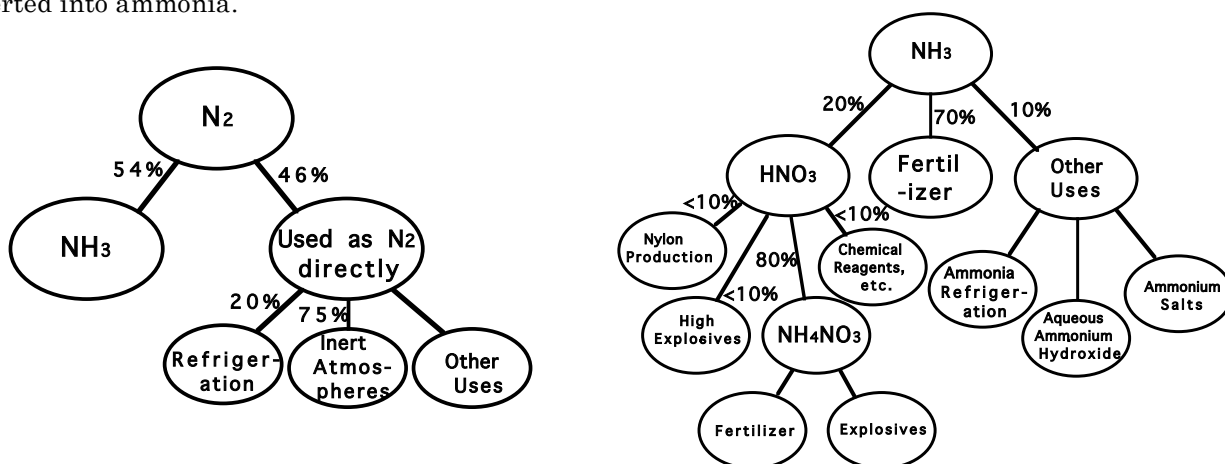


**C. Nitrogen's oxidation states.** Nitrogen forms compounds with a wide range of oxidation states that range from -3 for the nitride ion to +5 in nitrates and nitric acid. An example of each of these oxidation states are given in the table.

Oxidation state:	Example:
-3	$\text{Li}_3\text{N}$
-2	$\text{NH}_2\text{NH}_2$
-1	$\text{HNNH}$
0	$\text{N}_2$
+1	
+2	$\text{NO}$
+3	$\text{HNO}_2$
+4	$\text{NO}_2$
+5	$\text{HNO}_3$

While  $\text{N}_2$  has a notoriously strong triple bond, its single bond is one of the weakest in all of chemistry. Compared to its neighbor carbon, in which the C-C single bond strength is 347 kJ/mol, the N-N single bond strength is only 160 kJ/mol. The effect of this is that nitrogen is unlikely to catenate like carbon.

**D. Uses.** Nitrogen is obtained from the fractional distillation of air. Air contains 78% nitrogen. As shown in the left figure below, about half of the nitrogen “produced” is used directly as nitrogen and about half is converted into ammonia.



The main use of nitrogen gas is as an inert blanket in iron and steel industry as well as in related metallurgical and chemical activities where an inert atmosphere is required. Another important, large-scale use of nitrogen blankets is in the glass industry. Plate glass is floated over molten tin in order to make nearly perfectly smooth surface. The molten tin would rapidly oxidize if it were not for the blanket of nitrogen present. Nitrogen blankets are also employed in the electronics industry during construction of computer chips, transistors, diodes, etc.

A large amount of gaseous nitrogen is used as a purge gas in the petrochemical industry. Reactors and equipment are purged of oxygen and petroleum vapors before they are serviced in order to prevent explosions and fires.

Approximately 10% of all  $\text{N}_2$  produced is used as a refrigerant in the form of liquid nitrogen. Rubbery or sticky substances cannot be machined or ground unless they are first frozen. Freeze grinding is also used to make hamburger. Because most materials shrink when cooled, liquid nitrogen is used in shrink fitting and assembly operations. Liquid nitrogen is used to quick freeze foods and to maintain refrigeration of frozen foods as they are transported over the highway. For example, McDonalds transports its hamburgers frozen in liquid nitrogen to their destinations.

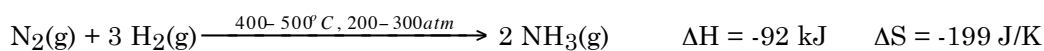
**E. Ammonia.** Ammonia production is the largest consumer of nitrogen and, as described in the previous section, is the gateway compound to most other nitrogen compounds produced industrially. Prior to Haber process, ammonia was made by destructive distillation of animal parts (hoofs, horns, etc.) As a result, ammonia was commonly called “Spirits of Hartshorn.”

Ammonia is a colorless gas with sharp irritating odor. Its density is about half that of air's, thus it tends to rise in a still room. The odor is detectable to the human nose at 20 - 50 ppm and becomes irritating to the eyes at 100 -200 ppm.

Ammonia is extremely soluble in water. Household ammonia is 2 M NH<sub>3</sub> mixed with some detergent. Ammonia was the first complex molecule to be identified in interstellar space and solid NH<sub>3</sub> makes up the rings on Saturn. Ammonia is a weak base with a pK<sub>b</sub> = 4.76 at 25 °C. Its melting point is -77.7 °C and boiling point is -33.3 °C. The density of liquid ammonia is 0.6826 g/mL.

The structure of ammonia, predicted by VSEPR is that of a trigonal pyramid. At room temperature ammonia molecules undergo an inversion or flip via a trigonal planar transition state. The lone pair on nitrogen and the three hydrogens invert to the opposite side. At room temperature the inversion rate is a remarkable 24 billion times per second!

Industrially, ammonia is prepared from the Haber process. Nitrogen and hydrogen are combined under high pressure and temperature in the presence of a nickel catalyst:



The reaction is exothermic, however entropy does not favor the forward reaction. Thus the reaction is spontaneous at lower temperatures. Unfortunately, the reaction is kinetically slow except at higher temperatures. The conditions employed strikes a compromise between thermodynamics and kinetics. The use of high pressures utilizes LeChatelier's principle to drive the reaction in the direction of the fewest number of moles of gas.

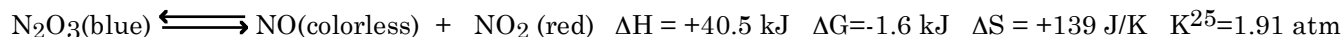
**F. Nitrogen oxides.** There are six principal oxides of nitrogen. They are N<sub>2</sub>O, NO, N<sub>2</sub>O<sub>3</sub>, NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, and N<sub>2</sub>O<sub>5</sub>. The trademark of their chemistry is their ability to interconvert so it is difficult to study any one pure oxide. All of these oxides are acid anhydrides.

**Nitrous oxide, N<sub>2</sub>O.** The proper IUPAC name N<sub>2</sub>O is dinitrogen monoxide, however its common name, nitrous oxide, is widely used. It is also simply called *nitrous*. Nitrous oxide was discovered by Joseph Priestley in 1771 by carefully heating ammonium nitrate to 250 °C. Write the reaction that takes place given that water is the other product.

N<sub>2</sub>O supports combustion because it is a good oxidant and actually contains a higher percentage of oxygen than ordinary air. Nitrous is colorless, rather unreactive, gas. Its boiling point is -88.5 °C and its melting point is -90.9 °C. The Lewis structure of nitrous oxide exhibits two important resonance structures. Sketch them, given that the atoms are connected N-N-O. What are the formal charges?

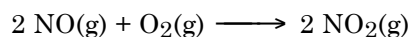
**Nitrogen oxide, NO, (nitric oxide).** Nitrogen monoxide is the proper name for the molecule NO, however, the common name, nitric oxide, is still in widespread use. Nitric oxide is a colorless, paramagnetic gas. Its melting point is -163.6 °C and its boiling point is -151.8 °C. Nitric oxide is the simplest thermally stable odd-electron molecule known in chemistry. It is extremely reactive. Sketch its structure.

**Dinitrogen trioxide, N<sub>2</sub>O<sub>3</sub>.** Dinitrogen trioxide forms a dark blue solid with a melting point of -100.1 °C. As a liquid, it dissociates into NO and NO<sub>2</sub>, the extent of which increases with an increase in temperature above -100.1°C.

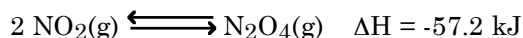


In the gas phase (bp +3.5 °C) N<sub>2</sub>O<sub>3</sub> is unstable towards the dissociation shown above. Nitrogen is in the +3 oxidation state in N<sub>2</sub>O<sub>3</sub>. Dinitrogen trioxide is formally the acid anhydride of nitrous acid, which is also unstable. Write the hydrolysis reaction for N<sub>2</sub>O<sub>3</sub>. Nitrous acid is a weak acid, pK<sub>a</sub> = 5.22.

**Nitrogen dioxide, NO<sub>2</sub> and dinitrogen tetroxide, N<sub>2</sub>O<sub>4</sub>.** Nitrogen dioxide is a red-brown, paramagnetic, reactive gas. It is readily formed from the oxidation of NO(g) in air:



The dynamic interconversion between NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> makes it impossible to study either of these species alone:

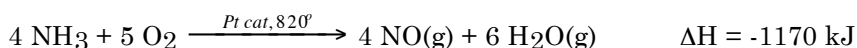


In both forms, the nitrogen is in the +4 oxidation state. Dinitrogen tetroxide is a colorless, diamagnetic gas that dissociates reversibly as shown above. Its melting point is -11.2 °C and its boiling point is 21.2 °C.

Nitrogen dioxide/dinitrogen tetroxide are components of urban smog. Collectively, these two nitrogen oxides are referred to as NO<sub>x</sub> and are caused inside of automobile engines and are some of the pollutants that the catalytic converter is designed to eliminate. The reddish skyline in urban areas is due to nitrogen dioxide. Does the LeChatelier theory predict there will be more or less NO<sub>2</sub> at the very low pressures found in the atmosphere (say compared with a 1 atm sample)?

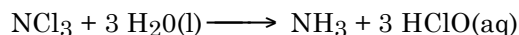
**Dinitrogen pentoxide, N<sub>2</sub>O<sub>5</sub>.** Dinitrogen pentoxide is colorless and ionic as a solid. It crystallizes as NO<sub>2</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup> and has a melting point of 41 °C. As a gas, both of the nitrogen atoms in N<sub>2</sub>O<sub>5</sub> are in the +5 oxidation state. Dinitrogen pentoxide is an unstable covalent molecule and the anhydride of nitric acid (although nitric acid is not made from N<sub>2</sub>O<sub>5</sub>)

**G. Nitric acid.** W. Ostwald studied the production of nitric acid and by 1901 had perfected the following sequence of reactions, which starts out with the combustion of ammonia:



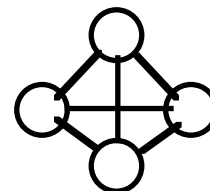
**H. Nitrogen halides.** The common halides of nitrogen include NF<sub>3</sub>, NCl<sub>3</sub>, NBr<sub>3</sub> < and NI<sub>3</sub>, which vary wildly in stability. NF<sub>3</sub> is very stable gas with a melting point of -206.8 °C and a boiling point of -129 °C. NF<sub>3</sub> does not react with water and has the expected trigonal pyramid structure with FNF angle of 102.5 °.

$\text{NCl}_3$  is a dense, volatile, explosive liquid (mp =  $-40\text{ }^\circ\text{C}$ ; bp =  $71\text{ }^\circ\text{C}$ ;  $d^{20} = 1.65\text{ g/cm}^3$ ) It decomposes explosively to elements and hydrolyzes easily to form  $\text{NH}_3$  and  $\text{HClO}$ :

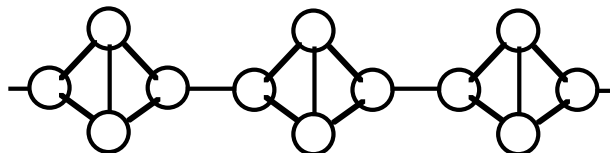


The main use for  $\text{NCl}_3$  is as a dilute gas is to bleach flour.  $\text{NBr}_3$  is so unstable that it cannot be studied. It is deep a red, temperature-sensitive volatile solid.

**I. Phosphorus.** Phosphorus exists in three allotropic forms. White phosphorus (sometimes called yellow) is a waxy white solid which sometimes appears yellow or even orange due to impurities. When it is ultrapure, it is actually colorless. White phosphorus is soft and waxy at warmer temperatures but hard and brittle under cool temperatures. It has formula  $\text{P}_4$  and has a tetrahedral pyramid structure in which each P atom is bonded to three other P atoms. The  $\text{sp}^3$  lone pair is directed outwards from each atom. White phosphorus is extremely reactive. It catches fire immediately in air and is usually stored under water in which it is insoluble. White phosphorus must never be directly handled because it will cause serious burns. It is exceptionally poisonous and 50 mg constitutes a fatal dose.

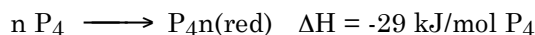


White phosphorus slowly darkens to a yellow and then a to a deep red when stored under water for prolonged periods of time. The color change corresponds to a slow conversion to a more stable allotropic form, red phosphorus. Pure red phosphorus is polymeric material with a structure consisting of joined tetrahedra in which one of the six P—P bonds in white  $\text{P}_4$  has been broken to form the polymeric units.



Like most polymers, P(red) is non-volatile. It is sold as an amorphous powder, will not ignite in air and thus can be stored indefinitely.

Red phosphorus was discovered in 1848 by A. Schrötter, 179 years after the discovery of white phosphorus. It is prepared by heating white phosphorus to  $250\text{ }^\circ\text{C}$  without air or by exposing it to sunlight. The transition is exothermic:

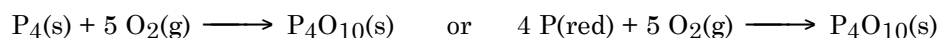


When red is heated to  $600\text{ }^\circ\text{C}$ , it depolymerizes back to white  $\text{P}_4$ .

Red phosphorus does not phosphoresce in air as does white phosphorus. It does not spontaneously ignite and is not as dangerous to handle and is not as toxic. The polymeric material does not crystallize so the solid is called amorphous.

Black phosphorus is the least common allotropic modification of phosphorus. P(black) is a network covalent solid with a sheet structure similar to that of graphite only puckered due to the  $\text{sp}^3$  angles involved. The sheets form several types of crystalline solids depending on the conditions.

**Oxides.** Red phosphorus burns in air if ignited with a match or heated above  $260\text{ }^\circ\text{C}$ . Both forms of phosphorus oxidize to  $\text{P}_4\text{O}_{10}$ :



The molecule  $\text{P}_4\text{O}_{10}$  has a tetrahedral structure similar to that of  $\text{P}_4$ . Compared to  $\text{P}_4$ ,  $\text{P}_4\text{O}_{10}$  has an P-O-P in place of each of the six P-P bonds in  $\text{P}_4$ . Additionally, each of the lone pairs on phosphorus hosts an oxygen atom. Sketch  $\text{P}_4\text{O}_{10}$  here.

Tetraphosphorus decaoxide is the acid anhydride for phosphoric acid. Write the reaction between  $P_4O_{10}$  and  $H_2O$  here.

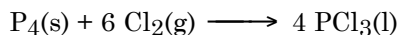
**J. Phosphates.** Phosphorus exists exclusively in the earth's crust in the form of inorganic phosphates. The element is widespread in the earth's crust. While there are several hundred phosphate minerals known, the vast majority of naturally occurring phosphate belongs to the **apatite** class of minerals which include these three most common members.

hydroxyapatite	$Ca_{10}(OH)_2(PO_4)_6$
fluorapatite	$Ca_{10}F_2(PO_4)_6$
chlorapatite	$Ca_{10}Cl_2(PO_4)_6$

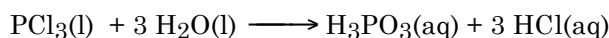
The formula for apatite minerals corresponds to three units of  $Ca_3(PO_4)_2$  plus one unit of  $Ca(OH)_2$ ,  $CaF_2$ , or  $CaCl_2$ , respectively. Collectively the apatites are known as **phosphate rock**. Large deposits located in Florida, Utah, Idaho and Tennessee in the USA and in Russia and Morocco. Phosphate rock is the initial material for all phosphorus compounds as shown in the diagram.

**Phosphorus halides.** All of the halogens form compounds with phosphorus. Three possible formulations exist. They are:  $P_2X_4$ ,  $PX_3$ , and  $PX_5$ . The oxidation states on phosphorus in these forms are +2, +3, and +5, respectively.

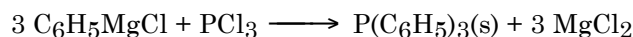
Phosphorus trichloride (mp  $-112\text{ }^\circ\text{C}$ , bp  $74\text{ }^\circ\text{C}$ ) is an important compound in organic synthesis and in the synthesis of organophosphines. It is prepared the direct combination of the elements:



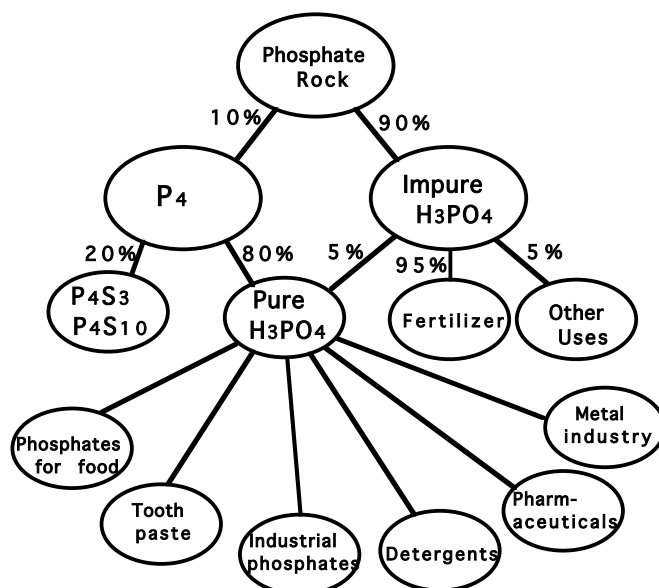
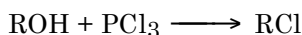
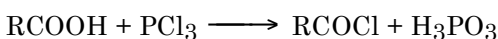
$PCl_3$  is also extremely reactive towards water producing phosphorous acid:



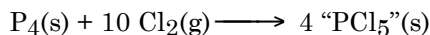
$PCl_3$  is used in Grignard syntheses to make organophosphines such as triphenylphosphine:



The reagent is also widely used to convert organic alcohols into chlorides and organic acids into acid chlorides:



“Phosphorus pentachloride” is produced from the reaction of phosphorus with excess chlorine:



It also hydrolyzes, however it produces phosphoric acid. Write the hydrolysis reaction here.

As a solid,  $\text{PCl}_5$  actually has an ionic structure consisting of  $\text{PCl}_4^+$  cations and  $\text{PCl}_6^-$  anions. Sketch these two ions here.

## 7. Oxygen, sulfur, selenium, tellurium.

**A. Physical properties.** Oxygen is a colorless, odorless and tasteless gas at room temperature and pressure. It can be condensed to a faint blue liquid by cooling to  $-183\text{ }^\circ\text{C}$  (90 K) at a pressure of one atmosphere. Liquid oxygen, often called *LOX*, reacts explosively with organic substances and must be handled with great care. Oxygen freezes at  $-218\text{ }^\circ\text{C}$  (55 K) at a pressure of one atmosphere. Oxygen dissolves in water to the extent of  $30.8\text{ cm}^3$  at STP per liter of water at  $20\text{ }^\circ\text{C}$ . It is also soluble in numerous non-aqueous solvents.

Sulfur is a yellow, tasteless, odorless solid. Sulfur is insoluble in water but dissolves readily in certain non-polar organic solvents, most notably carbon disulfide,  $\text{CS}_2$ . In terms of physical properties, sulfur is similar to selenium and tellurium with predictable periodic trends defining the differences between the elements. Oxygen, in many respects is quite unlike S, Se, and Te.

	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Molecular Formula	$\text{O}_2$	$\text{S}_8$			
Color	colorless	yellow	gray	silvery metal	
melting point ( $^\circ\text{C}$ )	-218.8	115	221	450	
boiling point ( $^\circ\text{C}$ )	-183.0	445	685	1009	
Pauling electronegativity	3.5	2.5	2.4	2.1	2.0
Atomic radius (pm)	60	100	115	140	190
density at $20\text{ }^\circ\text{C}$ ( $\text{g}/\text{cm}^3$ )	$1.33 \times 10^{-3}$	1.96	4.79	6.24	
1st ionization energy, MJ/mol	1.31	1.00	0.941	0.869	0.812
$\Delta H_{\text{fus}}$ kJ/mol	0.443	1.72	5.44	17.5	
$\Delta H_{\text{vap}}$ kJ/mol	6.82	8.37		50.6	

**B. Molecular oxygen.** Recall our discussion of the bonding that takes place in  $\text{O}_2$ . Molecular orbital theory predicts two unpaired electrons.

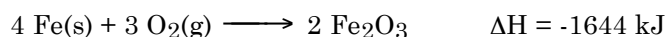
**C. Compounds of oxygen.** Oxygen reacts with most of the other elements except the halogens, noble gases and a few non-reactive metals such as gold. The oxides of the elements are capable of behaving as an

acid, a base or neither. The periodic trend of acid/base/amphoteric behavior is summarized below for the main group elements.

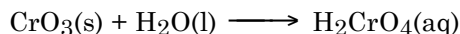
Li	Be	B	C	N	O	F	Ne	Basic	Amphoteric
Na	Mg	Al	Si	P	S	Cl	Ar	Acidic	Neither
K	Ca	Ga	Ge	As	Se	Br	Kr		

Fluorine forms an oxide, OF<sub>2</sub>, which has neither acid or basic properties.

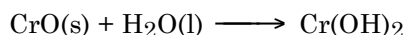
**Ionic compounds of oxygen.** Oxygen's most common oxidation state is -2, the oxide ion. Metal oxides are conveniently thought of in purely ionic terms. Oxygen reacts with most metals to form metal oxide salts. In many cases simply exposing a metal to oxygen will cause oxidation to occur. The rate of oxidation is enhanced by heating the metal.



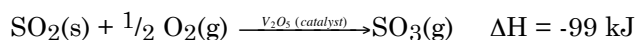
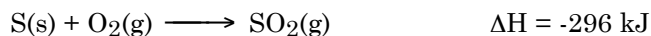
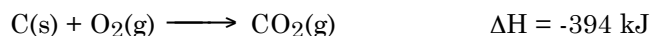
The transition metals were omitted from the figure above. Their oxides can have either acidic or basic properties depending on a variety of factors. The most important factor is the oxidation state. In general, transition metal oxides in high formal oxidation states are usually acid anhydrides. Oxides in which the same metal is in a lower oxidation state are often base anhydrides. For example, CrO<sub>3</sub> features chromium in its maximum oxidation state, +6. It functions as the acid anhydride of chromic acid:



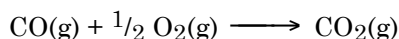
CrO, however, functions as a base anhydride:



**Covalent-molecular compounds of oxygen.** As we move from left to right across the periodic table, the electronegativities of the elements increase. Oxygen's electronegativity (3.5) is quite large and second only to fluorine's. All of the non-metals have electronegativities that are greater than 2.0 so the difference in electronegativities between a non-metal and oxygen is always less than 1.5. Electronegativity differences less than 1.7 are indicative of bonds that have predominantly covalent character. In very simple terms, all bonds between oxygen and non-metallic elements can be conveniently thought of in terms of having predominantly covalent character. The oxides of carbon and sulfur are gaseous and form by simple combustion of the element. At least two different oxides exist for each of these elements:



Carbon monoxide, a poisonous gas, is formed when carbon is combusted with limited supplies of oxygen. Carbon monoxide burns to produce carbon dioxide. Calculate  $\Delta H$  for the reaction:



Combustion of sulfur initially produces SO<sub>2</sub>. Further oxidation to sulfur trioxide is enthalpy favored to occur but is kinetically slow unless a catalyst (usually V<sub>2</sub>O<sub>5</sub>) is present.

Covalent bonds between oxygen and other elements are among the strongest in chemistry. — in contrast to the oxygen-oxygen single bond which is perhaps the weakest single bond in covalent chemistry. Only fluorine makes stronger covalent bonds than oxygen. The table summarizes important single bond strengths involving oxygen. Notice that the bond strength decreases as the bond polarity (difference in electronegativity) decreases. To fully appreciate how thermodynamically stable some of these bonds are we can compare them to the carbon-carbon bond (347 kJ/mol) which is thought of as quite stable.

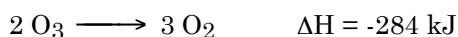
Bond	$\Delta H_{\text{cov}}$ (kJ/mol)	$\Delta \text{Electro-}$ <b>negativity</b>
O-B	536	1.5
O-H	459	1.4
O-Si	452	1.7
O-C	358	1.0
O-S	347	1.0
O-P	335	1.4
O-Cl	205	0.5
O-I	201	1.0
O-Br	201	0.7
O-N	201	0.5
O-F	190	0.5
O-O	142	0.0

The unusual strength of covalent bonds to oxygen gives us a useful predictive tool regarding certain chemical reactions. The formation of thermodynamically stable bonds such as the first six given in the table drive the course of a reaction and determine the products that can be expected.

**D. Peroxides and superoxides.** These ions were discussed briefly with the alkali metals. Use molecular orbital theory to complete the table below under the titles “Paramagnetic?” and “Bond order”

	MO Electron Configuration:	Paramagnetic?	Bond order:	Bond length:	Bond energy:
O <sub>2</sub> <sup>+</sup>	( $\sigma_s$ ) <sup>2</sup> ( $\sigma_s^*$ ) <sup>2</sup> ( $\sigma_p$ ) <sup>2</sup> ( $\pi$ ) <sup>4</sup> ( $\pi^*$ ) <sup>1</sup>			112 pm	640 kJ/mol
O <sub>2</sub>	( $\sigma_s$ ) <sup>2</sup> ( $\sigma_s^*$ ) <sup>2</sup> ( $\sigma_p$ ) <sup>2</sup> ( $\pi$ ) <sup>4</sup> ( $\pi^*$ ) <sup>2</sup>			121 pm	506 kJ/mol
O <sub>2</sub> <sup>-</sup>	( $\sigma_s$ ) <sup>2</sup> ( $\sigma_s^*$ ) <sup>2</sup> ( $\sigma_p$ ) <sup>2</sup> ( $\pi$ ) <sup>4</sup> ( $\pi^*$ ) <sup>3</sup>			126 pm	370 kJ/mol
O <sub>2</sub> <sup>-2</sup>	( $\sigma_s$ ) <sup>2</sup> ( $\sigma_s^*$ ) <sup>2</sup> ( $\sigma_p$ ) <sup>2</sup> ( $\pi$ ) <sup>4</sup> ( $\pi^*$ ) <sup>4</sup>			149 pm	160 kJ/mol

**E. Ozone.** Ozone is the second allotrope of oxygen. It is a light blue gas with a characteristic odor that is associated with the smell of the air after thunderstorms. Liquid ozone (bp -112 °C) explodes to produce oxygen:

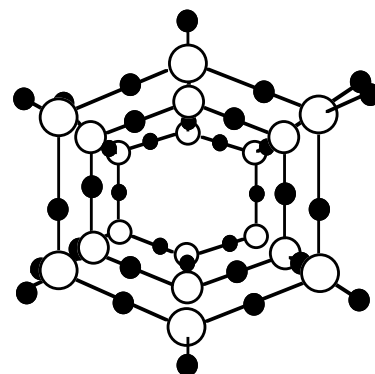


The structure of ozone is bent and is isostructural with SO<sub>2</sub> and NO<sub>2</sub>. Sketch the Lewis dot structure for ozone and give resonance forms if necessary.

The O-O-O angle is 117° and the oxygen-oxygen distance is 128 pm which is midway between the normal oxygen-oxygen single bond (149 pm) and double bond (121 pm) lengths. In both resonance forms the central oxygen has a formal charge of +1 while the single-bonded oxygen has a formal charge of -1. Resonance forms with adjacent opposite charges are inherently associated with unstable structures. If all the resonance

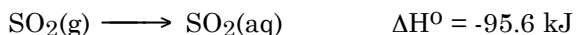
structures of a molecule have charge separation problems, the molecule is frequently thermodynamically unstable. Such is the case for ozone, which is so reactive that it must be generated (by electrical discharge) and used as needed. Ozone is the second strongest common oxidizing agent, exceeded by  $F_2$ . In Europe and Canada ozone is generated and used to disinfect water much like chlorine is used in the USA.

**F. Water.** Water is one of a very few substances for which the density of its solid phase is less than that of its liquid phase. Most liquid substances form solids that are more dense and therefore sink in the liquid upon solidifying. This unusual property of water is essential in the support of life on earth. If ice sank, aquatic life could not exist. The ice formed in winter would sink to the bottom and be insulated from the heat of summer. Only the top several meters of the frozen oceans and lakes would melt each summer. The fact that the density of water as a solid ( $0.917 \text{ g/cm}^3$ ) is less than that of the liquid ( $1.000 \text{ g/cm}^3$  at  $4^\circ\text{C}$ ) is also attributed to hydrogen bonding. The figure shows the crystal lattice for the most common form of ice. The structure is similar to that of diamond. Each oxygen is in a four-coordinate tetrahedral ( $sp^3$ ) environment. Each hydrogen is two-coordinate (covalently bonded to one oxygen and hydrogen bonded to another oxygen). The large voids that exist explain why solid water is less dense than the liquid form. In liquid water the crystal lattice breaks down to an extent and water molecules can pack more tightly. Considerable association between water molecules exists in the liquid phase, however. Extended solution lattices exist with a structure similar to that of ice and involving four or more molecules.



**G. Sulfur.** The most common form of elemental sulfur,  $S_8$ . The molecular structure is that of a puckered, 8-member ring. What angles are predicted from the ABE formula for a sulfur in  $S_8$ ?

**H. Sulfur oxides.** Sulfur dioxide is highly soluble in water. The dissolving process is highly exothermic:

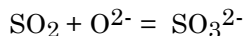


The actual solubility is  $200 \text{ g SO}_2/\text{L}$ .  $SO_2$  is often thought of as the 'anhydride of sulfurous acid'. However, it is questionable if sulfurous acid exists at all. If it does, the equilibrium constant is so small that fewer than 1 molecule per billion is in the form of sulfurous acid:

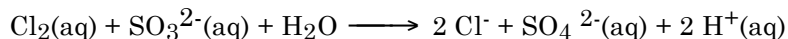


Sulfur dioxide has a number of important uses. It is used to disinfect food and is extensively used in the brewing industry. Numerous foodstuffs, including wines, use it as a preservative. It is used as a bleaching agent for paper, textiles, oils, etc. And, as Homer reported, it is used as a fumigant.

Sulfur dioxide and "sulfurous acid" feature sulfur in the +4 oxidation state. Similarly, the sulfite ion has a sulfur in the +4 oxidation state. One can think of the relationship between  $SO_2$  and  $SO_3^{2-}$  as differing by an oxide:



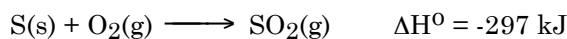
Thus, sulfite is the anion of the mythical sulfurous acid. Both bisulfite ( $HSO_3^-$ ) and sulfite ( $SO_3^{2-}$ ) salts are stable for most cations. Both are mild reducing agents. For example, sulfites can be used to destroy chlorine or any of the other halogens:



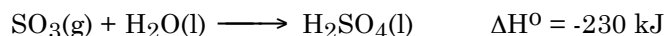
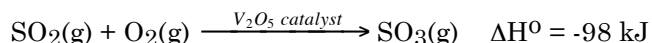
Sulfites are used to destroy unwanted permanganate solutions. Products include  $\text{Mn}^{+2}$  and sulfate. Balance this net ionic equation in acidic solution.

**Sulfur trioxide, sulfate, and sulfuric acid.** In all three cases, sulfur is in the +6 oxidation state. Sulfuric acid is the world's most important industrial chemical and also the least expensive acid available. The production of sulfuric acid dates back to 1793 in the USA (John Harrison, Philadelphia) and dates back over two centuries earlier in Europe. As a pure compound it has a mp = 10.37 °C and a density of 1.827 g/cm<sup>3</sup> at 25 °C. Sulfuric acid does not have a boiling point but decomposes at about 300 °C.

The modern industrial production of sulfuric acid involved several steps, collectively called the **contact process**. The oxidation of elemental sulfur forms  $\text{SO}_2(\text{g})$  according to the reaction:



The  $\text{SO}_2(\text{g})$  must be converted into  $\text{SO}_3(\text{g})$  and then hydrolyzed with one equivalent of water according to the equations:



**I. Chalcophilic metals.** In nature, a number of elements exist as sulfur ores. These tend to include the soft metal cations such as  $\text{Rh}^{+2}$ ,  $\text{Pd}^{+2}$ ,  $\text{Ag}^+$ ,  $\text{Cd}^{+2}$ ,  $\text{Pt}^{+2}$ ,  $\text{Hg}^{+2}$ ,  $\text{Pb}^{+2}$ ,  $\text{Cu}^{+1}$ , etc. The most familiar of these is iron pyrite, commonly called 'fools gold.' Iron pyrite is also an important source of both iron and sulfur. Despite what its formula suggests, iron is not in the +4 oxidation state. Rather, the sulfurs are present as disulfides,  $\text{S}_2^{2-}$  similar in structure and oxidation state to peroxides,  $\text{O}_2^{2-}$ . The structure of pyrite can be thought of as having a distorted NaCl structure. The linear  $\text{S}_2^{2-}$  units are centered on the chloride sites but are oriented away from the cubic cell axis. The  $\text{Fe}^{+2}$  ions are located at the sodium position. Sketch one unit cell for  $\text{FeS}_2$  here.

## 8. Halogens: fluorine, chlorine, bromine, and iodine.

**A. Physical properties** for the atomic and molecular halogen elements are given in the tables below. In most cases smooth periodic trends are observed. Electronegativity decreases from fluorine, the most electronegative of all elements to iodine. For comparison purposes, oxygen and nitrogen have electronegativities of 3.5 and 3.0, respectively. The first ionization energy is expected to decrease as the valence electrons populate shells with increasing quantum number, n.

	<b>F</b>	<b>Cl</b>	<b>Br</b>	<b>I</b>
AM (g/mol)	18.998403	35.453	79.904	126.9045
Electronic Configuration	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>5</sup>	[He]3s <sup>2</sup> 3p <sup>5</sup>	[Ar]4s <sup>2</sup> 3d <sup>10</sup> 4p <sup>5</sup>	[Kr]5s <sup>2</sup> 4d <sup>10</sup> 5p <sup>5</sup>
Electronegativity	4.0	3.2	3.0	2.7
Ionization energy, (kJ/mol)	1681	1250	1139	1007
Electron affinity (kJ/mol)	328	349	324	295
Atomic radius (pm)	71	99	114	133
Ionic radius (pm)	136	181	195	216

Electron affinity is the energy released when an electron is added. Thus, in terms of  $\Delta H_{\text{rxn}}$  for these reductions, all are exothermic.



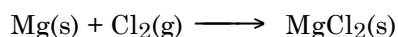
The trend in electron affinity for Cl, Br, and I follows the trend in electronegativity. However, fluorine does not follow the predicted trend and has an electron affinity that is significantly less than that of chlorine's. The reason is understood by considering the differences between electronegativity and electron affinity. Fluorine's electronegativity is a relative measure of the desire of the neutral atom to gain more electron density. However, the small size of fluorine's 2p-orbitals (when compared to chlorine's 3p-orbitals) makes it less able to accommodate an electron. Atomic radius increases with increasing principal quantum number, n. Bear in mind that the changes in atomic radius across the period is one of decreasing from left to right. Thus, the halogens are smaller in size than the chalcogens (Group VI elements). The ionic radius is nearly twice the atomic radius for the halogens.

	<b>F<sub>2</sub></b>	<b>Cl<sub>2</sub></b>	<b>Br<sub>2</sub></b>	<b>I<sub>2</sub></b>
MM (g/mol)	37.996806	70.906	159.808	253.809
Isotopes	<sup>19</sup> F	<sup>35</sup> Cl, <sup>37</sup> Cl	<sup>79</sup> Br, <sup>81</sup> Br	<sup>127</sup> I
mp (°C)	-219.62	-100.98	-7.2	113.5
bp (°C)	-188.14	-34.6	58.78	184.35
$\Delta H_{\text{fus}}$ (kJ/mol)	0.51	6.41	10.57	15.52
$\Delta H_{\text{vap}}$ (kJ/mol)	6.54	20.41	29.56	41.95
Bond dissociation energy (kJ/mol)	155	243	192	150
density at 20 °C (g/cm <sup>3</sup> )	(gas)	(gas)	3.119	4.93

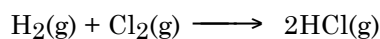
**B. Fluorine** is the most electronegative and reactive of all the elements. It is a colorless, corrosive gas that reacts with practically all other substances. Even water "burns" in fluorine with a bright flame! The commercial uses for fluorine are all rather new; most have developed since 1950. Fluorine's chemistry is understood in terms of covalent bond strengths to other atoms. A segment of the table first presented in the section on hydrogen is reproduced here. It shows that five out of the six strongest single bonds in all of chemistry are between fluorine and another atom. For example, Teflon is perfluoropolyethylene or  $(C_2F_2)_n$ .

Rank	Bond	$\Delta H$ (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

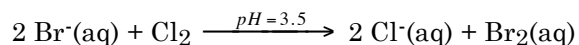
**C. Chlorine.** Chlorine is a pale green-yellow gas and does not occur in elemental form in nature. Chlorine is extremely reactive, but not as reactive as fluorine. It combines directly with most elements except carbon, nitrogen, oxygen and the noble gases. It combines directly with metals to form ionic salts such as  $MgCl_2$ :



and with non-metals to form covalent chlorides such as HCl:



**D. Bromine** is the only liquid non-metallic element. It is a red, heavy liquid with an appreciable vapor pressure at room temperature. The vapor is also red. Bromine has an odor similar to chlorine's and is extremely irritating to the eyes, skin and throat. Bromine is quite soluble in water. Industrial production of bromine involves oxidizing the bromide with chlorine to produce bromine and chloride, respectively:

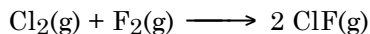


Bromine is removed from aqueous solution by blowing a current of air through the solution.

**E. The color of the halogens.** The ground state MO diagram for the halogens is  $(\sigma_s)^2(\sigma_s^*)^2(\sigma_p)^2(\pi)^4(\pi^*)^4(\sigma_p^*)^0$ . The energy gap between the  $\pi^*$  and the  $\sigma_p^*$  orbitals is small and the excited state  $(\sigma_s)^2(\sigma_s^*)^2(\sigma_p)^2(\pi)^4(\pi^*)^3(\sigma_p^*)^1$  is easily achieved. As a result, a small but significant portion of the halogen molecules have this excited state configuration. The intense purple color of iodine vapor is a result of ground state  $I_2$  to the excited state. (a) Sketch the MO diagram for this particular excited state. Label the energy gap between the ground state HOMO and LUMO. (b) Is the color observed due to an absorption (in which case include a color wheel to show what color is actually being absorbed) or an emission?

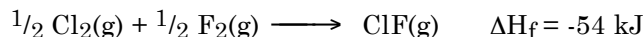
(a)	(b)
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**F. Interhalogens.** Chlorine monofluoride is a colorless gas prepared by heating  $\text{Cl}_2$  and  $\text{F}_2$  to 225 °C:

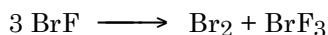


As noted earlier, the halogen homonuclear bond is particularly weak. Heteronuclear bonds between fluorine and any of the other halogens are significantly stronger. Thus, the heat of formation of  $\text{ClF}(\text{g})$  can be calculated to be -54 kJ:

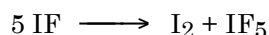
	<b>F</b>	<b>Cl</b>	<b>Br</b>	<b>I</b>
<b>F</b>	<b>155</b>	253	237	277
<b>Cl</b>	253	<b>243</b>	218	208
<b>Br</b>	237	218	<b>192</b>	175
<b>I</b>	277	208	175	<b>150</b>



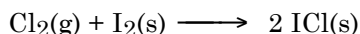
A comparison between the homonuclear and heteronuclear interhalogen bond strengths for each of the halogens shows that fluorine is the most likely to form heteronuclear interhalogen bonds from the purely thermodynamic standpoint. Nevertheless, these interhalogens may not settle on being 1:1 as did  $\text{ClF}$ . The list of simple 1:1 interhalogen compounds include  $\text{ClF}$ ,  $\text{BrF}$ ,  $\text{IF}$ ,  $\text{BrCl}$ ,  $\text{ICl}$  and  $\text{IBr}$ . Bromine monofluoride is a pale brown substance that is unstable at low temperatures; it dissociates into  $\text{Br}_2$  and  $\text{BrF}_3$ :



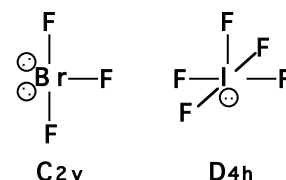
Similarly,  $\text{IF}$  is unstable and disproportionates into  $\text{I}_2 + \text{IF}_5$ :



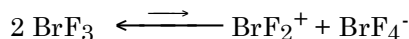
$\text{ICl}$  is a red crystalline compound formed by direct combination of the elements at room temperature:



Both  $\text{BrF}_3$  and  $\text{IF}_5$  are examples of expanded octet compounds. Their structures are T-shaped and square pyramidal, respectively.



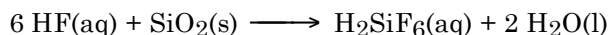
The halogen trifluorides include  $\text{ClF}_3$ , a colorless gas/liquid;  $\text{BrF}_3$ , a straw colored liquid, and  $\text{IF}_3$ , a yellow solid.  $\text{BrF}_3(\text{l})$  exhibits appreciable electrical conductivity. This is the result of some self-dissociation:



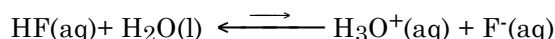
Sketch the Lewis dot structures of these two ions.

Higher interhalogens are known including  $\text{ClF}_5$ ,  $\text{BrF}_5$ , and  $\text{IF}_7$ . All are made by direct combination of the elements at elevated temperatures.  $\text{IF}_7$  has the structure of a pentagonal bipyramid. Sketch a pentagonal bipyramid.

**G. Hydrogen fluoride.** The properties of HF have been noted for centuries. In the 17th century, glass was etched with fluorspar,  $\text{CaF}_2$ , treated with acid; this produces HF which does the actual etching. An etched surface of glass is one in which the surface is microscopically pocked with countless divots. This creates a translucent effect which can be used to enhance the glass's beauty. The most familiar form of HF-etching today is the white 'frosted' light bulb. Chemically, the HF reacts with  $\text{SiO}_2$  in the glass to produce water-soluble  $\text{H}_2\text{SiF}_6$ . For this reason, HF(aq) is stored in plastic bottles.



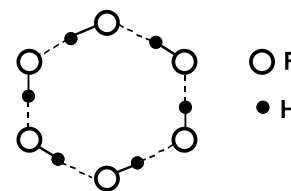
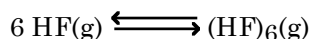
HF is the only weak acid in the family of hydrohalic acids. This is due to the unusual strength of HF covalent bond. At 25 °C, the  $K_a$  value is  $7 \times 10^{-4}$ .



HF exhibits very strong hydrogen bonding. In aqueous solution, HF forms the difluoride ion:



Even in gas phase, HF shows strong intermolecular forces and the monomer is known to exist in conjunction with the hexamer.



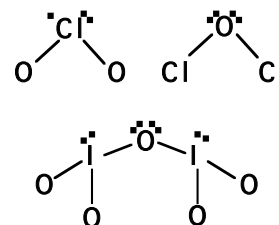
**H. Oxides.** A variety of halogen oxides are known and have been characterized. By halogens these include:

**Fluorine:**  $\text{F}_2\text{O}$ ,  $\text{F}_2\text{O}_3$

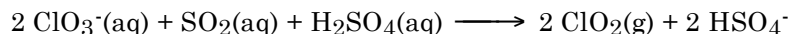
**Chlorine:**  $\text{Cl}_2\text{O}$ ,  $\text{Cl}_2\text{O}_3$ ,  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}_4$ ,  $\text{Cl}_2\text{O}_6$ ,  $\text{Cl}_2\text{O}_7$

**Bromine:**  $\text{Br}_2\text{O}$ ,  $\text{BrO}_3$ ,  $\text{BrO}_2$

**Iodine:**  $\text{I}_2\text{O}_4$ ,  $\text{I}_4\text{O}_9$ ,  $\text{I}_2\text{O}_5$



Most are of little importance to society except for  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}$  and  $\text{I}_2\text{O}_5$ .  $\text{ClO}_2$  is a yellow, paramagnetic gas (bp approx. 10 °C) with little tendency to dimerize. The O-Cl-O bond angle is 118 °.  $\text{ClO}_2$  is violently explosive gas which is more shock-sensitive than thermally sensitive.  $\text{ClO}_2$  is produced by the reaction of  $\text{KClO}_3$  with concentrated  $\text{H}_2\text{SO}_4$  and a reducing agent such as  $\text{SO}_2$ :



$\text{ClO}_2$  is water-soluble. In the light, it decomposes slowly to HCl and  $\text{HClO}_3$ . It is a powerful oxidizing agent and thus finds use as a commercial bleaching agent in the pulp, flour, and textile industries. Sometimes it is converted to  $\text{ClO}_3^-$  first. Sketch the Lewis dot structure of  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}$  and  $\text{I}_2\text{O}_5$ .