

8.6 Group 16 elements; sulfur production and use

Electronic structure of the group 16 elements

All the elements of the sulfur family exist in allotropic forms and, with the exception of oxygen, they are solids at ordinary temperatures. Their electronic configurations and ionization energies are shown in the table below. Notice that all these elements have 4 electrons in their outermost p orbitals. As a result, any atom can fill its shell either by gaining 2 electrons or by sharing 2 pairs of electrons (i.e. 4).

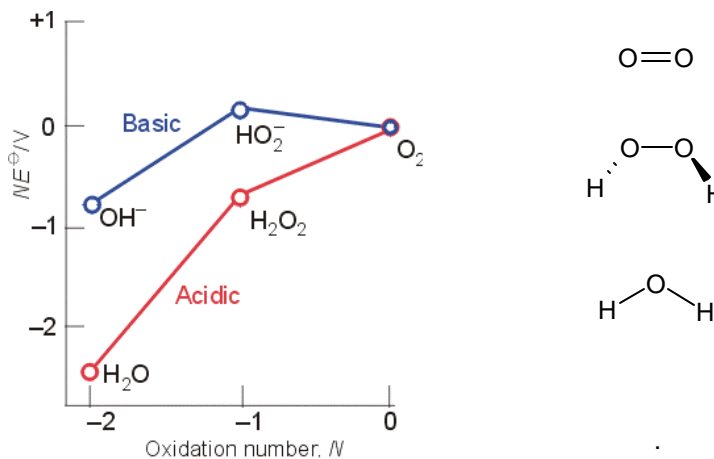
Element	Electronic structure	mp, °C	1st I.E., kJ mol ⁻¹	Electronegativity	Covalent radius
O	[He]2s ² 2p ⁴	-229	1314	3.50	0.73
S	[Ne]3s ² 3p ⁴	114	1000	2.44	1.04
Se	[Ar]3d ¹⁰ 4s ² 4p ⁴	221	941	2.48	1.17
Te	[Kr]4d ¹⁰ 5s ² 5p ⁴	452	869	2.01	1.37
Po	[Xe]4f ¹⁴ 6s ² 5d ¹⁰ 6p ⁴	254	812	1.76	?

Oxygen

Oxygen is one of the most abundant elements on earth. Large amounts of it are found in the molten mantle, in the crust that forms the great land masses, in the water of the vast oceans that cover most of the earth's surface, and in the gaseous atmosphere that surrounds the earth. Elemental oxygen can exist in two allotropic forms: diatomic molecules (O₂) and triatomic molecules (or ozone, O₃). Allotropy is a characteristic property of all elements of this group. Only in the atmosphere is oxygen found in the elemental forms, primarily as the dioxygen molecule, O₂. O₃ is however an important component of the stratosphere, in which it exists in equilibrium with O₂. The O₂/O₃ cycle acts as a filter for long-wavelength ultra-violet solar radiation, a process which is commonly referred to simply as "the ozone layer."

Dioxygen reacts so avidly with both metals and nonmetals that the presence of a large amount of free O₂ in the atmosphere raises the question: where did all of that O₂ come from? Studies over the past 200 years have provided the general outline of the answer, but some important details are still being actively investigated. Most of the dioxygen on earth has been produced by plants, from the smallest algae to the majestic redwoods. Plants use water, carbon dioxide (CO₂), and sunlight to form carbohydrates and oxygen in a complex process called photosynthesis. Animals reverse the process. They react carbohydrates with oxygen inside their cells in a process called respiration, forming CO₂ and water. So plants and animals exist together in a grand symbiotic cycle, each supplying the others' needs. The energy involved in this biological cycle is about 30 times the amount of energy expended each year by all of mankind's machines.

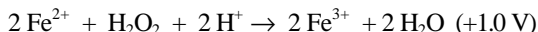
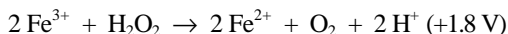
Oxygen can exist in two allotropic forms diatomic molecules (O₂) and triatomic molecules (or ozone, O₃).

Chemical preparation:A potent oxidizing agent:

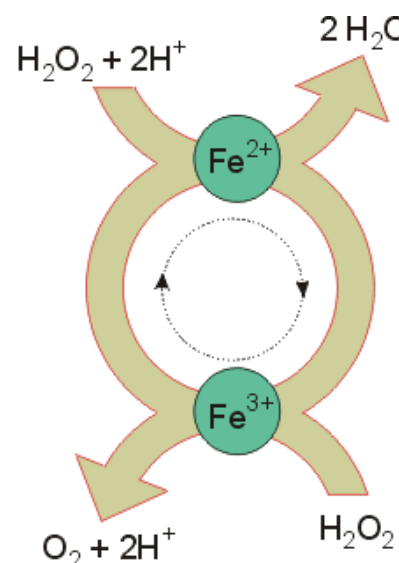
- Oxides of the metals are basic, give hydroxides with water
- Oxides of the non-metals are acidic, give hydronium ion with water

Hydrogen Peroxide

- Metastable (disproportionation)
- A stronger oxidizing agent than dioxygen (steeper slope)
- Catalyzed decomposition e.g. Fe^{3+} catalytic cycle at right:



- As both are favoured, Fe^{2+}/Fe^{3+} cycle is catalytic

Sulfur

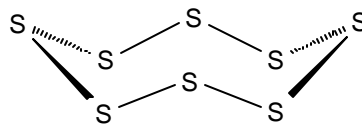
Sulfur can behave chemically in two ways. First a sulfur atom can acquire two electrons to complete its octet, thereby forming the stable sulfide ion, S^{2-} , with the $[Ar]$ electron configuration. It can also have positive oxidation states, particularly in the presence of such powerful oxidizers as fluorine and oxygen. Thus, as we already know, sulfur readily burns in air to form sulfur dioxide, a pungent gas. In this reaction sulfur forms a covalent bond with oxygen. But since oxygen atoms have a greater affinity for electrons than have sulfur atoms, the shared electrons shift towards the oxygen.

It should now be apparent that the way sulfur behaves in a particular reaction depends upon the nature of the element it combines with. If sulfur reacts with metals (or hydrogen), it is the more electronegative partner in the resulting bonds, and its oxidation number is -2 . On the other hand, if sulfur reacts with oxygen or fluorine, its oxidation number can be $+1$, $+2$, $+3$, $+4$, $+5$ or $+6$. Of these, the most common is $+4$, as in SO_2 and SF_4 . However, in the presence of a suitable catalyst, sulfur dioxide will also combine with oxygen to form sulfur trioxide, SO_3 , and SF_4 can be reacted with excess fluorine to make SF_6 . Interestingly, SF_6 is a very stable gas, and is used as an insulator in high-voltage electrical equipment, whereas SF_4 is a highly reactive compound. This is another example where a compound derives its stability from kinetic rather than from thermodynamic factors. SF_6 is unreactive because the crowded sulfur atom is kept away from nucleophiles by the six tightly-held fluorine atoms.

Properties of sulfur

Both sulfur and oxygen atoms have 6 electrons in their outermost energy levels. It would, therefore, be reasonable to expect that sulfur, like oxygen, would form diatomic molecules, S_2 . Actually sulfur forms diatomic molecules only at high temperatures. At ordinary temperatures it forms a ring of 8 sulfur atoms bound together by covalent bonds (Figure 1). The origin of this difference lies in the relative strengths of the single (e.g. $O-O$ vs $S-S$) and double bonds ($O=O$ vs $S=S$). Only for the elements of the second period of the periodic table is the bond energy of a double bond greater than the sum of two single bonds.

Figure 1
The crown shape of the
sulfur molecule, S₈



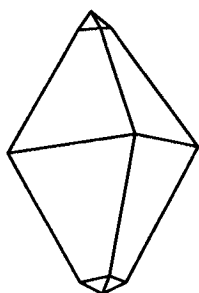
As one would expect, the van der Waal's forces are considerably greater in cyclic S₈ than in O₂. Sulfur molecules are nonpolar. In general we can say that nonpolar molecules mix with other nonpolar molecules but not with polar molecules. Sulfur will dissolve in such nonpolar liquids as carbon tetrachloride, carbon disulfide, and hexane, but not in water.

Allotropes of sulfur

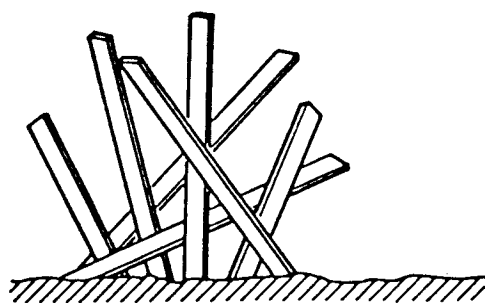
Sulfur has several allotropic forms, the most important being rhombic and monoclinic. Crystals of rhombic and monoclinic sulfur differ only in the internal arrangement of the crown-8 rings with respect to one another. The resulting crystals are observably different, belonging as they do to two different symmetry classes.

Rhombic sulfur consists of yellow octahedral crystals (see Figure 2). It is stable at ordinary temperatures, and is therefore the more familiar allotrope. It melts at 114°C, is insoluble in water, but quite soluble in carbon disulfide. Sizable crystals of rhombic sulfur can be grown by slowly evaporating a carbon disulfide solution of sulfur.

Monoclinic sulfur consists of long needleshaped crystals (see Figure 2). These can be formed by melting rhombic sulfur and then allowing it to cool and crystallize. This is because monoclinic sulfur is stable at temperatures above 96°C; it is unstable below this temperature and slowly reverts to the rhombic form. A more convenient way of preparing monoclinic sulfur is to let it crystallize from solution in hot toluene.



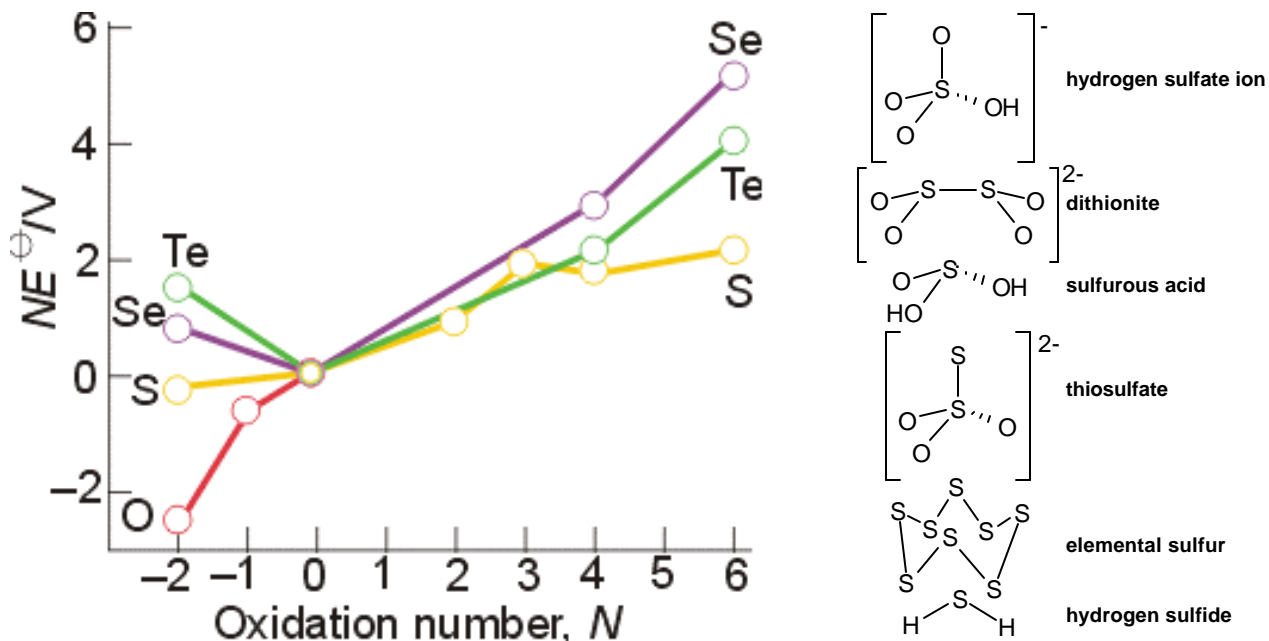
Typical habit of rhombic sulfur crystals



Typical habit of monoclinic sulfur crystals

Figure 2

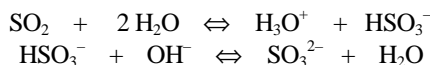
Near its melting point, sulfur is a mobile liquid, which is consistent with the interpretation that at this point it consists almost entirely of S₈ rings and that these rings interfere only slightly with each other's motion. However, as the temperature is raised, the kinetic energy of the molecules increases, causing bond-breaking and re-forming to occur. Thereby the rings become entangled and the viscosity of the liquid increases dramatically. As the temperature is raised still further, more extensive bond-breaking occurs, and a variety of short-chain sulfur molecules are formed. This allows some of the entangled chains to free themselves, and, as a result, the viscosity decreases. Finally, if the hot liquid is suddenly chilled by cold water, the chains again become so entangled that the sulfur solidifies and becomes rubber-like in texture. On long standing, the entangled chains eventually revert to S₈ rings, and this so-called plastic sulfur reverts to the rhombic crystalline form.



Sulfur oxides and oxo acids

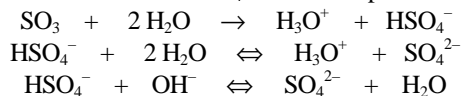
By sharing its electrons with more electronegative elements, such as oxygen, sulfur attains positive oxidation states. There are numerous sulfur oxides, and myriad oxo acids and anions, involving several sulfur oxidation states, and -S-O-S- catenation. We will consider only the most common ones here.

In sulfur dioxide, four of the sulfur electrons are involved in bonding with oxygen. SO_2 is the anhydride of sulfurous acid, H_2SO_3 , which is a weak acid, and forms some $\text{H}^+ + \text{HSO}_3^-$. In basic solutions the equilibria are shifted to the right, to form more bisulfite and sulfite ions and water.



SO_2 can be detected by the formation of a bright yellow precipitate when the gas is bubbled through an aqueous solution of hydroquinone. The crystals are composed of a hydroquinone clathrate. This is a type of cage structure in which SO_2 molecules are trapped in the holes formed when hydroquinone forms a hydrogen-bonded network solid. The cage only forms when "guest" molecules of certain size are added to the hydroquinone solution.

In sulfur trioxide all six of the sulfur electrons are involved in bonding. Sulfur trioxide is the anhydride of sulfuric acid, H_2SO_4 , one of the most important industrial inorganic chemicals. It is a strong acid whose aqueous solutions contain large concentrations of H^+ and HSO_4^- ions. In basic solutions the SO_4^{2-} ion is the predominant species.



A third sulfur oxide is known principally as the oxo anion, which is the thiosulfate ion. Note that in the thiosulfate ion the sulfur atom that replaces the oxygen in the sulfate structure may be assigned a -2 oxidation number and that the central sulfur atom has an oxidation number of $+6$, just as it has in sulfate. The $+2$ oxidation number assigned to sulfur in thiosulfate is obtained by finding the average of $+6$ and -2 , i.e. $(+6 - 2)/2 = +2$.

H_2SO_4 and SO_4^{2-} are mild oxidizing agents, whereas H_2S , S^{2-} , H_2SO_3 , SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$ are reducing agents. In addition, since S , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , and H_2SO_3 represent intermediate oxidation states, they can act as oxidizing agents with a strong reducing agent and as reducing agents with a strong oxidizing agent.

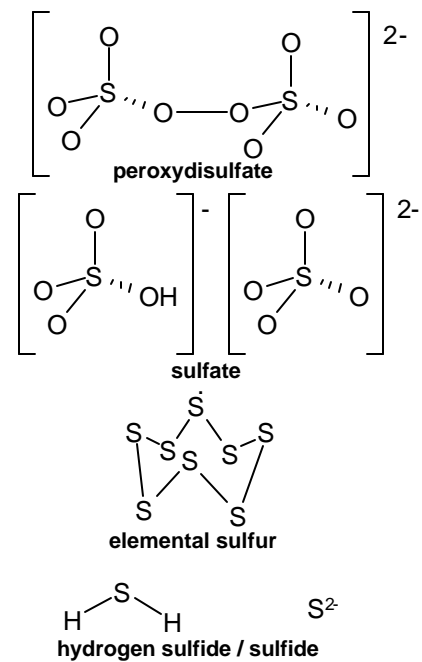
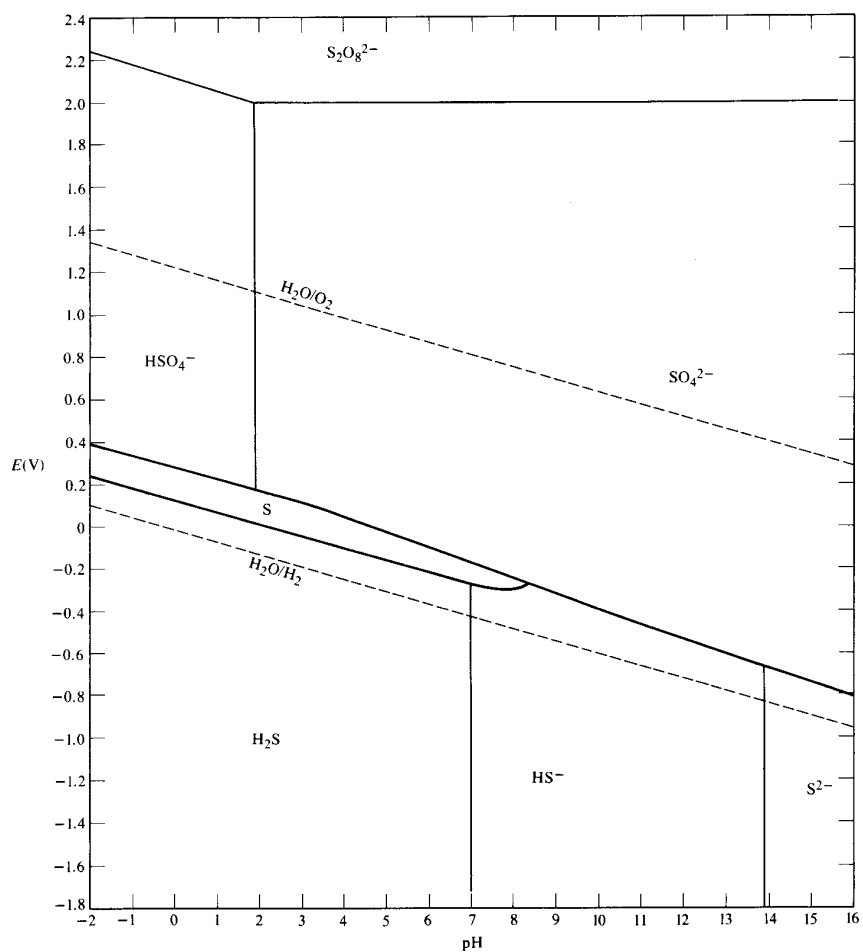


Figure 16.8 Pourbaix diagram for sulfur. [Adapted with permission from M. J. N. Pourbaix, in *Atlas of Electrochemical Equilibria in Aqueous Solution* (English translation, 2nd ed., by J. A. Franklin, National Association of Corrosion Engineering, Houston, TX, 1974, p. 551).]

Among the group 16 elements, sulfur and selenium are quite similar. Thus for most of the species shown in the Pourbaix diagram of sulfur, there are direct equivalents for selenium. A Pourbaix diagram for selenium is shown below. The most important general distinction between the two is the increased difficulty in oxidation for selenium. Thus elemental selenium occupies a much larger part of the diagram. The Se(VI) states are particularly difficult to attain. Note also that there is a huge overlap zone between the element and the neighbouring species.

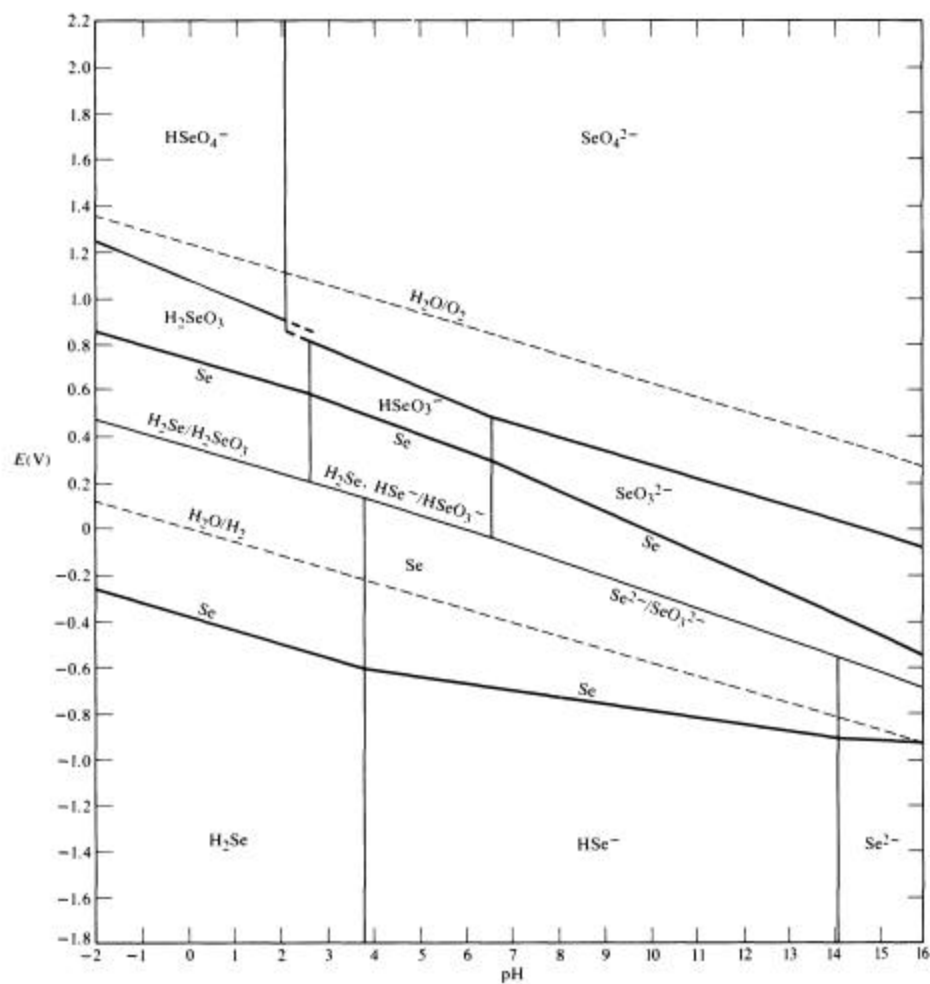


Figure 16.9 Pourbaix diagram for selenium. [Adapted with permission from M. J. N. Pourbaix, in *Atlas of Electrochemical Equilibria in Aqueous Solution* (English translation, 2nd ed., by J. A. Franklin, National Association of Corrosion Engineering, Houston, TX, 1974, p. 557).]

8.7 Group 17 elements; chlor-alkali production

Electronic structure of the group 17 elements

Under normal conditions fluorine is a yellowish gas, chlorine is a greenish gas, bromine is a dark red liquid, and iodine a black shiny solid. All the halogens are poisonous and should be handled with great care. It is interesting to note that the toxicity of the members of the halogen family decreases with increasing atomic number.

The ionization energies are usually high. As a result, the halogens do not normally tend to lose electrons in chemical reactions but instead they tend to gain them. This tendency is also apparent by examining the electron arrangement of the outermost orbitals. For fluorine it is $2s^2 2p^5$, for chlorine $3s^2 3p^5$ for bromine $4s^2 4p^5$, and for iodine it is $5s^2 5p^5$. In short, all the halogens have 7 electrons at the outermost quantum level or 5 electrons in the outermost p orbitals. And since the p orbitals can accommodate 6 electrons, the halogens often add a single electron in their reactions, thereby completing their corresponding inert gas configurations, and forming monatomic ions, the halide ions.

Ionization of halogens to positive oxidation states usually occurs only in compounds with more electronegative elements. For fluorine, there are none! For chlorine, there are a number of oxygen compounds ($\chi(\text{O}) = 3.50$). Bromine and iodine also form some (unstable) nitrogen compounds. In recent years an extensive chemistry of polyiodide cations has developed, with the help of "superacids".

Element	Electronic structure	mp, °C	1st I.E., kJ mol ⁻¹	Electronegativity	Covalent radius
F	[He]2s ² 2p ⁵	-219	1681	4.10	0.64
Cl	[Ne]3s ² 3p ⁵	-101	1255	2.83	0.99
Br	[Ar]3d ¹⁰ 4s ² 4p ⁵	-7	1140	2.74	1.14
I	[Kr]4d ¹⁰ 5s ² 5p ⁵	114	1008	2.21	1.33
At	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵	?	?	1.90	?

The tendency of the halogens to gain electrons in chemical reactions is consistent with their status as non-metals. This tendency is quantified by the electron affinity, or enthalpy of electron attachment, to use the more modern term (the signs used in the table below follow the latter definition). When a halogen atom acquires an electron to form an ion it releases energy, thereby entering a lower energy state, or a more stable state. Thus electron affinity can be defined as the energy released when an electron enters the outermost orbital of an atom.

Element	F	Cl	Br	I	At
Electron affinity	-328	-349	-325	-295	-270 (kJ mol ⁻¹)

However, the exact size of the electron affinity is not as easy to correlate with orbital character. For example, since fluorine is anomalously small, its electron affinity is reduced from what it might be due to electron-electron repulsion. When we look at chemical behaviour, however, we find that the oxidizing power of the halogens decreases as we proceed down the group from fluorine, to chlorine, to bromine to iodine, in accord with the predictions of simple theory. Because of their great chemical activity, it is not surprising that the halogens do not occur free in nature. Chlorine is by far the most abundant of the halogens. It occurs as chloride ion in seawater and as rock salt (NaCl) and Sylvite (KCl) in large mineral deposits.

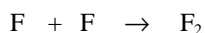
General characteristics of the halogens.

The halogens may complete their inert gas configurations either by gaining an electron to form an ionic bond or by sharing an electron to form a covalent bond. An example of the first kind of reaction is the combination of sodium and fluorine.



The electronegativity of fluorine is high and it captures an electron to form a stable ion, with little tendency for back donation of charge. The resulting compound is thus an ionic solid.

An example of the second kind of reaction is the combination of atoms of the same kind to form diatomic molecules, such as



It is apparent from their structure that halogen molecules are nonpolar. Thus a fluorine molecule, F_2 , shows no tendency to combine with another atom to form a larger molecule F_3 . Moreover, the van der Waal's forces between fluorine molecules are very weak and, as a result, there is little attraction between the molecules and little tendency for fluorine gas molecules to condense to a liquid. The boiling point of fluorine is -188°C . The van der Waal's forces become progressively stronger as the atomic number increases. (Why?) The boiling point of chlorine, which is -34°C , confirms this idea. The van der Waal's forces are still stronger for bromine, strong enough to hold the molecules together to form a liquid at ordinary temperatures. (The boiling point of bromine is 59°C .) The forces in iodine are so strong that the molecules condense to a solid at ordinary temperatures. (The boiling point of iodine is 183°C , although at atmospheric pressure iodine sublimates rather than forming a liquid.)

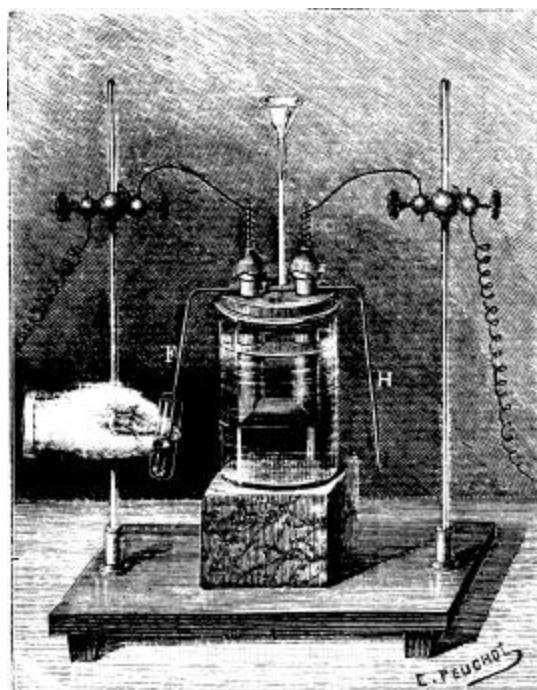
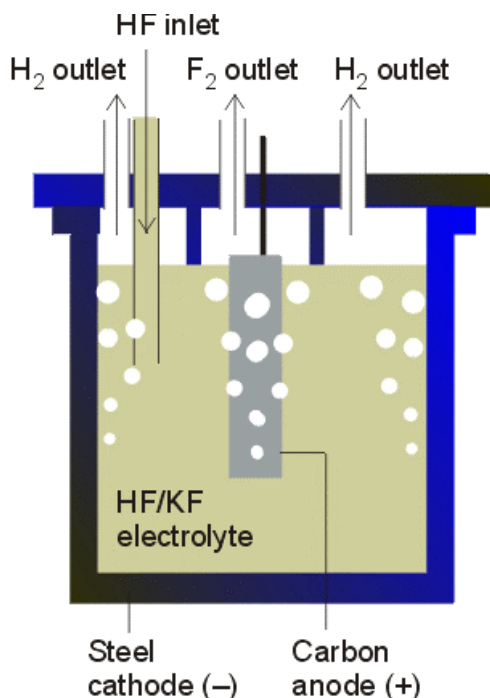
Fluorine is the most powerful of all oxidizers. The oxidation number of fluorine is -1 in all its compounds. Such a restriction does not apply to the other halogens, however.

Preparation and reactions of fluorine

Fluorine can only be prepared by electrolysis, and this was originally done by French chemist Henri Moissan in 1886. Historians of chemistry have concluded that several previous attempts to isolate elemental fluorine from its compounds probably did succeed, but that under the conditions used by the researchers, the fluorine ended up reacting immediately with other reactants in the mixture, and indeed often enough with the walls of the containers used for the preparation. The key to fluorine electrolysis is the use of a molten salt electrolyte, in practice this is composed of a mixture of concentrated hydrofluoric acid and potassium fluoride, along with certain catalytic impurities that enhance the reaction.

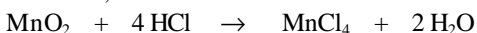
The diagrams below show a schematic of a modern HF electrochemical cell, as well as a sketch of Moissan's original 1886 cell. Key to the design of Moissan's original cell was the employment of an all-platinum design. Only platinum among the metals is sufficiently noble to resist direct reaction with elemental fluorine, the most powerful oxidizing agent known. The narrow platinum tubes labeled "H" and "F" on the diagram represent the sources of H_2 and F_2 gas, respectively. In his original experiments, Moissan simply held small samples of other elements under this gas stream using platinum deflagrating spoons. Virtually all elements on the periodic table spontaneously burst into flame when exposed to a stream of F_2 , yet this is a fluorine-flame, not an oxygen-flame.

The modern commercial HF cells, as well as smaller versions sometimes used in laboratories in lieu of gas cylinders of F_2 , differ little from Moissan's original design, except for a few direct technical improvements.



Preparation and reactions of chlorine

Chlorine is prepared in the laboratory by the chemical oxidation of the chloride ion. (Industrially it is prepared by the electrolysis of brine, which means in effect the electrochemical oxidation of chloride ion. This is known as the chlor-alkali process, and is discussed in detail in Section 8.7.2) Hydrochloric acid is a good source of chloride ions and manganese dioxide is a suitable oxidizer. When these substances react, the reaction occurs:



Manganese chloride, MnCl_4 , is unstable and decomposes to form manganous chloride (MnCl_2), and chlorine

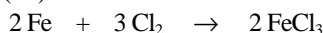


(a) Reactions with metals.

Chlorine is a strong oxidizer. It combines directly with most metals to form chlorides. For example,



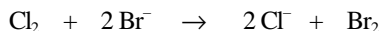
The vigor of the reaction depends upon the activity of the metal. Sodium, for instance, bursts into flame if placed in chlorine. The reaction with iron is interesting because iron (III) chloride is formed:



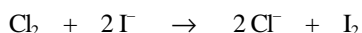
In this reaction, chlorine is a strong enough oxidizer to capture one of the "buried" electrons of iron, an electron in the next-to-the outermost shell. If iron reacts with chlorine, iron(III)chloride is formed; if iron reacts with hydrochloric acid, iron(II)chloride is formed. Chlorine is clearly a more powerful oxidizer than hydrogen ion.

(b) Replacement reactions.

Chlorine, being a stronger oxidizer than bromine or iodine, will displace bromine from bromides and iodine from iodides:



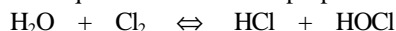
Similarly:



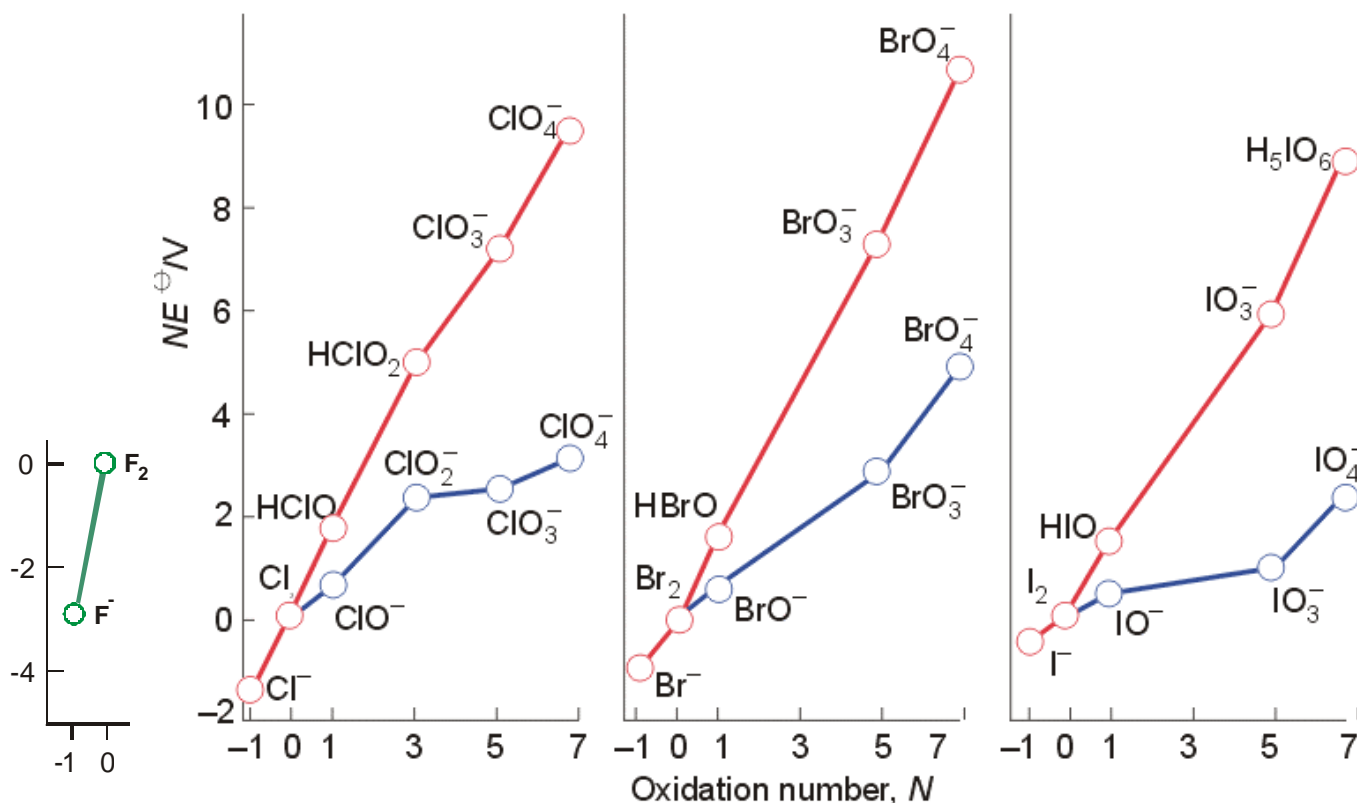
These replacement reactions serve as a test by which bromides and iodides can be identified.

(c) Reaction with water.

Chlorine dissolves in water to a small degree. The total concentration for a saturated aqueous solution at 25 C is 0.091 M. Of this total, $[\text{Cl}_2] = 0.061$ and $[\text{HOCl}] = 0.030$. The equilibrium for the disproportionation of Cl_2 in neutral solution is:



One chlorine atom forms chloride ion in water solution and the other forms a covalent bond with oxygen. The name of HOCl is hypochlorous acid; it is an oxyacid of chlorine. One of the chlorine atoms in this reaction is reduced and the other oxidized. As we covered in lecture, this disproportionation is favoured in basic solution, where quantitative solutions of NaOCl can be prepared (i.e. bleach)



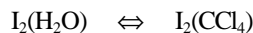
Preparation of and test for iodine in aqueous solution

Both industrially and in the laboratory iodine is prepared from iodide solutions (some natural brines have a high iodine content; otherwise iodine can be isolated from certain types of seaweed.) The reaction is that in (b) above, i.e. by using chlorine as an oxidizing agent to oxidize Γ^- to I_2 . Iodine is appreciably soluble in water, but the presence of even a small quantity of excess Γ^- sets up a powerful equilibrium as follows:



I_3^- is known as the triiodide ion.

Solutions of I_2 and I_3^- in water are brown in colour, due to a Lewis acid/base interaction with the water molecules. This makes it virtually impossible to tell aqueous Br_2 from aqueous I_2 , or to identify iodine in any kind of coloured solution. However, a positive identification of both these halogens is readily made by using a phase-transfer solvent. Normally CCl_4 is used, a totally non-polar liquid. Both Br_2 and I_2 are very soluble in this solvent, and as an additional benefit, there is no Lewis acid/base interaction to alter the colours. Thus Br_2 in CCl_4 is orange-brown in colour (depending on concentration), while I_2 in this solvent is deep purple. The solubility of I_2 in CCl_4 sets up a competing equilibrium with the triiodide equilibrium. However when doing an iodine test, always be sure to add sufficient chlorine water to lower the Γ^- concentration to the level where the reaction:



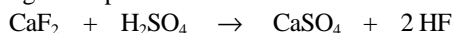
is will tend to go towards the product side. Otherwise the iodine may stay as I_3^- in aqueous solution despite the presence of CCl_4 .

Hydrogen halides.

A method of preparing hydrogen halides is to treat a metal halide with concentrated sulfuric acid. The principle is that the other acid must be a sufficiently strong Brønsted acid to protonate the halide ion, which is a Brønsted base. Concentrated sulfuric acid is used in the preparation of volatile acids because it is strong enough an acid, and because of its high boiling point, about 330 C, which enables the HX acids to be removed from solution by distillation.

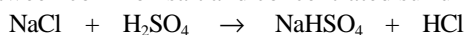
(a) Hydrogen fluoride.

Hydrogen fluoride is prepared by treating fluor spar with concentrated sulfuric acid:



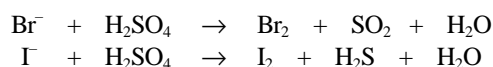
(b) Hydrogen chloride.

By far the most important of the hydrogen halides is hydrogen chloride. It is prepared by the reaction between common salt and concentrated sulfuric acid as shown in the equation:

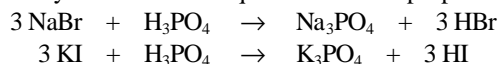


(c) Hydrogen bromide and hydrogen iodide.

Neither HBr nor HI can be prepared by the methods used to prepare HF and HCl. You can see from the Frost diagrams that the halogens are oxidizing agents and that, in oxidizing power, $F_2 > Cl_2 > Br_2 > I_2$. It follows that the halide ions are reducing agents and that, in reducing power, $\Gamma^- > Br^- > Cl^- > F^-$. Concentrated H_2SO_4 is a strong oxidizer. Bromide ions and iodide ions react with and reduce concentrated H_2SO_4 ; in one case sulfur dioxide is the reduction product and in the other, hydrogen sulfide. Or, as unbalanced equations,



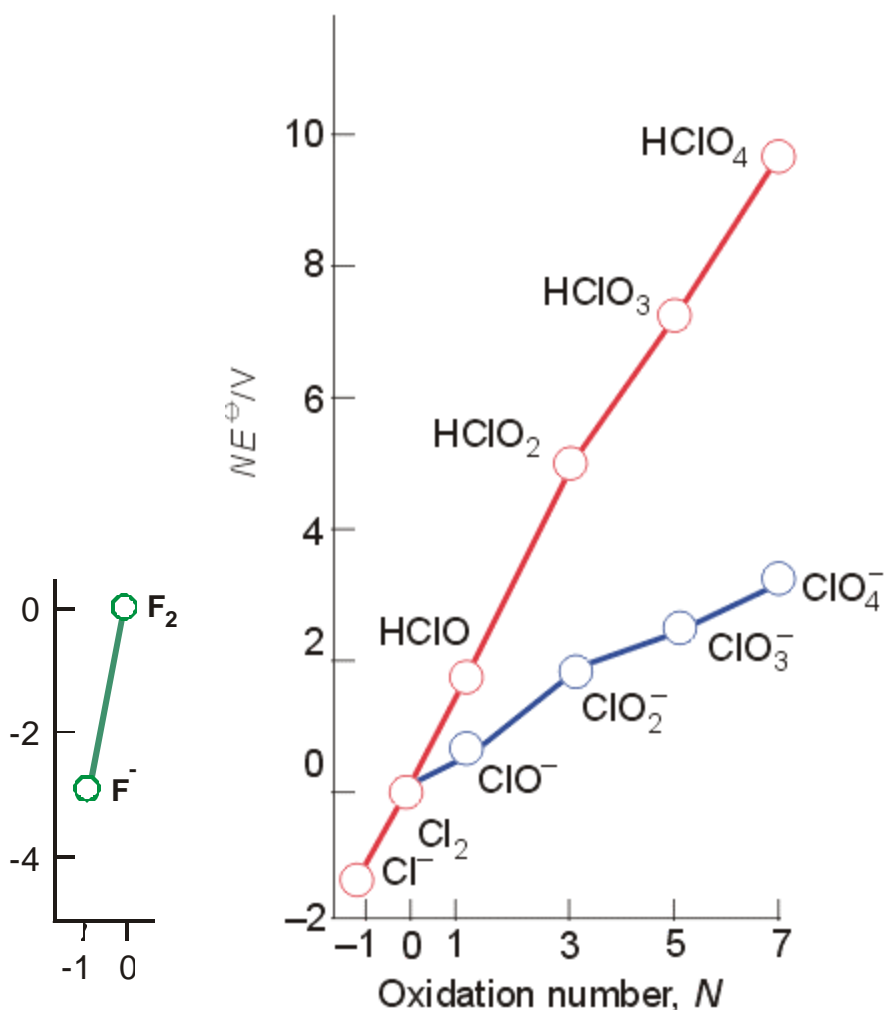
It should now be apparent that HBr and HI cannot be prepared from their halide salts by the reaction of an acid that is a strong oxidizer. Instead, phosphoric acid may be used. The equations for the preparation of these two gases would then be:

Fluorides, chlorides, bromides, and iodides of the elements

In general, the halides are quite soluble in water. There are, however, some exceptions to this rule: the chlorides, bromides and iodides of silver, mercury (I), and lead are only slightly soluble in water.

Halide ions are also capable of acting as ligands in transition metal coordination compounds, and replacing other ligands around the central atom. Halogen ions are commonly used as ligands also towards metals of the main group elements, including the metalloids. For example, the blood-red complex $FeSCN^{+2}$ can be converted to the colourless complex FeX_6^{-3} by excess halide, and the water molecules of hydration on blue $Cu^{+2}(aq)$ can be replaced by excess halide ion to form yellow or green CuX_4^{-2} complexes.

8.7.1 Reading the Frost Diagram for Fluorine and Chlorine in Acid and in Base solution

a) Slope

The steeper the slope, the stronger the oxidizing agent. (Compare the fluorine Frost diagram; we conclude that F_2 is a stronger oxidizing agent than is Cl_2 .)

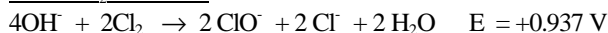
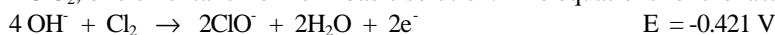
b) Bottom

A Frost diagram can display a thermodynamic well. There is none for Cl, so that the reactions tend to continue until Cl^- is reached. The thermodynamic end-point for chlorine is always Cl^- , the most common oxidation state for this element.

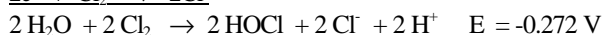
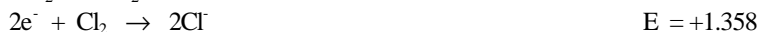
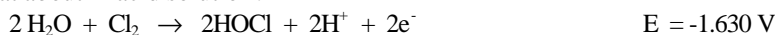
c) Disproportionation

If a species lies **above** the line connecting its neighbours, it is thermodynamically unstable towards disproportionation.

For example: $HClO_2$, or elemental chlorine in basic solution. The equations for the latter process are:



So elemental chlorine under these conditions is unstable! In fact, this is how household bleach is made, by bubbling Cl_2 through basic solution in a stirred reactor. The resulting solution is even more oxidizing than chlorine, and being ionic is soluble in water. But what about in acid solution?

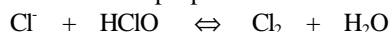


In acid solution, Cl_2 is stable! In fact, one should never acidify bleach, since chlorine gas will be liberated by a *comproportionation* reaction (the reverse of the indicated reaction, which has the opposite sign for the reaction).

The ClO^- in basic solution, when heated, is further oxidized to ClO_3^- , and a portion reduced back to Cl^- . (By suitable crystallization of the salts from this solution, the commercially important oxidant KClO_3 or the weed killers NaClO_3 and $\text{Ca}(\text{ClO}_3)_2$ may be obtained.)

d) Comproportionation

If a species lies **below** the line connecting its nearest neighbours, it can be formed from those neighbours in a comproportionation reaction. For example: Cl_2 in acid the comproportionation reaction is:



e) The Nernst Equation

We can look at this same question of pH control of E by using a general equation to correct for concentration changes in electrochemical reactions. This is the Nernst equation:

$$E_{\text{actual}} = E^\circ - \frac{0.0519\text{V}}{n} \log_{10} Q \quad (\text{at } 25^\circ\text{C only})$$

(Where Q is the reaction quotient. Q has the form of an equilibrium constant, but without the concentrations being equilibrium ones.)

Note that when $Q = 1$, $\log Q = 0$, and $E = E^\circ$.

Applying this to the redox states of chlorine, it is easiest to use the alkaline form of the equation (1):

$$E_{\text{actual}} = E^\circ - \frac{0.0519\text{V}}{n} \log_{10} \frac{[\text{ClO}^-]^2 [\text{Cl}^-]^2}{[\text{Cl}_2] [\text{OH}^-]^4}$$

What happens when $[\text{OH}^-]$ in this expression changes from 1 @ pH 14 to 10^{-14} @ pH 0? The term that changes if all other concentrations are held constant is:

$$\log \{1 / [10^{-14}]^4\} = \log 10^{56} = 56$$

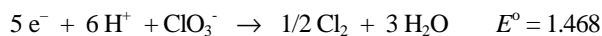
Hence, the value of the cell potential E becomes:

$$E = E^\circ - 0.05916/2 \times 56 = E^\circ - 1.65$$

In fact the change in redox potential is only 1.2 V, since half of the H^+ added is picked up by the weak acid HClO^- , but the general trend is there. This explains the major changes in redox potentials with pH. You can use the Nernst equation in a precise manner to actually calculate the new redox potential at certain specific concentrations. You can also use it in a qualitative sense to see trends.

- e.g. Is chloric acid a stronger or a weaker oxidizing agent in concentrated rather than in weak acid?

Solution:



$$E = E^\circ - 0.05916/5 \times \log [\text{Cl}_2]^4 / [\text{ClO}_3^-] [\text{H}^+]^6$$

Now, $\log 1 = 0$; $\log 0.1 = -1$. Thus raising $[\text{H}^+]$ from 1 to 6 or 10 M will make the log term into a more negative number. This will make the overall sign more positive, thus raising E . **It will be a stronger oxidizing agent in strong acid.** The same conclusion can be reached by considering Le Chatelier's principle applied to the equation. Since acid is consumed in the reaction, adding more acid will drive the reaction towards products!

f) Advantages of Graphic Display of Free Energies in volt-equivalents

To summarize the information from the Frost diagram: In acid, HOCl , HClO_2 and ClO_3^- are unstable to disproportionation.

In base, ClO_3^- , ClO_2^- , ClO^- and Cl_2 are unstable

Thus by comparing the blue and the red curves, we can **immediately** see that the chlorine compounds with oxidation state of 1 or greater are **much stronger oxidizing agents in acidic than in basic solution**. One important conclusion from this observation is that higher oxidation states of chlorine should *always* be synthesized under basic rather than under acidic conditions. Under basic conditions, it is possible to oxidize Cl^- (oxidation state -1) to free chlorine, $\text{Cl}_2(\text{g})$ (oxidation state 0), and then carry out a series of disproportionation reactions in which the chlorine is successively oxidized to the $+1$, $+5$, and finally the $+7$ oxidation states, as indicated on the Frost diagram.

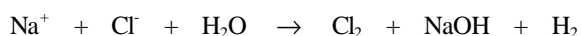
The exception to this rule is the production of perchlorate from the disproportionation of potassium chlorate. This reaction is actually done under neutral conditions using the potassium salt just above the melting point. Maintaining KClO_3 crystals at a temperature just above their melting point results in further auto-oxidation of the ClO_3^- to ClO_4^- , and reduces a portion of it to Cl^- . (Perchlorates are important oxidants in solid rocket fuels; see detailed information in the "Lecture 23" notes.)

8.7.1 Application of the Frost Diagram to the Chlor-Alkali process

This is one of the most important commercial chemical processes in Canada, and one that will become more controversial as time goes on. It has a number of variants, depending on the products.

Basically, a concentrated brine solution is prepared, NaCl(aq) . In an electrochemical cell, these are exposed to an electrolysis current. There are two major designs of cell, the older one was the mercury cell, in which mercury amalgam was used to remove the sodium for subsequent reaction with water to form sodium hydroxide. The newer design is the asbestos diaphragm design.

The cathode can be made of steel, since it is not exposed to chlorine. But the anode must be made of a resistant metal such as titanium. The basic reaction is:



This means that we are producing three important commodity chemicals, chlorine, hydrogen and sodium hydroxide. One of the main uses of these products is the pulp and paper industry. The chlorine and alkali are both used on site in the paper making and bleaching process. They have little use for the hydrogen. The mercury cell accomplishes the separation of the alkali from the brine; however its use in pulp and paper industry has led to the spreading of mercury into the environment. In fact, if the liquor is concentrated and cooled, most of the NaCl precipitates, leaving a salty solution of sodium hydroxide. These plants generally use the reagents in solution rather than isolating them. The residual salt in solution is not a major obstacle.

If instead of tapping off the chlorine, the mixture is stirred cold, NaOCl is produced, i.e. household bleach.

If the reactor is heated while being mixed, disproportionation to chlorate occurs.



The overall reaction is:



Hot concentrated hydroxide is required to drive this reaction at an acceptable rate. This is also done in a flow reactor. In some pulp plants it is not possible to provide a chlor-alkali plant. Then a common bleaching agent is chlorine dioxide, ClO_2 . It is a reactive radical compound, explosive in pure form. It is produced in situ where needed, for example by the reaction:



The dilute yellow-green gas is used directly in bleaching the pigments in the pulp, where it does not degrade the wood fibres.

All these chlorine bleach reactions are implicated in the production of PCB's and dioxins by the chlorination of organic matter in the pulp. This is a very, very small side reaction of the process, and since it is not clear what the constituents of wood pulp are, it is hard to know what factors control this by-product formation. But since these pollutants are known to be highly toxic, there is a strong push to replace chlorine in the pulp and paper industry. But it is not easy to see what can be used, which is any where near as effective a bleaching agent and anywhere near as cost effective as using Rock Salt and electricity as input materials.

In the next set of notes, "Lecture 23", I have provided some articles by industrial chemists on the chlor alkali industry. From these articles, you will be able to see the layout of a small plant, and read about some of the technical factors that must be taken into account.

