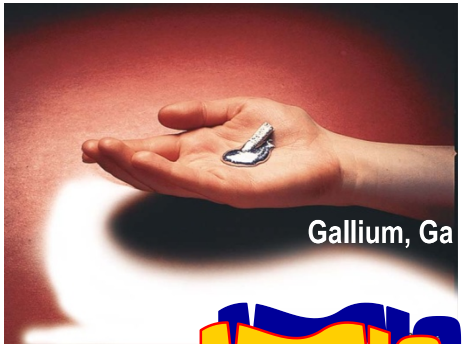
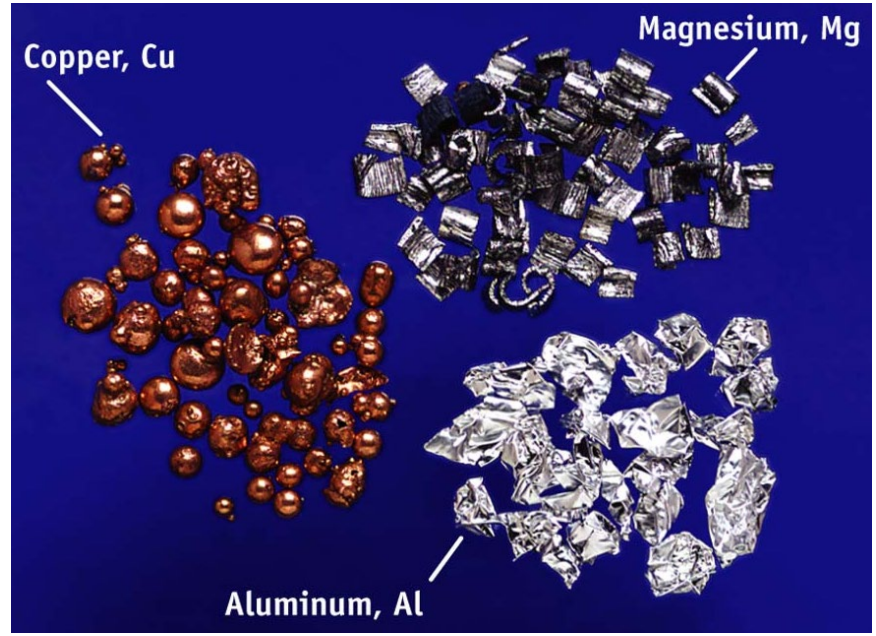


METALS



CHEMISTRY 1000

Topic #2: The Chemical Alphabet

Fall 2020

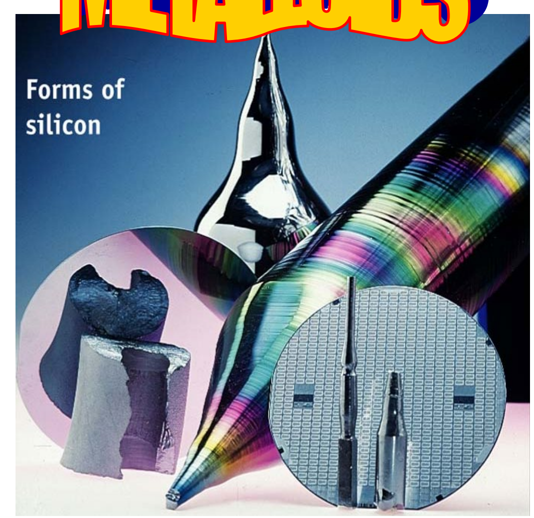
Dr. Susan Findlay

See Exercises 11.1 to 11.4

NONMETALS

Forms of Carbon

METALLOIDS

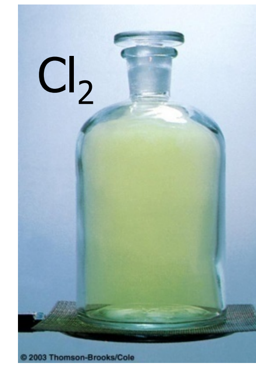


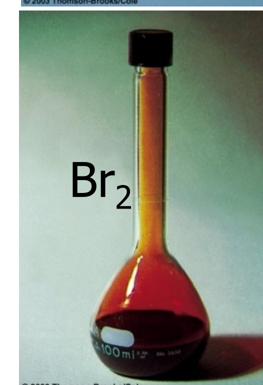
The Halogens (Group 17)

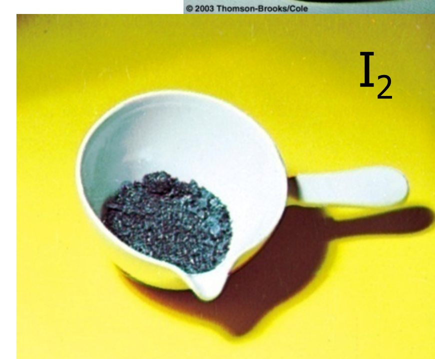
- What is a halogen?
  - Any element in Group 17 (the only group containing solids, liquids and gases at room temperature)
  - Exists as diatomic molecules (F_2, Cl_2, Br_2, I_2)

	Melting Point	Boiling Point	State (at 20 °C)	Density (at 20 °C)
Fluorine	-220 °C	-188 °C	Gas	0.0017 g/cm^3
Chlorine	-101 °C	-34 °C	Gas	0.0032 g/cm^3
Bromine	-7.25 °C	58.8 °C	Liquid	3.123 g/cm^3
Iodine	114 °C	185 °C	Solid	4.93 g/cm^3

  - A nonmetal
  - Volatile (evaporates easily) with corrosive fumes
  - Does not occur in nature as a pure element.
  - Electronegative; HCl, HBr and HI are strong acids; HF is one of the stronger weak acids







The Halogens (Group 17)

- What is a halogen?
  - Only forms one monoatomic anion (-1) and no free cations
  - Has seven valence electrons (valence electron configuration $[N.G.]ns^2np^5$) and a large electron affinity
  - A good **oxidizing agent** (good at gaining electrons so that <u>other</u> elements can be oxidized)

	First Ionization Energy (kJ/mol)	**Electron Affinity** (kJ/mol)	**Standard Reduction Potential** (V = J/C)
Fluorine	1681	328.0	+2.866
Chlorine	1251	349.0	+1.358
Bromine	1140	324.6	+1.065
Iodine	1008	295.2	+0.535

The Halogens (Group 17)

- Fluorine, chlorine and bromine are strong enough oxidizing agents that they can oxidize the oxygen in water! When fluorine is bubbled through water, hydrogen fluoride and oxygen gas are produced. Hypofluorous acid (HOF) is an intermediate:

The Halogens (Group 17)

Fluorine 18.9984 **F** 9
Chlorine 35.4527 **Cl** 17
Bromine 79.904 **Br** 35
Iodine 126.905 **I** 53
Astatine (210) **At** 85

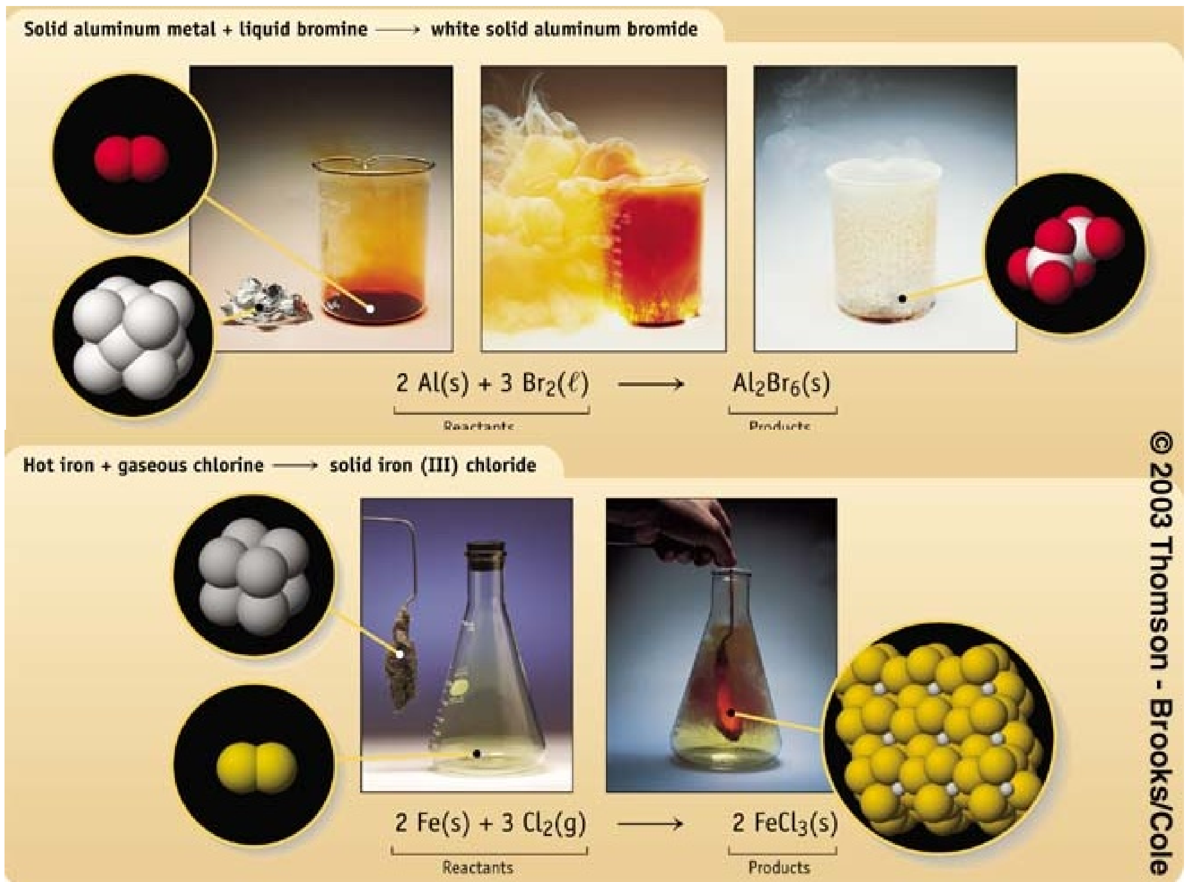
- Because they are weaker oxidizing agents than fluorine, chlorine and bromine will only perform this reaction in the presence of sunlight:

The oxygen produced in these reactions is particularly reactive, so moist chlorine gas is a much stronger oxidizing agent than anhydrous chlorine – as evidenced by the fact that it can bleach dyes like indigo, litmus and malachite green while anhydrous chlorine cannot.

The Halogens (Group 17)

Fluorine 18.9984	F 9
Chlorine 35.4527	Cl 17
Bromine 79.904	Br 35
Iodine 126.905	I 53
Astatine (210)	At 85

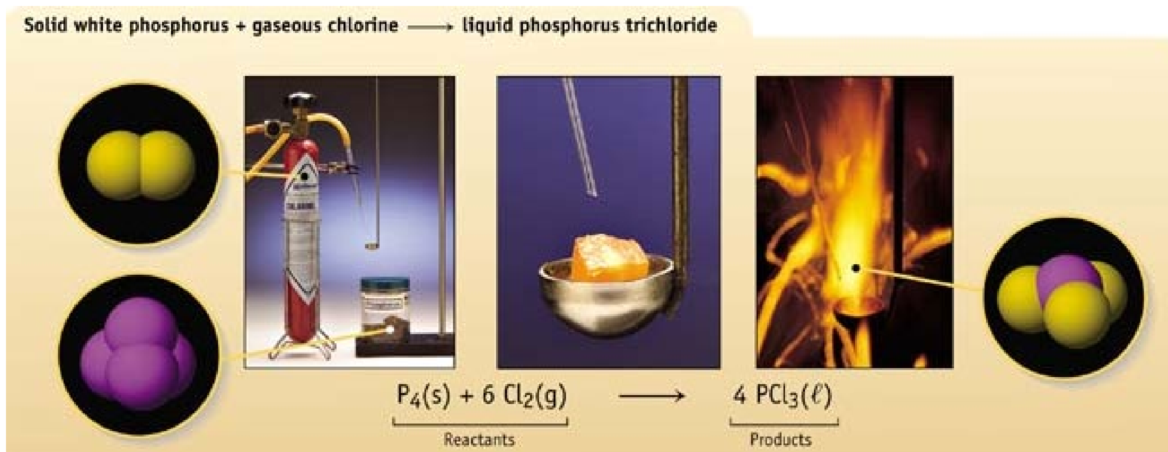
- What other reactions do halogens undergo?
  - We've already seen that halogens react violently with many metals:



The Halogens (Group 17)

Fluorine	18.9984	F	9
Chlorine	35.4527	Cl	17
Bromine	79.904	Br	35
Iodine	126.905	I	53
Astatine	(210)	At	85

- Halogens react with phosphorus (P_4) to give PX_3 or PX_5:
  (depending on the ratio of reactants)



The Halogens (Group 17)

- Halogens react with sulfur (S_8) to give a wide variety of compounds from S_2X_2 to SX_6:

- The long list of potential products includes, but is not limited to, SX_2, SX_4 and S_2X_4 *(depending on the ratio of reactants)*

The Halogens (Group 17)

Fluorine	18.9984	F	9
Chlorine	35.4527	Cl	17
Bromine	79.904	Br	35
Iodine	126.905	I	53
Astatine	(210)	At	85

- We saw in the Alkali Metals portion of the course that chlorine gas also reacts with the hydroxide in aqueous base:

- We also saw in the Alkali Metals portion of the course that chlorine gas is a product in the electrolysis of aqueous sodium chloride. This is how chlorine gas is produced industrially *(along with sodium hydroxide):*

The Halogens (Group 17)

- Oxoanions of the halogens
  - Fluorine, chlorine and bromine only occur naturally as monoatomic ions (fluoride, chloride and bromide). Iodine occurs naturally as iodide, but also in some oxygen-containing anions (**oxoanions**).
  - Chlorine, bromine and iodine are all capable of forming oxoanions in which an atom of halogen is surrounded by oxygen atoms.

The Halogens (Group 17)

- Because oxygen is more electronegative than all three of these halogens, the electron density is pulled out onto the oxygen atoms, leaving the halogen with a **positive oxidation state**:

Oxidation states are assigned similarly to formal charge, but treating every bond as 100% ionic, so that both electrons in the bond go to the more electronegative atom.

The Halogens (Group 17)

- Fluorine can only form one oxoanion.
  - What is it, and why is this the only one?
  - How is it different from the analogous oxoanion for chlorine, bromine or iodine?

The Halogens (Group 17)

Fluorine	18.9984	F	9
Chlorine	35.4527	Cl	17
Bromine	79.904	Br	35
Iodine	126.905	I	53
Astatine	(210)	At	85

- Draw Lewis diagrams for the four oxoanions of bromine, indicating the molecular geometry of each. Determine the oxidation state of each bromine atom.

- Because halogens are quite electronegative, they are quite reactive when they have large positive oxidation states. As such, oxoanions of halogens are even more reactive oxidizing agents than the halogens alone. Rank the oxoanions above by strength as an oxidizing agent.

The Halogens (Group 17)

- The name of an oxoanion depends on how many oxygen atoms surround the central atom. The table below shows the oxoanions you need to know for this course. You should already be familiar with many of them from lab. *It is important to know the correct charge as well as the number of oxygen atoms!*

	Cl	N	C	S	P
O	hypochlorite (ClO^-)				
O_2	chlorite (ClO_2^-)	nitrite (NO_2^-)			
O_3	chlorate (ClO_3^-)	nitrate (NO_3^-)	carbonate (CO_3^{2-})	sulfite (SO_3^{2-})	phosphite (PO_3^{3-})
O_4	perchlorate (ClO_4^-)			sulfate (SO_4^{2-})	phosphate (PO_4^{3-})

- To name an oxoanion which has had H^+ added, add **hydrogen** before the 'old' name. Remember that this adds +1 to the charge!
  e.g. HCO_3^- is "hydrogen carbonate"

The Halogens (Group 17)

- If enough H^+ have been added to render the oxoanion neutral, it is no longer an oxoanion. It is an **oxoacid**! In most* oxoacids, the hydrogen atoms are all attached to oxygen.

	Cl	N	C	S	P
	Hydrochloric acid (HCl)				
O	Hypochlorous acid ($HOCl$)				
O_2	Chlorous acid ($HClO_2$)	Nitrous acid (HNO_2)			
O_3	Chloric acid ($HClO_3$)	Nitric acid (HNO_3)	Carbonic acid (H_2CO_3)	Sulfurous acid (H_2SO_3)	Phosphorous acid* (H_3PO_3)
O_4	Perchloric acid ($HClO_4$)			Sulfuric acid (H_2SO_4)	Phosphoric acid (H_3PO_4)

*Phosphorous acid is an exception to this rule. Only two of its hydrogens are attached to oxygen.

The Halogens (Group 17)

Fluorine	18.9984	F	9
Chlorine	35.4527	Cl	17
Bromine	79.904	Br	35
Iodine	126.905	I	53
Astatine	(210)	At	85

- Draw the Lewis diagrams for sulfurous acid and sulfuric acid, and indicate the molecular geometry of each.

The Halogens (Group 17)

- As a general rule, the strength of an oxoacid increases as the number of oxygen atoms increases.

- We can quantify this trend using Pauling's rules for the strength of oxoacids:

$$\boxed{pK_a \approx 8 - 5p}$$

where the oxoacid has the formula $O_pE(OH)_q$.

- For oxoacids with multiple protons (i.e. $q > 1$), the pK_a increases by ~5 every time H^+ is removed (until none remain). Effectively, every H^+ is 100,000 times harder to remove than the last one.

The Halogens (Group 17)

- Use Pauling's rules to estimate pK_a values for sulfurous acid, sulfuric acid, hydrogen sulfite and hydrogen sulfate.