environment:

$$P_4\,(s,white) + excess\ O_2\,(g) \rightarrow P_4O_{10}\,(s)$$

- In water:

$$P_4O_6\,(s) + 6\,H_2O\,(g) \rightarrow 4\,H_3PO_3\,(aq)$$
$$P_4O_{10}\,(s) + 6\,H_2O\,(g) \rightarrow 4\,H_3PO_4\,(aq)$$



4 Phosphorous acid, H_3PO_3

Phosphorus Oxides and Oxoacids

- H_3PO_4, phosphoric acid's primary use is for fertilizers, food additives, and detergents.
- Many soft drinks owe their tart taste to low concentrations of phosphoric acid.
- Pure phosphoric acid, H_3PO_4, is a colorless solid with a melting point of 42 °C.
- It bonds readily with water and is usually only 85% H_3PO_4 when purchased. In this state, it is a syrupy liquid. Its high viscosity is due to extensive hydrogen bonding.

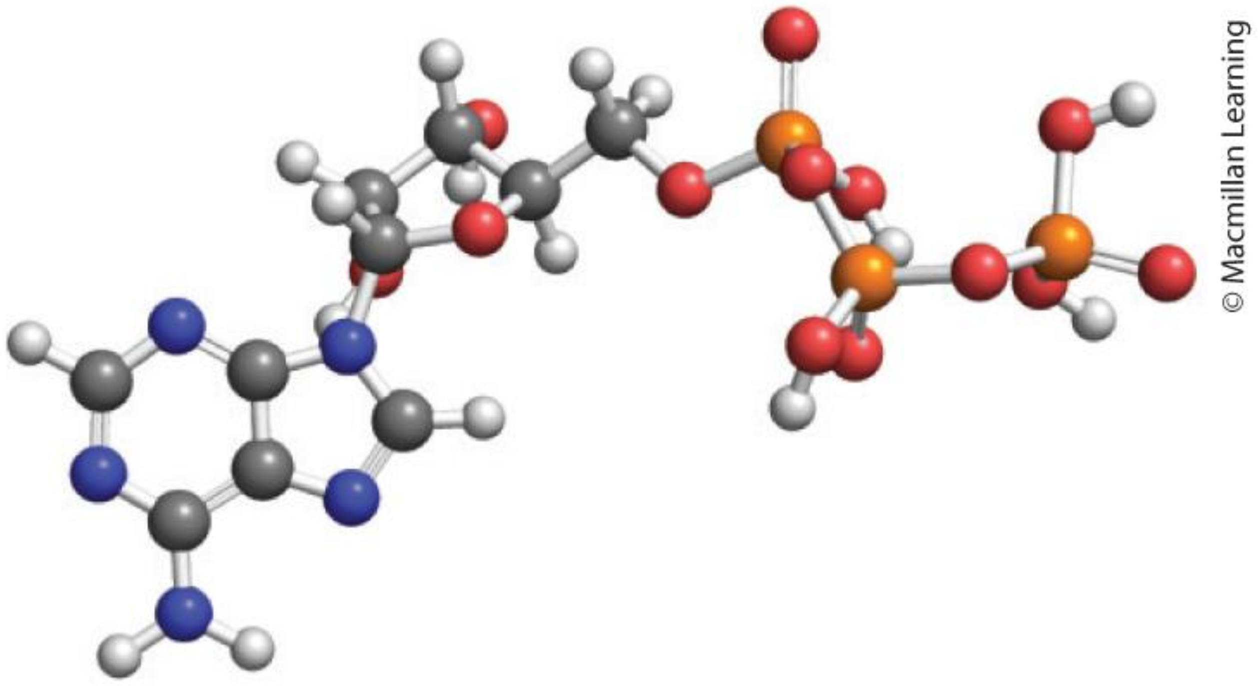
Phosphorus Oxides and Oxoacids

- Phosphates contain the tetrahedral PO_4^{3-} anion and are of great commercial importance.
- Phosphate rock is mined in huge quantities in Florida and Morocco.
- After being crushed, it is treated with sulfuric acid to give a mixture of sulfates and phosphates called superphosphate, a major fertilizer:

$$Ca_3(PO_4)_2\,(s) + 2\,H_2SO_4\,(l) \rightarrow 2\,CaSO_4\,(s) + Ca(H_2PO_4)_2\,(s)$$

ATP

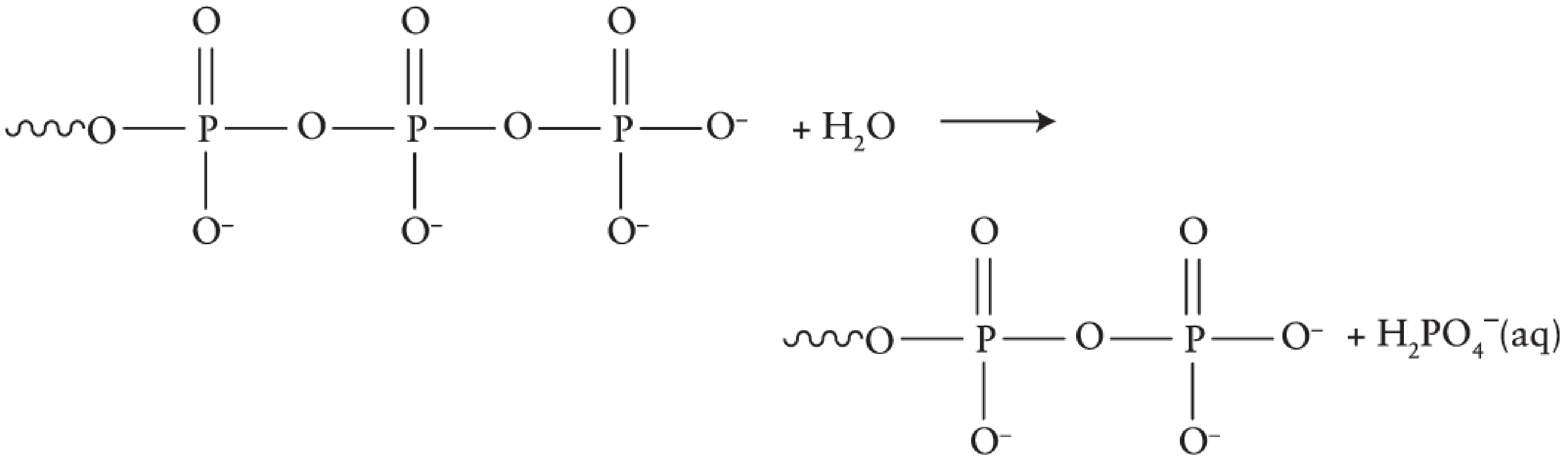
- The most important polyphosphoric acid is adenosine triphosphate, ATP.



7 Adenosine triphosphate, ATP

ATP

- Converting three phosphate groups into adenosine diphosphate, ADP (~~wiggly line indicates the rest of the molecule) releases a large amount of energy (ΔG° = –30 kJ at pH = 7), which is used to power energy-demanding cells.



Group 16: The Oxygen Family

- The elements become increasingly nonmetallic toward the right-hand ide of the periodic table. By Group 16, even polonium is best regarded as a metalloid.
- The valence electron configuration of the Group 16 elements is ns2np4, where n is the period number. The Group 16 elements are only two electrons short of a closed-shell, noble-gas configuration, and the effective nuclear charge is high.
- When elements in Group 16 form compounds with other nonmetals, they form covalent bonds. Electronegativities decrease down Group 16.

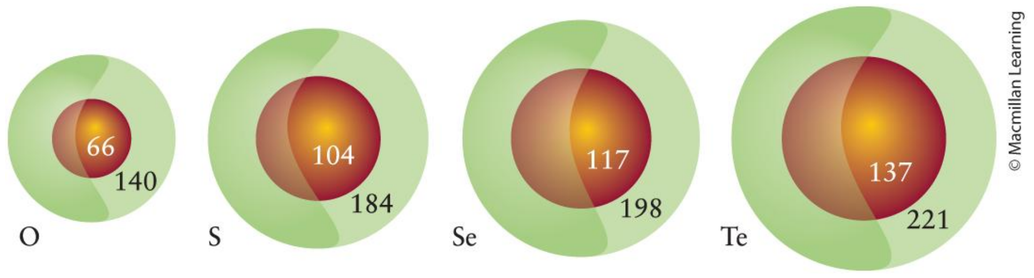
Group 16: The Oxygen Family

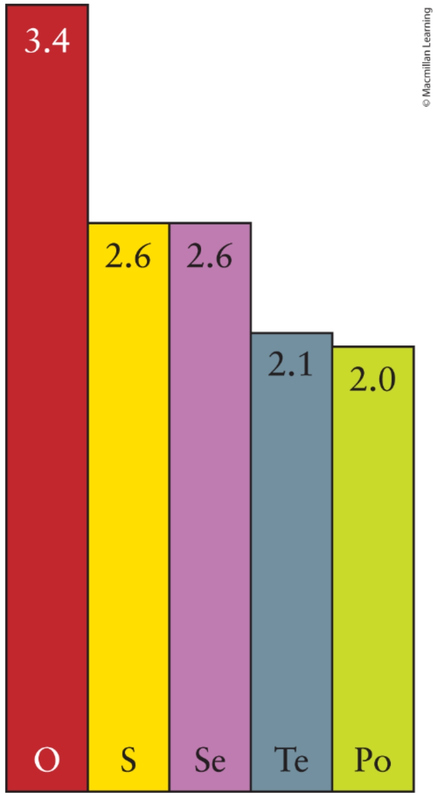
- Valence configuration: ns2np4

Z	Name	Symbol	Molar mass/ ($g \cdot mol^{-1}$)	Melting point/°C	Boiling point/°C	Density/ ($g \cdot cm^{-3}$)	Normal form*
8	oxygen	O	16.00	−218 −192	−183 −112	1.14† 1.35†	colorless paramagnetic gas (O_2) blue gas (ozone, O_3)
16	sulfur	S	32.06	115	445	2.09	yellow nonmetallic solid (S_8)
34	selenium	Se	78.96	220	685	4.79	gray nonmetallic solid
52	tellurium	Te	127.60	450	990	6.25	silver-white metalloid
84	polonium‡	Po	(209)	254	960	9.40	gray metalloid

The Group 16 Elements

- The members of the group are called chalcogens, broadly interpreted as “ore giver” as the elements are commonly found with metals in ores.
- Atomic and ionic radii increase down the group. Electronegativities decrease down the group.



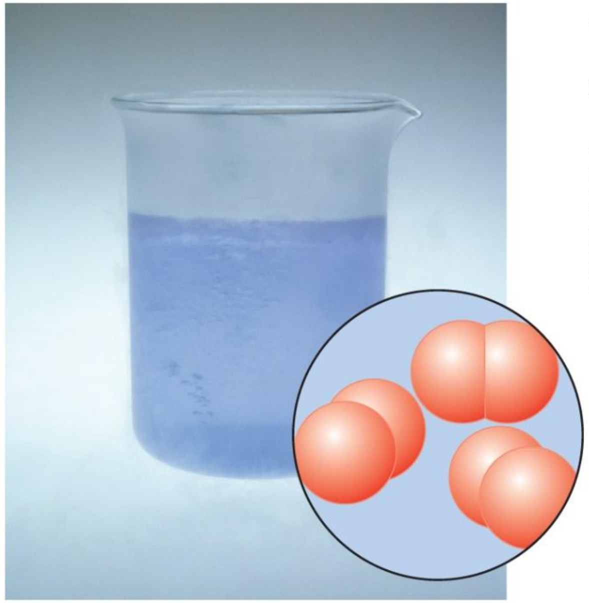


Oxygen

- Oxygen is the most abundant element in the Earth's crust, and the oxygen we breathe, O_2, is 23% of the atmosphere's mass. Oxygen is more reactive than nitrogen, which is the other major component of our atmosphere.
- The combustion of all living organisms in oxygen is thermodynamically spontaneous; however, plants and animals do not burst into flame at normal temperatures because combustion has a high activation energy.

Oxygen

- Oxygen, O_2, is a colorless, tasteless, odorless gas; it condenses as a pale-blue liquid at –183 °C. It is paramagnetic; it behaves like a tiny magnet in a magnetic field.
- More than 2 × 1010 kg of liquid oxygen is produced each year in the United States (80 kg per person) by fractional distillation of liquid air.
- The biggest consumer is the steel industry, where 1 t of oxygen (1 t = 103 kg) produces 1 t of steel.



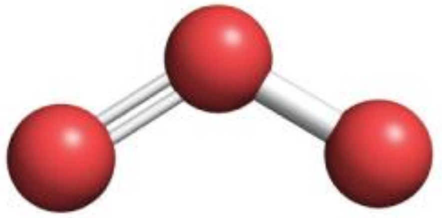
Oxygen

- Ozone, O_3, is an allotrope of oxygen, formed in the stratosphere by the solar bombardment on O_2 molecules. Its total atmospheric abundance is equivalent to a layer only 3 mm thick, yet it is vital to life on Earth. Ozone is present in smog, where it is produced by the reaction of oxygen molecules with oxygen atoms.

$$O\,(g) + O_2\,(g) \rightarrow O_3\,(g)$$

- The oxygen atoms are produced by the photochemical decomposition of NO_2.

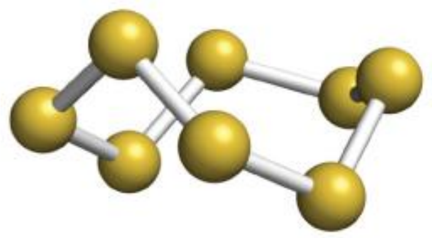
$$NO_2(g) \xrightarrow{UV\ radiation} NO\,(g) + O\,(g)$$



1 Ozone, O_3

Sulfur

- Sulfur has a striking ability to catenate, that is to form chains of atoms, whereas oxygen is limited to H_2O_2, O_3, and the anions O^{2-}, O_3^{2-}, and O_3^{2-}.
- Sulfur's S8 rings form long strands of "plastic sulfur" when sulfur is heated to about 200 °C and suddenly cooled.
- The –S–S– links are found in amino acids of proteins and keratin of our hair and is responsible for curly hair.



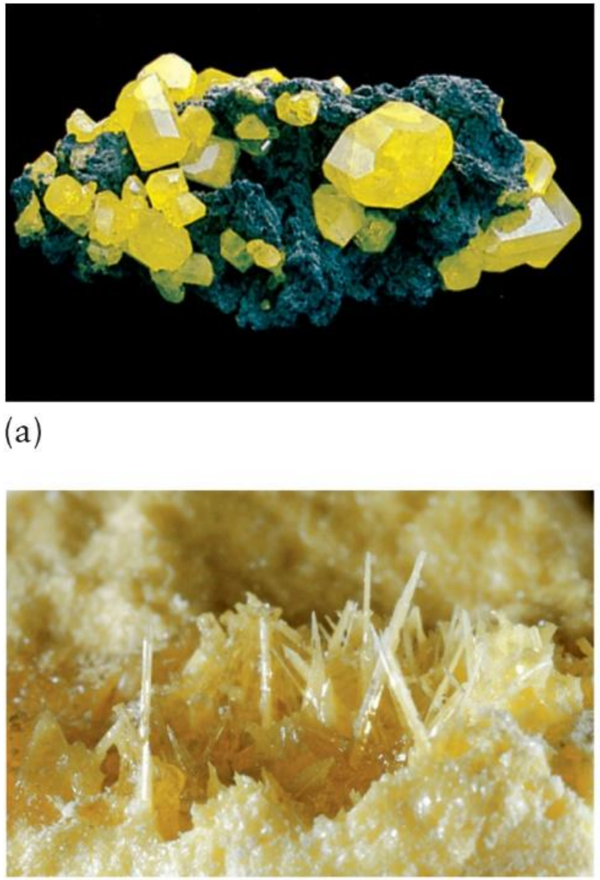
2 Sulfur, S_8

Sulfur

- Sulfur is widely distributed as sulfide ores, including (from left to right) galena, PbS; cinnabar, HgS; pyrite, FeS_2; and sphalerite, ZnS.
- Sulfur is found in its elemental solid or crystalline state, called brimstone, formed by bacterial action on H_2S.

Sulfur

- Sulfur is of major industrial importance. Most of the sulfur is used to make sulfuric acid, but an appreciable amount is used to vulcanize rubber.
- Elemental sulfur is yellow, tasteless, almost odorless, insoluble, nonmetallic molecular solid of crown-like S8 rings. Two common forms are (a) rhombic sulfur and (b) monoclinic sulfur.



(a)

(b)

Selenium, Tellurium, and Polonium

- Selenium, Se, and tellurium, Te, occur in sulfide ores; they are recovered during the electrolytic refining of copper. Both elements have several allotropes. Although the allotropes look like silver-white metals, they are poor conductors. When selenium is exposed to light its conductivity increases, so it is found in solar cells.

- Polonium is radioactive, a source of He-4 nuclei. The He nuclei is a good antistatic material used in the textiles industry.

Water

- Water is a common solvent, but it also a reactive compound.
- Water is an oxidizing agent.

$$2\ H_2O\ (l) + 2\ e^- \rightarrow 2\ OH^-\ (aq) + H_2\ (g)$$

- One example is its reaction with the alkali metals.

$$2\ Na\ (s) + H_2O\ (l) \rightarrow NaOH\ (aq) + H_2\ (g)$$

- However, unless the other reacant is a strong reducing agent, water acts as an oxidizing agent only at high temperatures.

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Water

- Water is also a very mild reducing agent.

$$4\,H^+\,(aq) + O_2\,(g) + 4\,e^- \rightarrow 2\,H_2O\,(l)$$

- Water is also a Lewis base and can donate one of its lone pairs to a Lewis acid to form complexes such as $Fe(H_2O)_6^{3+}$.

$$FeCl_3\,(s) + H_2O\,(l) \rightarrow Fe(H_2O)63^{+}\,(aq)$$

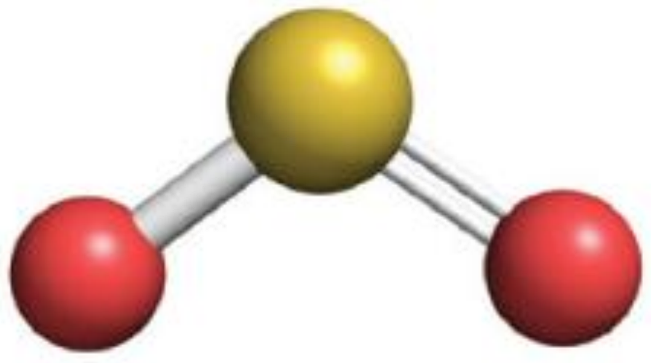
- Water's ability to act as a Lewis base is the basis for its ability to hydrolyze substances such as phosphorus pentachloride.

Other Group 16 Compounds with Hydrogen

- After oxygen, all other Group 16 binary compounds with hydrogen are offensive and toxic. The gases paralyze the olfactory nerve, and soon the victim can not smell the gas. Rotten eggs smell of hydrogen sulfide, H_2S, because egg proteins contain sulfur and give off the gas when they decompose.
- Sulfides, S_2^-, are soluble with s-block metals and insoluble with d-block metals.
- Sulfur can form peroxide-like molecules, polysulfanes, a cantenated form with a composition of $HS–S_n–SH$, where n = 1 through 6.

Sulfur Oxides and Oxoacids

- Sulfur forms several oxides. In atmospheric chemistry, these are referred to as SOx (read “sox”).
- The most important are the dioxide and trioxide as well as the corresponding sulfurous and sulfuric acids.
- SO_2 is produced in nature as well as from human activities in industry and transport. Naturally occuring H_2S is oxidized to dioxide by atmospheric oxygen.



4 Sulfur dioxide, SO_2

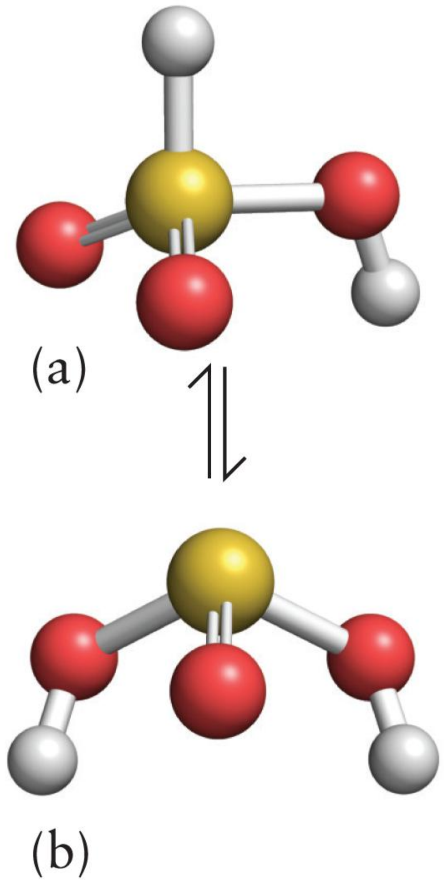
$$2\ H_2S\ (g) + 3\ O_2\ (g) \rightarrow\ 2\ SO_2\ (g) + 2\ H_2O\ (g)$$

- SO_2 reacts with water to make sulfurous acid.

$$SO_2\ (g) + 2\ H_2O\ (g) \rightarrow\ H_2SO_3\ (aq)$$

Sulfur Oxides and Oxoacids

- Sulfurous acid, H_2SO_3, is actually in equilibrium with SO_2 and water. Crystals of composition $SO_2{\cdot}x\ H_2O$, with x ≈ 7, are obtained when the solution is cooled.
- The molecules form into a cage called clathrates.
- Methane, carbon dioxide, and the noble gases also form clathrates with water.



5 Sulfurous acid, H_2SO_3

Sulfuric Acid (1 of 2)

- Sulfuric acid, H_2SO_4, is made through the contact process, in which sulfur burns in oxygen, then uses a V_2O_5 catalyst to make SO_3.

$$S\,(s) + O_2(g) \xrightarrow{1000\ ^\circ C} SO_2(g)$$

$$2\,SO_2(g) + O_2(g) \xrightarrow{500\ ^\circ C,\ V_2O_5} 2\,SO_3(g)$$

  SO_3 reacts with water vapor in the air. It transforms into oleum, a dense oily liquid which is an easier form to transport.

$$SO_3\,(g) + H_2SO_4\,(l) \rightarrow H_2S_2O_7\,(g)$$

- Oleum is then converted to sulfuric acid by reaction with water.

$$H_2S_2O_7\,(g) + H_2O\,(l) \rightarrow H_2SO_4\,(l)$$

Sulfuric Acid

- Sulfuric acid, H_2SO_4, is worldwide the most heavily produced inorganic chemical. The annual production in the United States alone is more than 4 × 1010 kg.
- The low cost of sulfuric acid production leads to its widespread use for the production of fertilizers, petrochemicals, dyestuffs, and detergents.
- H_2SO_4, is a very strong acid, and even its conjugate base HSO_4^- has a pKa of 1.92, which is a strong acid.

Group 17:
The Halogens

- The valence electron configuration of the Group 17 elements is ns2np5, where n is the period number. The Group 17 elements are only one electron short of a closed-shell configuration.
- To complete the octet of valence electrons, in the elemental state, all halogens form diatomic molecules, such as F2.
- With the exception of fluorine, halogens can also lose valence electrons and their oxidation numbers can range from −1 to +7.

Group 17: The Halogens

- Valence configuration: ns2np5

Z	Name	Symbol	Molar mass/ ($g \cdot mol^{-1}$)	Melting point/°C	Boiling point/°C	Density/ ($g \cdot cm^{-3}$)	Normal form*
9	fluorine	F	19.00	−220	−188	1.51	almost colorless gas
17	chlorine	Cl	35.45	−101	−34	1.66	yellow-green gas
35	bromine	Br	79.90	27	59	3.12	red-brown liquid
53	iodine	I	126.90	114	184	4.95	purple-black nonmetallic solid
85	astatine‡	At	(210)	300	350	–	nonmetallic solid

Fluorine

- Fluorine is the most abundant halogen in Earth's crust. Common minerals include fluorite (fluorspar), CaF_2; cryolite, Na_3AlF_6; and fluorapatite, $Ca_5(PO_4)_3F$.
- Since fluorine is the most strongly oxidizing element ($E° = +2.87$ V), it cannot be obtained by oxidation of another element.
- Fluorine is produced by electrolyzing molten KF and HF at about 75 °C with a carbon anode.
- Fluorine is a highly reactive, almost colorless gas of F_2 molecules.

Fluorine

- Most of the fluorine is used to make volatile solid UF_6 for processing nuclear fuel. The rest is used for producing SF_6 for electrical equipment.
- Fluorine is the most electronegative element and has an oxidation number of −1 in all its compounds. It is small and has a high effective nuclear charge. Therefore, its lattice energies are high, and its solubilities are low. Its low solubility is one of the reasons why the oceans are primarily chloride.
- Silver fluoride, AgF, is an exception. It is freely soluble in water because it is predominately ionic.

Chlorine

- Chlorine, Cl_2, is one of the most heavily manufactured chemicals worldwide. It is a pale yellow-green gas.
- It is obtained from sodium chloride by electrolysis of molten rock salt or brine.
- It reacts directly with nearly all the elements (except for carbon, nitrogen, oxygen, and the noble gases).
- Chlorine is used to manufacture of plastics, solvents, and pesticides. Bleach (NaClO) is added to paper, textiles and a disinfectant in water treatment.

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Bromine

- Bromine, Br, is a corrosive, red-brown fuming liquid of Br_2 molecules and has a penetrating odor. Chlorine is used to produce bromine from brine wells.

$$2\ \mathrm{Br^-}\,(\mathrm{aq})\ +\mathrm{CI_2}\,(\mathrm{g}) \rightarrow \mathrm{Br_2}\,(\mathrm{l}) + 2\ \mathrm{Cl^-}\,(\mathrm{aq})$$

- Bromine is used widely in synthetic organic chemistry.
- Organic bromides are incorporated into textiles as fire retardants and are used as pesticides; inorganic bromides, particularly silver bromide, are used in photographic emulsions.

Iodine and Astatine

- Iodine, I, occurs as iodide ions in brines and as an impurity in Chile saltpeter. It was once obtained from seaweed.
- Elemental iodine is produced by oxidation with chlorine.

$$2\ I^{-}\ (aq)\ +\ CI_2\ (g) \rightarrow I_2\ (l) + 2\ Cl^{-}\ (aq)$$

- I_2 is a blue-black lustrous solid that sublimes easily, forming a purple vapor. I_2 is slightly soluble in water, more so in ethanol. It is used as an antiseptic. Living organisms need trace amounts of iodine, so it is added to table salt (sold as “iodized salt.”)
- Astatine is radioactive and occurs with heavy elements like uranium.

Hydrogen Halides

- Hydrogen halides, HX, can be prepared by the direct reaction of the elements.

$$H_2\,(g) + X_2\,(g) \rightarrow 2\ HX\,(g)$$

- Fluorine reacts explosively by a radical chain reaction. Chlorine and hydrogen also explode when exposed to light. A more stable route to prepare hydrogen halides is the action of a nonvolatile acid on a metal halide.

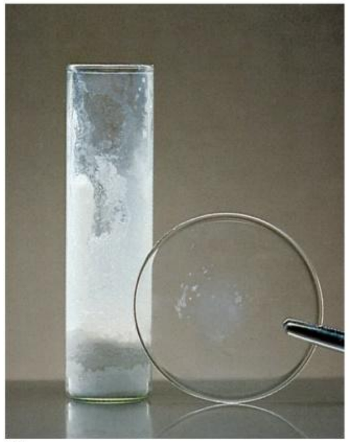
$$CaF_2\,(s)\ +\ 2\ H_2SO_4\,(aq) \rightarrow Ca(HSO_4)_2\,(aq)\ +\ 2\ HF\,(g)$$

- Bromine and iodine are oxidized by sulfuric acid, so phosphoric acid is used to prepare HBr and HI.

Hydrogen Halides

- HF can etch glass. Hydrofluoric acid attacks glass and silica. Interiors light bulbs are frosted with vapors of aqueous hydrofluoric acid and ammonium fluoride.
- HF, is used to make fluorinated carbon compounds, such as Teflon (polytetrafluoroethylene) and the refrigerant R134a (CF_3CH_2F) which does not contribute to global warming.
- Teflon is impervious to most acids, including hot nitric acid, so is used in cooking ware.

(a)



(b)

Halogen Oxoacids and Oxoanions

- Hypohalous acid, HXO, a halogen and water.

$$Cl_2\,(g) + H_2O\,(l) \rightarrow 2\,HClO\,(aq)\ +\ HCl\,(g)$$

- This is referred to as a disproportionation reaction since the Cl_2, 0 oxidation number, produces a +1 Cl in HClO, and a –1 Cl in HCl (the combined oxidation numbers are still 0).
- HClO is found in bleach as a disinfectant; it is also an oxidizing agent.

$$2\,HClO\,(aq) \rightarrow 2\,H^{+}\,(aq) + 2\,Cl^{-}\,(aq) + O_2\,(g)$$

- Oxygen is thought to oxidize organic matter.

Halogen Oxoacids and Oxoanions

- Chlorate ions, ClO_3^-, forms when chlorine reacts with hot, concentrated aqueous alkalis.

$$3\,Cl_2\,(g) + 6\,OH^-\,(aq) \rightarrow ClO_3^-\,(aq) + 5\,Cl^-\,(aq) + 3\,H_2O\,(l)$$

$$4\,KClO_3(s) \xrightarrow{\Delta} 3\,KClO_4(s) + KCl\,(s)$$

- Chlorates are strong oxidizing agents. A paste of KClO3 is added to match heads to help ignite phosphorus, also found in fireworks.

$$2\,KClO_3(s) \xrightarrow{\Delta, MnO_2} 2\,KCl\,(s) + 3\,O_2(g)$$

Halogen Oxoacids and Oxoanions

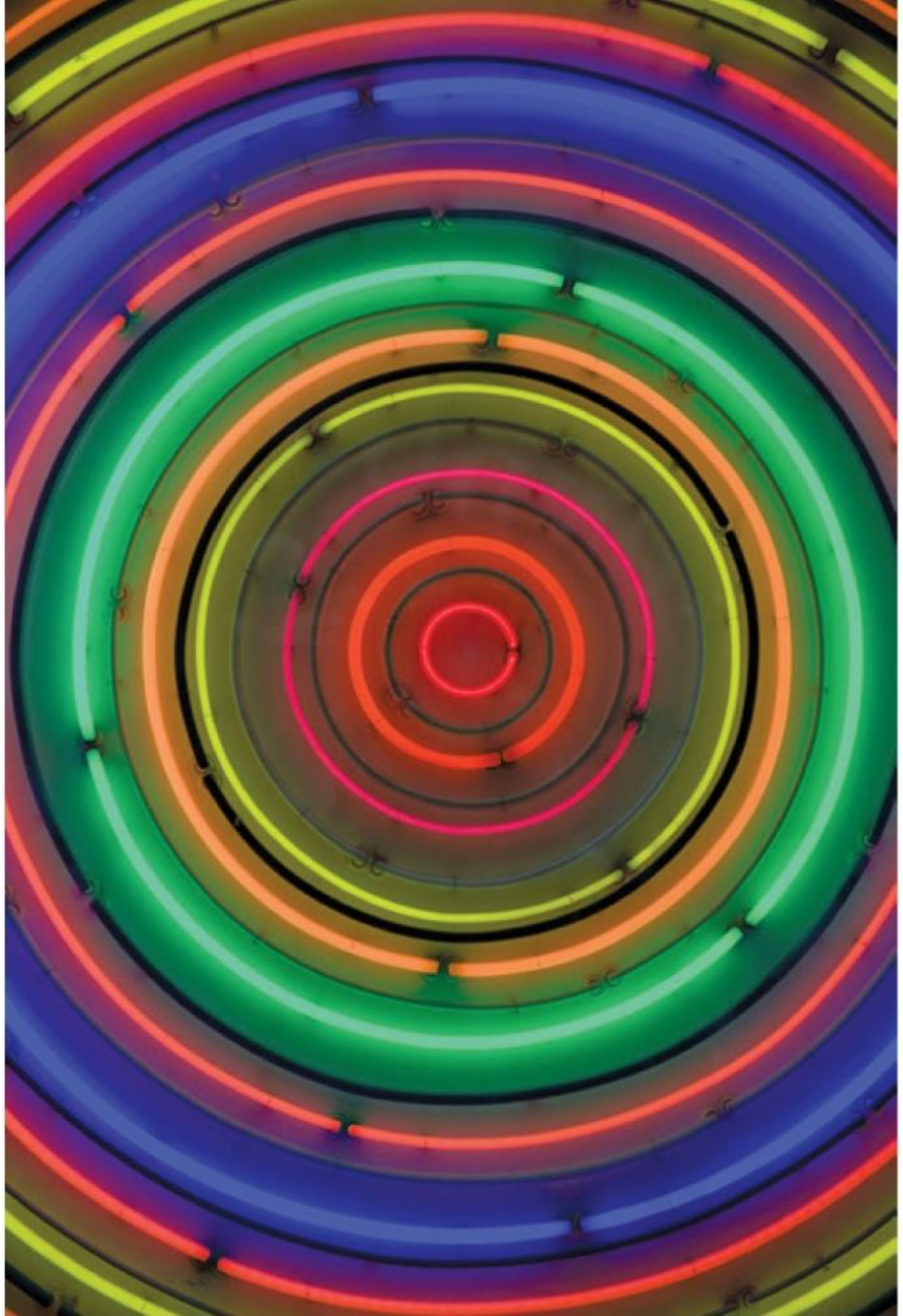
- The perchlorates, ClO_4^- (chlorine oxidation state +7), are prepared by electrolytic oxidation of aqueous chlorates.

$$ClO_3^-(aq) + H_2O\ (l) \rightarrow ClO_4^-(aq) + 2\ H^+(aq) + 2\ e^-$$

- One spectacular example of the oxidizing ability of perchlorates is their use in the booster rockets of space shuttles. This is a solid propellant.

NASA/Scott Andrews.

$$3\ NH_4ClO_4(s) + 3\ Al\ (s) \xrightarrow{Fe_2O_3} Al_2O_3(s) + AlCl_3(s) + 6\ H_2O\ (g) + 3\ NO\ (g)$$



Andrea Heselton/Alamy

Group 18: The Noble Gases

- The valence electron configuration of the Group 18 elements is ns2np6, where n is the period number. Noble gases get their group name from their very low reactivity.
- No compound of a noble gas was known until 1962. The British chemist Neil Bartlett synthesized the first noble-gas compound, xenon hexafluoroplatinate, XePtF6.
- Soon after, chemists at Argonne National Laboratory made xenon tetrafluoride, XeF4.

Group 18: The Noble Gases

- Common name: noble gases
- Valence configuration: ns2np6
- Normal form: colorless monatomic gas

Z	Name	Symbol	Molar mass/ $(g{\cdot}mol^{-1})$	Melting point/°C	Boiling point/°C
2	helium	He	4.00	–	−269 (4.2 K)
10	neon	Ne	20.18	−249	−246
18	argon	Ar	39.95	−189	−186
36	krypton	Kr	83.80	−157	−153
54	xenon	Xe	131.29	−112	−108
86	radon*	Rn	(222)	−71	−62

The Group 18 Elements

- All the Group 18 elements occur as gases in the atmosphere; together they make up about 1% of its mass.
- Argon is the third most abundant gas in the atmosphere, after nitrogen and oxygen.
- All the noble gases except helium and radon are obtained by fractional distillation of liquid air.

Helium

- Helium, the second most abundant element in the universe after hydrogen, is rare on Earth because it is so light that the molecules easily reach high speeds and escape from the atmosphere.
- Helium is mined (notably in Texas) where it has collected as a result of the emission of a particles by radioactive elements.
- Helium has a low density and is nonflammable, so it used to dilute oxygen for use in hospitals and in deep-sea diving, to pressurize rocket fuels, as a coolant, and in helium-neon lasers.

Helium

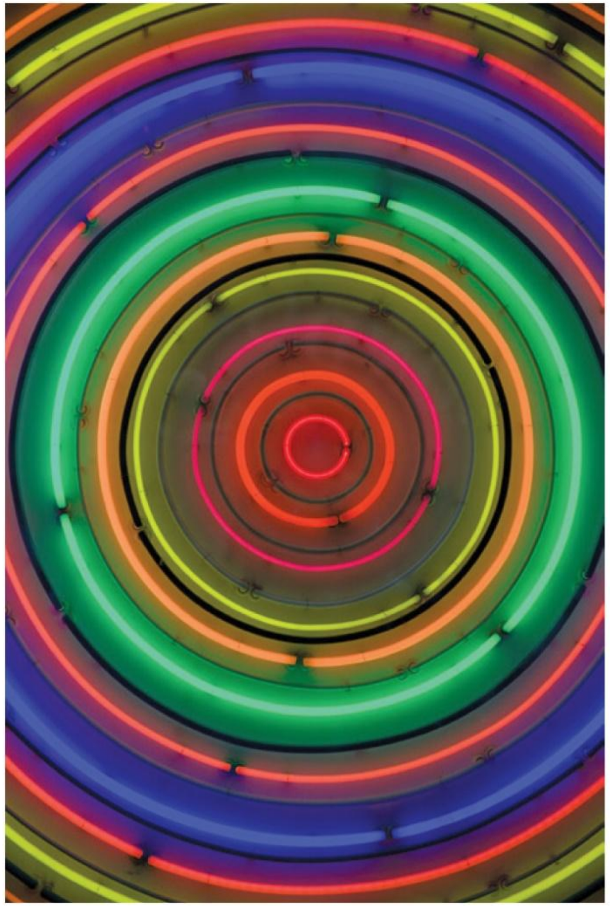
- Helium has the lowest boiling point of any substance (4.2 K). It does not freeze to a solid at any temperature unless pressure is applied. These properties make it useful in the study of cryogenics, the study of matter at very low temperatures, such as those for the study of superconductivity.
- Helium is the only substance to have more than one liquid phase. Below 2K, liquid helium-II shows the property of superfluidity, the ability to flow without viscosity.

Neon, Argon, Krypton, and Xenon

- Neon emits an orange-red glow when an electric current flows through it, so it is used in advertising signs and displays.
- Argon is used to provide an inert atmosphere for welding (to prevent oxidation) and to fill some types of light bulbs.
- Krypton gives an intense white light when electrically excited. Krypton is a nuclear fission by-product and is used as a way to measure worldwide nuclear activity.
- Xenon is used in halogen lamps, high-speed photographic flash tubes and is being investigated as an anesthetic.

Neon, Argon, Krypton, and Xenon

- The colors of the fluorescent lighting art are due to emission from noble-gas atoms. Neon is responsible for the red light; when it is mixed with a little argon, the color becomes blue-green. The yellow is achieved by coating the inside of the glass with phosphors that give off yellow light when excited.



Andrea Heselton/Alamy.

Compounds of the Noble Gases

- No compounds of helium, neon, and argon exist, except under very special conditions, such as the capture of atoms of He and Ne inside a buckminsterfullerene cage.
- Argon fluoride can be created transiently as an active medium in lasers. Argon fluorohydride, HArF, is only stable below 27 K.
- Krypton only forms one known stable molecule, KrF2. A molecule with a Kr–N bond has been reported, but it is only stable below −50 °C.

Compounds with Xenon

- Xenon difluoride, XeF2, and xenon tetrafluoride, XeF4, are made by heating the elements to 400 °C at 6 atm.
- The xenon fluorides are powerful fluorinating agents.

$$Pt\,(s) + XeF_4\,(s) \rightarrow Xe\,(g) + PtF_4\,(s)$$

Argonne National Laboratory/Science Source.

XeF_4, reported in 1962