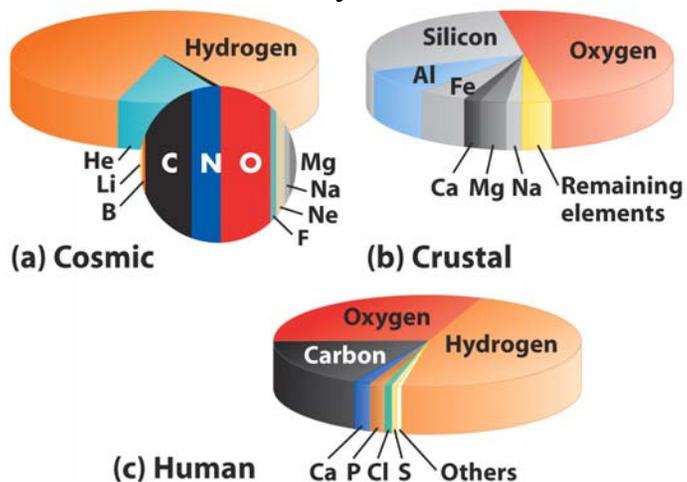


Lecture 23: Main Group Chemistry

An Introduction

We have spent the better part of the school year developing physical models to describe atomic structure, chemical bonding and the thermodynamics and kinetics physical and chemical phenomena. In all of that, however, we have been just as content to use generic symbols like $A + B \rightarrow C + D$ or to describe a weak acid as HA, as to actually assign it a real chemical structure with real chemical reactivity.



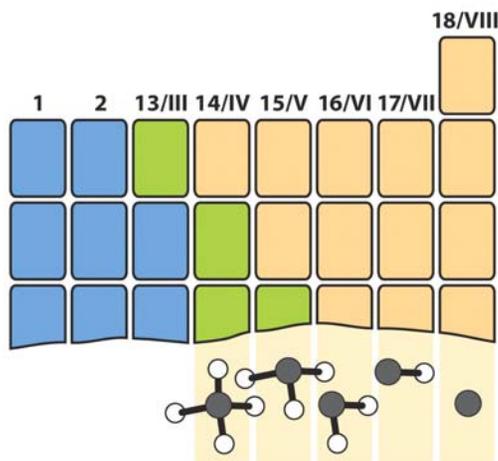
In this chapter we right this wrong, working systematically through the main groups of the periodic table, learning for each group and particularly significant elements in those groups:

- The natural forms in which the elements are found, including the hydrides and oxides
- The famous chemical reactions that involve the chemical compounds containing those elements
- The important practical uses of the compounds containing those elements.

Common themes in Main Group Chemistry:

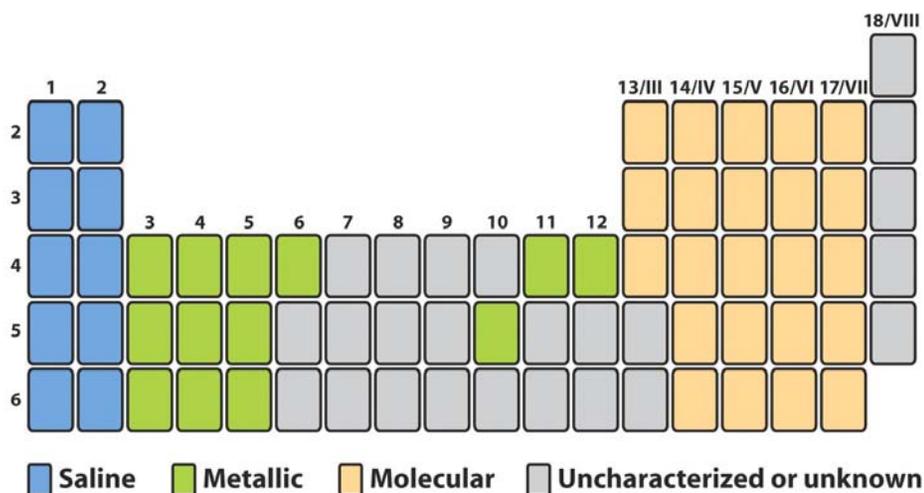
We must have learned something useful during the year that will help to explain the chemistry of the main group elements. Here are some important themes that appear to explain pretty much everything that happens

1. The number of valence electrons in atoms drive the chemistry of a compound. And the main group number corresponds to the number of valence electrons



2. Compounds formed by main group elements pretty much always satisfy the octet rule if they can, achieving noble gas-like electronic configurations
3. There are trends in the periodic table that are pretty much determined by the effective nuclear charge and overall number of electrons in an atom. These trends are:
 - a) atomic radius decreases moving to the right and up the periodic table
 - b) ionization energy increases moving to the right and up the periodic table
 - c) electronegativity increases to the right and up the periodic table
 - d) polarizability increases to the right and down the periodic table
 - e) non-metallic character increases to the right and up the periodic table
4. The second row of the periodic table is very special because overlap of adjacent 2p orbitals creates π bonding and because the significance of intermolecular hydrogen bonding forces. In contrast, third and higher rows create expanded orbitals to accommodate additional electrons in mushy low energy bonds.

5. Pretty much every element except the noble gases forms very stable compounds with itself, whether through metallic bonding, network solids like C, or small covalent molecules like N₂ or P₄.
6. Pretty much every compound forms hydrides (reacts with hydrogen). Basic ionic hydrides like NaH are found to the left on the periodic table and increasingly covalent acidic hydrides like HCl are found to the right on the periodic table.



7. Pretty much every compound forms oxides. Basic oxides are found to the left on the periodic table, a remarkable array of transitional metal and metalloid oxides with varied oxidation number make up the earth crust and give us the wealth of materials (from glass to gemstones) that make our lives interesting, and end at the right side of the table with the molecular oxides, like CO₂ or SO₃, that form oxyacids in water.

If you walked around thinking about these 7 ideas all the time, you would have the makings of a pretty good inorganic chemist.

Hydrogen Belongs to No Group

We would like to start with Group I, but first we need to get H out of the way. It doesn't really belong to any group given its chameleon-like nature. Perhaps the biggest clue for this is that it has an EN of 2.1 which would position it right smack in the middle of row 2 where it is remarkably adept at picking up a single electron like the halogens to be Noble gas-like, and equally adept at losing an electron to form the proton.

Common forms for elemental hydrogen.

TABLE 14.1 Physical Properties of Hydrogen

Valence configuration: $1s^1$

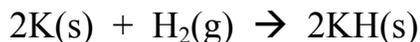
Normal form*: colorless, odorless gas

Z	Name	Symbol	Molar mass ($\text{g}\cdot\text{mol}^{-1}$)	Abundance (%)	Melting point ($^{\circ}\text{C}$)	Boiling point ($^{\circ}\text{C}$)	Density ($\text{g}\cdot\text{L}^{-1}$) [†]
1	hydrogen	H	1.008	99.98	-259 (14 K)	-253 (20 K)	0.089
1	deuterium	^2H or D	2.014	0.02	-254 (19 K)	-249 (24 K)	0.18
1	tritium	^3H or T	3.016	radioactive	-252 (21 K)	-248 (25 K)	0.27

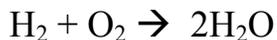
*Normal form means the state and appearance of the element at 25°C and 1 atm.

[†]The density refers to the same conditions.

There are three isotopes of hydrogen with almost all of it consisting of a single electron surrounding a single proton which means it has a $1s^1$ configuration meaning it would be happy both gaining and losing an electron.. Looking around the universe hydrogen is king, with 90% of all the atoms. On earth, its elemental form is dihydrogen, H_2 , a flammable gas that is so light it just floats off into space. On the bright side hydrogen reacts with just about everything to form hydrides



or



(like in water) or any of the hydride forming reactions in the table

TABLE 14.2 Chemical Properties of Hydrogen

Reactant	Reaction with hydrogen
Group 1 metals (M)	$2 \text{ M(s)} + \text{H}_2(\text{g}) \longrightarrow 2 \text{ MH(s)}$
Group 2 metals (M, not Be or Mg)	$\text{M(s)} + \text{H}_2(\text{g}) \longrightarrow \text{MH}_2(\text{s})$
some <i>d</i> -block metals (M)	$2 \text{ M(s)} + x \text{ H}_2(\text{g}) \longrightarrow 2 \text{ MH}_x(\text{s})$
oxygen	$\text{O}_2(\text{g}) + 2 \text{ H}_2(\text{g}) \longrightarrow 2 \text{ H}_2\text{O(l)}$
nitrogen	$\text{N}_2(\text{g}) + 3 \text{ H}_2(\text{g}) \longrightarrow 2 \text{ NH}_3(\text{g})$
halogen (X_2)	$\text{X}_2(\text{g,l,s}) + \text{H}_2(\text{g}) \longrightarrow 2 \text{ HX(g)}$

so there is plenty of H around, if not exactly in the forms we prefer.

So why to people love hydrogen? Because as dihydrogen, H_2 , it produces the most energy per mass of any fuel in the reaction



So obviously being able to find or create H_2 is lucrative as drilling for oil.

So what are some ways to make H_2 ? Industrially it is done using a Nickel catalyst to drive the reforming reaction:

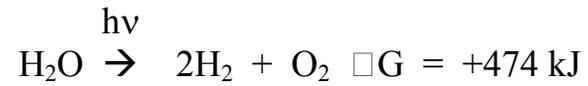


And in the lab you can generate it easily using:



You can even do it in the privacy of your own home by throwing a battery in water.

But ideally we want to do it with as inexpensive a source of energy as possible, and the holy grail of all chemical reactions these days is the photochemical decomposition of water. Using sunlight rather than that expensive battery to drive the electrolysis of water.



Reactions of H₂

So what do people do with H₂ when they make it?

- Drive cars in the 21st century
- Extract pure metals like copper from ore: $\text{M}^+ + \text{H}_2 \rightarrow \text{Cu} + 2\text{H}^+$ when ΔG is negative
- React it in the Haber Process to make NH₃ which is used to fertilize the earth.

Group I: The Alkali Metals

TABLE 14.3 Group 1 Elements: The Alkali Metals

Valence configuration: ns^1

Normal form*: soft, silver-gray metals

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

*Normal form means the state and appearance of the element at 25°C and 1 atm.

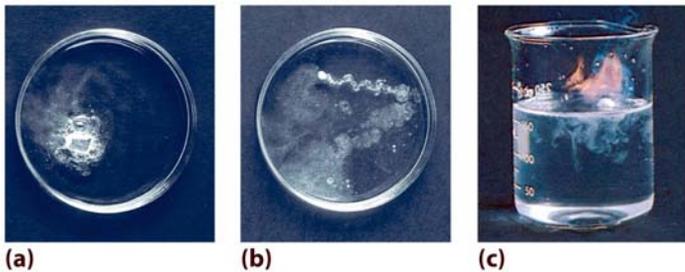
Alkali metals are a general chemistry student's friend. There is no ambiguity about them. Every one of them:

- Has a $1s^1$ electronic configuration
- Has a really low ionization energy
- Behaves like a metal (easily oxidized) in donating an electron to form a mono-cation that are ALWAYS +1 oxidation state no matter the compound
- Has really low boiling and melting points and weak bonding
- are highly reactive in water and with just about anything.
- Forms basic hydrides and oxides.

These materials are the metals stored in glycerin that I trot out every couple of weeks, clean up, slice to expose a shiny large surface area, and then step back to watch explode according to the following displacement reaction:



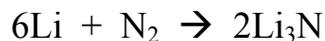
Note that a base is formed and that the hydrogen gas generated actually catches fire from the heat evolved.



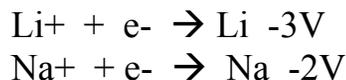
A similar reaction of the hydride also occurs, but Debra doesn't let me do this exciting demo.



And as proof that the alkali metals react with everything, here is Lithium that I don't even get to bring out in the air because it reacts with nitrogen in the air:



No wonder that when you look at the table of half cell reactions, right at the top of the table of reduction potentials are



Which means that the reverse reactions, the oxidations, are as good as it gets and that these metals are the best reducing agents out there, and prime targets for making batteries, like say, the Li ion battery.

And finally, the ubiquitous nature of the cations:

Li^+ , Na^+ , K^+ etc means they have found their way into our daily lives in a couple of ways:

- They are the salty taste in your foods
- They are the colors you see when you start to burn stuff, like the yellow in a match flame from the sodium ion.
- They are vital in neurological and metabolic processes in the body in which the relative concentrations of ions like Li^+ and K^+ and Na^+ matter. But that is biology which I know nothing about.

Group II--Alkali Earths.

TABLE 14.4 Group 2 Elements

Valence configuration: ns^2

Normal form*: soft, silver-gray metals

Z	Name	Symbol	Molar mass ($\text{g}\cdot\text{mol}^{-1}$)	Melting point ($^{\circ}\text{C}$)	Boiling point ($^{\circ}\text{C}$)	Density ($\text{g}\cdot\text{cm}^{-3}$)
4	beryllium	Be	9.01	1285	2470	1.85
12	magnesium	Mg	24.31	650	1100	1.74
20	calcium	Ca	40.08	840	1490	1.53
38	strontium	Sr	87.62	770	1380	2.58
56	barium	Ba	137.33	710	1640	3.59
88	radium	Ra	(226)	700	1500	5.00

*Normal form means the state and appearance of the element at 25°C and 1 atm.

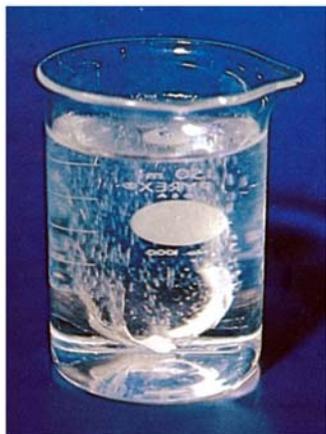
These metals are quite reactive so you will not find them as metals in their pure form, but rather as oxides, carbonates or phosphates. A particularly famous one of these is the rare gem emerald, which is what you get when beryllium oxide is doped with Cr^{+3} ions.



Emerald

Now chemically, and unlike the group I elements, the group II start to show some variety as Be contrasts with the later elements by forming covalent bonds and consequently forming some interesting molecules. Beginning with Mg, the rest of the elements are metallic. Here are some common reactions.

The metals react in hot water in a displacement reaction with products like the alkali metals. Look at the picture of H₂ bubbling away when Ca is added to hot water:



Alkali metal oxides also are basic and react in water to form hydroxide.



Some important applications of alkali earth chemistry.

To begin, the calcium ion finds itself in a wide array of structural materials like bone and concrete and tooth enamel. Why? It forms a relatively small doubly charged ion with a lot of charge density and the right size to create powerful material with polyanions like phosphate and carbonate.

The most common form of calcium is calcium carbonate, which, is what we call chalk or limestone and is the material on which the city of Austin rests. One of the key reactions of limestone is to heat it to form Calcium oxide, CaO, which is also called quicklime.



We have seen just how nasty quicklime is—we added water to it and it boiled so violently that it boiled an egg in CH301.

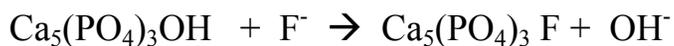


Now calcium is found not just in building materials like cements and mortar, it is also a building block for structure in the body, stuff like bones and teeth. So here is something you might not have known. How tooth decay works:

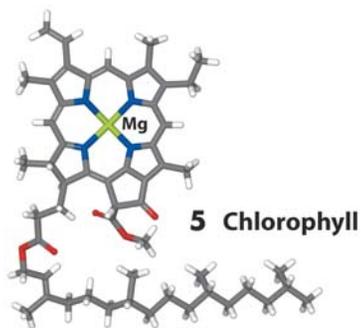
In the first reaction you will notice that tooth enamel, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, is attacked by acid and falls apart.



But if you could replace the OH^- group in the tooth enamel with something that was about the same size but no where near as reactive with protons (like just about anything but hydroxide) you might reduce tooth decay. So what about fluoride, which as shown in the reaction below, is allowed to replace the hydroxide. It is many orders of magnitude less reactive than the hydroxide compound.



But of all the Group II metals, the one that has the most important role, is Magnesium, and it comes in a very unusual way, as part of the molecule chlorophyll. As shown in the structure below, an Mg ion is strategically placed in the middle of a ring structure in the organic part of the molecule. One of the responsibilities of the Mg is to keep the ring structure rigid so the energy cascade to form ATP can happen. Alternate routes for energy loss (like vibrations) would prevent the desired energy process from occurring.



Group III—The B Group

The Group III elements are the first to really distinguish non-metallic and metallic character in the group. Boron, with an electronegativity of 2.0, very much forms covalent bonds. And given its odd number of electrons and inability to form four bonds to achieve an octet configuration, is involved in forming some remarkable compounds.

Aluminum is by far the most important of the elements in the row for two reasons, it is third only to Si and O in the earth's crust and it is a smallest non-reactive metal, which makes it important in manufacturing.

Elemental forms of B and Al.

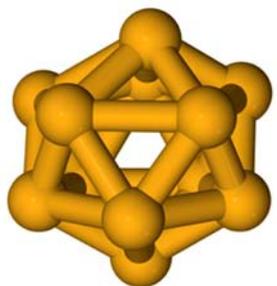
TABLE 14.5 Group 13/III Elements

Valence configuration: ns^2np^1

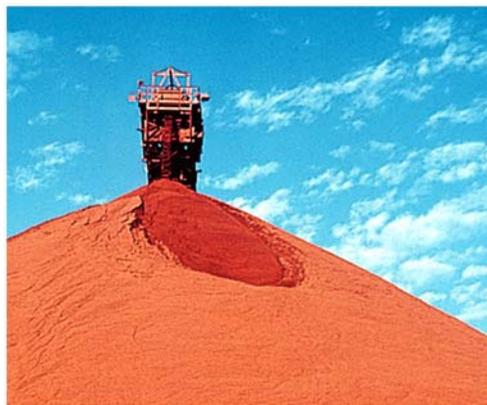
Z	Name	Symbol	Molar mass (g·mol ⁻¹)	Melting point (°C)	Boiling point (°C)	Density (g·cm ⁻³)	Normal form*
5	boron	B	10.81	2300	3931	2.47	powdery brown metalloid
13	aluminum	Al	26.98	660	2467	2.70	silver metal
31	gallium	Ga	69.72	30	2403	5.91	silver metal
49	indium	In	114.82	156	2080	7.29	silver-white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

*Normal form means the state and appearance of the element at 25°C and 1 atm.

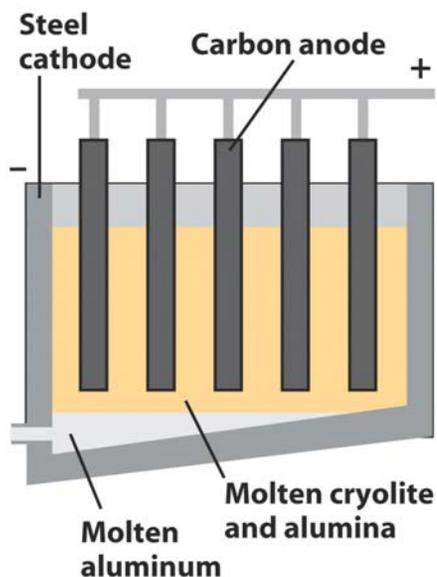
There are a variety of allotropes of boron, the most famous being B_{12} —all of them are formed in odd ways to achieve an octet configuration. Boron is actually extracted from the earth as $Na_2B_4O_7$ (borax). The red color of the material is due to an iron contaminant.



6 B_{12}



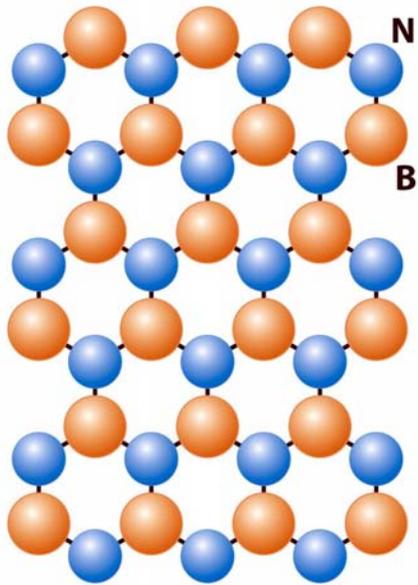
Aluminum is the most abundant compound in elemental form in the earth's crust and the most common element in metallic form, although it is not readily mined as a metal. Instead, aluminum is mined as Bauxite, an impure aluminum oxide, and turned into alumina (Al_2O_3) by the Bayer process. But the real triumph in manufacturing came when a process was created for producing Aluminum in relatively inexpensive way called the Hall Process. Aluminum is removed from the earth as Na_3AlF_6 , cryolite, melted with Alumina in an electrochemical process with the following overall reaction to produce metallic Al:



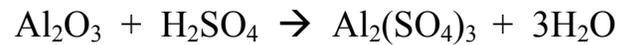
Applications of B and Al.

- $\text{B}(\text{OH})_3$ is a Lewis acid, boric acid that people love to call the “natural” or “organic” way to kill pests. Sure.
- Boron also forms some very interesting compounds with nitrogen called boron nitrides which have the same electronic configuration as graphite and C_{60} and consequently have prompted a lot of interest in them for new materials.





Aluminum is used in many manufacturing processes, most famously, the production of paper. Aluminum sulfate is known as papermaker's alum.



Aluminum oxides are also the basis of many valuable gems when combined with trace metals.



Ruby

Sapphire

Topaz

the trace metals added to get the color:

Cr⁺³

Fe⁺³ and Ti⁺⁴

Fe⁺³

Group IV—the Carbon Group

You might think that having spent a couple of lectures on organic compounds that we had already covered carbon and the Group IV compounds. But actually, not even close.

A look at the elements shows off the remarkable array of elements that form the basis of much of what makes our daily lives more livable.

TABLE 14.6 Group 14/IV Elements

Valence configuration: ns^2np^2

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

*Normal form means the state and appearance of the element at 25°C and 1 atm.

[†]The symbol s denotes that the element sublimes.

For example, we have the allotropes of elemental carbon:

Diamond graphite C₆₀

And we have all the silicon-based compounds which are very likely dominant, seeing as how, after oxygen, it is the most abundant element in the crustal.

And then we have to deal with the metalloid properties of silicon and germanium that make for a pretty important class of compounds called transistors

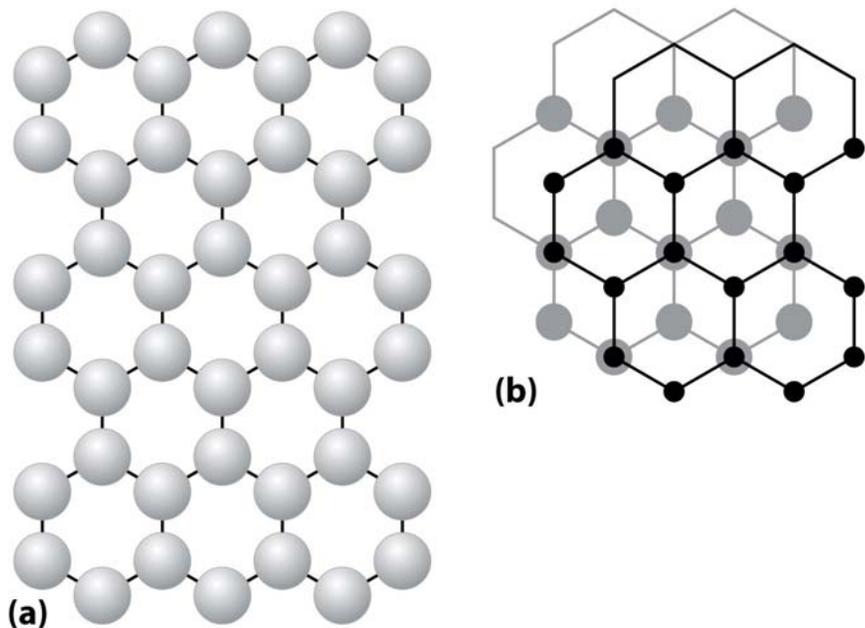
And who can forget the tin can or that lead has the kind of properties that shield Superman from Kryptonite.

Carbon Allotropes.

Of the three allotropes of carbon, graphite is the most apparent to us. It is what makes up soot, activated charcoal, and of course, pencil lead.

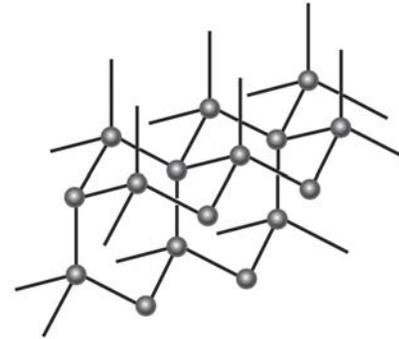
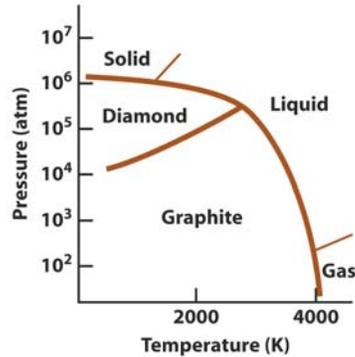
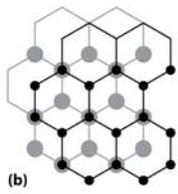
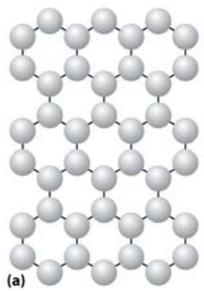
What is quite interesting about graphite is its structure, a series of hexagons with sp^2 hybridization. This might prompt you to ask what happens with the other p electron in carbon, and the answer is that it is part of an elaborate π -bonding structure between sheets of the σ -bonding C hexagons.

Among other properties, these free floating electrons contribute to electrical conductivity, which means, oddly enough, that Carbon electrodes for electrochemistry are very common.



Note, also, that this is a structure analogous to what is formed with boron-nitride compounds as described in the section on Group III compounds.

Diamond, of course, is the allotrope of carbon everyone covets. For some it is because it is pretty and shiny, but engineers like it because it is the hardest compound known and also is the best heat conductor known. This means that being able to make it synthetically by subjecting graphite to high pressures and temperatures, produces a really great abrasive (the best sandpaper known.) The structure of carbon is actually pretty boring—it is very simply a 3-dimensional series of sp^3 geometries (all sigma bond.) and so, lacking in π bonds, doesn't have a lot of electron movement and is an insulator.

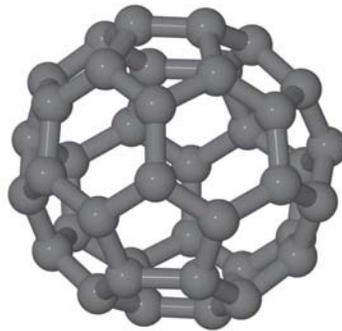


Graphite (conducting and sp_2)

at high pressure

makes diamond (insulating and sp_3)

A final, very recently discovered allotrope of carbon is C_{60} , a beautifully symmetrical molecule.

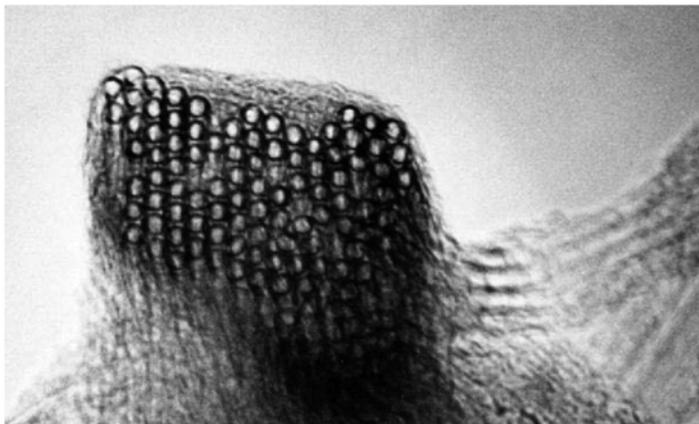


10 Buckminsterfullerene, C_{60}

C_{60} was discovered in the mid 80s, and has sent scientists into a frenzy because they have something new to play with. Some of the interesting things about C_{60} are that:

- it is conducting,
- it is a molecule and so can be dissolved in solvents (like benzene),
- is a cage that you can put things in, like metal that become superconducting at high temperatures,
- it is of a more general class that includes nanotubes.

Everyone likes tubes because of all the things you can do with tubes, like flow stuff through them. The idea that these nanotubes can be used in microelectronics and in nanosensors, has the folks over in the nanoscience building very excited.



Carbon Oxides.

I would be remiss to not mention the chemical compounds that we have built the city of Austin on. Carbonates, those compounds formed with the polyanion $\text{CO}_3^{=}$ are ubiquitous. They react with cations like the alkali metals and earths to form bones and chalk and as I said, the rocks we live on. Carbonates also participate in a rich acid/base equilibrium



which I have shown off throughout the course, for example, when I wanted to teach about polyprotic acids and when I wanted to show off the miscibility of gases like CO_2 in water when I had the two love birds from class blow through straws to make a solution of water acidic by commingling it with their shared exhalations of CO_2 .



Silicon.

Silicon is everywhere because sand and rocks are everywhere. And borrowing a page from carbon, the Group IV elements are capable of forming an amazing array of very stable chemical compounds.

I list a few of them here and then talk about them a bit.



Silicas (SiO_2) like amethyst, agate and onyx



Silicates, (SiO_4) like asbestos



aluminosilicates like mica

I won't bore you with learning the names of all the minerals formed from silicon-based compounds, but they are legion and vary based upon the level of metal and metal oxide impurities added to them. They form the basis for some of our most important synthetic materials including, most obviously, glasses (see mica above) and ceramics.

The manufactured glass we put in our houses is formed by taking sand (silica or SiO_2) and mixing it with varying amounts of metal oxides. For example:

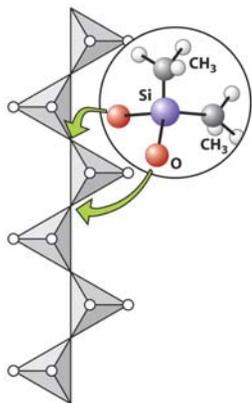
- Soda-line glass—made from melts of SiO_2 and sodium oxide and calcium oxide
- Borosilicates (Pyrex)—formed from melts of SiO_2 with B_2O_3 .

Silicones.

Another very common, but very different famous silicon-based compounds, are the silicones. These guys are not very rock-like because they have been modified with organic materials to create some useful properties. The basic form of silicone is a series of repeating Si-O units in a backbone



to which organic substituents can be added.



Note that by adding the organic functionality we can make a lot of different interesting compounds. The one most known to you is to add alkyl groups to the silicone to make a compound that repels water in windows frames sealants and in waterproofing fabrics.

Preparing for Groups V, VI and VII

Before launching into any detail about the rest of the main groups, it is important to stop and appreciate that these are the groups with the elements that produce the lion share of our chemical compounds. While it is nice that we have all those rocks and minerals from groups I-IV and the transition metals, the real work that makes the world go round, makes it possible to produce all the manufactured products you use, is because of the really nasty collection of reactive chemicals formed from Groups V, VI and VII.

It is unlikely that if you stopped someone on the street and said, quick, what are the top four chemicals produced in the world, that they would say:

Sulfuric acid

phosphoric acid

ammonia

chlorine

But if you want proof, at the following table from *Chemical and Engineering News*. and focus on the red highlights.

THOUSANDS OF TONS UNLESS OTHERWISE NOTED	PRODUCTION										
	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001 ^a
Aluminum sulfate ^b	1,185	1,047	1,050	1,140	1,144	1,197	1,161	1,166	1,196	1,091	
Ammonia ^{c,d}	17,169	17,924	17,195	17,869	17,403	17,923	17,891	18,475	17,337	16,806	
Ammonium nitrate ^e	7,819	7,981	8,280	8,568	8,489	8,498	8,604	9,079	7,630	7,498	
Ammonium sulfater	2,243	2,391	2,432	2,584	2,647	2,662	2,702	2,787	2,599	2,868	
Chlorine ^g	11,572	11,757	12,079	12,187	12,395	12,460	12,922	12,841	13,353	13,131	
Hydrochloric acid ^h	3,301	3,610	3,492	3,754	3,904	4,116	4,570	4,659	4,499	4,718	
Hydrogen, bcf, 100% ^{i,j}	153	162	213	331	352	386	526	552	454	481	
Nitric acid, 100% ^k	7,927	8,136	8,254	8,714	8,840	9,205	9,433	9,285	8,945	8,479	
Nitrogen gas, bcf, 100% ^{i,l}	770	818	796	870	844	816	809	871	858	933	
Oxygen, bcf, 100% ^l	470	515	547	605	630	682	743	676	685	661	
Phosphoric acid, P ₂ O ₅	12,109	12,826	11,515	12,792	13,134	13,210	13,159	13,891	13,708	13,143	
Sodium chlorate	449	555	539	559	617	662	626	779	818	939	
Sodium hydroxide	11,713	12,244	12,466	12,539	11,408	11,563	10,973	13,113	13,199	11,518	
Sodium sulfate ^m	794	609	592	652	711	664	706	629	660	509	569
Sulfuric acid ⁿ	43,466	44,524	39,839	44,813	47,519	47,770	47,929	48,512	44,756	44,032	40,054
Titanium dioxide ^o	1,095	1,253	1,279	1,380	1,382	1,352	1,466	1,459	1,493	1,547	1,463

Group V—Nitrogen Group

If you want to ask what would make for the most important compounds, they would be the ones that make it possible for us to eat (after oxygen which lets us breathe and is still free and does not need to be manufactured.) So eating requires food, and all food comes either from plants and things that eat plants, so it would be a good idea to grow a lot of plants. But plants need a lot of food themselves, in the form of fertilizers, so it is not surprising that

- ammonia, which is the useful form of N that plants love
- and phosphates, which are the useful form of P that plants love

are in such high demand.

So let's concentrate on the first two elements in the group.

TABLE 15.1 The Group 15/V Elements

Valence configuration: ns^2np^3

Z	Name	Symbol	Molar mass (g·mol ⁻¹)	Melting point (°C)	Boiling point (°C)	Density (g·cm ⁻³) at 25°C	Normal form*
7	nitrogen	N	14.01	-210	-196	1.04 [‡]	colorless gas
15	phosphorus	P	30.97	44	280	1.82	white or red nonmetal
33	arsenic	As	74.92	613s [†]	—	5.78	gray metalloid
51	antimony	Sb	121.76	631	1750	6.69	blue-white lustrous metalloid
83	bismuth	Bi	208.98	271	1650	8.90	white-pink metal

*Normal form means the appearance and state of the element at 25°C and 1 atm.

[†]The letter s denotes that the element sublimates.

[‡]For the liquid at its boiling point.

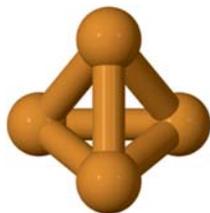
Sources of Elemental N and P

The source of elemental nitrogen is obvious—breathe. It is 75% of the earth's atmosphere. P₄ is more difficult to come by and requires a high temperature reaction with sand and carbon:



Reactions of Nitrogen and Phosphorus.

We start with nitrogen, which forms the most stable of all the non-Noble gas compounds with the triply-bonded diatomic nitrogen, N₂. And then one compound later in the group we are looking at phosphorus which is so reactive it explodes in the air. The reason for this difference is that nitrogen atom gets to achieve an octet rule like structure by forming second-row p-bonds while phosphorus can't form p-bonds and instead contorts itself to make P₄ which has really strained bond angles:



3 Phosphorus, P₄

Now the interesting consequence of these two observations is that the planet is filled with phosphorous, found in massive quantities as the rock, calcium phosphate, and the world is almost completely lacking in nitrogen compounds other N₂, which makes up 75% of air.

Which leads to the two very different ways we produce ammonia and phosphorous.

Nitrogen fixing.

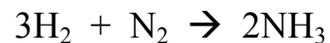
Elemental nitrogen is everywhere, it just isn't in the correct form. So we have to "fix" it. And the processes for doing this are:

- Relying on bolts of lightning to react with the elemental nitrogen
- To rely of bacteria that fix nitrogen (the organic farmers LOVE this stuff)



- To produce manufacture ammonia using the Haber process:

Haber Process:

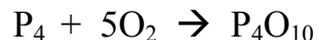


Which doesn't look all that exciting exempt that if we are going to make millions of tons of it, we are going to want to do it as efficiently as possible. Hence the enormous amount of work to optimize the process using just the right catalysts at the lowest temperature possible.

By the way, we know where the nitrogen comes from. But what is the industrial source of hydrogen (hint, look at the beginning of the notes.)

Phosphates.

We can create phosphoric acid fairly easily from white phosphorous, pretty much by sitting back and watching:



followed by

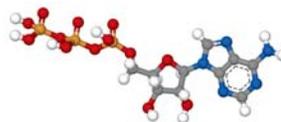


Phosphoric acid is used to make fertilizers, detergents and adds that zip to your soft drinks.

But the real source of phosphates used for fertilizers is to simply pull calcium phosphate out of the ground and react it with sulfuric acid (and this is the reason we need so much sulfuric acid.)



By the way, phosphates are a ubiquitous anion—they are also essential in metabolic processes in compounds like ATP or in nucleic acids.



7 Adenosine triphosphate (ATP)

Enough boring stuff. Anything interesting about N or P?

Well how about this. Nitrogen makes some very famous oxides of varying oxidation number.

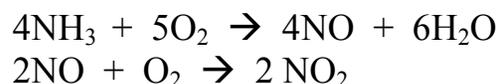
TABLE 15.2 The Oxides and Oxoacids of Nitrogen

Oxidation number	Oxide formula	Oxide name	Oxoacid formula	Oxoacid name
5	N_2O_5	dinitrogen pentoxide	HNO_3	nitric acid
4	NO_2^*	nitrogen dioxide	—	—
	N_2O_4	dinitrogen tetroxide	—	—
3	N_2O_3	dinitrogen trioxide	HNO_2	nitrous acid
2	NO	nitrogen monoxide	—	—
		nitric oxide		
1	N_2O	dinitrogen monoxide	$\text{H}_2\text{N}_2\text{O}_2$	hyponitrous acid
		nitrous oxide		

*2 $\text{NO}_2 = \text{N}_2\text{O}_4$.

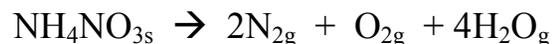
A couple of special applications include:

- N₂O is nitrous oxide, which as I understand it, is a delightful way to propel your whipped cream. It also is used in the dentist office to make you feel “different.”
- NO is nitric oxide, which, as I quote from Wikipedia in a delightfully scientific manner: causes: “the endothelium (inner lining) of blood vessels to signal the surrounding smooth muscle to relax, thus dilating the artery and increase blood flow. Whatever that means—all I know is that something called Viagra helps to make more NO in the body.
- Nitrogen dioxide, NO₂, is a nasty brown chemical that you can form by tossing a penny into nitric acid. It is a major component of air pollution.
- HNO₃ is nitric acid, not only one of the strong acids, but like sulfuric acid, a really fine oxidizing agent. It is made in vast quantities commercially using the Ostwald process in an 8-electron oxidation process:



Nitrogen and Bombs.

Finally, these nitrogen-containing compounds find themselves used in the production of explosives. And without going into detail, let’s just say that the reason things like TNT and nitroglycerin work, is the same reason that something as simple as ammonium nitrate can be explosive at high temperature:



Note that a solid has a Dn of 7 which means that a mole of solid, something you can cup in your hand, achieves a volume of many hundreds of liters. Do it fast enough, you have the potential for an explosive.

Group VI—The Oxygen Group

This group gets my vote for most underrated. After all, the real reason we are here, very simply, is that we are the beneficiaries of an atmosphere which is really reactive—my goodness, 25% of it is the extraordinarily dangerous compound called oxygen, and the only reason we didn't go up in a gigantic ball of flame the first time cavemen discovered fire is the activation barrier to all those combustion reactions we learned are spontaneous in thermodynamics.

TABLE 15.3 The Group 16/VI Elements

Valence configuration: ns^2np^4

Z	Name	Symbol	Molar mass (g·mol ⁻¹)	Melting point (°C)	Boiling point (°C)	Density (g·cm ⁻³) at 25°C	Normal form*
8	oxygen	O	16.00	-218 -192	-183 -112	1.14 [†] 1.35 [†]	colorless paramagnetic gas (O ₂) blue gas (ozone, O ₃)
16	sulfur	S	32.06	115	445	2.09	yellow nonmetallic solid (S ₈)
34	selenium	Se	78.96	220	685	4.79	gray nonmetallic solid
52	tellurium	Te	127.60	450	990	6.25	silver-white metalloid
84	polonium [‡]	Po	(209)	254	960	9.40	gray metalloid

*Normal form means the appearance and state of the element at 25°C and 1 atm.

[†]For the liquid at its boiling point.

[‡]Radioactive.

It is also not surprising that the most manufactured chemical compound, sulfuric acid, is found in this group either.

Elemental forms of O and S.

Oxygen in its elemental form has two allotropes, diatomic oxygen and triatomic oxygen (ozone.)

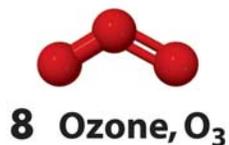


O₂



O₃

If you are trying to recall where you learned about ozone in this class, other than knowing that there is a hole in it, the reason is that back when we were learning about the VSEPR model for bonding, we trotted ozone out as a 24 electron resonance structure. I include its structure here so you can go, “now I remember.....”



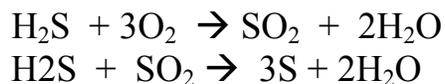
Elemental Sulfur.

Everyone has a recollection of elemental sulfur--it is that yellow powder you always see and has the structure S₈.

Sulfur is really everywhere, but because many of its compounds smell, we try to stay away from it, but, for example, there are many ores that contain sulfur. The third in collection of rocks containing S is called pyrite, or Fool's Gold, which nerd kids like me thought was pretty cool.



Sulfur is also an undesirable component of petroleum and natural gas where it is found as H₂S. As a result, it is not hard to produce the elemental form, especially given its relatively low melting point. The process used to claim it from petroleum is the Claus process in which the H₂S is first oxidized to SO₂.

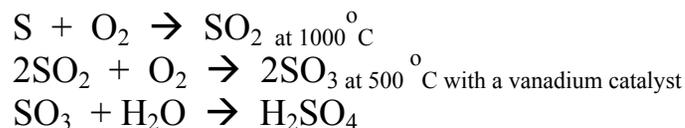


Reactions of Oxygen containing compounds.

O₂. Of course, the reactions of oxygen are the reactions that drive everything toward a higher oxidation state, from the combustion reactions I do in here daily to keep you awake, or the metabolic processes in biology that are utterly fascinating to pre-health professions students. I won't spend any time on these reactions since they are rammed down your throat your entire life as a scientist, but I will say, that end the end, everything rusts, everything get a much of Os attached. Stop fighting the inevitable.

Sulfuric acid. It is not surprising that I will spend some time talking about how to make the most important molecule this side of O₂ and how to use it.

The production of sulfuric acid is a multi-step effort, that believe me, has been perfectly. I list a grossly simplified form of it here so you can see how that S that we extract from petroleum gets turned into sulfuric acid.



And what would be do with this sulfuric acid? It happens to be great at three things:

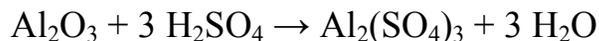
- It is a strong acid
- It is a strong oxidizing agent
- It is a great dehydrating agent (it removes water)

We have already seen it in action twice, now. Once to extract metals from the earth

And more recently, and most importantly (like 60% of its use) to create useful phosphates:

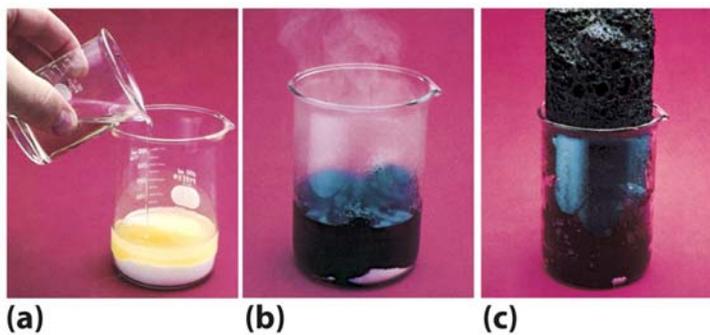
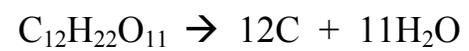


It is also used in the paper making process to make aluminum sulfate



Of course it finds its way into lead acid batteries where it is part of a famous battery

And of course, it is a staple of every chemistry circus, creating carbon out of sugar in a dehydrating reaction.



Group VII—The Halogens

TABLE 15.4 The Group 17/VII Elements

Valence configuration: ns^2np^5

Z	Name	Symbol	Molar mass (g·mol ⁻¹)	Melting point (°C)	Boiling point (°C)	Density (g·cm ⁻³) at 25°C	Normal form*
9	fluorine	F	19.00	-220	-188	1.51 [†]	almost colorless gas
17	chlorine	Cl	35.45	-101	-34	1.66 [†]	yellow-green gas
35	bromine	Br	79.90	27	59	3.12	red-brown liquid
53	iodine	I	126.90	114	184	4.95	purple-black nonmetallic solid
85	astatine [‡]	At	(210)	300	350	—	nonmetallic solid

*Normal form means the appearance and state of the element at 25°C and 1 atm.

[†]For the liquid at its boiling point.

[‡]Radioactive.

The halogens get a lot of publicity because they have a cool name (did you know the name for group VI is the chalcogens? See, Group VI needs to hire a better PR firm.) Halogens are especially useful to the chemistry educator because they sit at the extreme end of the periodic table and serve (excluding the Noble gases) as the:

- Compounds that are the smallest atoms and ions
- Compounds with the largest electronegativities
- Compounds with the largest ionization energies.
- Their elemental form is a very reactive oxidizing agent
- The compounds that just have to add a single electron to be happy.
- The second thing you think of when you make a salt

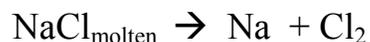
Elemental forms of halogen.

Like the alkali metals, there is a remarkable sameness to the halogens. They are all reactive diatomic gases. Also of interest, just as the second row Li has a souped up ability to react compared to the other alkali metals, F₂ has a souped up ability to react as well because of its very high electron affinity and small size.

Oh, and time out for a deep thought on why the oceans are filled with NaCl and F is nowhere to be found in the water. F is actually quite abundant in minerals on the planet—for example, it is the mainstay in the mineral cryolite, Na₃AlF₆, we pull out of the ground to make metallic Al. And yet, NaCl gets all the name recognition. Which can be traced to our friend “charge density”. Because F is so small, and the charge density larger in the rocks and minerals it forms, it is less able to dissolve in water compared to the Cl⁻ ion.

Despite all the excitement surrounding fluorine, and all the cool reactions it can do, like being the first compound people reach for when they want to make a really difficult reaction happen (for example, see the reactions of Noble gases), in the end most F used in manufacturing in the world ends up in the molecule UF_6 which is used to process nuclear fuels.

Chlorine. As you might have noticed from the table of industrial compounds manufactured in this country, Cl_2 battles next and next for the fourth position. The source of Cl_2 is the electrolysis reaction of NaCl .



You may recall that on the last day of electrochemistry, I pretended to melt some NaCl and toss a battery into it. Well if I had done it, I would have contributed to the way Cl_2 is manufactured. Something tells me, though, they do it a little more safely than I was about to try.

Once you have Cl_2 , what can you do with it?

Just about anything. Cl_2 is a very fine oxidizing agent that reacts with just about everything but C, N_2 and O_2 .

The compounds it forms are everything from bleaches to water purifiers to disinfectants to dry cleaning agents to pesticides.

Cl_2 is also readily converted into HCl and oxyacids



Which have many uses.

Group VIII—The Noble Gases

Every chemistry course begins by pointing that chemical reactions occur primarily to allow atoms to achieve electronic configurations that look like Noble gases. By that we mean having an ns^2np^6 configuration (with the exception of $n=1$). This is the source of the less sophisticated notion of satisfying the octet rule and the more sophisticated notion of achieving stable filled shells that are energetically favored.

The length to which compounds go to end up like this is remarkable, and for example, that is how we end up with a compound like elemental phosphorous, P_4 , which has a Noble gas configuration, but to do so has such strained bond angles that it is literally explosive in air.

Well you can imagine that once you achieve your goal of becoming electronically stable, you don't really feel like doing anything else, and that can certainly be said for the Noble gases shown below.

TABLE 15.6 The Group 18/VIII Elements (the Noble Gases)

Valence configuration: ns^2np^6

Normal form: colorless monatomic gas

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

*Radioactive.

They are, in fact, so okay being themselves that they aren't even interested in appreciable intermolecular interaction and as a consequence are gases at room temperature. We have to cool things way down to make liquid helium or neon or argon as you see above.

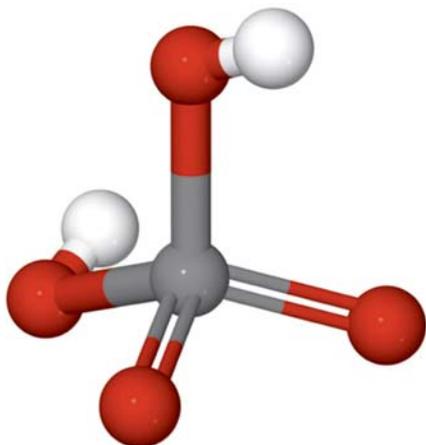
Of course being a really stable, unreactive, really cold material has a lot of really valuable uses, and that is why you see trucks of liquid Noble gases flying down the interstate all the time.

As for reactivity, even though the gases have a very high ionization energy, they can only stand so much electrocution before the electrons are excited to higher energy level and even ionized. And as the excited gases relax back to the ground state, they emit characteristic light that makes for exciting 6th Street and Bourbon Street images. (These are of course being replaced by 400 foot by 1000 foot LED displays of the latest Target ad campaign, as my recent trip to New York has confirmed, so look at the pretty picture below if there aren't any left in the real world.



Chemical reactivity. As mentioned, Noble gases don't react, which is exactly the kind of absolute statement that drives scientists to the lab to prove they can do it. And for years desire to be the first to make a molecule with a covalent Noble gas bond was something to do.

The first success was, not surprisingly, the consequence of taking a large polarizable Noble gas like Xe, with the most reactive stuff out there, F₂, to make the compound XeF₄ at high temperature and pressure. Lots of other compounds with Xe have been made since then like the acid below.



18 Xenic acid, H_2XeO_4

And for those of you thinking that maybe you would like to be the first to make some compounds with Kr, that has happened with the formation of, not surprisingly, KrF_2 .

And that is all I have to say about main group chemistry.

