

7.3: The Chemical Families

Learning Objectives

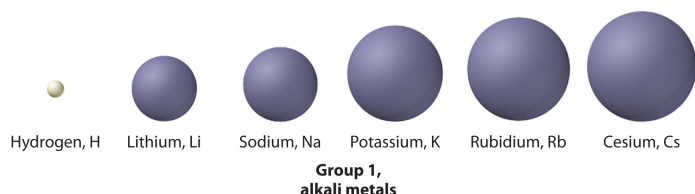
- To understand the correlation between the chemical properties and the reactivity of the elements and their positions in the periodic table

Periodic trends in properties such as atomic size and ionic size, ionization energy, electron affinity, and electronegativity illustrate the strong connection between the **chemical properties** and the reactivity of the elements and their positions in the periodic table. In this section, we explore that connection by focusing on two periodic properties that correlate strongly with the chemical behavior of the elements: valence electron configurations and Mulliken electronegativities.

The Main Group Elements

We have said that elements with the same valence electron configuration (i.e., elements in the same column of the periodic table) often have similar chemistry. This correlation is particularly evident for the elements of groups 1, 2, 3, 13, 16, 17, and 18. The intervening families in the *p* block (groups 14 and 15) straddle the diagonal line separating metals from nonmetals. The lightest members of these two families are nonmetals, so they react differently compared to the heaviest members, which are metals. We begin our survey with the alkali metals (group 1), which contain only a single electron outside a noble gas electron configuration, and end with the noble gases (group 18), which have full valence electron shells.

Group 1: The Alkali Metals



The elements of group 1 are called the *alkali metals*. *Alkali* (from the Arabic *al-qili*, meaning “ashes of the saltwort plant from salt marshes”) was a general term for substances derived from wood ashes, all of which possessed a bitter taste and were able to neutralize acids. Although oxides of both group 1 and group 2 elements were obtained from wood ashes, the alkali metals had lower melting points.

Potassium and sodium were first isolated in 1807 by the British chemist Sir Humphry Davy (1778–1829) by passing an electrical current through molten samples of potash (K_2CO_3) and soda ash (Na_2CO_3). The potassium burst into flames as soon as it was produced because it reacts readily with oxygen at the higher temperature. However, the group 1 elements, like the group 2 elements, become less reactive with air or water as their atomic number decreases. The heaviest element (francium) was not discovered until 1939. It is so radioactive that studying its chemistry is very difficult.

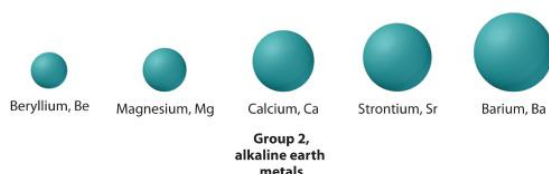
The alkali metals have ns^1 valence electron configurations and the lowest electronegativity of any group; hence they are often referred to as being *electropositive* elements. As a result, they have a strong tendency to lose their single valence electron to form compounds in the +1 oxidation state, producing the EX monohalides and the E_2O oxides.

Reducing agents are species that can lose an electron in a reaction. Alkali metals with only a single *s* electron, and very low ionization energies can easily do this and thus are powerful reducing agents. Sodium salts such as common table salt ($NaCl$), baking soda ($NaHCO_3$), soda ash (Na_2CO_3), and caustic soda ($NaOH$) are important industrial chemicals. Other compounds of the alkali metals are important in biology. For example, because potassium is required for plant growth, its compounds are used in fertilizers, and lithium salts are used to treat manic-depressive, or bipolar, disorders. The best modern batteries use lithium.

We can watch a video demonstration of the properties of lithium, sodium and potassium. Rubidium and cesium are extremely reactive and difficult to handle in the atmosphere when there is any water vapor present



Group 2: The Alkaline Earth Metals



The elements of group 2 are collectively referred to as the *alkaline earth metals*, a name that originated in the Middle Ages, when an “earth” was defined as a substance that did not melt and was not transformed by fire. Alkalies that did not melt easily were called “alkaline earths.”

Recall that the trend in most groups is for the lightest member to have properties that are quite different from those of the heavier members. Consistent with this trend, the properties of the lightest element—in this case, beryllium—tend to be different from those of its heavier *congeners*, the other members of the group. Beryllium is relatively unreactive but forms many covalent compounds, whereas the other group members are much more reactive metals and form ionic compounds. As is the case with the alkali metals, the heaviest element, radium, is highly radioactive, making its size difficult to measure. Radium was discovered in 1902 by Marie Curie (1867–1934; Nobel Prize in Chemistry 1903 and Nobel Prize in Chemistry 1911), who, with her husband, Pierre, isolated 120 mg of radium chloride from tons of residues from uranium mining.

All the alkaline earth metals have ns^2 valence electron configurations, and all have electronegativities less than 1.6. This means that they behave chemically as metals (although beryllium compounds are covalent) and lose the two valence electrons to form compounds in the +2 oxidation state. Examples include the dihalides (EX_2) and the oxides (EO).

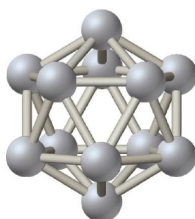
Compounds of the group 2 elements have been commercially important since Egyptian and Roman times, when blocks of limestone or marble, which are both $CaCO_3$, were used as building materials, and gypsum ($CaSO_4 \cdot 2H_2O$) or lime (CaO) was used as mortar. Calcium sulfate is still used in Portland cement and plaster of Paris. Magnesium and beryllium form lightweight, high-strength alloys that are used in the aerospace, automotive, and other high-tech industries. As you learned previously, one of the most impressive uses of these elements is in fireworks; strontium and barium salts, for example, give red or green colors, respectively. Except for beryllium, which is highly toxic when powdered, the group 2 elements are also important biologically. Bone is largely hydroxyapatite [$Ca_5(PO_4)_3OH$], mollusk shells are calcium carbonate, magnesium is part of the chlorophyll molecule in green plants, and calcium is important in hormonal and nerve signal transmission. Because $BaSO_4$ is so insoluble, it is used in “barium milk shakes” to obtain x-rays of the gastrointestinal tract. Reaction of the Alkaline earth metals with water is not quite so . . . exciting as that of the alkali metals as seen in this video from the University of Southampton



Group 13



Of the group 13 elements, only the lightest, boron, lies on the diagonal line that separates nonmetals and metals. Thus boron is a semimetal, whereas the rest of the group 13 elements are metals. Elemental boron has an unusual structure consisting of B_{12} icosahedra covalently bonded to one another; the other elements are typical metallic solids.



B_{12} icosahedron in elemental boron

No group 13 elements were known in ancient times, not because they are scarce—Al is the third most abundant element in Earth's crust—but because they are highly reactive and form extremely stable compounds with oxygen. To isolate the pure elements, potent reducing agents and careful handling were needed.

The elements of group 13 have ns^2np^1 valence electron configurations. Consequently, two oxidation states are important: +3, from losing three valence electrons to give the closed-shell electron configuration of the preceding noble gas; and +1, from losing the single electron in the np subshell. Because these elements have small, negative electron affinities (boron's is only -27.0 kJ/mol), they are unlikely to acquire five electrons to reach the next noble gas configuration. In fact, the chemistry of these elements is almost exclusively characterized by +3. Only the heaviest element (Tl) has extensive chemistry in the +1 oxidation state. It loses the single $6p$ electron to produce TlX monohalides and the oxide Tl_2O .

In the 19th century, aluminum was considered a precious metal. In fact, it was considered so precious that aluminum knives and forks were reserved for the French Emperor Louis Napoleon III, while his less important guests had to be content with gold or silver cutlery. Because of the metal's rarity the dedication of the Washington Monument in 1885 was celebrated by placing a 100 oz chunk of pure aluminum at the top. In contrast, today aluminum is used on an enormous scale in aircraft, automobile engines, armor, cookware, and beverage containers. It is valued for its combination of low density, high strength, and corrosion resistance. Aluminum is also found in compounds that are the active ingredients in most antiperspirant deodorants.

Compounds of boron, such as one form of BN, are hard, have a high melting point, and are resistant to corrosion. They are particularly useful in materials that are exposed to extreme conditions, such as aircraft turbines, brake linings, and polishing compounds. Boron is also a major component of many kinds of glasses, and sodium perborate $[Na_2B_2O_4(OH)_4]$ is the active ingredient in many so-called color-safe laundry bleaches.

Gallium, indium, and thallium are less widely used, but gallium arsenide is the red light-emitting diode (LED) in digital readouts in electronics, and MgGa_2O_4 produces the green light emitted in many xerographic machines. Compounds of thallium(I) are extremely toxic. Although Tl_2SO_4 is an excellent rat or ant poison, it is so toxic to humans that it is no longer used for this purpose.

Group 14



The group 14 elements straddle the diagonal line that divides nonmetals from metals. Of the elements in this group, carbon is a nonmetal, silicon and germanium are semimetals, and tin and lead are metals. As a result of this diversity, the structures of the pure elements vary greatly.

The ns^2np^2 valence electron configurations of group 14 gives rise to three oxidation states: -4 , in which four electrons are added to achieve the closed-shell electron configuration of the next noble gas; $+4$, in which all four valence electrons are lost to give the closed-shell electron configuration of the preceding noble gas; and $+2$, in which the loss of two np^2 electrons gives a filled ns^2 subshell.

The electronegativity of carbon is only 2.5, placing it in the middle of the electronegativity range, so carbon forms covalent compounds with a wide variety of elements and is the basis of all organic compounds. All of the group 14 elements form compounds in the $+4$ oxidation state, so all of them are able to form dioxides (from CO_2 to PbO_2) and tetrachlorides (CCl_4 and PbCl_4). Only the two metallic elements, Sn and Pb, form an extensive series of compounds in the $+2$ oxidation state. Tin salts are sprayed onto glass to make an electrically conductive coating, and then the glass is used in the manufacture of frost-free windshields. Lead sulfate is formed when your car battery discharges.

Carbon has at least four allotropes (forms or crystal structures) that are stable at room temperature: graphite; diamond; a group of related cage structures called fullerenes (such as C_{60}); nanotubes, which are cylinders of carbon atoms and are intermediate in structure between graphite and the fullerenes; and graphene which is a single atomic layer of carbon atoms covalently bonded. Graphite consists of extended planes of covalently bonded hexagonal rings. Because the planes are not linked by covalent bonds, they can slide across one another easily. This makes graphite ideally suited as a lubricant and as the “lead” in lead pencils mixed with a bit of clay as a binder. Graphite also provides the black color in inks and tires, and graphite fibers are used in high-tech items such as golf clubs, tennis rackets, airplanes, and sailboats because of their lightweight, strength, and stiffness.

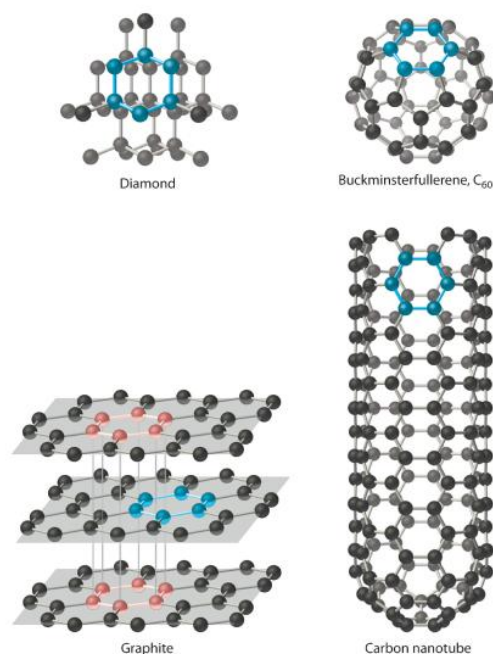


Figure 3.4.1 Four Allotropes of **Carbon**. Diamond consists of a rigid three-dimensional array of carbon atoms, making it one of the hardest substances known. In contrast, graphite forms from extended planes of covalently bonded hexagonal rings of carbon atoms that can slide across one another easily. Fullerenes are spherical or ellipsoidal molecules with six- and five-membered rings of carbon atoms, and nanotubes are sheets of graphite rolled up into a cylinder.

In contrast to the layered structure of graphite, each carbon atom in diamond is bonded to four others to form a rigid three-dimensional array, making diamond one of the hardest substances known; consequently, it is used in industry as a cutting tool. Fullerenes, on the other hand, are spherical or ellipsoidal molecules with six- and five-membered rings of carbon atoms; they are volatile substances that dissolve in organic solvents. Fullerenes of extraterrestrial origin have been found in meteorites and have been discovered in a cloud of cosmic dust surrounding a distant star, which makes them the largest molecules ever seen in space. Carbon nanotubes, intermediate in structure between graphite and the fullerenes, can be described as sheets of graphite that have been rolled up into a cylinder or, alternatively, fullerene cages that have been stretched in one direction. Carbon nanotubes are being studied for use in the construction of molecular electronic devices and computers. For example, fabrics that are dipped in an ink of nanotubes and then pressed to thin out the coating are turned into batteries that maintain their flexibility. This creates “wearable electronics” and allows for the possibility of incorporating electronics into flexible surfaces. When applied to a t-shirt, for example, the t-shirt is converted into an “e-shirt.”

Silicon is the second most abundant element in Earth’s crust. Both silicon and germanium have strong, three-dimensional network structures similar to that of diamond. Sand is primarily SiO₂, which is used commercially to make glass and prevent caking in food products. Complex compounds of silicon and oxygen with elements such as aluminum are used in detergents and talcum powder and as industrial catalysts. Because silicon-chip technology laid the foundation for the modern electronics industry, the San Jose region of California, where many of the most important advances in electronics and computers were developed, has been nicknamed “Silicon Valley.”

Elemental tin and lead are metallic solids. Tin is primarily used to make alloys such as bronze, which consists of tin and copper; solder, which is tin and lead; and pewter, which is tin, antimony, and copper.

In ancient times, lead was used for everything from pipes to cooking pots because it is easily hammered into different shapes. In fact, the term *plumbing* is derived from *plumbum*, the Latin name for lead. Lead compounds were used as pigments in paints, and tetraethyllead was an important antiknock agent in gasoline. Now, however, lead has been banned from many uses because of its toxicity, although it is still widely used in lead storage batteries for automobiles. In previous centuries, lead salts were frequently used as medicines. Evidence suggests, for example, that Beethoven’s death was caused by the application of various lead-containing medicines by his physician. Beethoven contracted pneumonia and was treated with lead salts, but in addition, he suffered from a serious liver ailment. His physician treated the ailment by repeatedly puncturing his abdominal cavity and then sealing the wound with a lead-laced poultice. It seems that the repeated doses of lead compounds contributed to Beethoven’s death.

Group 15: The Pnictogens



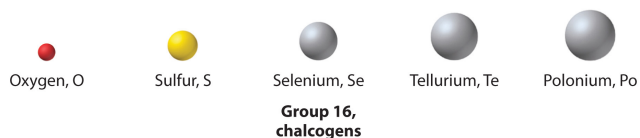
The group 15 elements are called the pnictogens. The elements in group 15 of the periodic table—from the Greek *pnigēin*, meaning “to choke,” and *genes*, meaning “producing”—ostensibly because of the noxious fumes that many nitrogen and phosphorus compounds produce. This family has five stable elements; one isotope of bismuth (^{209}Bi) is nonradioactive and is the heaviest nonradioactive isotope of any element. Once again, the lightest member of the family has unique properties. Although both nitrogen and phosphorus are nonmetals, nitrogen under standard conditions is a diatomic gas (N_2), whereas phosphorus consists of three allotropes: white, a volatile, low-melting solid consisting of P_4 tetrahedra; a red solid comprised of P_8 , P_9 , and P_{10} cages linked by P_2 units; and black layers of corrugated phosphorus sheets. The next two elements, arsenic and antimony, are semimetals with extended three-dimensional network structures, and bismuth is a silvery metal with a pink tint.

All of the pnictogens have ns^2np^3 valence electron configurations, leading to three common oxidation states: -3 , in which three electrons are added to give the closed-shell electron configuration of the next noble gas; $+5$, in which all five valence electrons are lost to give the closed-shell electron configuration of the preceding noble gas; and $+3$, in which only the three np electrons are lost to give a filled ns^2 subshell. Because the electronegativity of nitrogen is similar to that of chlorine, nitrogen accepts electrons from most elements to form compounds in the -3 oxidation state (such as in NH_3). Nitrogen has only positive oxidation states when combined with highly electronegative elements, such as oxygen and the halogens (e.g., HNO_3 , NF_3). Although phosphorus and arsenic can combine with active metals and hydrogen to produce compounds in which they have a -3 oxidation state (PH_3 , for example), they typically attain oxidation states of $+3$ and $+5$ when combined with more electronegative elements, such as PCl_3 and H_3PO_4 . Antimony and bismuth are relatively unreactive metals, but form compounds with oxygen and the halogens in which their oxidation states are $+3$ and $+5$ (as in Bi_2O_3 and SbF_5).

Although it is present in most biological molecules, nitrogen was the last pnictogen to be discovered. Nitrogen compounds such as ammonia, nitric acid, and their salts are used agriculturally in huge quantities; nitrates and nitrites are used as preservatives in meat products such as ham and bacon, and nitrogen is a component of nearly all explosives.

Phosphorus, too, is essential for life, and phosphate salts are used in fertilizers, toothpaste, and baking powder. One, phosphorus sulfide, P_4S_3 , is used to ignite modern safety matches. Arsenic, in contrast, is toxic; its compounds are used as pesticides and poisons. Antimony and bismuth are primarily used in metal alloys, but a bismuth compound is the active ingredient in the popular antacid medication Pepto-Bismol.

Group 16: The Chalcogens



The group 16 elements are often referred to as the chalcogens. The elements in group 16 of the periodic table—from the Greek *chalk*, meaning “copper,” and *genes*, meaning “producing”—because the most ancient copper ore, copper sulfide, is also rich in two other group 16 elements: selenium and tellurium. Once again, the lightest member of the family has unique properties. In its most common pure form, oxygen is a diatomic gas (O_2), whereas sulfur is a volatile solid with S_8 rings, selenium and tellurium are gray or silver solids that have chains of atoms, and polonium is a silvery metal with a regular array of atoms. Like astatine and radon, polonium is a highly radioactive metallic element.

All of the chalcogens have ns^2np^4 valence electron configurations. Their chemistry is dominated by three oxidation states: -2 , in which two electrons are added to achieve the closed-shell electron configuration of the *next* noble gas; $+6$, in which all six valence electrons are lost to give the closed-shell electron configuration of the *preceding* noble gas; and $+4$, in which only the four np electrons are lost to give a filled ns^2 subshell. Oxygen has the second highest electronegativity of any element; its chemistry is dominated by the -2 oxidation state (as in MgO and H_2O). No compounds of oxygen in the $+4$ or $+6$ oxidation state are known. In contrast, sulfur can form compounds in all three oxidation states. Sulfur accepts electrons from less electronegative elements to give H_2S and Na_2S , for example, and it donates electrons to more electronegative elements to give compounds such as SO_2 , SO_3 ,

and SF₆. Selenium and tellurium, near the diagonal line in the periodic table, behave similarly to sulfur but are somewhat more likely to be found in positive oxidation states.

Oxygen, the second most electronegative element in the periodic table, was not discovered until the late 18th century, even though it constitutes 20% of the atmosphere and is the most abundant element in Earth's crust. Oxygen is essential for life; our metabolism is based on the oxidation of organic compounds by O₂ to produce CO₂ and H₂O. Commercially, oxygen is used in the conversion of pig iron to steel, as the oxidant in oxyacetylene torches for cutting steel, as a fuel for the US space shuttle, and in hospital respirators.

Sulfur is the brimstone in "fire and brimstone" from ancient times. Partly as a result of its long history, it is employed in a wide variety of commercial products and processes. In fact, more sulfuric acid is produced worldwide than any other compound. Sulfur is used to cross-link the polymers in rubber in a process called *vulcanization*, which was discovered by Charles Goodyear in the 1830s and commercialized by Benjamin Goodrich in the 1870s. Vulcanization gives rubber its unique combination of strength, elasticity, and stability.

Selenium, the only other commercially important chalcogen, was discovered in 1817, and today it is widely used in light-sensitive applications. For example, photocopying, or xerography, from the Greek *xêrós*, meaning "dry," and *graphia*, meaning "writing," uses selenium films to transfer an image from one piece of paper to another, while compounds such as cadmium selenide are used to measure light in photographic light meters and automatic streetlights.

Group 17: The Halogens



The term *halogen*, derived from the Greek *hals*, meaning "salt," and *genes*, meaning "producing," was first applied to chlorine because of its tendency to react with metals to form salts. All of the halogens have an ns^2np^5 valence electron configuration, and all but astatine are diatomic molecules in which the two halogen atoms share a pair of electrons. Diatomic F₂ and Cl₂ are pale yellow-green and pale green gases, respectively, while Br₂ is a red liquid, and I₂ is a purple solid. The halogens were not isolated until the 18th and 19th centuries.

Because of their relatively high electronegativities, the halogens are nonmetallic and generally react by gaining one electron per atom to attain a noble gas electron configuration and an oxidation state of -1. *Halides* are produced according to the following equation, in which X denotes a halogen:



If the element E has a low electronegativity (as does Na), the product is typically an ionic halide (NaCl). If the element E is highly electronegative (as P is), the product is typically a covalent halide (PCl₅). Ionic halides tend to be nonvolatile substances with high melting points, whereas covalent halides tend to be volatile substances with low melting points. Fluorine is the most reactive of the halogens, and iodine the least, which is consistent with their relative electronegativities (Figure 3.3.11). As we shall see in subsequent chapters, however, factors such as bond strengths are also important in dictating the reactivities of these elements. In fact, fluorine reacts with nearly all elements at room temperature. Under more extreme conditions, it combines with all elements except helium, neon, and argon.

The halogens react with hydrogen to form the hydrogen halides (HX):



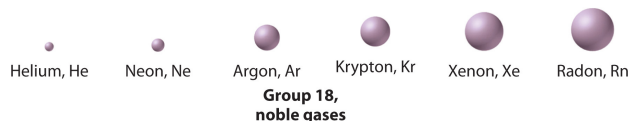
Fluorine is so reactive that any substance containing hydrogen, including coal, wood, and even water, will burst into flames if it comes into contact with pure F₂.

Because it is the most electronegative element known, fluorine never has a positive oxidation state in any compound. In contrast, the other halogens (Cl, Br, I) form compounds in which their oxidation states are +1, +3, +5, and +7, as in the *oxoanions*, XO_n⁻, where $n = 1-4$. Because oxygen has the second highest electronegativity of any element, it stabilizes the positive oxidation states of the halogens in these ions.

All of the halogens except astatine (which is radioactive) are commercially important. NaCl in salt water is purified for use as table salt. Chlorine and hypochlorite (OCl^-) salts are used to sanitize public water supplies, swimming pools, and wastewater, and hypochlorite salts are also used as bleaches because they oxidize colored organic molecules. Organochlorine compounds are used as drugs and pesticides. Fluoride (usually in the form of NaF) is added to many municipal water supplies to help prevent tooth decay, and bromine (in AgBr) is a component of the light-sensitive coating on photographic film. Because iodine is essential to life—it is a key component of the hormone produced by the thyroid gland—small amounts of KI are added to table salt to produce “iodized salt,” which prevents thyroid hormone deficiencies. The video shows the (some times explosive) reactions of the halogens



Group 18: The Noble Gases

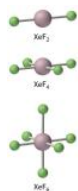


The noble gases are helium, neon, argon, krypton, xenon, and radon. All have filled valence electron configurations and therefore are unreactive elements found in nature as monatomic gases. The noble gases were long referred to as either “rare gases” or “inert gases,” but they are neither rare nor inert. Argon constitutes about 1% of the atmosphere, which also contains small amounts of the lighter group 18 elements, and helium is found in large amounts in many natural gas deposits. The group’s perceived “rarity” stems in part from the fact that the noble gases were the last major family of elements to be discovered.

The noble gases have $EA \geq 0$, so they do not form compounds in which they have negative oxidation states. Because ionization energies decrease down the column, the only noble gases that form compounds in which they have positive oxidation states are Kr, Xe, and Rn. Of these three elements, only xenon forms an extensive series of compounds. The chemistry of radon is severely limited by its extreme radioactivity, and the chemistry of krypton is limited by its high ionization energy (1350.8 kJ/mol versus 1170.4 kJ/mol for xenon). In essentially all its compounds, xenon is bonded to highly electronegative atoms such as fluorine or oxygen. In fact, the only significant reaction of xenon is with elemental fluorine, which can give XeF_2 , XeF_4 , or XeF_6 . Oxides such as XeO_3 are produced when xenon fluorides react with water, and oxidation with ozone produces the perxenate ion $[\text{XeO}_6^{4-}]$, in which xenon acquires a +8 oxidation state by formally donating all eight of its valence electrons to the more electronegative oxygen atoms. In all of its stable compounds, xenon has a positive, even-numbered oxidation state: +2, +4, +6, or +8. The actual stability of these compounds varies greatly. For example, XeO_3 is a shock-sensitive, white crystalline solid with explosive power comparable to that of TNT (trinitrotoluene), whereas another compound, Na_2XeF_8 , is stable up to 300°C.

Although none of the noble gas compounds is commercially significant, the elements themselves have important applications. For example, argon is used in incandescent light bulbs, where it provides an inert atmosphere that protects the tungsten filament from oxidation, and in compact fluorescent light bulbs (CFLs). It is also used in arc welding and in the manufacture of reactive elements, such as titanium, or of ultrapure products, such as the silicon used by the electronics industry. Helium, with a boiling point of only 4.2 K, is used as a liquid for studying the properties of substances at very low temperatures. It is also combined in an 80:20 mixture with oxygen used by scuba divers, rather than compressed air, when they descend to great depths. Because helium is less soluble in water than N_2 —a component of compressed air—replacing N_2 with He prevents the formation of bubbles in blood vessels, a

condition called “the bends” that can occur during rapid ascents. Neon is familiar to all of us as the gas responsible for the red glow in neon lights.



The Transition Metals, the Lanthanides, and the Actinides

As expected for elements with the same valence electron configuration, the elements in each column of the *d* block have vertical similarities in chemical behavior. In contrast to the *s*- and *p*-block elements, however, elements in the *d* block also display strong *horizontal* similarities. The horizontal trends compete with the vertical trends. In further contrast to the *p*-block elements, which tend to have stable oxidation states that are separated by *two* electrons, the transition metals have multiple oxidation states that are separated by only *one* electron.

Note the Pattern

The *p*-block elements form stable compounds in oxidation states that tend to be separated by two electrons, whereas the transition metals have multiple oxidation states that are separated by one electron.

The group 6 elements, chromium, molybdenum, and tungsten, illustrate the competition that occurs between these horizontal and vertical trends. For example, the maximum number of electrons that can be lost for all elements in group 6 is +6, achieved by losing all six valence electrons (recall that Cr has a $4s^1 3d^5$ valence electron configuration), yet nearly all the elements in the first row of the transition metals, including chromium, form compounds with the dication M^{2+} , and many also form the trication M^{3+} . As a result, the transition metals in group 6 have very different tendencies to achieve their maximum oxidation state. The most common oxidation state for chromium is +3, whereas the most common oxidation state for molybdenum and tungsten is +6.

Note the Pattern

The *d*-block elements display both strong vertical and horizontal similarities.

Groups 3 (scandium, lanthanum, actinium), 11 (copper, silver, gold), and 12 (zinc, cadmium, mercury) are the only transition metal groups in which the oxidation state predicted by the valence electron configuration dominates the chemistry of the group. The elements of group 3 have three valence electrons outside an inner closed shell, so their chemistry is almost exclusively that of the M^{3+} ions produced by losing all three valence electrons. The elements of group 11 have 11 valence electrons in an $ns^1(n-1)d^{10}$ valence electron configuration, and so all three lose a single electron to form the monocation M^+ with a closed $(n-1)d^{10}$ electron configuration. Consequently, compounds of Cu^+ , Ag^+ , and Au^+ are very common, although there is also a great deal of chemistry involving Cu^{2+} . Similarly, the elements of group 12 all have an $ns^2(n-1)d^{10}$ valence electron configuration, so they lose two electrons to form M^{2+} ions with an $(n-1)d^{10}$ electron configuration; indeed, the most important ions for these elements are Zn^{2+} , Cd^{2+} , and Hg^{2+} . Mercury, however, also forms the dimeric mercurous ion (Hg_2^{2+}) because of a subtle balance between the energies needed to remove additional electrons and the energy released when bonds are formed. The +3 oxidation state is the most important for the lanthanides. Any of the 14 elements between $Z=58$ (cerium) and $Z=71$ (lutetium) and for most of the actinides (Any of the 14 elements between $Z=90$ (thorium) and $Z=103$ (lawrencium).) Why? Here is a brief video on the properties of the Lanthanides



Example 8

Based on the following information, determine the most likely identities for elements D and E.

1. Element D is a shiny gray solid that conducts electricity only moderately; it forms two oxides (DO_2 and DO_3).
2. Element E is a reddish metallic substance that is an excellent conductor of electricity; it forms two oxides (EO and E_2O) and two chlorides (ECl and ECl_2).

Given: physical and chemical properties of two elements

Asked for: identities

Strategy:

A Based on the conductivity of the elements, determine whether each is a metal, a nonmetal, or a semimetal. Confirm your prediction from its physical appearance.

B From the compounds each element forms, determine its common oxidation states.

C If the element is a nonmetal, it must be located in the p block of the periodic table. If a semimetal, it must lie along the diagonal line of semimetals from B to At. Transition metals can have two oxidation states separated by one electron.

D From your classification, the oxidation states of the element, and its physical appearance, deduce its identity.

Solution:

1. **A** The moderate electrical conductivity of element D tells us that it is a semimetal. It must lie in the p block of the periodic table because all of the semimetals are located there. **B** The stoichiometry of the oxides tells us that two common oxidation states for D are +4 and +6. **C** Element D must be located in group 16 because the common oxidation states for the chalcogens (group 16) include +6 (by losing all six valence electrons) and +4 (by losing the four electrons from the p subshell). Thus D is likely to be Se or Te. **D** Additional information is needed to distinguish between the two.
2. **A** Element E is an excellent electrical conductor, so it is a metal. **B** The stoichiometry of the oxides and chlorides, however, tells us that common oxidation states for E are +2 and +1. **C** Metals that can have two oxidation states separated by one electron are usually transition metals. The +1 oxidation state is characteristic of only one group: group 11. Within group 11, copper is the only element with common oxidation states of +1 and +2. **D** Copper also has a reddish hue. Thus element E is probably copper.

Exercise

Based on the following information, determine the most likely identities for elements G and J.

1. Element G is a red liquid that does not conduct electricity. It forms three compounds with fluorine (GF , GF_3 , and GF_5) and one with sodium (NaG).
2. Element J is a soft, dull gray solid that conducts electricity well and forms two oxides (JO and JO_2).

Answer

1. Br
2. Sn or Pb

Summary

The chemical families consist of elements that have the same valence electron configuration and tend to have similar chemistry. The alkali metals (group 1) have ns^1 valence electron configurations and form M^+ ions, while the alkaline earth metals (group 2) have ns^2 valence electron configurations and form M^{2+} ions. Group 13 elements have ns^2np^1 valence electron configurations and have an overwhelming tendency to form compounds in the +3 oxidation state. Elements in group 14 have ns^2np^2 valence electron configurations but exhibit a variety of chemical behaviors because they range from a nonmetal (carbon) to metals (tin/lead). Carbon, the basis of organic compounds, has at least four allotropes with distinct structures: diamond, graphite, **fullerenes**, and carbon **nanotubes**. The **pnictogens** (group 15) all have ns^2np^3 valence electron configurations; they form compounds in oxidation states ranging from -3 to $+5$. The **chalcogens** (group 16) have ns^2np^4 valence electron configurations and react chemically by either gaining two electrons or by formally losing four or six electrons. The halogens (group 17) all have ns^2np^5 valence electron configurations and are diatomic molecules that tend to react chemically by accepting a single electron. The noble gases (group 18) are monatomic gases that are chemically quite unreactive due to the presence of a filled shell of electrons. The **transition metals** (groups 3–10) contain partially filled sets of d orbitals, and the **lanthanides** and the **actinides** are those groups in which f orbitals are being filled. These groups exhibit strong horizontal similarities in behavior. Many of the transition metals form M^{2+} ions, whereas the chemistry of the lanthanides and actinides is dominated by M^{3+} ions.

Key Takeaway

- Periodic properties and the chemical behavior of the elements correlate strongly with valence electron configurations and Mulliken electronegativities.

Conceptual Problems

- Of the group 1 elements, which would you expect to be the best reductant? Why? Would you expect boron to be a good reductant? Why or why not?
- Classify each element as a metal, a nonmetal, or a semimetal: Hf, I, Tl, S, Si, He, Ti, Li, and Sb. Which would you expect to be good electrical conductors? Why?
- Classify each element as a metal, a nonmetal, or a semimetal: Au, Bi, P, Kr, V, Na, and Po. Which would you expect to be good electrical insulators? Why?
- Of the elements Kr, Xe, and Ar, why does only xenon form an extensive series of compounds? Would you expect Xe^{2+} to be a good oxidant? Why or why not?
- Identify each statement about the halogens as either true or false and explain your reasoning.
 - Halogens have filled valence electron configurations.
 - Halogens tend to form salts with metals.
 - As the free elements, halogens are monatomic.
 - Halogens have appreciable nonmetallic character.
 - Halogens tend to have an oxidation state of -1 .
 - Halogens are good reductants.
- Nitrogen forms compounds in the $+5$, $+4$, $+3$, $+2$, and -3 oxidation states, whereas Bi forms ions only in the $+5$ and $+3$ oxidation states. Propose an explanation for the differences in behavior.
- Of the elements Mg, Al, O, P, and Ne, which would you expect to form covalent halides? Why? How do the melting points of covalent halides compare with those of ionic halides?
- Of the elements Li, Ga, As, and Xe, would you expect to form ionic chlorides? Explain your reasoning. Which are usually more volatile—ionic or covalent halides? Why?
- Predict the relationship between the oxidative strength of the oxoanions of bromine— BrO_n^- ($n = 1-4$)—and the number of oxygen atoms present (n). Explain your reasoning.
- The stability of the binary hydrides of the chalcogens decreases in the order $H_2O > H_2S > H_2Se > H_2Te$. Why?
- Of the elements O, Al, H, and Cl, which will form a compound with nitrogen in a positive oxidation state? Write a reasonable chemical formula for an example of a binary compound with each element.

12. How do you explain the differences in chemistry observed for the group 14 elements as you go down the column? Classify each group 14 element as a metal, a nonmetal, or a semimetal. Do you expect the group 14 elements to form covalent or ionic compounds? Explain your reasoning.
13. Why is the chemistry of the group 13 elements less varied than the chemistry of the group 15 elements? Would you expect the chemistry of the group 13 elements to be more or less varied than that of the group 17 elements? Explain your reasoning.
14. If you needed to design a substitute for BaSO_4 , the barium milkshake used to examine the large and small intestine by x-rays, would BeSO_4 be an inappropriate substitute? Explain your reasoning.
15. The alkali metals have an ns^1 valence electron configuration, and consequently they tend to lose an electron to form ions with +1 charge. Based on their valence electron configuration, what other kind of ion can the alkali metals form? Explain your answer.
16. Would Mo or W be the more appropriate biological substitute for Cr? Explain your reasoning.

Answer

- 1.
- 2.
- 3.
- 4.
- 5.
- 6.
- 7.
- 8.
- 9.
- 10.
11. Nitrogen will have a positive oxidation state in its compounds with O and Cl, because both O and Cl are more electronegative than N. Reasonable formulas for binary compounds are: N_2O_5 or N_2O_3 and NCl_3 .
- 12.
- 13.
- 14.
- 15.
- 16.

Numerical Problems

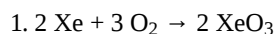
1. Write a balanced equation for formation of XeO_3 from elemental Xe and O_2 . What is the oxidation state of Xe in XeO_3 ? Would you expect Ar to undergo an analogous reaction? Why or why not?
2. Which of the *p*-block elements exhibit the greatest variation in oxidation states? Why? Based on their valence electron configurations, identify these oxidation states.
3. Based on its valence electron configuration, what are the three common oxidation states of selenium? In a binary compound, what atoms bonded to Se will stabilize the highest oxidation state? the lowest oxidation state?
4. Would you expect sulfur to be readily oxidized by HCl? Why or why not? Would you expect phosphorus to be readily oxidized by sulfur? Why or why not?
5. What are the most common oxidation states for the pnictogens? What factors determine the relative stabilities of these oxidation states for the lighter and the heavier pnictogens? What is likely to be the most common oxidation state for phosphorus and arsenic? Why?
6. Of the compounds NF_3 , NCl_3 , and NI_3 , which would be the least stable? Explain your answer. Of the ions BrO^- , ClO^- , or FO^- , which would be the least stable? Explain your answer.
7. In an attempt to explore the chemistry of the superheavy element ununquadium, $Z = 114$, you isolated two distinct salts by exhaustively oxidizing metal samples with chlorine gas. These salts are found to have the formulas MCl_2 and MCl_4 . What would be the name of ununquadium using Mendeleev's *eka*-notation?

8. Would you expect the compound CCl_2 to be stable? SnCl_2 ? Why or why not?
9. A newly discovered element (Z) is a good conductor of electricity and reacts only slowly with oxygen. Reaction of 1 g of Z with oxygen under three different sets of conditions gives products with masses of 1.333 g, 1.668 g, and 1.501 g, respectively. To what family of elements does Z belong? What is the atomic mass of the element?
10. An unknown element (Z) is a dull, brittle powder that reacts with oxygen at high temperatures. Reaction of 0.665 gram of Z with oxygen under two different sets of conditions forms gaseous products with masses of 1.328 g and 1.660 g. To which family of elements does Z belong? What is the atomic mass of the element?
11. Why are the alkali metals such powerful reductants? Would you expect Li to be able to reduce H_2 ? Would Li reduce V? Why or why not?
12. What do you predict to be the most common oxidation state for Au, Sc, Ag, and Zn? Give the valence electron configuration for each element in its most stable oxidation state.
13. Complete the following table.

	Mg	C	Ne	Fe	Br
Valence Electron Configuration					
Common Oxidation States					
Oxidizing Strength					

14. Use the following information to identify elements T, X, D, and Z. Element T reacts with oxygen to form at least three compounds: TO , T_2O_3 , and TO_2 . Element X reacts with oxygen to form XO_2 , but X is also known to form compounds in the +2 oxidation state. Element D forms D_2O_3 , and element Z reacts vigorously and forms Z_2O . Electrical conductivity measurements showed that element X exhibited electrical conductivity intermediate between metals and insulators, while elements T, D, and Z were good conductors of electricity. Element T is a hard, lustrous, silvery metal, element X is a blue-gray metal, element D is a light, silvery metal, and element Z is a soft, low-melting metal.
15. Predict whether Cs, F_2 , Al, and He will react with oxygen. If a reaction will occur, identify the products.
16. Predict whether K, Ar, O, and Al will react with Cl_2 . If a reaction will occur, identify the products.
17. Use the following information to identify elements X, T, and Z.
 1. Element X is a soft, silvery-white metal that is flammable in air and reacts vigorously with water. Its first ionization energy is less than 500 kJ/mol, but the second ionization energy is greater than 3000 kJ/mol.
 2. Element T is a gas that reacts with F_2 to form a series of fluorides ranging from TF_2 to TF_6 . It is inert to most other chemicals.
 3. Element Z is a deep red liquid that reacts with fluorine to form ZF_3 and with chlorine to form ZCl and ZCl_3 , and with iodine to form ZI . Element Z also reacts with the alkali metals and alkaline earth metals.
18. Adding a reactive metal to water in the presence of oxygen results in a fire. In the absence of oxygen, the addition of 551 mg of the metal to water produces 6.4 mg of hydrogen gas. Treatment of 2.00 g of this metal with 6.3 g of Br_2 results in the formation of 3.86 g of an ionic solid. To which chemical family does this element belong? What is the identity of the element? Write and balance the chemical equation for the reaction of water with the metal to form hydrogen gas.

Answers



The oxidation state of xenon in XeO_3 is +6. No, Ar is much more difficult to oxidize than Xe.

2.

3. The valence electron configuration of Se is $[\text{Ar}]4s^23d^{10}4p^4$. Its common oxidation states are: +6, due to loss of all six electrons in the 4s and 4p subshells; +4, due to loss of only the four 4p electrons; and -2, due to addition of two electrons to give an

[Ar]4s²3d¹⁰4p⁶ electron configuration, which is isoelectronic with the following noble gas, Kr. The highest oxidation state (+6) will be stabilized by bonds to highly electronegative atoms such as F (SeF₆) and O (SeO₃), while the lowest oxidation state will be stabilized in covalent compounds by bonds to less electronegative atoms such as H (H₂Se) or C [(CH₃)₂Se], or in ionic compounds with cations of electropositive metals (Na₂Se).

4.

5. All of the pnictogens have ns^2np^3 valence electron configurations. The pnictogens therefore tend to form compounds in three oxidation states: +5, due to loss of all five valence electrons; +3, due to loss of the three np^3 electrons; and -3, due to addition of three electrons to give a closed shell electron configuration. Bonds to highly electronegative atoms such as F and O will stabilize the higher oxidation states, while bonds to less electronegative atoms such as H and C will stabilize the lowest oxidation state, as will formation of an ionic compound with the cations of electropositive metals. The most common oxidation state for phosphorus and arsenic is +5.

6.

7. Uuq = *eka*-lead

8.

9. The ratios of the masses of the element to the mass of oxygen give empirical formulas of ZO, Z₂O₃, and ZO₂. The high electrical conductivity of the element immediately identifies it as a metal, and the existence of three oxides of the element with oxidation states separated by only one electron identifies it as a transition metal. If 1 g of Z reacts with 0.33 g O₂ to give ZO, the balanced equation for the reaction must be $2Z + O_2 \rightarrow 2ZO$. Using M to represent molar mass, the ratio of the molar masses of ZO and Z is therefore:

$$M_{ZO}:M_Z = (M_Z + M_O):M_Z = (M_Z + 16.0):M_Z = 1.33:1 = 1.33.$$

Solving for M_Z gives a molar mass of 48 g/mol and an atomic mass of 48 amu for Z, which identifies it as titanium.

10.

11. Alkali metals are powerful reductants because they have a strong tendency to lose their ns^1 valence electron, as reflected in their low first ionization energies and electronegativities. Lithium has a more positive electron affinity than hydrogen and a substantially lower first ionization energy, so we expect lithium to reduce hydrogen. Transition metals have low electron affinities and do not normally form compounds in negative oxidation states. Therefore, we do not expect lithium to reduce vanadium.

12.

	Mg	C	Ne	Fe	Br
Valence Electron Configuration	3s ²	2s ² 2p ²	2s ² 2p ⁶	4s ² 3d ⁶	4s ² 4p ⁵
Common Oxidation States	+2	-4, +4	0	+2, +3	-1, +1, +3, +5, +7
Oxidizing Strength	None	Weak	None	None	Strong

14.

15. $4\text{Cs(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{Cs}_2\text{O(s)}$ $2\text{F}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow \text{OF}_2\text{(g)}$ $4\text{Al(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Al}_2\text{O}_3\text{(s)}$ $\text{He} + \text{O}_2\text{(g)} \rightarrow \text{no reaction}$

16.

1. sodium or potassium
2. xenon
3. bromine

18.

Contributors

- Anonymous

Modified by Joshua Halpern

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