

Inorganic Chemistry with Doc M.

Day 13. The Main Group Elements

Topics:

1. Hydrogen
2. Group I. The Alkali Metals
3. Group II. The Alkaline Earth Metals
4. Group III. Boron, aluminum, gallium
5. Group IV. Carbon, silicon, germanium, tin and lead

Electronegativities of the Elements. The main group elements and their electronegativities are shown in the table below. Much of the main group chemistry is determined by whether the compounds are ionic or covalent. The alkali metals and alkaline earth metals form ionic compounds with more electronegative elements such as the halogens. Groups IA and IIA aside, the rest of the non-metal main group elements engage in bonding within the group that is largely covalent in nature. Most compounds are not purely ionic or covalent but somewhere in between. Ionic character increases with an increase in the difference in electronegativities.

H 2.1							He
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.5	Ar
K 0.8	Ca 1.0	Ga	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr
Rb 0.8	Sr 1.0	In	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe
Cs 0.7	Ba 0.9	Tl	Pb 1.9	Bi 1.9	Po	At	Rn

1. Hydrogen.

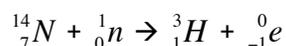
A. Introduction. Hydrogen is one of the most unique elements of the periodic table. Most people live their entire lives without ever encountering molecular hydrogen — yet we are constantly in contact with and dependent on compounds of hydrogen. The most familiar compound of hydrogen is water. Hydrogen makes up over 92% of all the atoms of the Universe. In other terms, this corresponds to 73.9% of the Universe's mass. Our sun, like many other stars, consists mostly of hydrogen. All of the other elements were (and still are being) formed from hydrogen and helium fusion reactions in stars. As the star ages, the percentage of hydrogen drops. The current hydrogen content of our sun is 30% by mass. Hydrogen is also known to be a major constituent of the larger planets. For example, Jupiter contains significant amounts of hydrogen. At some depth in the planet's core, it is

believed that the pressure is significant (in excess of one million atmospheres) to convert the hydrogen into the form of a close-packed metallic solid hydrogen.

B. Physical properties. Hydrogen is a colorless, odorless, and tasteless gas and is one of the most important of the chemical elements. Hydrogen's freezing point is 20.28 K. It is essentially insoluble in water.

C. Isotopes. Although isotopes of elements generally do not have names, the isotopes of hydrogen are named **protium**, **deuterium**, and **tritium**. Along with the names, comes the pseudo-atomic symbols for deuterium (D) and tritium (T). The most common isotope of hydrogen is protium, ${}^1_1\text{H}$, which has a single proton for its nucleus. Deuterium, ${}^2_1\text{H}$, the second most common isotope of hydrogen represents one hydrogen out of every 6400. It has a neutron and a proton in its nucleus and is thus approximately twice as dense as ${}^1_1\text{H}$. Deuterium is not radioactive and has many uses in chemistry. It is obtained from the fractional distillation of water.

Tritium, ${}^3_1\text{H}$, occurs in nature in trace levels (1 atom in 10^{17} hydrogen atoms) and is readily produced in nuclear reactors. In nature, tritium is constantly being produced in the upper atmosphere by the reaction between cosmic neutrons and ${}^{14}\text{N}$:



Tritium is a β -emitter with a half-life of 12.5 years. Write the nuclear reaction that takes place when tritium emits a β -particle.

D. Hydrogen and the Periodic Table. Hydrogen is typically placed at the top of the alkali metals on the periodic table because of its electronic configuration, $1s^1$. However, hydrogen exists as a covalent, diatomic gas, H_2 which is unlike the alkali metals. While both the alkali metals and hydrogen exhibit the oxidation states 0 and +1, hydrogen also exhibits a third -1 oxidation state similar to that of a halogen.

Property:	Hydrogen	Lithium	Fluorine
Ionization Energy (kJ/mol)	1312	520	1681
Electron affinity (kJ/mol)	-73	-58	-328
Electronegativity	2.1	1.0	4.0
Stable cation	H^+	Li^+	none
Stable anion	H^-	none	F^-
Stable molecular form	H_2	metal	F_2
Phase of element (standard conditions)	gas	metal	gas
Valence electronic configuration	$1s^1$	$2s^1$	$2s^2 2p^5$

There are important differences between hydrogen and the alkali metals within the +1 oxidation state. The alkali metals utilize the +1 oxidation state in all of their common ionic salts and thus exhibit ionic character. Hydrogen in the +1 oxidation state is generally covalent. For example, hydrogen exhibits the +1 oxidation state in all of these covalent compounds: NH_3 , CH_4 , H_2O , and HCl .

Comparison of hydrogen's atomic properties with those of lithium and fluorine helps to understand the dilemma. Hydrogen has atomic properties which resemble both of these elements. The ionization energy for hydrogen is large and similar to that of fluorine, however, the resulting +1 oxidation state is common for hydrogen but not for fluorine. Molecular hydrogen is a diatomic gas like fluorine while lithium is a metal. Unlike the halogens, hydrogen is a reducing agent - much like the alkali metals. Its electron affinity is similar to that of lithium and its electronegativity is in between those for lithium and fluorine.

E. Hydrogen forms strong covalent bonds to all non-metallic elements with the exception of the noble gases. Compounds of hydrogen that involve metals are generally thought of as ionic with the hydrogen functioning as a hydride, H^- .

Covalent bonds between hydrogen and other elements are among the strongest in chemistry. Hydrogen ranks with fluorine and oxygen in its ability to form strong covalent bonds. The table below lists the twenty strongest covalent bonds for which reasonable values are known. Nearly half of the entries on this list involves hydrogen including all of the elements between hydrogen and the second period non-metals (B, C, N, O, and F). Bonds to third period non-metals are somewhat weaker although they are still quite strong. The unusual strength of most covalent bonds to hydrogen is not explained by the same reasoning that applies to oxygen and fluorine. The ability of O and F to form strong single bonds is attributed to the large electronegativity of these elements which provides polar character to the covalent bonds. In fact, without polar

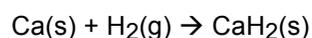
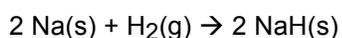
Rank	Bond	ΔH (kJ/mol)
1	B-F	613
2	F-Si	565
3	H-F	565
4	B-O	536
5	F-P	490
6	C-F	485
7	H-O	459
8	B-Cl	456
9	O-Si	452
10	H-H	432
11	H-Cl	428
12	H-C	412
13	H-B	389
14	H-N	389
15	Si-Cl	381
16	B-Br	377
17	B-C	372
18	H-S	363
19	H-Br	362
20	C-O	358

character, covalent bonds involving O and F are notoriously weak. The bond strengths for O-O, F-F and O-F are all less than 200 kJ/mol. Hydrogen's electronegativity is 2.1 which is fairly average for the non-metals so bonds between hydrogen and most non-metals have little polar character (with the exception of H-N, H-O, H-F, and H-Cl). The unusual strength of the non-polar bonds involving hydrogen is attributed to hydrogen's ability to create stable molecular orbitals involving the overlap of hydrogen's 1s orbital with most other atomic orbitals.

The stability of covalent bonds to hydrogen provides a useful predictive tool regarding certain chemical reactions. Under mild reaction conditions, bonds to hydrogen often remain intact. For example, in organic reactions, the C-H bonds do not usually break during the course of the reaction.

The H-H bond ranks 10th in strength for single bonds in the table. This is consistent with the argument that the excellent orbital overlap involving hydrogen's 1s orbital results in energetically stable bonds. This also explains the surprisingly unreactive nature of hydrogen. Many exothermic reactions involving hydrogen require a catalyst to occur. Even the combustion with oxygen requires some sort of initiator such as a spark. This suggests that the energy of activation is large, in part due to the thermodynamic stability of all bonds to hydrogen.

F. Hydrides. The alkali metals and alkaline earths combine directly with hydrogen at elevated temperatures to form ionic metal hydrides in which the hydrogen is present as the anion, H⁻.



Hydrides of Group 1 and 2 are called **saline hydrides**. These compounds react readily with water or oxygen. The reaction with water is often violent because the hydrogen generated sprays water.



Write the reaction between CaH₂(s) and O₂(g):

Boron and aluminum form two fundamentally important hydrides that have numerous applications as reducing agents in organic and inorganic chemistry. These are sodium borohydride, NaBH₄, and lithium aluminum hydride, LiAlH₄. The anion in each case can be thought of as a hydride anion coordinated to a Lewis acid (for example, BH₄⁻ = H⁻ + BH₃). Chemically, hydrides are useful reducing agents. For example, aldehydes are reduced to alcohols with the use of hydride reductants.

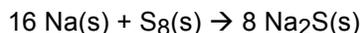
2. The Alkali Metals.

A. Physical properties. The alkali metals are typical metals in some respects and bizarrely different from other metals in other respects. To start with the typical, the alkali metals have luster, are malleable, ductile, conduct electricity and heat much like metals in general. Now on to the bizarre. The table below shows that the densities of lithium and sodium are actually less than that of water — the metals would float if they didn't react with water. Their melting points are unusually low, too. Both of these properties are the result of large atomic radii and lattices that are not close-packed.

Some Physical Properties of the Alkali Metals

	Density (g/mL)	Melting Point (°C)	Boiling Point (°C)	Unit cell	Atomic Radius (pm)
Li	0.53	180.5	1326	bcc	152
Na	0.97	97.8	883		186
K	0.86	63.7	756		227
Rb	1.53	39.0	688		248
Cs	1.88	28.6	690		265

B. Chemical Reactions. Reactions involving the alkali metals are generally predictable: the alkali metal reduces the non-metal forming an alkali metal cation. For example, sodium reacts with sulfur and after gentle heating to initiate the reaction, it proceeds violently:



Alkali metals react with halogens as expected, however, the kinetic rates are sometimes surprising. For example, lithium and sodium appear to barely react with bromine while the other alkali metals react violently with bromine. What is the reaction expected between potassium and bromine:

C. Ionic radii. The cations produced in the above reactions, as expected are considerably smaller than the parent element as shown in the next table and graph.

	Atomic Radius (pm)		Ionic Radius (pm)
Li	152	Li ⁺	86
Na	186	Na ⁺	112
K	227	K ⁺	144
Rb	248	Rb ⁺	158
Cs	265	Cs ⁺	184

D. Reaction with water. All of the alkali metals react with water to form hydrogen and alkali metal hydroxide:



Lithium reacts the slowest (seconds), sodium reacts quickly and the heat generated melts the sodium which floats on the surface as it reacts violently with water. Potassium reacts almost explosively with water. This may be explained in part due to the ease of ionization as one descends the group.

E. Ionization energies. As we've discussed, the alkali metals, like all elements, undergo ionization as an endothermic process. The second ionization energy is so high in each case that the +2 ion is not known.

Valence Electronic Configuration	1st I. E. (kJ/mol)	2nd I. E. (kJ/mol)
Li, $2s^1$	520	7300
Na, $3s^1$	496	4560
K, $4s^1$	419	3070
Rb, $5s^1$	403	2640
Cs, $6s^1$	376	2260

F. Reaction with oxygen. The alkali metals react with oxygen, however the products are a bit surprising. Lithium forms the expected lithium oxide, but sodium forms sodium peroxide as the dominant product and potassium, rubidium and cesium form the paramagnetic superoxide, $KO_2(s)$. Write the balanced reactions between oxygen and lithium, sodium and potassium:

G. Covalent chemistry. An important exception to the generalization that bonds between alkali metals and non-metals are ionic is the lithium-carbon bond. These bonds are more covalent than ionic. Compounds such as $LiCH_3$ readily dissolve in non-polar solvents such as hexane. What is the difference in electronegativity between lithium and carbon? Is the bond "mostly" covalent or ionic? Sketch the structure with labels such as " δ^+ ."

H. Gas phase alkali metals. When the alkali metals are vaporized, they form diatomic molecules much like hydrogen. The dissociation energies of these purely covalent bonds are known. For example, the sodium-sodium bond in $Na_2(g)$ has a bond strength (dissociation energy) of 73.3 kJ/mol. Would you expect Na_2 to have a MO diagram similar to that of H_2 ?

I. Reaction with nitrogen. Chemists and chemical manufactures frequently use nitrogen or argon as an inert atmosphere to prevent degradation (oxidation or hydrolysis) of their chemicals. The alkali metals (and alkaline earth's), however, react with nitrogen to produce nitrides. Lithium reacts fairly rapidly to produce the ruby red crystalline nitrides Li_3N .

3. The Alkaline Earth Metals.

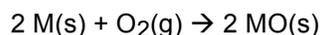
A. Physical Properties. As a family, the alkaline earth metals (or simply alkaline earths) can be compared to the alkali metals. With smaller atomic radii, the densities are larger (none are less than water's), and the melting points are higher — generally, they behave more like traditional metals.

	Density (g/mL)	Melting Point ($^{\circ}\text{C}$)	Electro-negativity	1st Ionization energy (kJ/mol)	2nd Ionization energy (kJ/mol)	Atomic Radius (pm)	Ionic Radius (pm)
Be	1.85	1278	1.5	899	1757	112	34
Mg	1.74	651	1.2	737	1450	160	78
Ca	1.55	843	1.0	590	1145	197	106
Sr	2.63	769	1.0	549	1059	215	127
Ba	3.62	725	0.9	503	960	222	143
Ra	5.5	700	0.9	509	975	225	157

The alkaline earth metals exhibit periodic trends in density, and electronegativity. The trend in melting points for these metals shows an unusually low value for magnesium. The atomic and ionic radii follow the expected periodic trend. Note that the cations are much smaller than the neutral atoms due to their +2 charge. In the case of Be^{+2} , the ionic radius is so small that Be^{+2} is the smallest metallic ion in chemistry. Compared to atomic Be, the volume of the cation is only 3% that of the neutral atom.

B. Reaction Chemistry: Forming +2 cations. Like the alkali metals, the alkaline earth metals are easily oxidized, do not exist in nature in the free form, and exhibit a chemistry that is mostly ionic. The most important difference is the oxidation states of the two groups. While the alkali metals formed +1 salts that are generally water-soluble, the alkaline earths form +2 ions, for which the salts are frequently insoluble. The additional charge makes it difficult for solvation energies to overcome the coulombic attraction between the +2 cation and an anion.

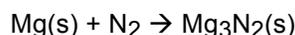
C. Oxides. All of the alkaline earths are air-sensitive, producing films of white metal **oxide** upon exposure to air.



The rate increases down the group. Magnesium can be easily stored in plastic bags or bottles in which the exposure to air and moisture has been minimized. Calcium, strontium and barium readily react with both oxygen and nitrogen so that they must be carefully stored under argon. All of the alkaline earth oxides exhibit the NaCl structure.

Alkaline earth oxides are all **base anhydrides** because they form basic solutions upon hydrolysis. Write the reaction:

D. Nitrides. As with oxygen, the reaction with nitrogen increases from Be to Ba. Magnesium only forms **nitrides** at very high temperatures while the heavier alkaline earths cannot be stored under nitrogen atmospheres.

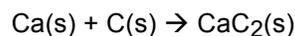


E. Reaction with water. The alkaline earths are all moisture sensitive, producing hydrogen and metal hydroxides. Write the reaction:

F. Hydrides. The alkaline earths form hydrides when the metals are heated with hydrogen. The hydrides are all highly reactive in the way one would expect for metal hydrides. Write the reaction for calcium + H₂:

G. Halides. In the reaction with halogens, the expected MX₂ salt is always obtained. Write the reaction:

H. Carbide. The reaction between calcium and carbon at high temperatures produces calcium acetylide (C₂²⁻):



Acetylides hydrolyze to form acetylene. Coal miners used this reaction to generate acetylene for illumination underground. The acetylene has to be ignited.



I. Covalent chemistry. Normally one does not think of covalent bonding when considering the alkaline earth metals. However, for beryllium and magnesium, the extremely small ionic radii produces a strong point charge

which can polarize electron density away from anions. This amounts to converting ionic bonding into covalent bonding and is most likely to occur when the anion is readily polarizable. The most familiar example of this is the **Grignard reagents**, RMgBr, in which the carbon-magnesium bond has considerable covalent character.

4. Group III. Boron, Aluminum, Gallium, Indium, and Thallium.

A. Introduction. The alkali metals and alkaline earth metals both provided us with an impression of the general similarities that exist within each group. Differences were subtle. Starting with Group 3, the differences within each group are more striking than the similarities. For example in Group IV, black, non-metallic carbon does not seem to have much in common with tin or lead. In Group V, it is not initially clear what gaseous nitrogen and metallic antimony (used to make pewter) have in common. These facts thwarted many 19th century attempts at producing a periodic table. In Group III, boron is a non-metal and the rest of the elements are metals.

B. Boron is the first member of Group III on the periodic table. In most respects, it is unlike the other members of the group. It is the only non-metal in the group. Boron is a black-brown, hard, brittle solid that physically resembles carbon or silicon more than it does any other Group III element. Even the chemistry of boron resembles carbon's or silicon's to a certain extent; a large number of covalent molecular compounds are known. Along with carbon, boron is the only other element with a propensity for catenation — forming bonds to oneself. With a valence of 3 electrons, however, many of the covalent compounds of boron are subvalent and thus function as Lewis acids. Whenever that occurs, the Lewis acidity of the compound drives the reaction chemistry.

C. Aluminum was first isolated as a metal in 1827 by the chemist Wohler. The name, **aluminum**, was proposed by Davy twenty years earlier (1807) and is derived from the chemical name **alum** ($\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) which was known to the ancient Greeks and Romans and used as an astringent (an agent that contracts body tissue and thus checks bleeding from capillaries) and as a mordant (a binder used to affix dyes to cloth). Shortly thereafter, the ending was changed from aluminum to aluminium to conform with the ending given most elements. The pronunciation became al-you-**min**-ee-yum. The new spelling was used in the USA too, until 1925 when the American Chemical Society decided to use 'aluminum' thereafter in its publications.

Between 1827 when metallic aluminum was first made and 1886 when the Hall process was discovered, metallic aluminum was a precious rarity. Globules of the metal were displayed next to the crown jewels at the 1855 Paris Exposition and Emperor Louis Napoleon III used aluminum cutlery on state occasions. In 1852, aluminum sold for \$550 per pound. At the turn of the century, and less than 20 years after the introduction of the Hall process, aluminum sold for \$0.33 per pound.

D. Physical properties. The physical properties of boron, aluminum and gallium are given in the table. Of the properties listed in the table, the atomic radius and density exhibit the expected periodic behavior. The

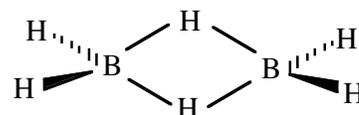
electronegativity decreases from boron to thallium, however, gallium's is slightly higher and an exception to the periodic trend.

	B	Al	Ga
Atomic radius (pm)	85	125	130
Pauling Electronegativity	1.9	1.5	1.6
mp ($^{\circ}\text{C}$)	2300	660	30
bp ($^{\circ}\text{C}$)	2550 ^a	2467	2403
density (g/cm^3)	2.34	2.70	5.90

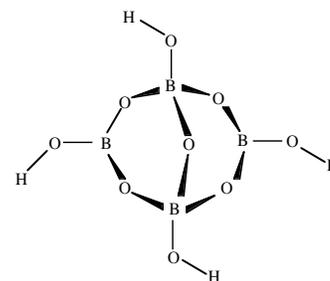
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E. Boranes.

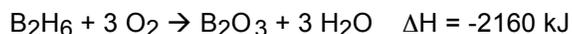
Boron a large number of compounds with hydrogen, as does carbon. The boranes, however, are not nearly as stable and exhibit unusual bonding arrangements. All boranes are air-sensitive and some react quite violently with air, specifically oxygen. In terms of bonding, boron has only 3 valence electrons and attempts to stretch the electron it gets from hydrogen by making 3-center, 2-electron bonds:



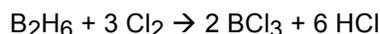
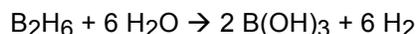
B_2H_6 , or diborane is the simplest of the boranes. The series continues and more complicated arrangements are also utilized such as 4-center, 3-electron bonds, and so on. The electron-poor structures are no match for a Lewis base. For example, boron in nature exists in a variety of oxyanions, including the most important one, borate, $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ as found in the minerals borax and kernite, shown at right.



Many boron hydrogen compounds (boranes) are flammable. Diborane (bp $-93\text{ }^{\circ}\text{C}$) is spontaneously flammable in air:



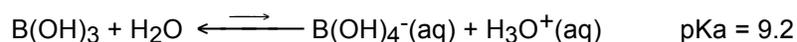
Diborane also reacts with water and chlorine to produce boric acid and boron trichloride, respectively:



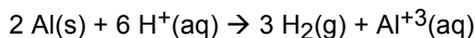
F. Oxides. Like the familiar aluminum oxide, Al_2O_3 , diboron trioxide has the formula B_2O_3 . It is one of the principle components in borosilicate glass, commonly sold under the brand name Pyrex.

G. Boric acid. Boric acid is a feebly weak acid. Its formula is usually written as H_3BO_3 , which misrepresents the molecular structure — it is actually that of a boron bonded to three OH groups. Sketch the structure of boric acid:

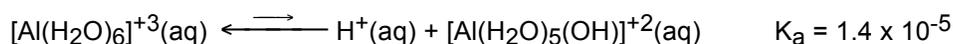
In general chemistry you have learned that acids are proton donors. This is not true for boric acid which owes its acidity to the fact that it is a Lewis acid and thus a hydroxide acceptor:



H. Aluminum reacts with acids and bases. Aluminum reacts readily with hydrochloric acid producing hydrogen while aluminum is oxidized:

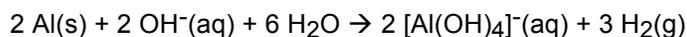


The aluminum product, shown as $\text{Al}^{+3}(\text{aq})$, is actually a hexaquo complex, $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$ which exists with an octahedral geometry. The ion $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$ is also fairly acidic and has a K_a value that is similar to that of acetic acid:



Sketch these complex ions ($[\text{Al}(\text{H}_2\text{O})_6]^{+3}$ and $[\text{Al}(\text{H}_2\text{O})_5(\text{OH})]^{+2}$), which are both octahedral in shape

Metallic aluminum readily reacts with strong bases - even faster than it does with a strong acid. The reaction again involves the oxidation of aluminum and the production of hydrogen:

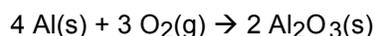


The complex ion $[\text{Al}(\text{OH})_4]^-$ consists of an Al^{+3} surrounded by a tetrahedral arrangement of hydroxide ligands.

I. Aluminum oxide. Aluminum forms a protective, transparent oxide coating. In your daily experiences with aluminum (cookware, food containers and foil wrap aluminum), you have probably observed that the metal behaves as though it is chemically inert. Indeed aluminum debris persists in nature for a long time. Aluminum metal is actually quite reactive; its oxidation potential is large and positive indicating a relative ease with which the metal should be oxidized:

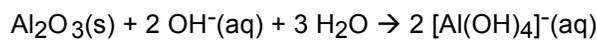
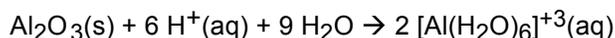


The oxidation is indeed facile and occurs quickly in air to fresh surfaces of aluminum producing Al_2O_3 , which forms an impervious, coating through which further exposure to air is prevented.



This protects the underlying aluminum metal from further oxidation. It's for this reason alone that we are able to use aluminum in so many applications. The coating is extremely thin and nearly invisible to the eye. It gives aluminum metal its somewhat dulled appearance that we usually attribute to the metal.

J. Amphoterism. Aluminum oxide readily reacts with acids as well as bases, as shown in these two equations:



In the reaction between Al_2O_3 and acid, the Al_2O_3 is a proton acceptor and is thus reacting as though it were a base. The product, $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$ is water soluble. In the reaction between Al_2O_3 and hydroxide, the Al_2O_3 undergoes an acid-base reaction in which it plays the role of the acid. Thus, Al_2O_3 functions as a base towards acids and as an acid towards bases. This property is called **amphoterism** - the ability to function as either an acid or a base.

5. Group IV. Carbon, silicon, germanium, tin and lead.

A. General. The group four elements include non-metallic carbon, semi-metal silicon and germanium, and the metals tin and lead. Unlike carbon, the rest of the Group IV elements do not generally exhibit catenation. Silicon is a possible exception: compounds containing Si-Si bonds can be made in the lab, however they are generally not stable. In addition, silicon and all elements in Periods 3, 4, 5, and 6, do not tend to form double bonds. This is due to the fact that the bond lengths are larger for these larger elements and orbital overlap involving p-orbitals that would by symmetry form p-bonds are simply too far apart. A most poignant example is CO_2 and SiO_2 . Carbon dioxide is a covalent molecular compound that is a gas and silicon dioxide is a network covalent compound with only single bonds and known as the mineral quartz.

B. Physical properties. The most interesting comparison of the Group 4 elements is the transition exhibited by the group from non-metallic (C), to metalloid (Si and Ge) to metallic (Sn and Pb). The physical properties listed in the table demonstrate a smooth transition in properties. Covalent radius, first ionization energy and electronegativity all follow predicted periodic trends. The trend in melting points reflects the transition from network covalent, non-metals with high melting points to purely metallic forces operating for Sn and Pb. Electrical conductivity, is low for the metalloids and much higher for the metals. Carbon's conductivity is relatively high for the graphite form, reported here, due to the ability of the 2-dimensional sheets of aromatic carbons to conduct electricity through the p-manifold of orbitals.

	Carbon	Silicon	Germanium	Tin	Lead
Covalent radius, pm	77.2	117.6	122.3	140.5	146
First ionization potential (V)	11.26	8.151	7.899	7.344	7.416
Pauling electronegativity	2.55	1.90	2.01	1.96	2.33
mp (°C)	4100 ^a	1685	1210	505	601
bp (°C)	4470 ^a	3540	3107	2876	2023
density (g/cm ³)	2.62	2.33	5.32	7.30	11.4
$\Delta H_{\text{vaporization}}$ (kJ/mol)	356	384	331	296	178
Elect. conductivity (mW ⁻¹ cm ⁻¹) ^b	6.1×10^{-4}	2.5×10^{-12}	1.5×10^{-8}	9.2×10^{-2}	4.8×10^{-2}

C. Lanthanide contraction. Notice that lead doesn't follow the expected periodic trend in terms of electronegativity, ionization energy, and ionization potential. This is the result of the 4f orbitals that are filled prior to the 6p orbitals. All of these trends are explained by the effective nuclear charge. Calculate the Slater shielding and effective nuclear charge that is expected for each of the Group IV elements.

C

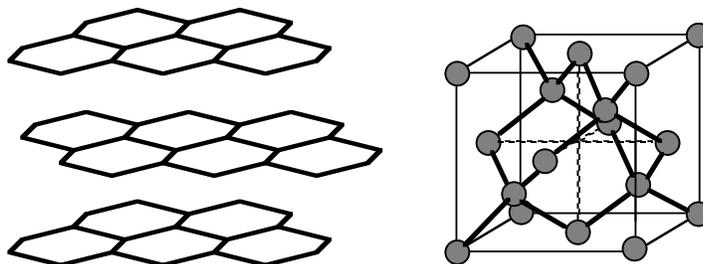
Si

Ge

Sn

Pb

D. Allotropes of carbon. Elemental carbon is a black, non-metallic element. Carbon exists in three forms or **allotropes**. These forms include graphite, which is one of the softest of the solid elements and diamond which is the hardest. (Graphite has a hardness of 1.0 on the geologist's hardness scale and diamond defines a hardness of 10.0.) A third allotrope of carbon was discovered in 1985 and is called **buckminsterfullerene**. The table below summarizes important physical properties of the three allotropes although very few data are available for buckminsterfullerene.



The structure of graphite consists of sp^2 carbons in a hexagonal pattern of flat sheets. The C-C bond distance is 141.5 pm within the sheets and 335.4 pm between the sheets. Van der Waals forces hold the adjacent sheets together. These forces are easily overcome and the sheets easily slide past each other - giving graphite its property of being a good lubricant. Note also that the **resistivity** of graphite varies by a factor of several thousands depending along which crystal axis the measurement is being made. Resistivity is large when measured perpendicular to the graphite's sp^2 sheets. When measured along either of the planar axes, the resistivity is low because electrons are conducted through the network of p-orbitals (p-manifold). Diamond has an sp^3 network covalent structure. It utilizes a cubic style unit cell with a C-C bond length of 154.45 pm. As indicated by its resistivity, diamond is a non-conductor

Property	a-Graphite	Diamond	buckminsterfullerene
Formula	C(s)	C(s)	C ₆₀ (s)
Hybridization	sp^2	sp^3	sp^2
Hardness	1.0	10.0	?
Density	2.266 g/cm ³	3.514 g/cm ³	1.7 g/cm ³
Resistivity	ca 4×10^{-4} ohm cm ^a and 0.2 - 1.0 ohm cm ^b	ca 10^{14} - 10^{16} ohm cm	
ΔH_f	0.00 kJ/mol	1.90 kJ/mol	
phase changes	sublimes: 3367 +/- 25 °C; bp 4827 °C	mp: 4100 +/- 200 °C at 125 kbar	

^aAlong base; ^balong axis

E. Inorganic Carbon. As a simple way to differentiate between organic and inorganic carbon, let's say that generally organic carbon includes compounds that exhibit carbon-carbon or carbon-hydrogen bonds and inorganic carbon generally does not. Inorganic carbon compounds include: elemental carbon, C, carbides (C₂²⁻, C⁴⁻), carbonates (CO₃²⁻), carbonic acid (H₂CO₃), bicarbonates (HCO₃⁻), carbon monoxide (CO), carbon

dioxide (CO_2), carbon disulfide, (CS_2), oxalates ($\text{C}_2\text{O}_4^{2-}$), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), carbon tetrachloride, (CCl_4). In addition, there are numerous compounds that are considered either organic or inorganic. Methane and all other non-catenated forms of carbon are examples. Thus, chloromethane, methylene chloride, formic acid (methanoic acid), formaldehyde (methanal), methanol, urea (NH_2CONH_2) are examples.

F. Silicon. Although silicon does not exist as a free element in nature, the element constitutes 26% by mass of the earth's crust. Only the element oxygen is more plentiful and together these two elements exist as silicates.

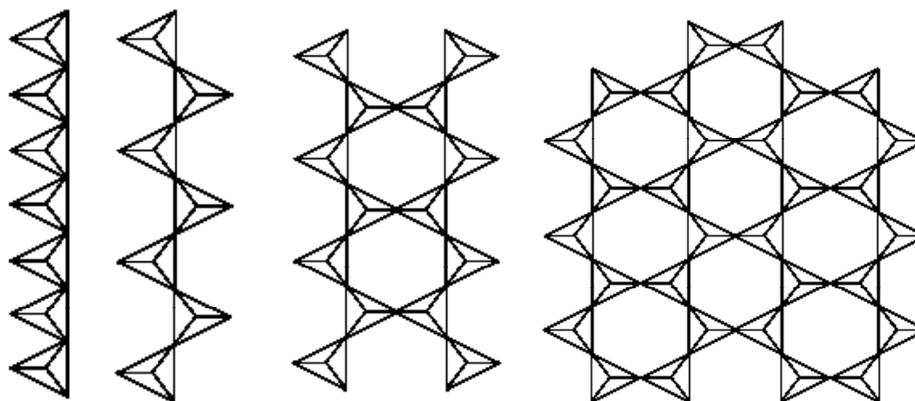
G. Silicates. Most of the silicon in the earth's crust is in the form of silicates, polymeric silicon-oxygen anions such as monomeric SiO_4^{4-} and polymeric $(\text{SiO}_3^{3-})_n$, $n = \text{millions}$. Silicates constitute over 90% of the earth's crust. The table lists some silicate-based minerals with relatively simple formulas.

We have already encountered orthosilicate SiO_4^{4-} and pyrosilicate, $\text{Si}_2\text{O}_7^{6-}$. Condensed rings of three and six SiO_4 units are also possible. Sketch these using the tetrahedral pyramid notation and give their charges:

The most familiar example of the polysilicate anion with six SiO_4 is the mineral beryl which is usually referred to by its gem name: emerald. The cations include Be^{+2} and Al^{+3} . The green color of emerald is due to trace amounts of Cr^{+3} .

Mineral Name:	Formula:
phenakite	Be_2SiO_4
willemite	Zn_2SiO_4
olivine	$(\text{Mg, Fe})_2\text{SiO}_4$
pyrope	$\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$
almandine	$\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$
grossular	$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$
uvarovite	$\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$
andradite	$\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$
zircon	ZrSiO_4

The chain silicates can further condense to form double chain structures such shown below in the two left figures. Keep in mind that only a small segment of a linear polymeric chain is shown here — and the cations are not shown. This complicated structure is the result of condensing the pyroxene anion chain (with its mirror image). What is the empirical formula and charge for these two silicates?



The double chain polysilicate shown as the third figure above is called an amphibole. These can form fibrous materials providing that the polymeric chains crystallize in a parallel fashion. A familiar example of a fibrous amphibole is asbestos in which case the cations are magnesium and calcium. What is its empirical formula of the anion? Show work here or on the drawing.

Polysilicates can also form 2-dimensional sheets of condensed tetrahedra. A portion of such a sheet is shown in the rightmost figure above. What is its empirical formula of the anion?

As you might imagine, there is considerable bond strength in the 2-dimensional sheet of silicate tetrahedra. The cations hold these sheets together. In some cases, the cations are all located between alternate sheets - they do not occur between every sheet; alternate sheets are held together only by dispersion forces. For this reason, sheets are easily cleaved from one another. The extremely soft mineral talc (talcum powder) is an example of this sheet-type polysilicate. Talc has the empirical formula $\text{Mg}_3(\text{OH})_2\text{Si}_4\text{O}_{10}$. Micas also utilize the sheet polysilicate structure, however in the case of micas, the cations exist between all sheets. There is a wide variety of minerals that belong to the mica group. The list of mica cations include H^+ , K^+ , Al^{+3} , Li^+ , Mg^{+2} , and Fe^{+2} .

There is one final degree of polysilicate condensation that is possible. This joins the 2-dimensional sheets into a three dimensional structure with empirical formula SiO_2 . The mineral quartz has this structure.

F. Organosilanes. Compounds with carbon-silicon bonds have been made in large number. None occur in nature and all are air and moisture sensitive. The tendency to oxidize to form very thermodynamically stable Si-O bonds drives silicon chemistry. The simplest carbon-like compound is silane, SiO_4 . It immediately bursts into flames upon exposure to air. Other carbon-like compounds include $\text{Si}(\text{CH}_3)_4$, $\text{Si}(\text{CH}_3)_3\text{Cl}$, $\text{Si}_2(\text{CH}_3)_6$, SiCl_4 , and so on. Because Si-H bonds are so unstable, and silicon is larger than carbon, the analogy to ethane, with a C_2 backbone, is with a Si_2 backbone is $\text{Si}_2(\text{CH}_3)_6$; methyls are used instead of hydrogen atoms to add a little more stability. All of the organosilanes cited as examples are low-boiling liquids.

Review for ACS Final.

1. Which element is known for its +1 and +3 oxidation states?
(a) Ta (b) Tc (c) Te (d) Ti (e) Tl
2. Which element exists in allotropic forms?
(a) Br (b) Cu (c) Ar (d) Si (e) P
3. Which of following statements about sodium is false?
(a) Na is more reactive towards air and water than lithium, but less so than K.
(b) Sodium forms dimers, Na_2 , in the gas phase.
(c) The first ionization energy for Na is endothermic.
(d) Sodium forms sodium peroxide when exposed to air.
(e) Sodium forms polar covalent bonds in most of its compounds.
4. Which metal reacts with $\text{NaOH}(\text{aq})$ to form hydrogen?
(a) iron (b) cobalt (c) aluminum (d) copper (e) lead
5. Which oxide is a base anhydride?
(a) Li_2O (b) Fe_2O_3 (c) Al_2O_3 (d) P_2O_5 (e) SO_2
6. Which statement is NOT true for sodium metal?
(a) Sodium is more reactive than potassium.
(b) The ionization energy of sodium is greater than that of potassium.
(c) The electronegativity of sodium is less than that of lithium.
(d) The atomic radius of sodium is less than that of potassium.
(e) The electron affinity of sodium is greater than that of cesium.
7. Which elemental calcium is added to water, what occurs?
(a) The solution becomes acidic.
(b) Hydrogen is formed.
(c) Calcium dissolves.
(d) Calcium rapidly forms calcium oxide.
(e) Calcium hydride forms over time.

Answers: e, e, e, c, a, a, b

Answers to Day 12.

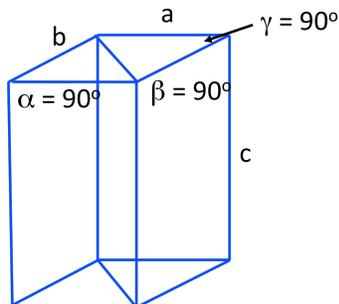
1. Bravis fundamental lattice types

$\alpha = 78^\circ$; $\beta = 77^\circ$; and $\gamma = 86^\circ$.

Two of the eight balls in the triclinic model, actually exhibit all three cell angles to be less than 90° .

It is possible to have a monoclinic or triclinic unit cell with two cell dimensions exactly the same length as a coincidence

(d) figure at right



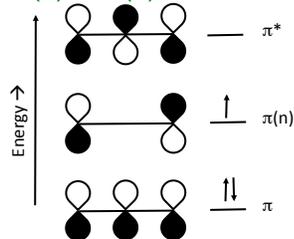
2. Silicates.



3. Semiconductors A. Conjugated ene systems.

1. The left one is bonding (0 nodes) and the right one is anti-bonding (1 node). (b) and (c)

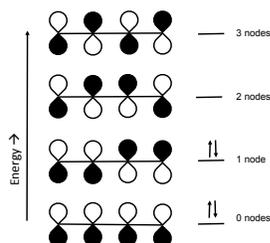
2. (a) and (d)



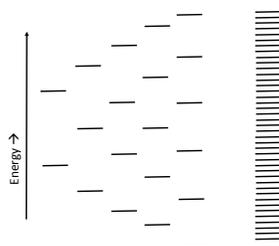
	AO (C1)	AO (C2)	AO (C3)	sum
MO(π^*)	1/4	1/2	1/4	1
MO($\pi(n)$)	1/2	0	1/2	1
MO(π)	1/4	1/2	1/4	1
sum	1	1	1	

(e) For the allyl radical, there is a node at C2. The radical electron is on C1 and C3

3.



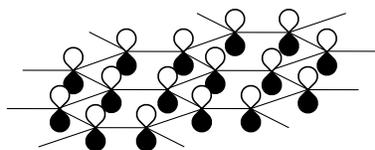
B. Extended conjugated ene systems. The lower half of each of these MO diagrams are filled.



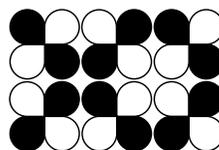
C. Network covalents.

2. (a) diamond NC (b) tin M (c) calcium carbide I
 (d) silicon carbide NC (e) silicon SM (f) silicon tetrachloride CM
 (g) sodium silicide I (h) graphite NC (g) copper M

3.

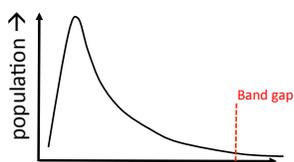


4.



D. Band theory. 2. From L → R: conductor, semi-conductor, insulator; 3. The MO diagrams were made from s and d orbitals (6 orbitals) per atom. They are, in order, Sc, Cr, Co, and Zn. The bond order is largest for the half-filled figure, and that corresponds to Cr. Chromium has a high melting point and is hard and strong. Zinc, cadmium and mercury must use p-orbitals as well in their valence manifold. This way they can have some bond order and be able to conduct electricity.

3. (a) Silicon be a non-conductor at 0 K. (b):



E. Semi-conductors. 1a.



F. Diodes: p-n junctions. 2a. The p-type is slightly **negative** and the n-type is slightly **positive**. (b) Left half is δ^- .
3. The energies of orbitals on cations are **lower** than on their neutral or negative counterparts.
4. When the voltage is applied in a forward bias situation, electrons flow as per the arrow. When the battery is switched, electrons do not flow. The diode "rectifies" alternating current, turning it into phased direct current



G. Photosensitive switches.

H. Photovoltaic cells

I. LEDs

