

Chemistry of The Main Group Elements

1. Hydrogen

Hydrogen is the most abundant element in the universe, but it accounts for less than 1% (by mass) in the Earth's crust. It is the third most abundant element in the living system. There are three naturally occurring isotopes of hydrogen: hydrogen (^1H) - the most abundant isotope, deuterium (^2H), and tritium (^3H) which is radioactive. Most of hydrogen occurs as H_2O , hydrocarbon, and biological compounds.

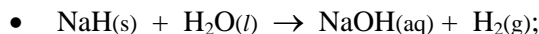
Hydrogen is a colorless gas with m.p. = -259°C (14 K) and b.p. = -253°C (20 K). Hydrogen is placed in Group 1A (1), together with alkali metals, because of its single electron in the valence shell and its common oxidation state of +1. However, it is physically and chemically different from any of the alkali metals. Hydrogen reacts with reactive metals (such as those of Group 1A and 2A) to form metal hydrides, where hydrogen is the anion with a "-1" charge. Because of this hydrogen may also be placed in Group 7A (17) together with the halogens. Like other nonmetals, hydrogen has a relatively high ionization energy (I.E. = 1311 kJ/mol), and its electronegativity is 2.1 (twice as high as those of alkali metals).

Reactions of Hydrogen with Reactive Metals to form Salt like Hydrides

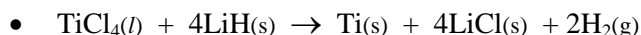
Hydrogen reacts with reactive metals to form ionic (salt like) hydrides:



The hydrides are very reactive and act as a strong base. It reacts violently with water to produce hydrogen gas:



It is also a strong reducing agent and is used to reduce TiCl_4 to titanium metal:

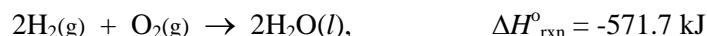


Reactions of Hydrogen with Nonmetals

Hydrogen reacts with nonmetals to form covalent compounds such as HF, HCl, HBr, HI, H_2O , H_2S , NH_3 , CH_4 , and other organic and biological compounds. In most covalent compounds, hydrogen is assigned the oxidation state of +1 because the other nonmetal has a higher electronegativity. Fluorine is the only element that reacts with hydrogen at room temperature to form hydrogen fluoride:



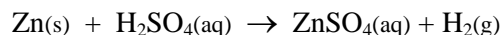
A mixture of H_2 and O_2 gases remain indefinitely without reacting until a spark is introduced, which will cause an explosive reaction:



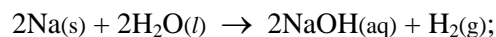
The reaction is exothermic and explosive, but has very high activation energy. A mixture of hydrogen and oxygen gas will not spontaneously react unless initiated by a flame or spark.

Preparation of Hydrogen Gas

Hydrogen can be prepared in the lab by reaction of certain metals with dilute hydrochloric or sulfuric acid (but not nitric acid):



Hydrogen is also produced when reactive metals such as Na, K and Ca react with water:



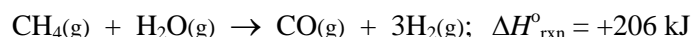
But this is not a good way to prepare hydrogen gas, because the reaction is very violent.

Hydrogen gas is also formed when steam is passed over burning coke at temperature over 1000°C, which also produce carbon monoxide gas.



The mixture is called “*syngas*”, which at one time was used as fuel. The practice was stopped because carbon monoxide is toxic and hazardous to health.

Industrial production of hydrogen gas is carried out by the steam reformation of hydrocarbons, such as the reaction of methane gas with steam at very high temperature and in the presence of catalyst (such as Ni). The following reaction is normally carried out above 900°C and at 7 atm using Ni-catalyst:

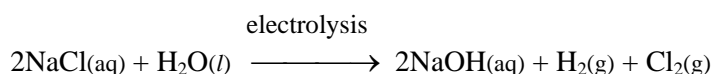


The reaction is endothermic, but has a positive entropy change. The reaction becomes spontaneous and goes to completion when carried out at high temperature (>900°C). More hydrogen is obtained if the CO gas is piped into another reactor where it is further reacted with steam in a reaction known as the *water-gas shift reaction*. This reaction is exothermic:

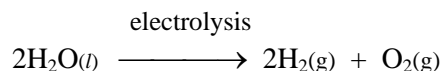


(The CO₂ gas can be absorbed by calcium oxide, CaO, thus leaving a fairly pure hydrogen gas.)

Hydrogen is also industrially produced as a by-product in the manufacture of sodium hydroxide, NaOH, by electrolysis of concentrated aqueous NaCl:



The electrolysis of water also yields H₂ gas, but the operation is too costly for a large scale production of hydrogen:



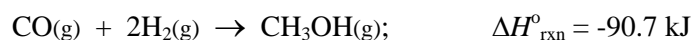
Primary Uses of Hydrogen Gas

The largest amount of hydrogen gas is used in the manufacture of ammonia by the Haber process, where hydrogen is reacted with nitrogen at ~300°C and ~250 atm:

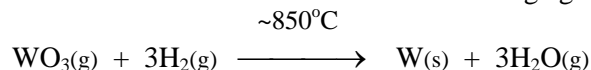


Although the reaction is thermodynamically favored at room temperature, it is extremely slow to be practically viable. Therefore, the industrial reaction is carried out at higher temperature and in the presence of a catalyst to speed up the reaction, although the yield is compromised.

Hydrogen is also needed to produce methanol. The reaction with CO gas is carried out at temperature ~300°C and 150 atm over pellets of Cr₂O₃-ZnO, which act as catalysts:



Large quantities of hydrogen are also used for the hydrogenation of vegetable oil to make shortenings and margarine. It is also used as rocket fuel and as a reducing agent for the extraction of certain metals:



Most of the hydrogen needed for manufacturing purposes is produced in the same plant where it is needed.

2. Trends Across the Periodic Table: The Second Period Elements

General trends of physical and chemical properties across (left-to-right) the period 2 elements: Li, Be, B, C, N, O, F, and Ne.

- Atomic number changes from 3 to 10;
- Electron configuration of valence shell changes from $2s^1$ through $2s^2 2p^6$; number of electrons in the *valence shell* increases from 1 (in Group 1A) to 8 (in Group 8A).
- Effective nuclear charge increases across the period;
- Atomic size generally decreases with increasing effective nuclear charge; anomalous behavior is observed at Be and B ($\text{Be} < \text{B}$), and at N and O ($\text{N} < \text{O}$)
- Ionization energy generally increases; anomalous behavior is observed at Be and B ($\text{Be} > \text{B}$), and at N and O ($\text{N} > \text{O}$)
- Electronegativity increases gradually from left to right across period (exclude noble gas);
- Metallic character decreases with increasing nuclear charge;
- Reactivity is highest on the left end (for metal) and right end (for nonmetal) of the period, and decreasing towards the middle;
- Chemical bonding between atoms of an element changes from metallic (Li & Be) to covalent in network structure (B & C) to covalent in individual molecules (N_2 , O_2 , & F_2) to none in Ne.
- Bonding between each element and an active nonmetal (such as F_2) changes from ionic to polar covalent, to nonpolar covalent.
- The acid-base characteristics of the common oxides changes from most basic to mild basic to weakly acidic to strongly acidic;
- The reducing strength decreases through the metals; oxidizing strength increases through the nonmetal (exclude noble gases).
- The trend in physical properties of the second period elements is such that it goes from soft and light metal with low melting point (for Li) followed by a hard metal with high mp (for Be) to very hard metalloid with extremely high mp (for B). Then the nonmetal starts with Carbon (middle of the period), which is the only nonmetal that is a solid. Important natural allotropes of carbon are *graphite* and *diamond*, which are physically very different. Graphite is opaque, soft and flaky, while diamond is very hard and shiny. The other nonmetals (N_2 , O_2 , F_2 , and Ne) are all gases. All gaseous elements have very low mp and bp, with Neon having the lowest mp and bp.

Various Uses of the Second Period Elements and Their Compounds

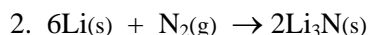
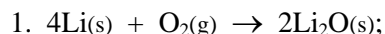
- Lithium is used as additive in lubricant in auto industries; high voltage and light weight batteries (such as batteries used in pacemakers and cameras); for making strong light alloys used in space; isotopes of lithium hydride are used in thermonuclear bombs; Li_2CO_3 is used for treating manic-depressant.
- Beryllium is used in X-ray tube window; to make alloys for springs and gears (especially those used in watches), and spark free tools.
- The compounds of boron are used as cleaning agent (borax), eyewash antiseptic (boric acid), borosilicate glass; B_4C is used in armor; regulator in nuclear plants; composite for making tennis rackets.

- Carbon is one of the primary elements in the molecules of life; it is the second most abundant element in the human body. It forms the skeletons of all organic compounds; Graphite is used as lubricant, to make strong structural fiber, in steel making, as pencil lead, manufacture of plastics. Diamond is used in jewelry, cutting tools, protective films.
- Nitrogen is one of the primary elements in the molecules of life, especially proteins and nucleic acids; used in the manufacture of ammonia, fertilizers, explosive, rocket fuel, nitric acid; nitric oxide in atmosphere is responsible for acid rain and smog; nitrogen gas is used as inert blanket for electronic equipments; liquid nitrogen is used as refrigerant and in cryogenic surgery.
- Oxygen is the most abundant element in the Earth's crust; oxygen gas is essential for life; it is needed for combustion; used in water purification and in steel production; water is 88.9% oxygen (by mass) and it is essential for life.
- Fluorine compounds are used as additives in tooth paste; for making Teflon; in uranium enrichment, and CFCs is used as refrigerant, but causes the depletion of ozone layer.
- Neon is used in elemental form primarily in neon lighting for advertising signs, in fog lamps, TV and monitor tubes, laser and voltage detectors.

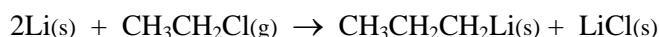
3. Group 1A(1): The Alkali Metals

The alkali metals are the most reactive of all metals; the reactivity increases down the group. As a group, they contain elements with the *largest atomic size* and the *lowest first ionization energy*. Alkali metals are light and soft – can easily be cut with a knife.

They also have a *low heat of atomization* (ΔH_{atom}) and *low ionization energy* (I.E.). The relatively weak effective nuclear charge makes it easier to remove the single electron from the valence shell. Thus, an alkali metal readily loses its single valence electron to a nonmetal. All compounds of the alkali metals are invariably ionic, except in organo-lithium compound, such as alkyl lithium, where lithium is covalently bonded to a carbon atom of the alkyl group. Lithium exhibits some atypical properties. It is the only member that forms simple oxide and nitride when reacted with oxygen and nitrogen gases, respectively:



Lithium reacts with organic halides to form alkyl lithium, which is a molecular compound:



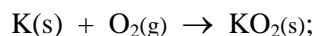
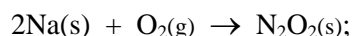
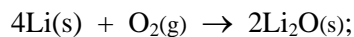
Important Reactions

Alkali metals are strong reducing agents:

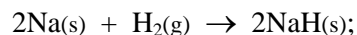
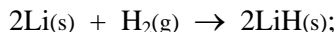
1. They reduce hydrogen in water to hydrogen gas and form hydroxides:



2. The reaction with oxygen gas produces different types of oxides: lithium forms a simple oxide, Li_2O ; sodium forms peroxide, Na_2O_2 ; potassium, rubidium and cesium form superoxide:



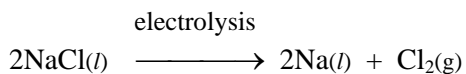
3. Alkali metals react with hydrogen gas to form ionic (salt like) hydrides:



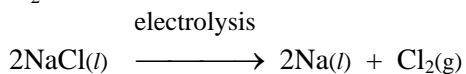
4. They react violently with the halogens to form halides:



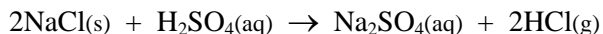
5. Sodium chloride is the most important alkali halide. It is the source of sodium metal and chlorine gas and the starting material in the manufacture of sodium hydroxide. In the Downs process, molten sodium chloride is electrolyzed to produce Na and Cl_2 :



In the Chlor-alkali process, brine solution (concentrated NaCl solution) is electrolyzed to produce NaOH, H_2 , and Cl_2 :



NaCl reacts with sulfuric acid to form sodium sulfate and hydrogen chloride gas:



Sodium sulfate is an important ingredient in paper industry; HCl is used in steel, plastics, and textile.

6. Sodium hydroxide and chlorine gas is used for making bleaching solutions:



7. LiCl and LiBr are used in dehumidifiers and air-conditioning units because of their positive heat of solution. Li_2CO_3 is used to make porcelain enamels, in glass making to produce tough glasses, and as a drug for treating manic-depression.
8. Na_2CO_3 is used in glass manufacture and as industrial base. NaHCO_3 is used as baking powder and in fire extinguishers because it decomposes to produce CO_2 gas and the reaction is endothermic, therefore reduces heat.

4. The Alkaline Earth Metals

The alkaline Earth metals are generally harder than the alkali metals; they have higher m.p. and b.p. The presence of two valence electrons makes metallic bonds stronger than they are in the alkali metals. The alkaline earth metals also have higher effective nuclear charge than the alkali metals, which leads to higher ionization energy. In general, the alkaline earth metals are relatively less reactive than their alkali metal counterparts.

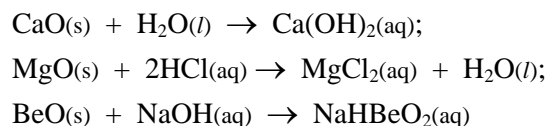
Like alkali metals, the alkaline Earth metals are strong reducing agent, with the reactivity increasing down the group. With the exception of beryllium, alkaline Earth metals react with oxygen and halogens to form ionic compounds. The oxides are alkaline – they dissolve in water to form basic solution.

Like lithium, compounds of beryllium are mainly molecular. Even BeF_2 , which is the most ionic of all beryllium compounds, has a low m.p. and the melt has a low conductivity, indicating that the compound is not completely ionic.

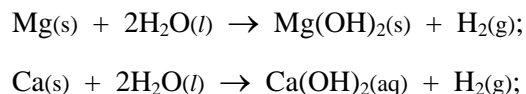
Important Reactions and Compounds

1. $2\text{Mg(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{MgO(s)};$
2. $3\text{Mg(s)} + \text{N}_2\text{(g)} \rightarrow \text{Mg}_3\text{N}_2\text{(s)}$
3. $\text{Ba(s)} + \text{O}_2\text{(g)} \rightarrow \text{BaO}_2\text{(s)};$

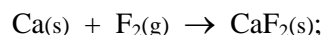
The oxides of alkaline earth metals are basic, except BeO which is amphoteric:



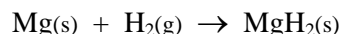
4. Ca, Sr, and Ba react with water to form hydroxides and produce hydrogen gas. Mg does not react with water, but it reacts with steam to form Mg(OH)_2 and H_2 ; while Be does not react with either water or steam:



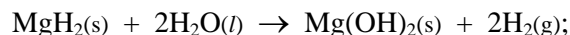
5. They react with halogens to form halides; the halides of beryllium are mostly molecular:



6. With the exception of beryllium, all alkaline earth metals react with hydrogen to form ionic hydrides:



The hydrides react with water to produce hydrogen gas and can be a source of fuel:



7. All carbonates of alkaline earth metals undergo thermal decomposition to the oxide:



CaO , which reacts with water to form Ca(OH)_2 , is used for making cement and mortar:

5. Group 3A Elements

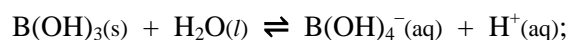
In this group, Boron is a metalloid, others are metals. Boron forms a covalent network solid and it is the hardest element in the group, with extremely high m.p. and b.p. Boron atom is the smallest and it has the highest ionization energy. However, there is very little variation in the ionization energy of the other group members. Ionization energy in kJ/mole: B(800), Al(577), Ga(579), In(558), and Tl(589). The trend in ionization energy is rather inconsistent due to the inconsistent changes in the effective nuclear charges. The number of protons increases by 8 from B to Al, but increases by 18 from Al to Ga and from Ga to In (because of transition metals), and from In to Tl the number increases by 32 (because of transition metal and lanthanide series). These additional charges found among the heavier metals of Group 3A results in a lower increase of atomic size than would be expected if the transition and lanthanide series were not present. As a result, the increase in density are relatively large between Al ($d = 2.70 \text{ g/cm}^3$) and Ga ($d = 5.90 \text{ g/cm}^3$), and between In ($d = 7.31 \text{ g/cm}^3$) and Tl ($d = 11.85 \text{ g/cm}^3$).

Elements of Group 3A(13) also exhibit a wide range of chemical behaviors. Boron is a metalloid and all its compounds are molecular covalent. It is much less reactive compared to other elements in the same group. The chemical behavior of boron is very different from that of the other members in the group. For examples:

- all boron compounds are covalent;
- boron forms network covalent compounds with metals, H, O, N, and C.
- In a simple molecule, the boron atom has an incomplete octet, and therefore, they act as a Lewis acid:
- $\text{BF}_3(\text{g}) + \text{:NH}_3(\text{g}) \rightarrow \text{F}_3\text{B}-\text{NH}_3(\text{g})$;

The above reaction is called Lewis acid-base reaction.

- Boric acid, $\text{B}(\text{OH})_3$, when dissolved in water does not release hydrogen ion, but instead it acts as Lewis acid and accepts a pair of electron from water, and the reaction produces H^+ :

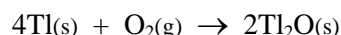


- Boron forms boron nitride with nitrogen, a covalent network compound with structure very similar to graphite. It is used as control rods in nuclear reactors.
- In many hydrides of boron (such as diboranes), boron attains the octet state by forming two bridges through the hydrogen atoms. Each bridge is a one-electron covalent bond.

The compounds of the other members of Group 3A elements are ionic with a significant covalent characteristic. For example, the halides of aluminum can exist in the gas phase as covalent dimers and its oxide is *amphoteric*.

Important Reactions

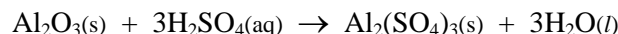
All elements react with oxygen gas, especially at high temperature:



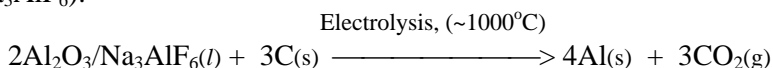
Aluminum oxide, Al_2O_3 , readily forms when aluminum metal is exposed to air. However, the oxide forms a continuous coating layer, which prevents further oxidation of the metal. This makes aluminum somewhat resistant toward corrosion.

The properties of oxides changes from weakly acidic (B_2O_3) to amphoteric (Al_2O_3) to mildly basic (Ga_2O_3 and In_2O_3), and to very basic (Tl_2O). Boron oxide (B_2O_3) is used in the production of borosilicate glasses. Aluminum oxide (Al_2O_3) is the major constituent in bauxite - the natural source of Al metal. It is used as abrasive in sand paper and sanding tools. It is also used to strengthen ceramics and metals.

Aluminum oxide reacts with H_2SO_4 to form aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, which is used in water purification.



Aluminum sulfate and CaO form a colloidal mixture in water and is used in water treatment plant for removing suspended solids. Aluminum metal is produced by electrolysis of molten Al_2O_3 in cryolite (Na_3AlF_6):



Thalium is a component in the super conducting ceramic, $\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Ca}_2\text{Cu}_3\text{O}_{10}$.

6. Group 4A(14) Elements – Valence-shell Configuration: ns^2np^2

This group contains a nonmetal (C), two metalloids (Si & Ge), and two metals (Sn & Pb). Carbon exhibits the most interesting and versatile chemical properties. Carbon is the most important element in organic, molecular, and polymer chemistry, where it forms the primary structural features of these compounds. Silicon is the second most abundant element in the Earth's crust and it shares some of the chemical characteristics of carbon, such as the ability to form polymer molecules.

The types of bonding found among elements of Group 4A affect some of their physical characteristics, such as hardness, m.p. and b.p. The large decrease in m.p. between C and Si, where both form covalent network solids, is due to longer and weaker bonds in the Si structure; the large decrease between Ge and Sn is due to the change from covalent network to metallic bonding. The large increase across the period between Al and Si is also due to the change from metallic bonding to covalent network bonding.

Allotropes

Carbon exists in three different physical forms or allotropes, namely: diamond, graphite, and the “bucky-ball”. Diamond and graphite are physically very different; whereas the former is very hard, the latter is soft and flakes off rather easily. The difference in their physical characteristics is due to the nature of bonding in diamond and graphite. In diamond, carbon atoms are covalently bonded to one another forming an extensive, three dimensional covalent networks solid. This makes diamond the hardest natural substance on Earth. It is used as cutting materials, such as in drill bits used for drilling rocks. In graphite, the carbon atoms are arranged in layers; within each layer, atoms are covalently bonded to one another, but the interactions between carbon atoms of one layer with those of the neighboring layers are weak van der Waals dispersion forces. These weak forces makes graphite soft so that it is used as lubricants, and the layers flake off rather easily, suitable to be used as pencil leads. The third allotrope of carbon that was only discovered in 1980s is called *buckminsterfullerene* (or the “bucky-ball”). The basic feature of this allotrope is its soccer ball-like molecule containing 60 carbon atoms covalently bonded to each other. Interest in the physical and chemical properties of the bucky-ball has been growing quite steadily since its discovery, especially in its selective conductivity potentials.

The group 4A(14) elements also display a wide range of chemical behavior, from the covalent compounds of carbon to the ionic compounds of lead. Like carbon, Si and Ge also form covalent compounds with nonmetals; whereas Sn and Pb form ionic as well as covalent compounds with nonmetals. Tin and lead can acquire the oxidation states of +2 and +4. Compounds in which Sn and Pb have the +2 oxidation state are primarily ionic, as indicated by their high m.p. and the conductivity of their melt and aqueous solutions. While compounds in which Sn or Pb has the +4 oxidation state are primarily covalent, as indicated by their low m.p. and the melt does not conduct electricity. For example, SnCl_2 and PbCl_2 are primarily ionic – they are white solid with high m.p., and their aqueous solution or the melt conduct electricity. Whereas, SnCl_4 is a volatile liquid, soluble in organic solvent such as benzene, and PbCl_4 is an oily substance. The physical properties of SnCl_4 and PbCl_4 suggest that they are covalent compounds. The oxides, SnO and PbO , are primarily ionic and more basic than SnO_2 and PbO_2 .

Important Features in Carbon Chemistry.

Carbon is the most versatile element in the periodic table; it can bond with many elements as well as with itself. Carbon exhibits the sp^3 , sp^2 , and sp hybridization, and therefore, can form single, double and triple bonds. As a result, carbon can form chains, branches and rings that lead to myriad of structures containing carbon skeletons. The entire organic and biological compounds are based on the carbon skeletons. A wide array of organic compounds containing only carbon and hydrogen (thus called

hydrocarbon) are found in nature. The small atomic size of carbon enables the formation of π -bonds in addition to σ -bonds between carbon atoms, which leads to multiple bond formation. Because the atomic size of the other member elements is large, the formation of π -bond by sidewise overlap does not occur. For example, whereas CO_2 is a discrete molecule in which carbon is double bonded to each oxygen in the molecule, SiO_2 is a network solid - π -bond between Si and O atom cannot form because the Si atom is too large.

Metal carbonates, especially calcium carbonate (CaCO_3), are the most important inorganic compounds containing carbon. CaCO_3 makes up the limestone, marble, coral, and chalk. CaCO_3 is the starting material in the production of quick lime (CaO), which is used for making cement and mortar. It is also an ingredient in common antacid formulation because it reacts with HCl(aq) in the stomach acid:



Similar reactions with sulfuric acid and nitric acid protect lakes bounded by limestone deposits from the harmful effects of acid rain.

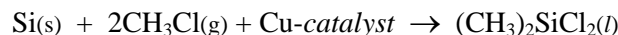
Carbon reacts with oxygen gas to form two common gaseous oxides: CO and CO_2 . While the former is toxic and should be eliminated from the surrounding, the latter gas is essential for plant life. Plants absorb CO_2 gas and water to manufacture carbohydrates during photosynthesis. CO_2 gas in the atmosphere also helps keep our Earth environment warm and livable. However, too much CO_2 in the atmosphere leads to global warming.

Carbon also reacts with halogens to form a wide array of compounds, such as carbon tetrachloride (CCl_4), dichloromethane (CH_2Cl_2) and chloroform (CHCl_3), which are important organic solvents. The chlorofluorocarbons (CFCs, or freon) have important industrial uses, but their exceptional stability and persistent presence in the environment has created some major problems like the depletion of ozone layer.

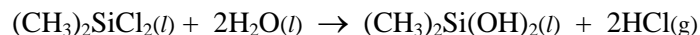
Highlights of Silicon Chemistry

Silicon is a metalloid and very important element in the electronic industries because of its semi-conducting property. Silicon dioxide (SiO_2), perhaps the second most abundant substance on the Earth crust, is a covalent network solid, but does not exist in a discrete molecular form like CO_2 . Silica (sand), silicates and silicones (the silicon-based polymers), consist of repeating —Si—O— units.

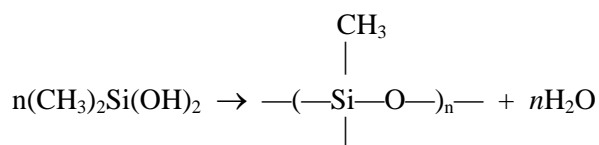
1. *Silicate minerals* are the most abundant substance outside the living systems. The building unit of silicates is the *orthosilicate group*, $\text{—SiO}_4\text{—}$, in which four oxygen atoms are covalently bonded to a central silicon atom forming the tetrahedral unit. Some of the well known minerals contain single SiO_4^{4-} ions or a number of them linked together, such as in the gemstone zircon, ZrSiO_4 ; hemomorphite, $\text{Zn}_4(\text{OH})_2\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$, and in beryl, $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$, which is the major source of beryllium.
2. *Silicone Polymers* are synthetic polymers containing short to long chains of —Si—O— units. A key starting material is the *dimethylsilicon dichloride*, which is formed by catalytic reaction of silicon with methyl chloride:



Dimethylsilicon dichloride reacts with water to form *dimethylsilicon dihydroxide*:



which polymerizes to form *polydimethylsiloxane*?





Important Compounds

1. CO is produced and used in the industrial production of methanol. It is also used in the purification of nickel. It is a toxic gas and inhalation of a certain amount of CO gas can be fatal because of its strong affinity for hemoglobin; thus prevents the binding of oxygen molecules to the hemoglobin.
2. CO₂ is important to photosynthetic plants to make carbohydrates and O₂. CO₂ is the final oxidation product of carbon-based fuels; its increase in the atmosphere is suspected to cause the apparent global warming. It is used in industry as a refrigerant gas, blanketing gas in fire extinguishers, and effervescence gas in beverages. NH₃ and CO₂ are reactants in the production of urea; the latter is used as fertilizer and for the manufacture of plastic monomers.
3. Methane, CH₄, is the primary component is natural gas and used as fuel; it is also a reactant in the industrial production of hydrogen gas which is an important constituent in the manufacture of ammonia, methanol and in the production of certain metals (such as tungsten).
4. C₃H₈, C₄H₁₀, and C₈H₁₈ are important fuels; C₆H₁₄ and C₆H₆ are important organic solvents;
5. C₂H₄, C₂H₃Cl, CF₄, H₂N(CH₂)₆NH₂, and ClOC(CH₂)₄COCl (among others) are important monomers in polymer industries, such as plastic, PVC, Teflon, and nylon.
6. Silica, SiO₂, occurs in many amorphous (glassy) and crystalline forms, quartz being the most common. It is used to make glass and an inert support material in thin layer and column chromatography.
7. Silicon carbide, SiC, or carborundum, is a major industrial abrasive and used for making tough and temperature resistant ceramics.

Important Reactions

1. $\text{E(s)} + 2\text{X}_2 \rightarrow \text{EX}_4$ (E = C, Si, Ge)
SnX₂ and PbX₂ are more stable than SnX₄ and PbX₄
2. $\text{E(s)} + \text{O}_2(\text{g}) \rightarrow \text{EO}_2$ (E = C, Si, Ge, and Sn)
3. $\text{C(s)} + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + \text{H}_2(\text{g});$
4. $\text{CH}_4(\text{g}) + \text{H}_2\text{O(g)} \rightarrow \text{CO(g)} + 3\text{H}_2(\text{g});$
5. $\text{CO(g)} + \text{H}_2\text{O(g)} \rightarrow \text{CO}_2(\text{g}) + \text{H}_2(\text{g});$
6. $\text{CaC}_2(\text{s}) + \text{H}_2\text{O(g)} \rightarrow \text{C}_2\text{H}_2(\text{g}) + \text{Ca(OH)}_2(\text{aq});$
7. $\text{CCl}_4(\text{l}) + \text{HF(g)} \rightarrow \text{CFCl}_3(\text{g}) + \text{HCl(g});$
8. $\text{SiO}_2(\text{s}) + 2\text{C(s)} \rightarrow \text{Si(s)} + 2\text{CO(g)};$
9. $\text{SiO}_2(\text{s}) + 4\text{HF(g)} \rightarrow \text{SiF}_4(\text{g}) + 2\text{H}_2\text{O(l)};$
10. $\text{SiF}_4(\text{g}) + 2\text{Mg(s)} \rightarrow \text{Si(s)} + 2\text{MgF}_2(\text{s});$

7. Group 5A(15): The Nitrogen Family

This group contains two nonmetals, nitrogen and phosphorus (the former being a gas and the latter solid); two metalloids, arsenic and antimony; and a metal (Bi).

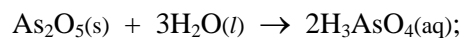
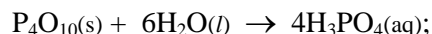
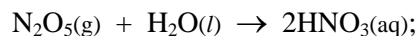
Nitrogen exists as stable diatomic molecules and is the most abundant gas (~79%) in the Earth's atmosphere. The triple bonds in N₂ make nitrogen molecules very stable and almost chemically inert. Dispersion forces between N₂ molecules are very weak and nitrogen gas has a b.p. at about 77 K (-196°C).

Phosphorus occurs in several allotropes - the white and red forms are the most common, but the two exhibit different physical and chemical properties. The white phosphorus consists of individual tetrahedral P₄ molecules and is very reactive. When exposed to air, it ignites spontaneously. The white phosphorus also has a low melting point (44.1°C), and soluble in nonpolar solvents. The red phosphorous consists of linear chains of the P₄ molecules; it is less reactive and has a much higher melting point (~600°C), and is insoluble.

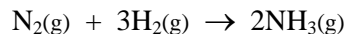
Important Trends in The Chemical Behaviors of the Group 5A Elements

Elements of Group 5A overwhelming form covalent compounds. Whereas nitrogen can form a maximum of four covalent bonds, the rest of the elements in the group can form more than four covalent bonds by utilizing one or more of the *nd* orbitals. Nitrogen and phosphorus form simple anion with “-3” charge when reacted with active metals such as those of Group 1A and 2A metals: Li₃N, Mg₃N₂, Na₃P, and Ca₃P₂ are examples. Bismuth form mainly covalent compounds, but it forms ionic compounds with F₂ gas and nitric acid: BiF₃ and Bi(NO₃)₃.

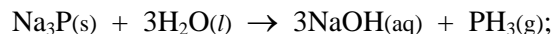
Nitrogen exhibits every possible oxidation states the element can acquire, such as: -3 (in NH₃), -2 (in N₂H₄), -1 (in NH₂OH), 0 (in N₂), +1 (in N₂O), +2 (in NO), +3 (in N₂O₃), +4 (in NO₂), and +5 (in N₂O₅). Only the +3 and +5 states are common for phosphorus (P), arsenic (As), and antimony (Sb), but bismuth (Bi) exhibits only the +3 oxidation state. The oxides of nitrogen, phosphorus, and arsenic are acidic; those of antimony, Sb₂O₃ are amphoteric, but Sb₂O₅ is acidic; while Bi₂O₃ is basic. N₂O₅ forms strong acid when dissolved in water, while P₄O₁₀, As₂O₅ and Sb₂O₅ form weak acids:



All the Group 5A elements form hydrides. NH₃ is formed by the catalytic reaction of the gases:

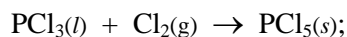
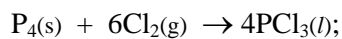
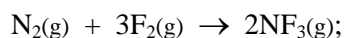


The other hydrides are prepared from the phosphide, arsenide, etc, with water, and they are extremely:

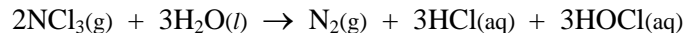


Among the hydrides, NH₃ forms hydrogen bonds with each other and has the highest bp.

All elements of Group 5A form trihalides, EX₃, but P, As and Sb also form pentahalides, EX₅.

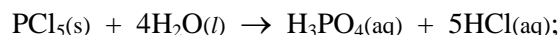


Among the trihalides of nitrogen, NF_3 is the most stable and somewhat unreactive, but NCl_3 react with water explosively:



NBr_3 can only be prepared below -87°C ; $\text{NI}_3 \cdot \text{NH}_3$ explodes at the slightest touch.

The pentahalides react with water to form hydrogen halides and the oxoacid of the element:

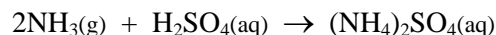
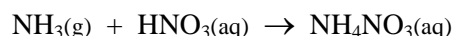


Highlights of Nitrogen Chemistry

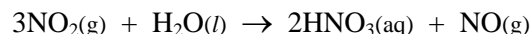
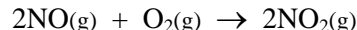
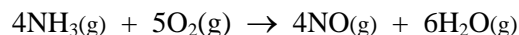
Our atmosphere consists of about 78% nitrogen gas, which is almost an inert gas. It reacts with the atmospheric oxygen only at very high temperature ($>2000^\circ\text{C}$) or when a lightning bolt strikes. Yet nitrogen and oxygen form an array of oxides in which nitrogen exhibits a whole range of oxidation state from +1 to +5: N_2O , NO , N_2O_3 , NO_2 , N_2O_4 , and N_2O_5 . At high temperature, nitrogen gas also reacts with H_2 , Li , the Group 2A elements, B , Al , C , Si , Ge , and many transition elements.

Atmospheric nitrogen is fixed naturally by bacteria in nodules found on roots of plants belonging to the legume family, such as peas, beans, and clover. Lightning bolt also cause nitrogen in the atmosphere to react with oxygen and form NO gas, which is quickly converted to NO_2 gas. Industrial nitrogen fixation is carried out by the Haber process in the production of ammonia: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

The reaction is carried out at high temperature and pressure ($\sim 300^\circ\text{C}$ and 200 atm). About 70% of the ammonia produced are converted into fertilizers, such as NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, $(\text{NH}_4)_3\text{PO}_4$, and urea.

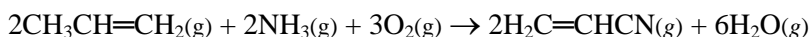


About 20% of the ammonia produced is used for the production of HNO_3 in the Oswald process:

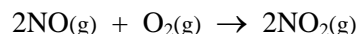


Nitrogen is an essential element as it is needed for growth and for syntheses of protein, nucleic acids and other essential molecules that support growth. Nitric oxide, NO , is an odd-electron molecule with vital biochemical function. Plants absorb the fixed nitrogen (in the form of NH_4^+ or NO_3^- ions) from soil and water to make protein and nucleic acids.

Some of the ammonia is also used in the production hydrazine, N_2H_4 , which is used to make rocket fuel. Ammonia is also used for producing certain monomers for making nylon or other synthetic polymers. For example, acrylonitrile, $\text{H}_2\text{C}=\text{CHCN}$, a monomer for polyacrylonitrile (such as Acrilan and Orlon), is made from propylene, ammonia, and oxygen gas. The reaction is carried out at high temperature and pressure in the presence of catalyst.



Although nitrogen and oxygen in the atmosphere do not react under normal condition, at high temperature such as one inside an internal combustion engine that is in operation for more than 10 minutes, these two gases react to form NO. Once formed, NO is readily oxidized to the brown gas, NO₂:



The latter is responsible, to some extent, for the formation of acid rain and the photochemical smog. The NO₂ gas released into the environment during the morning rush hours undergoes photochemical decomposition to NO and O during the later part of the day:



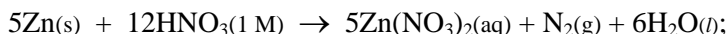
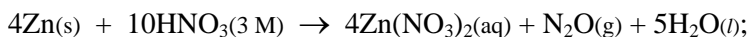
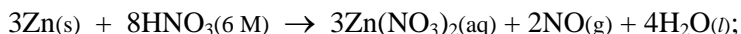
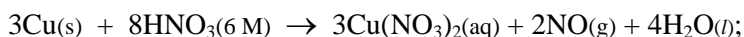
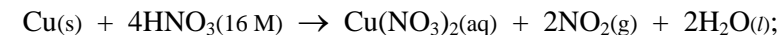
The reactive O atoms react with O₂ gas to form ozone, O₃: $\text{O}_2\text{(g)} + \text{O(g)} \rightarrow \text{O}_3\text{(g)}$.

A complex series of reactions occur between NO₂, O₃, and unburned hydrocarbons in gasoline fumes to form *peroxyacylnitrates* (PANs), a group of atmospheric pollutants responsible for the brown smog and potent nose and eye irritants.

Oxoacids and Oxoanions of Nitrogen

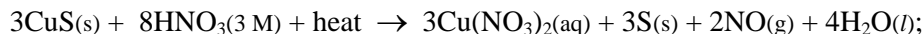
Nitric acid (HNO₃) and nitrous acid (HNO₂) are the two common oxoacids of nitrogen. Nitric acid is a strong acid and a very powerful oxidizing agent. It oxidizes almost all metals it comes in contact with, except gold and platinum. Unlike the reactions of metals with other strong acid (such as HCl and H₂SO₄), the reactions of nitric acid with metals do not produce H₂ gas. This is because the nitrate ion, NO₃⁻, is a stronger oxidizing agent; therefore, redox reactions involving the nitrate ions occurs before one that involve the H⁺ ions. The products of the reactions with metals vary with the metal reactivity and the HNO₃ concentration.

The following reactions are some of the examples:



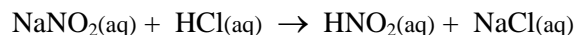
Note that, the higher the concentration of the nitric acid used in the reaction, the less the change in the oxidation state of nitrogen. This seems reasonable because in concentrated nitric acid, there are more nitrate ions to be reduced. Each nitrate ion can obtain only a small number of electrons. In a dilute acid, there are fewer nitrate ions competing for electrons, and each gets more.

Nitric acid oxidizes compounds as well as elements. For example, copper(II) sulfide, which is very insoluble, can be dissolved by treatment with hot nitric acid, which oxidizes the sulfide ion:



However, concentrated nitric acid does not dissolve aluminum, although the metal is reacted by other acids such as HCl(aq) and H₂SO₄(aq). This is because the initial reaction of the metal with nitric acid produces aluminum oxide, Al₂O₃, which forms a continuous protective coating and prevents further attack by the acid. The oxide itself does not dissolve in the acid.

Nitrous acid, HNO₂, is a weak acid and can be prepared by the reaction of a metal nitrite with a strong acid, such as:

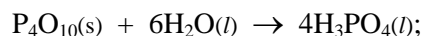
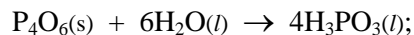


Highlights of Phosphorus Chemistry

Phosphorus forms two important oxides, P_4O_6 and P_4O_{10} , in which phosphorus has an oxidation state of +3 and +5, respectively. P_4O_6 is formed in the presence of limited oxygen gas, and in the presence of excess O_2 , P_4O_{10} is formed:

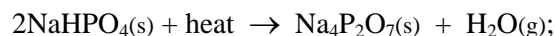


Both oxides react with water to form the oxoacids - phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4):

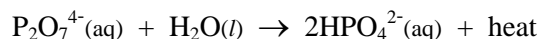


Both phosphorous and phosphoric acids are weak acids, with phosphoric acid being the stronger acid. H_3PO_3 is a diprotic acid, while H_3PO_4 is a triprotic acid, but the third H^+ ion is only released at $pH > 12$. Phosphoric acid is one of the “Top-10” most important compounds in chemical manufacturing. One of its major use is in the manufacture of fertilizers, such as ammonium phosphate. It is also used as a polishing agent for aluminum surfaces, for making phosphate buffer, and as additive in soft drinks. Na_3PO_4 is a strong base and is used in scouring powders and paint removers. A phosphorus sulfide, P_4S_3 , is used in “strike-anywhere” match heads.

Polyphosphates are formed by heating hydrogen phosphate, such as sodium hydrogen phosphate which loses a water molecule upon heating forming sodium diphosphate:



The diposphate ion reacts with water to form HPO_4^{2-} and releases heat:



In living cells, diphosphate and triphosphate compounds plays important role in the storage and production of energy needed for myriad of cellular functions. Sodium triphosphate, $Na_5P_3O_{10}$, is a component in some synthetic detergents. Extended polyphosphate chains consist of tetrahedral PO_4 units which are structurally similar to silicate chains.

8. Group 6A(16): The Oxygen Family

This group consists of two nonmetals (O & S), two semi-metals (Se & Te), and a radioactive metal (Po). The composition of Group 6A(16) is very similar to that of Group 5A(15). For example, ionization energy and electronegativity decrease down the group as atomic size increases; conductivity increases as bonding changes from pure covalent to metalloid network to metallic solid.

Oxygen is the most abundant element and accounts for 49.5% (by mass) of all elements found in the Earth's crust; it is also the most abundant element (about 65% by mass) in the human body. Elemental oxygen makes up about 23% (by mass, or 21% by volume) of the Earth's atmosphere. Oxygen is a colorless gas containing diatomic molecules, O_2 , (like N_2 in nitrogen gas). At 1 atm, oxygen boils at 90 K, which is higher than that of nitrogen (b.p. = 77 K). This difference in boiling points enables us to separate oxygen and nitrogen from the air by fractional distillation.

Allotropes are more common among the Group 6A elements than in Group 5A. Oxygen occurs in two forms - the normal oxygen gas (O_2) and ozone gas (O_3). The latter is a very powerful oxidizing agent and its presence in the stratosphere plays a very important role in protecting the Earth surface from direct uv

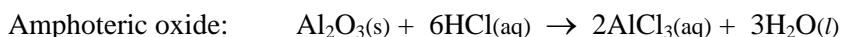
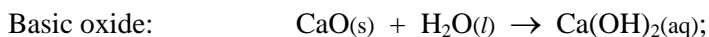
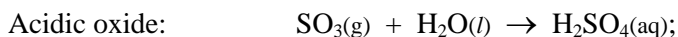
radiation from the sun. The thinning of the ozone layer, especially above the South Pole, means that more UV radiation will reach the Earth's surface, with potentially hazardous effect.

Sulfur can exist in more than 10 different allotropic forms, depending on the temperature and pressure conditions. The ability of S atoms to form bonds to each other resulted in numerous rings and chains. At room temperature, sulfur exists as a crown-shape 8-membered ring, called *cyclo-S₈*. The most stable allotrope is *orthorhombic α-S₈*, which is made up entirely of the S₈ molecules. All other allotropes of sulfur eventually revert to this form.

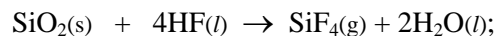
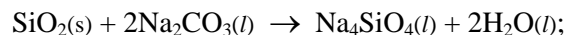
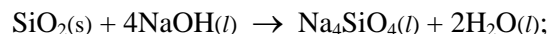
The Group 6A elements exhibit the widest range of atomic properties. At the top, oxygen has the highest electronegativity of 3.5 and is a strong oxidizing agent. Every element (except He, Ne, and Ar) forms at least one oxide. In most compounds oxygen is anion with an oxidation state of -2; in peroxides it is assigned the o.s. of -1.

A broad range of properties characterize the oxides. Most oxides of nonmetals are gases; while oxides of metals are solids with very high m.p. (BeO melts at 2530°C). Water, the most abundant of all natural oxides on Earth, is very essential to life. It is a very stable oxide that is a liquid at room temperature, but has a relatively high m.p., bp, and specific heat. The presence of large bodies of water helps to moderate the Earth's climate. Its high specific heat and enthalpy of vaporization enable water to absorb a large amount of heat during the day and releases it at night, but causes only a small change in its temperature. In industry, water is used in the cooling systems.

The metal oxides can be nonconductors (MgO), semiconductors (NiO), conductors (ReO₃), and superconductors (YBa₂Cu₃O₇). Some oxides have positive enthalpy of formation ($\Delta H_f^\circ = +90.3$ kJ/mol for NO), whereas others have negative enthalpy of formation ($\Delta H_f^\circ = -393.5$ kJ/mol for CO₂). Most of them are thermally stable, but some like HgO decomposes when heated. Some oxides like Li₂O are chemically reactive, while others, like Fe₂O₃ are inert. Some oxides, such as CO, NO₂, and SO₂, are very toxic. The oxides of nonmetals are acidic (form acidic solutions when dissolve in water), whereas oxide of metals are basic or amphoteric. The oxides of semimetals (SiO₂) are very weakly acidic.



SiO₂ is attacked by hot molten NaOH and Na₂CO₃, but it is resistant to acid except HF:



S, Se and Te also form anion with “2-” charge when they react with active metal, but with other nonmetals, its o.s. can be +2, or +4. All Group 6A elements form hydrides, but for water, all other hydrides have foul smelling and toxic. Some of hydrogen sulfide is naturally formed in swamps from the breakdown of organic matter. H₂S is a very toxic gas and has a foul smell of a rotten egg. Other hydrides, such as H₂Se and H₂Te are about 100 times more toxic.

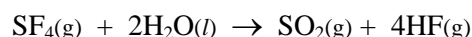
Some of the interesting features of the hydrides are:

- only water can form hydrogen bonds. Because of H-bonding, water has a much higher mp and bp than the other hydrides of Group 6A elements.

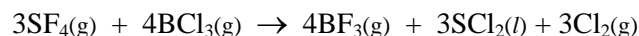
- The E—H bond length increases down the group, hence the bond strength decreases down the group. For example, H₂Te decomposes above 0°C.
- The bond angle in water is 104.5°, a value quite close to that of a tetrahedral geometry (109.5°). It is proposed that bonding in water involves sp³ hybridized orbitals of oxygen atom. However, for other hydrides, the bond angle is 90°, suggesting that the central atom uses unhybridized *p* orbitals.

The Group 6A elements also form a wide range of halides, except oxygen.

- Sulfur forms many stable fluorides, a few chlorides, one bromide, but no stable iodides.
- As the central atom becomes larger, the halides become more stable. Tetrachlorides and tetrabromides are known for Se, Te, and Po, but tetraiodides only occur with Te and Po. Hexafluorides are known for S, Se, and Te.
- The bond lengths in halides increase and bond strength decreases down the group.
- Crowding and orbital availability seem to affect the reactivity of the halides. For example, SF₄ has a see-saw shape and a lone pair of electrons on the central atom and it is very reactive. It reacts with moisture to form SO₂ and HF:



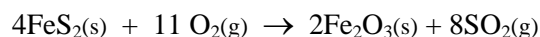
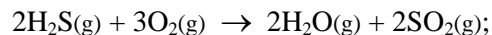
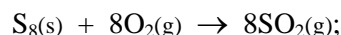
It is also used to fluorinate many compounds:



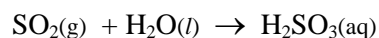
- SF₄ reacts by donating the lone pair electrons or by accepting a pair of electrons into one of the empty 3*d* orbitals. The see-saw shape exposes a large portion of the sulfur atom to chemical attacks.
- In contrast, SF₆ which has no lone pair on the central atom to be donated in a chemical reaction and has octahedral shape (thus more crowding by F atoms), is almost as inert as a noble gas; it is odorless, tasteless, nonflammable, nontoxic, and insoluble; it is not affected by hot metals, boiling HCl, molten KOH, or high-pressure steam. SF₆ is often used as insulating gas in high-voltage generators, withstanding over 10⁶ volts across electrodes only 50 mm apart.

Highlights of Sulfur Chemistry: Oxides, Oxoacids, and Sulfides

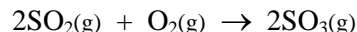
Sulfur forms two important oxides: SO₂ and SO₃, in which sulfur has the oxidation state +4 and +6, respectively. SO₂ is easily formed when the element sulfur, H₂S, or a metal sulfide burns in air:



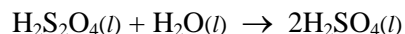
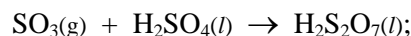
SO₂ gas also dissolves in water to form sulfurous acid, H₂SO₃, which is a weak acid:



SO₂ is used in the production of sulfuric acid, H₂SO₄. SO₂ is reacted with O₂ in the presence of V₂O₅/K₂O catalyst at about 600°C to form SO₃.

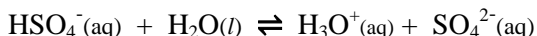
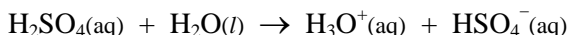


Sulfur trioxide is reacted with concentrated sulfuric acid to form disulfuric acid, H₂S₂O₇, which in turn is re-converted to concentrated sulfuric acid by reaction with water:



Over 150 million tons of sulfuric acid is annually produced worldwide. Sulfuric acid is widely used in the manufacture of fertilizers, metal processing, pigment production, textile processing, manufacture of soap and detergent, organic synthesis and production of plastics. Commercially available sulfuric acid is 98% H_2SO_4 by mass.

Sulfuric acid is a strong acid, which ionizes completely when dissolved in water forming hydronium ion, H_3O^+ , and hydrogen sulfate ion, $\text{HSO}_4^-(\text{aq})$. The latter is a weak acid, which dissociate partially to establish ionic equilibrium in aqueous solution.



Concentrated sulfuric acid is an excellent dehydrating agent. It dehydrates wood, carbohydrates, natural fibers and many organic substances by removing water from the molecular structure, leaving behind a black carbonaceous mass.

Another important compound of sulfur is the thiosulfate, $\text{S}_2\text{O}_3^{2-}$, which is an important reducing agent in chemical analysis. Its largest chemical use is in photography, where sodium thiosulfate pentahydrate, $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (known as “hypo”) is involved in fixing the image.

Sulfur reacts with most metals to form metal sulfides. Most heavy metal ores occur naturally in the form of sulfide: CuFeS_2 , ZnS , PbS , FeS_2 , etc.

9. Group 7A (17): The Halogens

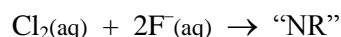
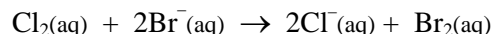
This group contains nonmetals that are generally very reactive and each of them can form compounds with most elements. At the top of the group we find fluorine, which is the most electronegative and most reactive of all nonmetals. Both fluorine and chlorine are gases containing diatomic molecules (F_2 and Cl_2), Bromine is a volatile liquid and iodine is solid, both contain diatomic molecules. The last element in the group, astatine, is radioactive and extremely rare. The change from gas to liquid and to solid as we go down the group is a reflection of the trend of increasing dispersion (London) forces as molecular size get larger going down the group.

What makes halogens chemically reactive is that: (1) the diatomic molecule contains relatively weak single bond and can be broken rather easily. Bond energies (in kJ/mol) are: 159 in F_2 , 243 in Cl_2 , 193 in Br_2 , and 151 in I_2 . (2) Each halogen atom contains 7 electrons in the valence shell (one less than the “octet state”), and therefore can easily acquire an electron to achieve the “octet state”. A halogen atom acquires the octet state either by:

- Gaining an electron from a metal atom and becomes anion in an ionic compound;
- Sharing a pair of electron with a nonmetal atom to form a covalent bond.

Fluorine, the most electronegative element, reacts with every element (except He, Ne, and Ar). Compounds made up of Xenon and fluorine (such as XeF_2 , XeF_4 and XeF_6) has been prepared in the lab. The exceptional reactivity of fluorine is also related to the weak $\text{F}-\text{F}$ bond (with bond energy = 159 kJ/mol). Since fluorine atom is small, the $\text{F}-\text{F}$ bond is short and repulsions between electron pairs of one atom and those of the other are strong, thus weaken the bond.

In most chemical reactions, halogen act as oxidizing agents, and oxidizing ability decreases down the group – halogens higher in the group can oxidize halide ions lower down:



The halogens also under disproportionation (redox) reaction are aqueous solution. For example,



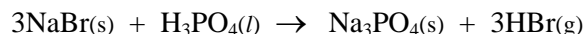
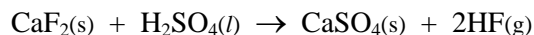
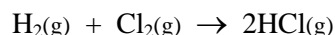
This equilibrium shift to the right in basic solution:



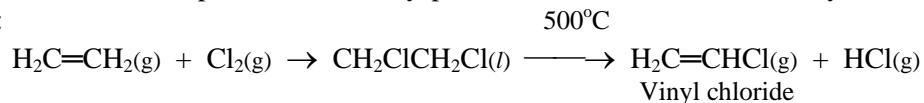
Sodium hypochloride solution, $\text{NaOCl}(\text{aq})$, is a bleaching solution.

Highlights of Halogen Chemistry

Hydrogen Halides – halogens form gaseous hydrogen halides, HX , by direct combination with H_2 or by the reaction of a concentrated acid on the metal halide:



Most commercial HCl is produced as a by-product in the manufacture vinyl chloride for plastics production:

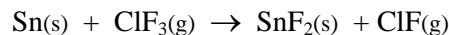


Vinyl chloride is used in the manufacture of PVC plastics.

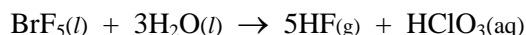
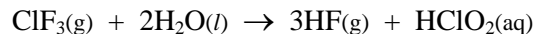
Hydrogen halides react with water to form *hydrohalic acid*, $\text{HX}(\text{aq})$. Only $\text{HF}(\text{aq})$ is a weak acid, while $\text{HCl}(\text{aq})$, $\text{HBr}(\text{aq})$, and $\text{HI}(\text{aq})$ are strong acids. Acid strength increases in the order: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$.

The Interhalogen Compounds

Halogens react with one another to form many *interhalogen compounds*, and the reactions are exothermic. Interhalogen compounds containing diatomic molecules of various combination have been prepared. Some fluorine-containing interhalogen compounds are used as fluorinating agents. For example:



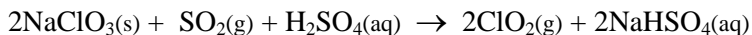
Fluorine-containing interhalogen compounds react explosively with water producing HF and an oxoacid. For example,



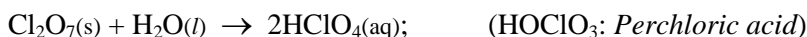
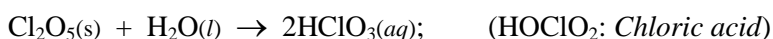
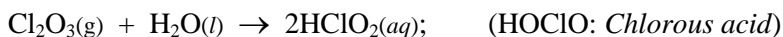
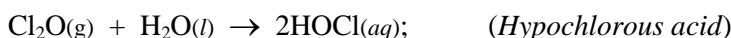
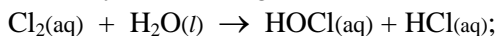
In their compounds, fluorine has the oxidation number -1 , but Cl , Br , and I may have the oxidation numbers: -1 , $+1$, $+3$, $+5$, and $+7$. For example, the oxidation number of the other halogen in the following hydrohalogen and fluorohalogen compounds are shown in parenthesis, such as $\text{HCl} (-1)$, $\text{ClF} (+1)$, $\text{ClF}_3 (+3)$, $\text{BrF}_5 (+5)$, and $\text{IF}_7 (+7)$.

Halogen Oxides, Oxoacids, and Oxoanions.

The oxides of halogen are powerful oxidizing agents and dissolve in water to form weak and strong acids. For example, dichlorine monoxide (Cl_2O) and chlorine dioxide (ClO_2) are used to bleach paper. Since ClO_2 is rather unstable to heat and shock, it has to be prepared on site:



The extremely reactive nature of ClO_2 is due to the presence of unpaired electron and Cl has the unusual +4 oxidation state. Chlorine achieves the highest oxidation state of +7 in the dichlorine heptoxide, Cl_2O_7 , which is very toxic. Halogen and their oxides dissolve in water to form oxoacids:

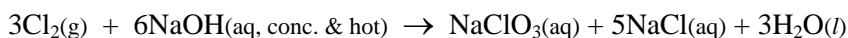
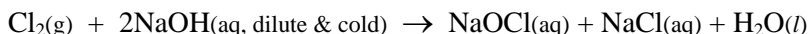


Except for fluorine, halogens form four oxoacids, namely, hypohalous acid (HOX), halous acid (HOXO), halic acid (HOXO₂), and perhalic acid (HOXO₃). For example, hypochlorous acid (HOCl), chlorous acid (HOClO), chloric acid (HOClO₂), and perchloric acid (HOClO₃). The strength of the oxoacid solution is in the order:



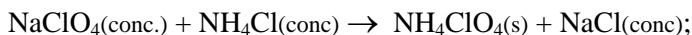
That is, the more oxygen atoms bonded to the halogen (also means the higher the oxidation number of the halogen), and/or the more electronegative the central (halogen) atom, the stronger is the acid.

The salt of oxoacid may be prepared by reaction of the halogen or oxoacid with a strong base. For example, sodium hypochlorite (NaOCl) and sodium chlorate (NaClO_3) are formed by the reaction of chlorine gas with sodium hydroxide under different condition:

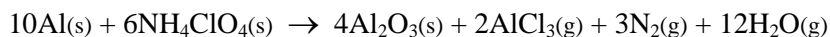


Most of sodium chlorate produced (>70%) are used to make chlorine dioxide (ClO_2) for bleaching paper pulps. Potassium chlorate (KClO_3) is also prepared by the reaction of chlorine gas with hot concentrated KOH solution. It is mainly used as an oxidizer in fireworks and for making match heads.

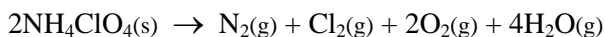
Sodium perchlorate (NaClO_4) is produced by electrolytic oxidation of NaClO_3 and is used for preparing perchloric acid (HOClO_3) and other perchlorates. Over 50% of NaClO_4 produced are converted to ammonium perchlorate (NH_4ClO_4);



Ammonium perchlorate is a powerful oxidant, and together with aluminum, it is used as fuel in booster rockets for the space shuttle.



Each space shuttle launch uses about 730 metric tons (7.3×10^5 kg) of ammonium perchlorate. Ammonium perchlorate decomposes exothermically when heated to above 200°C. The reaction is both enthalpy and entropy driven:



10. Group 8A (18) – Noble Gases

This group consists of the unreactive “inert” gases (He, Ne, Ar, Kr, Xe, and Rn; the last element is radioactive). Each atom in these element contains 8 electrons in the valence shell (except He which has two electrons only), and therefore achieves the most stable octet state. Each atom is stable by itself and, therefore, there is no need to form molecules.

Occurring at the right end of the period in the periodic table, these elements have the smallest atomic size and highest ionization energy compared with other elements in the same period. Because of their small size, dispersion (London) forces are very weak, and they occur as gases containing single atoms and having very low boiling points. No natural compound of the noble gas elements exists, but some compounds of xenon, such as, XeF_2 , XeF_4 , XeF_6 , XeO_4 , and XePtF_4 , have been prepared in the lab. Xenon is the largest nonradioactive noble gas element. It has a relatively low ionization energy (just above radon). Thus, excitation of electrons in a xenon atom that lead to the formation of covalent bonds is possible.
