

P-Block Elements

The nitrogen family is element group 15 of the periodic table. The nitrogen family consists of nitrogen, phosphorus, arsenic, antimony and bismuth. Nitrogen family elements consists of atoms having 5 electrons in their outer energy level. A pnictogen is one of the chemical elements in group 15 of the periodic table. This group is also known as the nitrogen family.

Z	Element	No. of electrons/shell
7	nitrogen	2, 5
15	phosphorus	2, 8, 5
33	arsenic	2, 8, 18, 5
51	antimony	2, 8, 18, 18, 5
83	bismuth	2, 8, 18, 32, 18, 5

Like other groups, the members of this family show similar patterns in electron configuration, especially in the outermost shells.

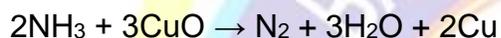
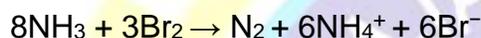
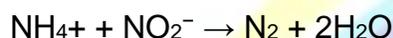
This group has the defining characteristic that all the component elements have 5 electrons in their outermost shell, that is 2 electrons in the s subshell and 3 unpaired electrons in the p subshell. They are therefore 3 electrons short of filling their outermost electron shell in their non-ionized state. The most important elements of this group are nitrogen (N), which in its diatomic form is the principal component of air, and phosphorus (P), which, like nitrogen, is essential to all known forms of life.

The pnictogens consist of two nonmetals (one gas, one solid), two metalloids, one metal, and one element with unknown chemical properties. All the elements in the group are solids at room temperature, except for nitrogen which is gaseous at room temperature. Nitrogen and bismuth, despite both being pnictogens, are very different in

their physical properties. For instance, at STP nitrogen is a transparent nonmetallic gas, while bismuth is a silvery-white metal.

Nitrogen

Nitrogen can be produced by fractional distillation of air. Nitrogen can also be produced in a large scale by burning hydrocarbons or hydrogen in air. On a smaller scale, it is also possible to make nitrogen by heating barium azide. Additionally, the following reactions produce nitrogen:



Phosphorus

The principal method for producing phosphorus is to reduce phosphates with carbon in an electric arc furnace.

Arsenic

Most arsenic is prepared by heating the mineral arsenopyrite in the presence of air. This forms As_4O_6 , from which arsenic can be extracted via carbon reduction. However, it is also possible to make metallic arsenic by heating arsenopyrite at 650 to 700 °C without oxygen.

Antimony

With sulfide ores, the method by which antimony is produced depends on the amount of antimony in the raw ore. If the ore contains 25% to 45% antimony by weight, then crude antimony is produced by smelting the ore in a blast furnace. If the ore contains 45% to 60% antimony by weight, antimony is obtained by heating the ore, also known as liquidation. Ores with more than 60% antimony by weight are chemically displaced with iron shavings from the molten ore, resulting in impure metal.

If an oxide ore of antimony contains less than 30% antimony by weight, the ore is reduced in a blast furnace. If the ore contains closer to 50% antimony by weight, the ore is instead reduced in a reverberatory furnace.

Antimony ores with mixed sulfides and oxides are smelted in a blast furnace

Bismuth

Bismuth minerals do occur, but it is more economic to produce bismuth as a by-product of lead. In China, bismuth is also found in tungsten and zinc ores

The nitrogen family includes the following compounds: nitrogen (N), phosphorus (P), arsenic(As), antimony (Sb), and bismuth (Bi). All Group 15 elements have the electron configuration ns^2np^3 in their outer shell, where n is equal to the principal quantum number. The nitrogen family is located in the p-block in Group 15, as shown below.

Periodic Trends

All Group 15 elements tend to follow the general periodic trends:

- Electronegativity (the atom's ability of attracting electrons) decreases down the group.
- Ionization energy (the amount of energy required to remove an electron from the atom in its gas phase) decreases down the group.
- Atomic radii increase in size down the group.
- Electron affinity (the ability of the atom to accept an electron) decreases down the group.
- Melting point (amount of energy required to break bonds to change a solid phase substance to a liquid phase substance) increases down the group.
- Boiling point (amount of energy required to break bonds to change a liquid phase substance to a gas) increases down the group.
- Metallic character increases down the group.

Properties of Group 15 Element

Element/Symbol	Atomic Number	Mass	Electron Configuration	Covalent Radius (pm)	Electronegativity	First Ionization Energy (kJ/mol)	Common Physical Form(s)
<u>Nitrogen (N)</u>	7	14.01	$1s^2 2s^2 2p^3$	75	3	1402	Colorless Gas
<u>Phosphorus (P)</u>	15	30.97	$[\text{Ne}]3s^2 3p^3$	110	2.1	1012	White Solid / Red Solid
<u>Arsenic (As)</u>	33	74.92	$[\text{Ar}] 3d^{10} 4s^2 4p^3$	121	2	947	Yellow Solid / Gray Solid
<u>Antimony (Sb)</u>	51	121.76	$[\text{Kr}] 4d^{10} 5s^2 5p^3$	140	1.9	834	Yellow Solid / Silver-White Metallic Solid
<u>Bismuth (Bi)</u>	83	208.98	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^3$	155	1.9	703	Pink-White Metallic Solid

Group 15 Element

There are two allotropic elements in Group 15, phosphorus and arsenic. Phosphorus exists in several allotropic forms. The main ones (and those from which the others are derived) are white, red, and black (the thermodynamically stable form at room temperature). Only white and red phosphorus are of industrial importance. Phosphorus was first produced as the common white phosphorus, which is the most volatile, most reactive, and most toxic, but the least thermodynamically stable form of phosphorus, α -P₄. White phosphorus is a waxy, nonconductor and reacts with air—the phosphorescent reaction of oxygen with the vapour above the solid producing the yellow-green chemiluminescent light, which gives phosphorus its name (after the Greek god, Eosphoros, the morning star, the bringer of light). The phosphorus in commercial use is amorphous red phosphorus, produced by heating white phosphorus in the absence of air at about 300°C. It melts

around 600°C and was long thought to contain polymers formed by breaking a P-P bond of each P₄ tetrahedron of white phosphorus then linking the "opened" tetrahedral.

A variety of crystalline modifications (tetragonal red, triclinic red, cubic red), possibly with similar polymeric structures can also be prepared by heating amorphous red phosphorus at over 500°C.

The most thermodynamically stable, and least reactive, form of phosphorus is black phosphorus, which exists as three crystalline (orthorhombic-, rhombohedral- and metallic, or cubic) and one amorphous, allotrope. All are polymeric solids and are practically nonflammable. Both orthorhombic and rhombohedral phosphorus appear black and graphitic, consistent with their layered structures.

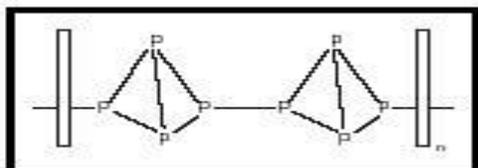


Figure a. Linkage of P₄ units in red phosphorus.

A violet crystalline allotrope, monoclinic phosphorus, or Hittorf's phosphorus, after its discoverer, can be produced by a complicated thermal electrolytic procedure. The structure is very complex, consisting of tubes of

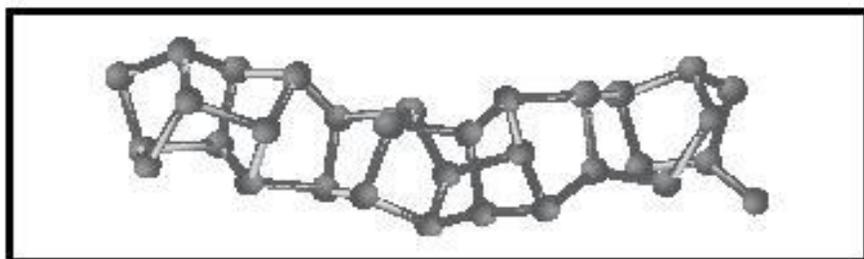


Figure (b). Linkage of P_4 units in red phosphorus.

pentagonal cross section joined in pairs to form double layers, which are repeated through the crystal. The tubes are formed from cage-like P_8 and P_9 groups, linked by P_2 units.

At least six forms of solid arsenic have been reported, of which three are amorphous. The most stable and most common form of arsenic at room temperature is a brittle, steel-gray solid (α -As) with a structure analogous to that of rhombohedral black phosphorus. Arsenic vapor contains tetrahedral As_4 molecules, which are thought to be present in the yellow unstable arsenic formed by condensation of the vapor. Arsenic occurs naturally as α -As and also as the mineral arsenolamprite, which may have the same structure as orthorhombic black phosphorus.

Reactions and Compounds of Nitrogen

Like carbon, nitrogen has four valence orbitals (one 2s and three 2p), so it can participate in at most four electron-pair bonds by using sp^3 hybrid orbitals. Unlike carbon, however, nitrogen does not form long chains because of repulsive interactions between lone pairs of electrons on adjacent atoms. Nitrogen is the only pnictogen that normally forms multiple bonds with itself and other second-period elements, using π overlap of adjacent np orbitals. Thus the stable form of elemental nitrogen is N_2 , whose $N\equiv N$ bond is so strong ($DN\equiv N = 942 \text{ kJ/mol}$) compared with the $N-N$ and $N=N$ bonds ($DN-N = 167 \text{ kJ/mol}$; $DN=N = 418 \text{ kJ/mol}$) that all compounds containing $N-N$ and $N=N$ bonds are thermodynamically unstable with respect to the formation of N_2 . In fact, the formation of the $N\equiv N$ bond is so thermodynamically favored that virtually all compounds containing $N-N$ bonds are potentially explosive. Again in contrast to carbon, nitrogen undergoes only two important chemical reactions at room temperature: it reacts with metallic lithium to form lithium

nitride, and it is reduced to ammonia by certain microorganisms. Few binary molecular compounds of nitrogen are formed by direct reaction of the elements. At elevated temperatures, N_2 reacts with H_2 to form ammonia, with O_2 to form a mixture of NO and NO_2 , and with carbon to form cyanogen ($N\equiv C-C\equiv N$); elemental nitrogen does not react with the halogens or the other chalcogens. Nonetheless, all the binary nitrogen halides (NX_3) are known. Except for NF_3 , all are toxic, thermodynamically unstable, and potentially explosive, and all are prepared by reacting the halogen with NH_3 rather than N_2 . Both nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are thermodynamically unstable, with positive free energies of formation. Unlike NO , NO_2 reacts readily with excess water, forming a 1:1 mixture of nitrous acid (HNO_2) and nitric acid (HNO_3)



Nitrogen also forms N_2O (dinitrogen monoxide, or nitrous oxide), a linear molecule that is isoelectronic with CO_2 and can be represented as $-N=N+=O$. Like the other two oxides of nitrogen, nitrous oxide is thermodynamically unstable. The structures of the three common oxides of nitrogen are as follows:

Physical Properties And Oxidation States

Physical properties include physical state, metallic character, melting and boiling points, density, and allotropy. Nitrogen is a diatomic gas, while the remaining elements are solids. As we move down a group, metallic character increases & the ionisation enthalpy of the elements decrease with an increase in their atomic size.

Trends in melting and boiling points:

The melting point increases from nitrogen to arsenic due to the gradual increase in atomic size. The very low melting point of nitrogen is due to its discrete diatomic molecules. On the other hand, the high melting point of arsenic is attributed to its giant layered structure in which the layers are closely packed.

Although the atomic size increases from arsenic to antimony, there is a decrease in their melting points. Although antimony has a layered structure, it has a low melting point than arsenic because of the relatively loose packing of atoms. Furthermore, the melting point of bismuth is less than antimony due to the loose packing of atoms by metallic bonding. On the other hand, the boiling point gradually increases from nitrogen to bismuth.

Allotropy: All the elements in group fifteen, except for bismuth, show allotropy. Nitrogen exists in two allotropic forms, that is, alpha nitrogen and beta nitrogen. Phosphorus exists in many allotropic forms. Of these, the two important allotropic forms are white phosphorus and red phosphorus. Arsenic exists in three important allotropic forms - yellow, grey and black. Antimony also has three important allotropic forms, namely, yellow, explosive and metallic.

Oxidation states: All the elements of group 15 have 5 electrons in their outermost orbit. They need only 3 electrons to complete their octet configuration. The octet can be achieved either by gaining 3 electrons or by sharing 3 electrons by means of covalent bonds. As a result, the common negative oxidation state of these elements is -3. As we move down the group, the tendency to exhibit -3 oxidation state decreases. This is due to the increase in atomic size and metallic character.

Group 15 elements also show positive oxidation states of +3 & +5 by forming covalent bonds. Due to the inert pair effect the stability of +5 oxidation state decreases down the group, while that of +3 oxidation state increases. Nitrogen has only s- and p-orbitals, but no d-orbitals in its valence shell.

Therefore, nitrogen can show a maximum covalency of 4. A covalency of four is obtained by sharing its lone pair of electron with another atom or ion.

Phosphorus and the remaining elements can exhibit a covalency of five and a maximum covalency, also called expanded covalency of six. This is possible because of the presence of vacant d-orbitals in the valence shell. All the compounds of group fifteen elements, which exhibit a +5 oxidation state, are covalent.

In group fifteen elements, the covalent character decreases from nitrogen to bismuth. Nitrogen, because of its smaller size, high electro-negativity and strong tendency to form p pi – p pi multiple bonds, it exhibits various oxidation states from -3 to +5.

Oxidation State and Chemical Properties

The elements of group 15 generally exhibit -3, +3 and +5 oxidation states. The tendency to exhibit -3 oxidation state decreases as we move down the group due to increase in the size of the atom and the metallic character. Bismuth hardly forms any compound in oxidation state -3. In fact the stability of +5 state also decreases as we move down the group. BiF_5 is the only well characterized Bi (V) compound.

Due to inert pair effect, the stability of +5 state decreases and +3 state increases as we move down the group in the periodic table. Nitrogen reacts with oxygen and also exhibits +1, +2, +4 oxidation states. On the other hand phosphorus shows +1 and +4 states in some oxoacids.

In nitrogen, the oxidation states from +1 to +4 tend to disproportionate in acidic solution. In case of phosphorus the intermediate oxidation states disproportionate into +5 and -3 in both acids and alkalis. Whereas

considering the case of arsenic, antimony and bismuth, the +3 state is stable with respect to disproportionation.

Nitrogen has only 4 electrons in its outermost shell (one in s orbital and 3 in p) which is available for bonding, hence it exhibits a maximum covalency of 4. The heavier elements have a vacant d orbital in the valence shell which is used for bonding.

Anomalous properties of Nitrogen- The bond enthalpy of nitrogen molecule is very high due to the presence of triple bond between the two atoms. Other elements form only single bonds with their own atoms and other atoms too. The N-N is weaker than P-P because of high interelectronic repulsions of the non-bonding electrons in N-N due to the small size of N-atom .

Reactivity towards hydrogen:- All the elements of Group 15 form hydrides of the type $E H_3$ where $E = N, P, As, Sb$ or Bi . The stability of hydrides decreases from NH_3 to BiH_3 due to decrease in their bond dissociation enthalpy. Consequently, the reducing character of the hydrides increases. Ammonia is only a mild reducing agent while BiH_3 is the strongest reducing agent amongst all the hydrides. Basicity also decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$. Basicity decreases because electron density around the central atom decreases.

Reactivity towards oxygen

All these elements form two types of oxides: E_2O_3 and E_2O_5 . The oxide in the higher oxidation state of the element is more acidic than that of lower oxidation state. Their acidic character decreases down the group. The oxides of the type E_2O_3 of nitrogen and phosphorus are purely acidic, that of arsenic and antimony amphoteric and those of bismuth is predominantly basic.

Reactivity towards halogens

- These elements react to form two series of halides: EX_3 and EX_5 .
- Nitrogen does not form pentahalide due to non-availability of the d orbitals in its valence shell.
- Pentahalides are more covalent than trihalides.
- In case of nitrogen, only NF_3 is known to be stable due to high polarizing nature of F-atom
- Trihalides except BiF_3 are predominantly covalent in nature. BiF_3 is ionic due to high metallic character of Bismuth.

Reactivity towards metals-

All these elements react with metals to form their binary compounds exhibiting -3 oxidation state

1. PH_3 has lower boiling point than NH_3 because PH_3 molecules do not form intermolecular hydrogen bonding in liquid state. That is why the boiling point of PH_3 is lower than NH_3 .

2. NH_3 is soluble in water whereas PH_3 is insoluble.

Preparation, Properties and Uses – Dinitrogen

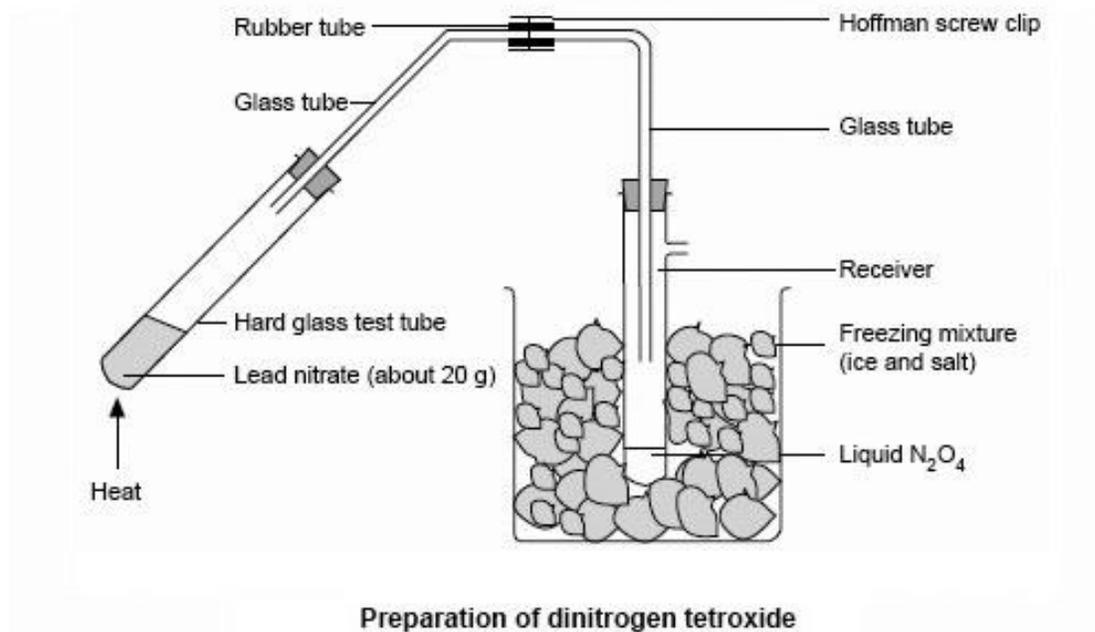
Dinitrogen makes up to 78% of the earth's atmosphere and it is the most abundant element present in the air and the seventh most abundant uncombined element found in the universe. This element was first discovered

in the year 1772 by a Scottish physician Daniel Rutherford. The symbol of this chemical element is N and 7 is its atomic number.

Preparation of dinitrogen:

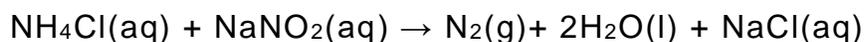
Nitrogen is obtained commercially by liquefaction and fractional distillation of air. This process mainly involves two steps:

Step 1: Air is reduced to liquid air by applying high pressure ranging between 100 to 200 atmospheres. This compressed air is then passed through fine jet where it undergoes expansion. This method is repeated several times which results in the formation of liquid air.



Step 2: The liquid formed undergoes fractional distillation. The boiling point of dinitrogen is lower than that of the liquid oxygen and hence it distils out, leaving behind liquid oxygen. Nitrogen is obtained from the impure liquid.

In laboratory, dinitrogen is obtained by reacting aqueous solution of ammonium chloride with sodium nitrite.



The products obtained consists of impurities such as NO and HNO₃ which can be removed by thermal decomposition of ammonium dichromate. Another method to remove the impurities is to pass the gaseous mixture through sulphuric acid containing potassium dichromate.



Decomposition of sodium or barium azide in the presence of high temperature also results in the formation of pure nitrogen.

Physical properties of Dinitrogen:

- Nitrogen is a colourless, odourless and diamagnetic in nature. It is a non-toxic gas.
- It is sparingly soluble in water.
- Nitrogen undergoes condensation to form a colourless liquid which on solidification results in the formation of snow like mass.

Chemical properties of Dinitrogen:

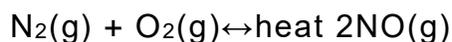
- Dinitrogen has a high bond enthalpy due to the N = N bond. Due to this it is inert at room temperature. However the reactivity increases as the temperature increases. At high temperatures, nitrogen molecules react with

metals to form respective ionic nitrides and with non-metals to form covalent nitrides.

$6\text{Li} + \text{N}_2 \xrightarrow{\text{heat}} 2\text{Li}_3\text{N}$ At about 773 K it reacts with hydrogen to form ammonia in Haber's Process.



- Nitric oxide is formed when nitrogen molecule reacts with oxygen molecule at a temperature of 2000 K.



Uses of Dinitrogen:

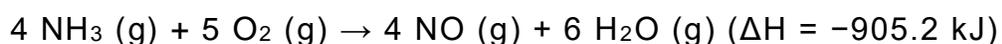
- It is mainly used in the industrial manufacturing of compounds such as ammonia, calcium cyanamide etc.
- It is used in the manufacturing industries such as iron and steel to obtain an inert atmosphere.
- Liquid nitrogen is used in food industries as a preservative and as a refrigerant.

Ostwald process

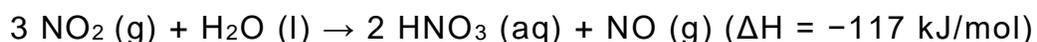
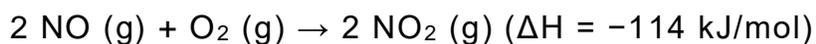
The Ostwald process is a chemical process for making nitric acid (HNO_3). Wilhelm Ostwald developed the process, and he patented it in 1902. The Ostwald process is a mainstay of the modern chemical industry, and it provides the main raw material for the most common type of fertilizer.

production. Historically and practically, the Ostwald process is closely associated with the Haber process, which provides the requisite raw material, ammonia (NH₃).

Ammonia is converted to nitric acid in 2 stages. It is oxidized by heating with oxygen in the presence of a catalyst such as platinum with 10% rhodium, to form nitric oxide and water. This step is strongly exothermic, making it a useful heat source once initiated:

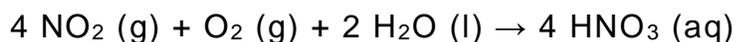


Stage two encompasses two reactions and is carried out in an absorption apparatus containing water. Initially nitric oxide is oxidized again to yield nitrogen dioxide. This gas is then readily absorbed by the water, yielding the desired product (nitric acid, albeit in a dilute form), while reducing a portion of it back to nitric oxide:



The NO is recycled, and the acid is concentrated to the required strength by distillation.

Alternatively, if the last step is carried out in air:



Typical conditions for the first stage, which contribute to an overall yield of about 98%, are:

- pressure between 4 and 10 atmospheres (approx. 400-1010 kPa or 60-145 psig) and
- temperature is about 500 K (approx. 217 °C or 422.6 °F.).

Compounds of nitrogen

Red phosphorus



Red phosphorus structure

Red phosphorus may be formed by heating white phosphorus to 300 °C (572 °F) in the absence of air or by exposing white phosphorus to sunlight. Red phosphorus exists as an amorphous network. Upon further heating, the amorphous red phosphorus crystallizes. Red phosphorus does not ignite in air at temperatures below 240 °C (464 °F), whereas pieces of white phosphorus ignite at about 30 °C (86 °F). Ignition is spontaneous at room temperature with finely divided material. Heating red phosphorus in the presence of moisture creates phosphine gas, which is both highly flammable and toxic.

Applications

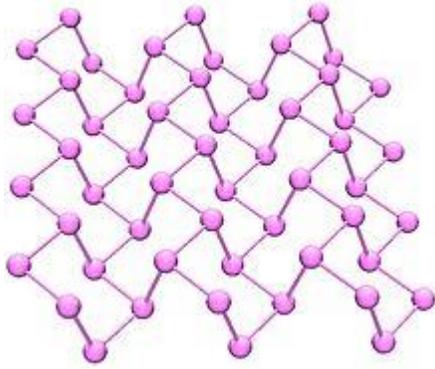
Red phosphorus can be used as a very effective flame retardant, especially in thermoplastics (e.g. polyamide) and thermosets (e.g. epoxy resins or

polyurethanes). The flame retarding effect is based on the formation of polyphosphoric acid. Together with the organic polymer material, this acid creates a char which prevents the propagation of the flames. The safety risks associated with phosphine generation and friction sensitivity of red phosphorus can be effectively reduced by stabilization and micro-encapsulation. For easier handling, red phosphorus is often used in form of dispersions or masterbatches in various carrier systems.

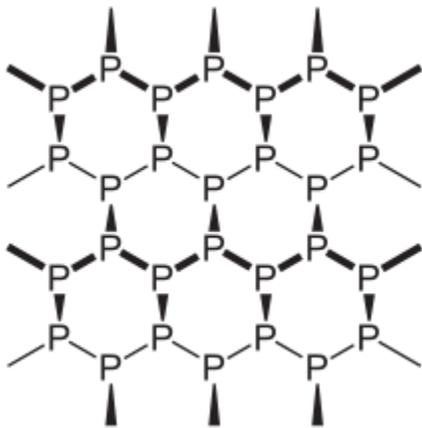
Reactions of violet phosphorus

It does not ignite in air until heated to 300 °C and is insoluble in all solvents. It is not attacked by alkali and only slowly reacts with halogens. It can be oxidised by nitric acid to phosphoric acid.

If it is heated in an atmosphere of inert gas, for example nitrogen or carbon dioxide, it sublimates and the vapour condenses as white phosphorus. If it is heated in a vacuum and the vapour condensed rapidly, violet phosphorus is obtained. It would appear that violet phosphorus is a polymer of high relative molecular mass, which on heating breaks down into P₂ molecules. On cooling, these would normally dimerize to give P₄ molecules (i.e. white phosphorus) but, in vacuo, they link up again to form the polymeric violet allotrope.



Black phosphorus



Black phosphorus structure

Black phosphorus is the thermodynamically stable form of phosphorus at room temperature and pressure. It is obtained by heating white phosphorus under high pressures (12,000 atmospheres). In appearance, properties, and structure, black phosphorus is very much like graphite with both being black and flaky, a conductor of electricity, and having puckered sheets of linked atoms.

Black phosphorus has an orthorhombic structure and is the least reactive allotrope, a result of its lattice of interlinked six-membered rings where each

atom is bonded to three other atoms. Black and red phosphorus can also take a cubic crystal lattice structure. A recent synthesis of black phosphorus using metal salts as catalysts has been reported.

Diphosphorus molecule

The diphosphorus allotrope (P_2) can normally be obtained only under extreme conditions (for example, from P_4 at 1100 kelvin). In 2006, the diatomic molecule was generated in homogenous solution under normal conditions with the use of transition

Diphosphorus is the gaseous form of phosphorus, and the thermodynamically stable form between 1200 °C and 2000 °C. The dissociation of tetraphosphorus (P_4) begins at lower temperature: the percentage of P_2

at 800 °C is $\approx 1\%$. At temperatures above about 2000 °C, the diphosphorus molecule begins to dissociate into atomic phosphorus.

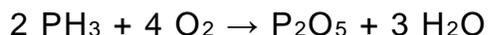
Phosphine.

Phosphine (IUPAC name: phosphane) is the compound with the chemical formula PH_3 . It is a colorless, flammable, toxic gas. Pure phosphine is odorless, but technical grade samples have a highly unpleasant odor like garlic or rotting fish, due to the presence of substituted phosphine and diphosphane (P_2H_4). With traces of P_2H_4 present, PH_3 is spontaneously flammable in air, burning with a luminous flame. Phosphines are also a group of organophosphorus compounds with the formula R_3P (R = organic derivative). Organophosphines are important in catalysts where they complex to various metal ions; complexes derived from a chiral phosphine can catalyze reactions to give chiral, enantioenriched products.

Structure and properties

PH₃ is a trigonal pyramidal molecule with C_{3v} molecular symmetry. The length of the P-H bond is 1.42 Å, the H-P-H bond angles are 93.5°. The dipole moment is 0.58 D, which increases with substitution of methyl groups. The aqueous solubility of PH₃ is slight; 0.22 mL of gas dissolve in 1 mL of water. Phosphine dissolves more readily in non-polar solvents than in water because of the non-polar P-H bonds. It is technically amphoteric in water, but acid and base activity is poor. Proton exchange proceeds via a phosphonium(PH₄⁺) ion in acidic solutions and via PH₂⁻ at high pH, with equilibrium constants K_b = 4 × 10⁻²⁸ and K_a = 41.6 × 10⁻²⁹.

Phosphine burns producing a dense white cloud of phosphorus pentoxide:



Preparation

Phosphine may be prepared in a variety of ways. Industrially it can be made by the reaction of white phosphorus with sodium or potassium hydroxide, producing sodium or potassium hypophosphite as a by-product.



Alternatively the acid-catalyzed disproportioning of white phosphorus yields phosphoric acid and phosphine. Both routes have industrial significance; the acid route is preferred method if further reaction of the phosphine to substituted phosphines is needed. The acid route requires purification and pressurizing. It can also be made (as described above) by the hydrolysis of a metal phosphide, such as aluminium phosphide or calcium

phosphide. Pure samples of phosphine, free from P_2H_4 , may be prepared using the action of potassium hydroxide on phosphonium iodide (PH_4I).

Laboratory routes

It is prepared in the laboratory by disproportionation of phosphorous acid



Phosphine evolution occurs around 200 °C. Alternative methods involve the hydrolysis of aluminium and calcium phosphides.

Phosphorus tri chloride

Phosphorus trichloride is a chemical compound of phosphorus and chlorine, having the chemical formula PCl_3 . It has a trigonal pyramidal shape. It is the most important of the three phosphorus chlorides. It is an important industrial chemical, being used for the manufacture of organophosphorus compounds for a wide variety of applications.

Chemical Properties

The phosphorus in PCl_3 is often considered to have the +3 oxidation state and the chlorine atoms are considered to be in the -1 oxidation state. Most of its reactivity is consistent with this description.

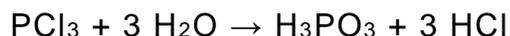
Redox reactions PCl_3 is a precursor to other phosphorus compounds, undergoing oxidation to phosphorus pentachloride (PCl_5), thiophosphoryl chloride ($PSCl_3$), or phosphorus oxychloride ($POCl_3$).

If an electric discharge is passed through a mixture of PCl_3 vapour and hydrogen gas, a rare chloride of phosphorus is formed, diphosphorus tetrachloride (P_2Cl_4).

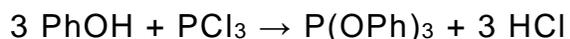
PCl_3 as an electrophile

Phosphorus trichloride is the precursor to organophosphorus compounds that contain one or more P(III) atoms, most notably phosphites and phosphonates. These compounds do not usually contain the chlorine atoms found in PCl_3 .

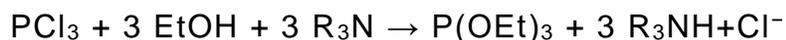
PCl_3 reacts rapidly and exothermically with water to form phosphorous acid, H_3PO_3 and HCl :



A large number of similar substitution reactions are known, the most important of which is the formation of phosphite esters by reaction with alcohols or phenols. For example, with phenol, triphenylphosphite is formed:

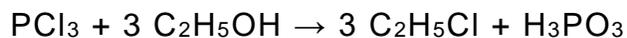


where "Ph" stands for phenyl group, $-\text{C}_6\text{H}_5$. Alcohols such as ethanol react similarly in the presence of a base such as a tertiary amine

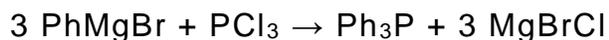


Of the many related compounds can be prepared similarly, triisopropylphosphite is an example.

In the absence of base, however, the reaction produces phosphonic acid and an alkyl chloride, according to the following stoichiometry:



Aminophosphonates are widely used as sequestering and antiscaling agents in water treatment. The large volume herbicide glyphosate is also produced this way. The reaction of PCl_3 with Grignard reagents and organolithium reagents is a useful method for the preparation of organic phosphines with the formula R_3P (sometimes called phosphines) such as triphenylphosphine, Ph_3P .



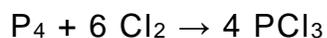
Under controlled conditions PCl_3 can be used to prepare PhPCl_2 and Ph_2PCl .

PCl_3 as a nucleophile

Phosphorus trichloride has a lone pair, and therefore can act as a Lewis base, for example with the Lewis acids BBr_3 it forms a 1:1 adduct, $\text{Br}_3\text{B} \cdots \text{PCl}_3$. Metal complexes such as $\text{Ni}(\text{PCl}_3)_4$ are known. This Lewis basicity is exploited in one useful route to organophosphorus compounds using an alkyl chloride and aluminium chloride:

Preparation

World production exceeds one-third of a million tonnes. Phosphorus trichloride is prepared industrially by the reaction of chlorine with a refluxing solution of white phosphorus in phosphorus trichloride, with continuous removal of PCl_3 as it is formed (in order to avoid the formation of PCl_5).



Industrial production of phosphorus trichloride is controlled under the Chemical Weapons Convention, where it is listed in schedule 3. In the laboratory it may be more convenient to use the less toxic red phosphorus. It is sufficiently inexpensive that it would not be synthesized for laboratory use.

Uses

PCl_3 is important indirectly as a precursor to PCl_5 , POCl_3 and PSCl_3 , which are used in many applications, including herbicides, insecticides, plasticisers, oil additives, and flame retardants.

For example oxidation of PCl_3 gives POCl_3 , which is used for the manufacture of triphenyl phosphate and tricresyl phosphate, which find application as flame retardants and plasticisers for PVC. They are also used to make insecticides such as diazinon. Phosphonates include the herbicide glyphosate.

PCl_3 is the precursor to triphenylphosphine for the Wittig reaction, and phosphite esters which may be used as industrial intermediates, or used in the Horner-Wadsworth-Emmons reaction, both important methods for making alkenes. It can be used to make trioctylphosphine oxide (TOPO), used as an extraction agent, although TOPO is usually made via the corresponding phosphine.

PCl_3 is also used directly as a reagent in organic synthesis. It is used to convert primary and secondary alcohols into alkyl chlorides, or carboxylic acids into acyl chlorides, although thionyl chloride generally gives better yields than PCl_3 . Phosphorus pentachloride is the chemical compound with the formula PCl_5 . It is one of the most important phosphorus chlorides, others

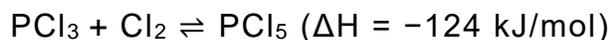
being PCl_3 and POCl_3 . PCl_5 finds use as a chlorinating reagent. It is a colourless, water- and moisture-sensitive solid, although commercial samples can be yellowish and contaminated with hydrogen chloride.

Structure

The structures for the phosphorus chlorides are invariably consistent with VSEPR theory. The structure of PCl_5 depends on its environment. Gaseous and molten PCl_5 is a neutral molecule with trigonalbipyramidal (D_{3h}) symmetry. The hypervalent nature of this species can be explained with the inclusion of non-bonding MOs (Molecular orbital theory) or resonance (Valence bond theory). This trigonalbipyramidal structure persists in non-polar solvents, such as CS_2 and CCl_4

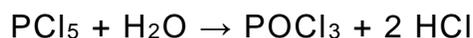
Preparation

PCl_5 is prepared by the chlorination of PCl_3 . This reaction is used to produce ca. 10,000,000 kg/y of PCl_5 (as of 2000).

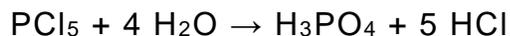


PCl_5 exists in equilibrium with PCl_3 and chlorine, and at 180 °C the degree of dissociation is ca. 40%. Because of this equilibrium, samples of PCl_5 often contain chlorine, which imparts a greenish colouration.

In its most characteristic reaction, PCl_5 reacts upon contact with water to release hydrogen chloride and give phosphorus oxides. The first hydrolysis product is phosphorus oxychloride:



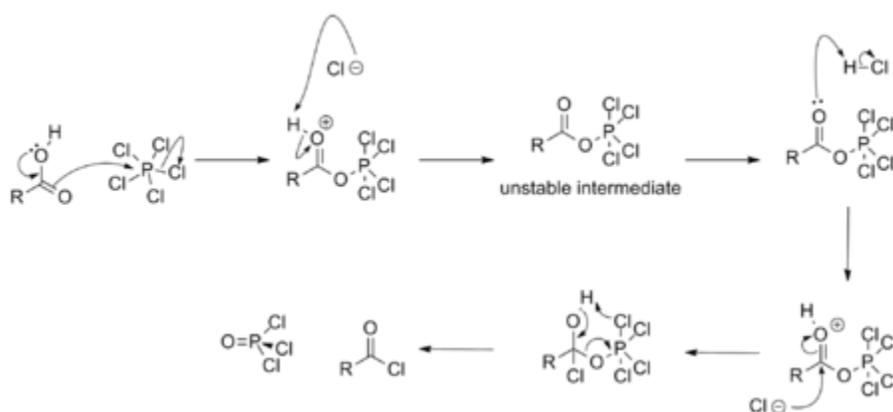
In hot water, hydrolysis proceeds completely to ortho-phosphoric acid:



Chlorination of organic compounds

In synthetic chemistry, two classes of chlorination are usually of interest: oxidative chlorinations and substitutive chlorinations. Oxidative chlorinations entail the transfer of Cl_2 from the reagent to the substrate. Substitutive chlorinations entail replacement of O or OH groups with chloride. PCl_5 can be used for both processes.

PCl_5 will convert carboxylic acids to the corresponding acyl chloride through the following mechanism:



It also converts alcohols to alkyl chloride. Thionyl chloride is more commonly used in the laboratory because the SO_2 is more easily separated from the organic products than is POCl_3 .

PCl_5 and PCl_3 bear some resemblance to SO_2Cl_2 , as both serve often as sources of Cl_2 . Again for oxidative chlorinations on the laboratory

scale, SO_2Cl_2 is often preferred over PCl_5 since the gaseous SO_2 by-product is readily separated.

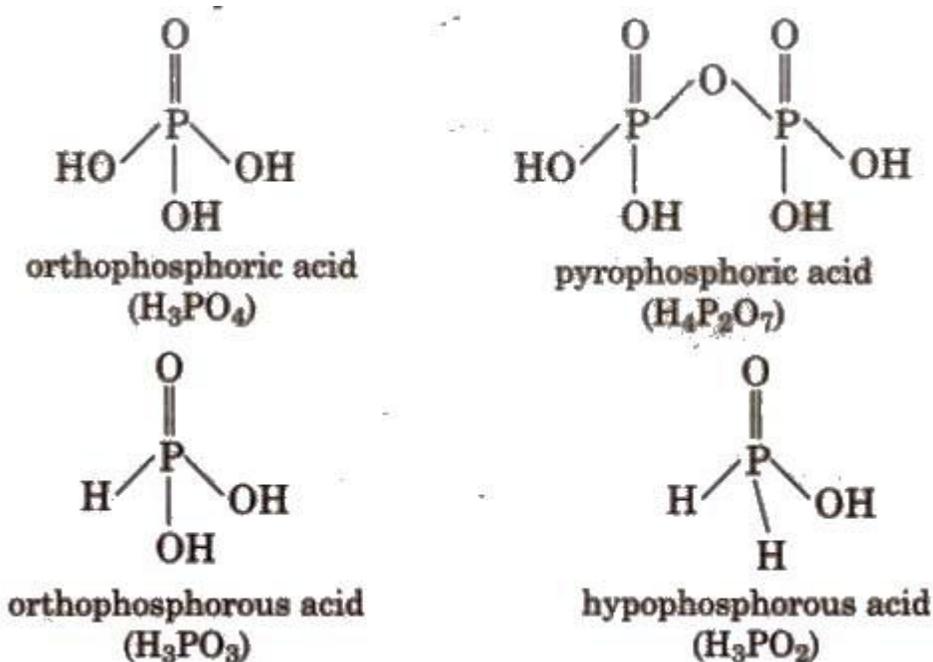
PCl_5 reacts with a tertiary amides, such as DMF, to give dimethyl chloro methylene ammonium chloride, which is called the Vilsmeier reagent, $[(\text{CH}_3)_2\text{NCClH}]\text{Cl}$. More typically, a related salt is generated from the reaction of DMF and POCl_3 . Such reagents are useful in the preparation of derivatives of benzaldehyde by formylation and for the conversion of C-OH groups into C-Cl groups

In contrast to PCl_3 , the pentachloride replaces allylic and benzylic CH bonds and is especially renowned for the conversion of C=O groups to CCl_2 groups.

The electrophilic character of PCl_5 is highlighted by its reaction with styrene to give, after hydrolysis, phosphonic acid derivatives

Oxoacids of Phosphorus

Oxoacids are basically the acids that contain oxygen. Phosphorus forms a number of oxoacids, for example: H_3PO_4 , H_3PO_3 , etc. In oxoacids of phosphorus, phosphorus is tetrahedrally surrounded by other atoms. Generally, all these acids are known to form at least one P=O bond and one P-OH bond. P-P or P-H bonds are also found in addition to P=O bonds and P-OH bonds in oxoacids of phosphorus where the oxidation state of phosphorus is less than +5. These acids are generally seen to disproportionate to higher and lower oxidation states. For example, phosphorous acid on heating disproportionates to give phosphoric acid and phosphine.



Oxoacids of Phosphorus

The P-H bonds in oxoacids are not ionisable to give H⁺ ions whereas the H atoms which are attached with oxygen in P-OH form are ionisable. Hence we can say that only the H atoms attached with oxygen cause basicity. As a result phosphorous acid, H₃PO₃ is dibasic due to the presence of two P-OH bonds whereas phosphoric acid, H₃PO₄ is tribasic due to the presence of three P-OH bonds. Oxoacids of phosphorus having P-H bonds have strong reducing properties. For example: hypophosphorous acid containing two P-H bonds acts as a good reducing agent.

Phosphorous acid, H₃PO₃ Phosphorous acid is a diprotic acid that is, it ionizes two protons. It is better described with the structural formula HPO(OH)₂. Phosphorous acid is prepared by hydrolysis of phosphorus trichloride with acid or steam.

Phosphoric acid, H_3PO_4 : Phosphoric acid is a triprotic acid that is, it ionizes three protons. It is a non-toxic acid, when pure and is a solid at room temperature and pressure. Phosphoric acid is prepared by adding sulfuric acid to tricalcium phosphate rock:

Group 16 Element The chalcogens are the chemical elements in group 16 of the periodic table. This group is also known as the oxygen family. It consists of the elements oxygen (O), sulfur (S), selenium (Se), tellurium (Te), and the radioactive element polonium (Po). The chemically uncharacterized synthetic element livermorium (Lv) is predicted to be a chalcogen as well. All of the chalcogens have six valence electrons, leaving them two electrons short of a full outer shell. Their most common oxidation states are -2 , $+2$, $+4$, and $+6$. They have relatively low atomic radii, especially the lighter ones.

Properties Atomic and physical

Chalcogens show similar patterns in electron configuration, especially in the outermost shells, where they all have the same number of valence electrons, resulting in similar trends in chemical behavior:

<u>Z</u>	<u>Element</u>	<u>No. of electrons/shell</u>
8	oxygen	2, 6
16	sulfur	2, 8, 6
34	selenium	2, 8, 18, 6
52	tellurium	2, 8, 18, 18, 6
84	polonium	2, 8, 18, 32, 18, 6
116	livermorium	2, 8, 18, 32, 32, 18, 6

Oxygen's most common allotrope is diatomic oxygen, or O_2 , a reactive paramagnetic molecule that is ubiquitous to aerobic organisms and has a

blue color in its liquid state. Another allotrope is O_3 , or ozone, which is three oxygen atoms bonded together in a bent formation. There is also an allotrope called tetraoxygen, or O_4 and six allotropes of solid oxygen including "red oxygen", which has the formula O_8 .

There are only three allotropic elements in Group 16, oxygen, sulfur, and selenium. Only two oxygen allotropes are known—dinuclear "oxygen" (dioxygen, O_2) and trinuclear ozone (O_3) (Figure 6). Both are gases at room temperature and pressure. Dioxygen exists as a diradical (contains two unpaired electrons) and is the only allotrope of any element with unpaired electrons. Liquid and solid dioxygen are both pale blue because the absorption of light excites the molecule to a higher energy (and much more reactive) electronic state in which all electrons are paired ("singlet" oxygen). Gaseous dioxygen is probably also blue, but the low concentration of the species in the gas phase makes it difficult to observe.

Ozone is a V-shaped, triatomic dark blue gaseous molecule with a bond order of $1\frac{1}{2}$. It is usually prepared from dioxygen by electric discharge (e.g., lightning) and can be detected by its characteristic "sharp" smell—from which it gets its name (after the Greek *ozein* : to smell). Ozone is thermodynamically unstable and reverts spontaneously to dioxygen.

The dark blue color of O_3 is important because it arises from the intense absorption of red and ultraviolet (UV) light. This is the mechanism by which ozone in the atmosphere (the ozone layer) protects Earth from the Sun's UV radiation. After F_2 , ozone is the most powerful oxidant of all the elements.

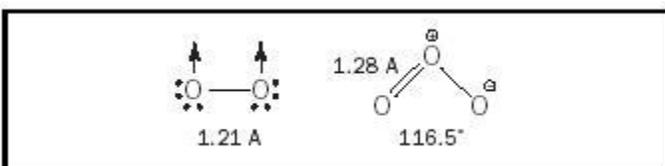


Figure 6. Dioxxygen and ozone, the allotropes of oxygen.

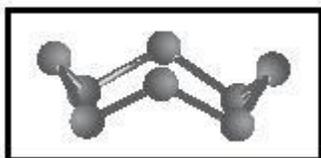


Figure a. Sulfur allotrope, S₈.

Sulfur (S) is second only to carbon in the number of known allotropes formed. The existence of at least twenty-two sulfur allotropes has been demonstrated. The simplest allotrope of sulfur is the violet disulfur molecule, S₂, analogous to the dioxygen molecule. Unlike O₂, however, S₂ does not occur naturally at room temperature and pressure. It is commonly generated in the vapor generated from sulfur at temperatures above 700°C. It has been detected by the Hubble Space Telescope in volcanic eruptions on Jupiter's satellite,

The most thermodynamically stable of all of the sulfur allotropes and the form in which sulfur ordinarily exists is orthorhombic sulfur, α-S₈, cyclooctasulfur, which contains puckered eight-membered rings, in which each sulfur atom is two-coordinate (Figure a).

The second allotrope of sulfur to be discovered was cyclohexasulfur (sometimes called rhombohedral sulfur), first reported in 1891. It is the densest of the sulfur allotropes and forms air-sensitive orange-red crystals containing chair-shaped, six-membered rings. Sulfur forms an extensive series of generally yellow crystalline allotropes, S_n (where species with n up to 30 have been identified). The color of liquid sulfur changes from pale yellow to orange, then red and finally to black, near the boiling point (445°C).

At about 159°C, the viscosity increases as polymeric sulfur is formed. The liquid is thought to contain chains of sulfur atoms, wound into helices.

Selenium (Se) also exists in several allotropic forms—gray (trigonal) selenium (containing Se n helical chain polymers), rhombohedral selenium (containing Se 6 molecules), three deep-red monoclinic forms— α -, β -, and γ -selenium (containing Se 8 molecules), amorphous red selenium, and black vitreous selenium, the form in industrial usage. The most thermodynamically stable and the densest form is gray (trigonal) selenium, which contains infinite helical chains of selenium atoms. All other forms revert to gray selenium on warming. In keeping with its density, gray selenium is regarded as metallic, and it is the only form of selenium that conducts electricity. A slight distortion of the helical structure would produce a cubic metallic lattice.

The trend from nonmetallic to metallic character upon going down the group is exemplified by the conductivities of these elements. Sulfur is an insulator, selenium and tellurium are semiconductors, while the conductivity of polonium is typical of a true metal . In addition, the conductivities of sulfur, selenium, and tellurium increase with increasing temperature, behavior typical of nonmetals, whereas that of polonium increases at lower temperatures, typical of metals.

Species	Bond Order	Number of Unpaired e ⁻	O–O Distance (pm)*
O ₂ ⁺	2.5	1	112
O ₂	2	2	121
O ₂ ⁻	1.5	1	133
O ₂ ²⁻	1	0	149
density (g/cm ³) at 25°C		1.31 (g/L)	2.07

atomic radius (pm)	48	88
first ionization energy (kJ/mol)	1314	1000
normal oxidation state(s)	-2	+6, +4, -2

Oxidation state of elements (Group 16): The chalcogens

The group 16 elements, also known as the chalcogens have 6 valence electrons, and hence they can achieve noble gas configuration either by gaining 2 electrons or by sharing two electrons i.e., by forming M^{2-} ions, or forming two covalent bonds. Oxidation state of elements is defined as the number of electrons gained or lost to form a bond and its sign is the indication of ionic charge on the element. Oxygen is the most electronegative element after fluorine. The difference in electronegativity between metals and oxygen is generally very high. We know that ionic bond is formed when the difference in electronegativity of any two elements is very high. Thus, metals and oxygen combine to form metal oxide with oxygen attaining O^{2-} form, so the oxidation state of oxygen is mostly (-II). Electronegativity of chalcogens decreases down the group in periodic table. Other chalcogen elements like sulphur, selenium and tellurium reacts with more electronegative element of group 1, 2 and lanthanides i.e., the uppermost elements of group 1, 2 and lanthanides to form sulphides, selenides and tellurides. These compounds are the most stable compounds formed by these elements. Compounds formed above can be denoted as S^{2-} , Se^{2-} , and Te^{2-} . The electronegativity difference between the compounds (sulphides, selenides and tellurides) shows that they are at the borderline of 50% ionic and 50% covalent characters as in the case of PCl_5 .

Metallic character decreases as you move across the periodic table from left to right. This occurs as atoms more readily accept electrons to fill a valence shell than lose them to remove the unfilled shell. Metallic to lose as the atomic radius increases. The increase in atomic radius decreases attraction

between the positive nucleus and the negative electrons, causing the electrons to be held more loosely character increases as you move down the periodic table. This is due to the fact that the electrons become easier. **Oxidation states:** The elements of this group have a configuration of $ns^2 np^4$ in their valence shell, they may attain noble gas configuration either by gaining two electrons, forming M^{-2} , or by sharing two electrons, thus forming two covalent bonds. Hence, these elements show both negative and positive oxidation states. The common oxidation states exhibited by the elements of group 16 include minus two, plus two, plus four and plus six.

Symbol	Element	Oxidation States
${}^8\text{O}$	Oxygen	-2,-1,+1,+2
${}^{16}\text{S}$	Sulphur	-2,+2,+4,+6
${}^{34}\text{Se}$	Selenium	-2,+2,+4,+6
${}^{52}\text{Te}$	Tellurium	-2,+2,+4,+6
${}^{84}\text{Po}$	Polonium	+2,+4

The electro-negativity of oxygen is very high. It exhibits a negative oxidation state of -2 in all its metal oxides. In addition to -2 oxidation state, oxygen shows -1 oxidation state in peroxides and $-1/2$ oxidation state in superoxides.

Oxygen shows positive oxidation state only in its compounds with fluorine, since fluorine is more electro-negative than oxygen. It shows +2 oxidation state in OF_2 & +1 in O_2F_2 .

The other elements of the group, apart from exhibiting +2 oxidation state, also exhibit +4 and +6 oxidation states due to the availability of d-orbitals in their atoms. Oxygen differs considerably from the rest of the elements in its group. Due to its small size and high electro-negativity and the absence of d-orbitals in the valence shell.

Atomicity:

Oxygen is diatomic and gaseous, while the other elements exist as solids.

Formation of M^{-2} ions:

Oxygen, due to its high electro-negativity, shows negative oxidation state and does not show any positive oxidation state, except in OF_2 & O_2F_2 .

Maximum covalency:

Oxygen covalency is limited to two, but the covalency exceeds four in the other elements due to the availability of d-orbitals in them.

Hydrogen bond formation:

Because of its small size and high electro-negativity, oxygen forms strong hydrogen bonds. The other elements in the group have comparatively low electro-negativities, and do not form hydrogen bonds.

Chemical properties:

The elements of this group react with hydrogen to form hydrides of the type H_2E , where E could be oxygen, sulphur, selenium, tellurium or polonium.



Hydrogen Group 16 Element

Physical states of hydrides: Water is a colourless and odourless liquid, while the hydrides of all the other elements of the group are colourless, poisonous gases with unpleasant odours. The boiling point of the hydrides markedly decreases from water to hydrogen sulphide, and then increases. Water has an abnormally high boiling point because its molecules are associated with each other by means of hydrogen bonds in its solid as well as liquid states.

Acidic character of hydrides:

Acidic nature of hydrides increases from H_2O to H_2Te . The increase in acidic character is due to the decrease in the H-E bond dissociation enthalpy from H_2O to H_2Te . Except for water, all the other hydrides act as reducing agents. The reducing property of these hydrides increases from H_2S to H_2Te .

All the elements of this group react with oxygen to form dioxides and trioxides. Both these types of oxides are acidic in nature. Sulphur trioxide is the only important trioxide in this group. At room temperature, sulphur trioxide is a solid and exists in three distinct forms - alpha, beta and gamma.

Group 16 elements form a large number of halides of the type EX_6 , EX_4 and EX_2 , where E is a group 16 element and X is a halogen. Among hexahalides, only hexafluoride are stable. They undergo sp^3d^2 hybridisation, and hence, have octahedral geometry. SF_6 is extremely inert. Among the tetra fluorides SF_4 is a gas, SeF_4 is a liquid and TeF_4 is a solid. Except for selenium, all the other elements of this group form dichlorides and dibromides.

The trends of their properties in this group are interesting. Knowing the trend allows us to predict their reactions with other elements. Most trends are true for all groups of elements, and the group trends are due mostly to the size of

the atoms and number of electrons per atom. The trends are described below:

1. The metallic properties increase in the order oxygen, sulfur, selenium, tellurium, or polonium. Polonium is essentially a metal. It was discovered by M. Curie, who named it after her native country Poland.
2. Electronegativity, ionization energy (or ionization potential IP), and electron affinity decrease for the group as atomic weight increases.
3. The atomic radii and melting point increase.
4. Oxygen differs from sulfur in chemical properties due to its small size. The differences between O and S

are more than the differences between other members.

Metallic character increases down the group, with tellurium classified as a metalloid and polonium as a metal. Melting point, boiling point, density, atomic radius, and ionic radius all increase down the group. Ionization energy decreases down the group. The most common oxidation state is -2; however, sulfur can also exist at a +4 and +6 state, and +2, +4, and +6 oxidation states are possible for Se, Te, and Po.

Catenation

One of the most unusual properties of this family of elements is that of catenation or the bonding of an atom to another identical atom. Although oxygen shows this property only in the existence of ozone, sulfur is second only to carbon in exhibiting this mode of combination; the chalcogens beyond

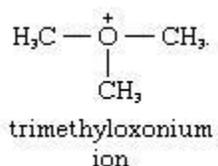
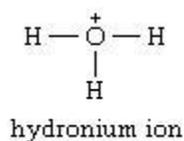
sulfur show it to diminishing degrees, polonium having no tendency to catenate. This type of bonding is found in the many ring systems of sulfur and selenium as well as in long zigzag chain structures. Catenation also occurs in the sulfanes and the metal polysulfides, compounds that have the formulas H_2S_x and M_2S_x , in which x may take the values of 2, 3, 4, or more, and M represents a singly charged metal ion. In comparing the catenation of sulfur atoms with that of carbon atoms, it may be noted that the number of molecular species having $(-S-)_x$ structures is very large, as is that of the analogous hydrocarbon compounds $(-CH_2-)_x$. The analogy between molecules containing rings of sulfur atoms and cyclic hydrocarbons is limited because only S_6 and S_8 have sufficient stability to permit proper comparison to be made. The general similarity extends to molecules of the form $Z(-S-)_xZ$ and $Z(-CH_2-)_xZ$, which are represented by compounds in which Z is H, SO_3H , and CF_3 .

Covalent links between sulfur atoms have some of the character of multiple bonds—that is, more than one pair of electrons is shared, at least to some extent. Such interactions may involve overlap of p orbitals of one sulfur atom with d orbitals of another. Although not all investigators feel alike on the subject of d-orbital participation in the bonding of sulfur compounds, partial occupation of these orbitals is consistent with certain properties such as the colours of S_8 and S_2 molecules, the rigidity of chains and rings of sulfur atoms, and other features of the chemistry of sulfur compounds.

Similarities of sulfur and oxygen are exhibited in certain compounds in which these elements interchange for one another. Examples include sulfates and thiosulfates (such as Na_2SO_4 and $Na_2S_2O_3$), phosphates and thiophosphates (containing the ions PO_4^{3-} , PO_3S^{3-} , $PO_2S_2^{3-}$, POS_3^{3-} , and PS_4^{3-}), and a similar series of arsenates and thioarsenates.

Ores of heavy metals often are found as sulfides, MS , and selenides, MSe , or even with MS_xSe_y structures. The similarity in structures as well as properties accounts for the chalcogens' being found together in nature.

The number of atoms to which an element of Group 16 can form covalent bonds increases from oxygen to sulfur. An oxygen atom usually combines with two other atoms, as in the compounds water (H_2O), oxygen fluoride (OF_2), or dimethyl ether ($H_3C-O-CH_3$); the unshared pairs of electrons and the partial negative charge on the oxygen atom in most of these compounds allows bonding to another atom, as in the hydronium ion or trimethyloxonium ion.



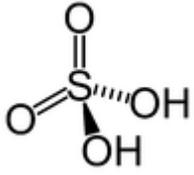
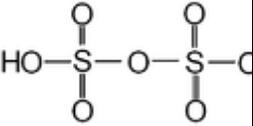
Heavier members of the group associate or coordinate with other atoms or groups of atoms in numbers commensurate with the size of both the chalcogen and the coordinating group. Thus, sulfur tetrafluoride (SF_4) and sulfur hexafluoride (SF_6) are stable compounds, although sulfur hexaiodide (SI_6) is not known because of the very large size of the iodine atom. A closely related property is that of anionic complex formation: there is little evidence for the ion SF_6^{2-} , but there are ions such as $TeCl_6^{2-}$, TeF_6^{2-} , and

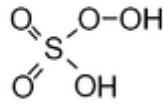
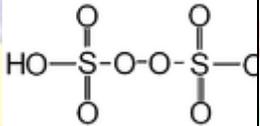
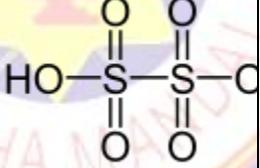
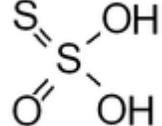
Sulfur oxoacid

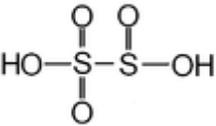
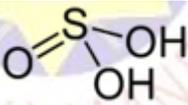
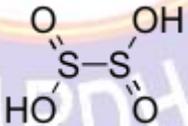
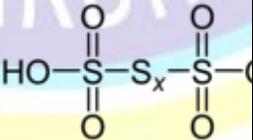
The sulfur oxoacids are chemical compounds that contain sulfur, oxygen and hydrogen. The best known and most important industrially is sulfuric acid. Sulfur has a number of oxoacids; however, some of these are known only

from their salts (these are shown in italics in the table below). The acids that have been characterised contain a variety of structural features, for example:

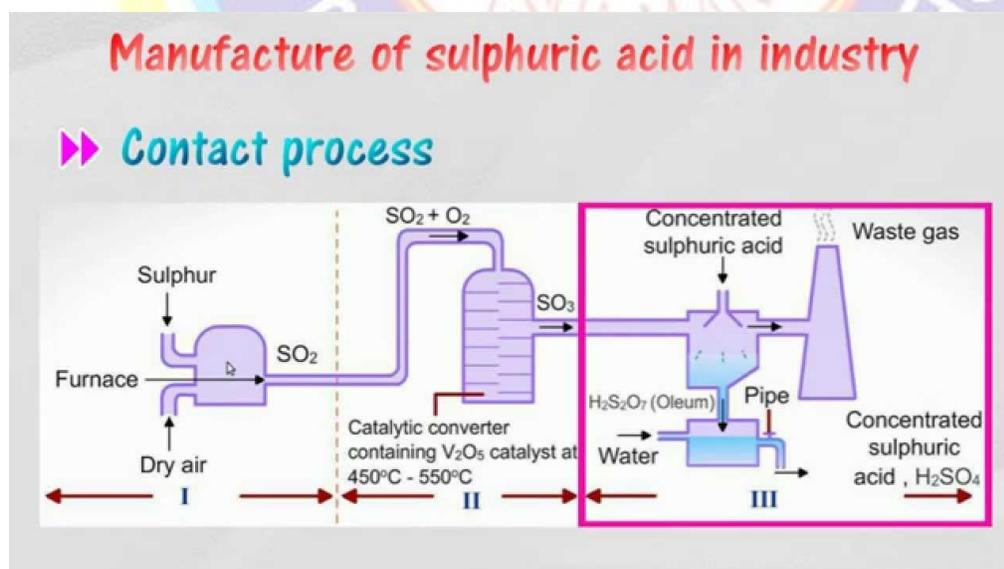
- tetrahedral sulfur when coordinated to oxygen
- terminal and bridging oxygen atoms
- terminalperoxo groups
- terminal S=S
- chains of (-S-)

Acid	Formula	Oxidation state(s)	Structure	Related anions	Notes
<u>Sulfuric acid</u>	H ₂ SO ₄	VI		<u>Sulfate</u> , SO ₄ ²⁻ and hydrogen sulfate commonly known as <u>bisulfate</u> , HSO ₄ ⁻	Best known and industrially significant.
Polysulfuric acids including <u>disulfuric acid</u> or pyrosulfuric acid	H ₂ SO ₄ .nS O ₃	VI		Disulfate (commonly known as <u>pyrosulfate</u>), S ₂ O ₇ ²⁻ and trisulfate,	Pure disulfuric acid melts at 36 °C. Present in

				$S_3O_{10}^{2-}$	fuming sulfuric acid, <u>oleum</u> . Examples known for n=1,2.
<u>Peroxymonosulfuric acid</u>	H_2SO_5	VI		<u>Peroxymonosulfate</u> , $OOSO_3^{2-}$	"Caro's acid", a solid melting at 45 °C
<u>Peroxydisulfuric acid</u>	$H_2S_2O_8$	VI		<u>Peroxydisulfate</u> , $O_3SOOSO_3^{2-}$	A solid melting at 65 °C.
<u>Dithionic acid</u>	$H_2S_2O_6$	V		<u>Dithionate</u> , $O_3SSO_3^{2-}$	Not isolated in pure form, only concentrated solutions have been prepared
<u>Thiosulfuric acid</u>	$H_2S_2O_3$	-II (for the terminal sulfur)		<u>Thiosulfate</u> , $S_2O_3^{2-}$ <u>Hydrogen thiosulfate</u> $HS_2O_3^-$	Aqueous solutions decompose.

		, VI (for the central atom)		(ammonium salt prepared in anhydrous methanol at $-80\text{ }^{\circ}\text{C}^{[1]}$)	
<u>Disulfurous acid</u> or <u>pyrosulfurous acid</u>	$\text{H}_2\text{S}_2\text{O}_5$	V (of the sulfur atom bonded to 3 oxygen atoms), III (of other sulfur atom)		Disulfite commonly known as <u>metabisulfite</u> , $\text{S}_2\text{O}_5^{2-}$	Not known.
<u>Sulfurous acid</u>	H_2SO_3	IV		<u>Bisulfite</u> , HSO_3^- and <u>sulfite</u> , SO_3^{2-}	Not known.
<u>Dithionous acid</u>	$\text{H}_2\text{S}_2\text{O}_4$	III		<u>Dithionite</u> , $\text{O}_2\text{SSO}_2^{2-}$	Not known.
<u>Polythionic acids</u>	$\text{H}_2\text{S}_x\text{O}_6$	0 (for the bridging S atoms), V (for the terminal		<u>Polythionates</u> , $\text{O}_3\text{S}(\text{S}_{x-2})\text{SO}_3^{2-}$. Example <u>trithionate</u> , <u>tetrathionate</u> , <u>pentathionate</u> , <u>hexathionate</u> , <u>heptathionate</u> ,	Examples known with $x=3, 4, 5, 6, 7, 8, 10, 12, 14$.

		I central S atoms)		<u>octathionate</u> , <u>nonathionate</u> , <u>decathionate</u> , <u>undecathionate</u> , <u>dodecathionate</u> , <u>tridecathionate</u> and <u>tetradecathionate</u> e.	
<u>Thiosulfurous acid</u>	$\text{H}_2\text{S}_2\text{O}_2$	-I (for the exterior sulfur atom), III (for the central atom)	$\begin{array}{c} \text{O} \\ \parallel \\ \text{HO}-\text{S}-\text{SH} \end{array}$	<u>Thiosulfites</u>	Not known



Group 17 Element

The halogens or halogen elements are a group in the periodic table consisting of five chemically related elements: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). The artificially created element 117 (ununseptium) may also be a halogen. In the modern IUPAC nomenclature, this group is known as group 17.

The name 'halogen' means 'salt-producing'. When halogens react with metals they produce a wide range of salts, including calcium fluoride, sodium chloride (common salt), silver bromide and potassium iodide.

The group of halogens is the only periodic table group that contains elements in three of the four main states of matter at standard temperature and pressure. All of the halogens form acids when bonded to hydrogen. Most halogens are typically produced from minerals or salts. The middle halogens, that is chlorine, bromine and iodine, are often used as disinfectants. Organobromides are the most important class of flame retardants. Elemental halogens are lethally to dangerously toxic.

Characteristics

The halogens show trends in chemical bond energy moving from top to bottom of the periodic table column with fluorine deviating slightly. (It follows trend in having the highest bond energy in compounds with other atoms, but it has very weak bonds within the diatomic F_2 molecule.) This means, as you go down the periodic table, the reactivity of the element will decrease because of the increasing size of the atoms.

Halogens are highly reactive, and as such can be harmful or lethal to biological organisms in sufficient quantities. This high reactivity is due to the

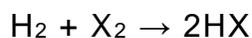
high electronegativity of the atoms due to their high effective nuclear charge. Because the halogens have seven valence electrons in their outermost energy level, they can gain an electron by reacting with atoms of other elements to satisfy the octet rule. Fluorine is one of the most reactive elements, attacking otherwise-inert materials such as glass, and forming compounds with the usually inert noble gases. It is a corrosive and highly toxic gas. The reactivity of fluorine is such that, if used or stored in laboratory glassware, it can react with glass in the presence of small amounts of water to form silicon tetrafluoride (SiF_4). Thus, fluorine must be handled with substances such as Teflon (which is itself an organofluorine compound), extremely dry glass, or metals such as copper or steel, which form a protective layer of fluoride on their surface.

The high reactivity of fluorine allows paradoxically some of the strongest bonds possible, especially to carbon. For example, Teflon is fluorine bonded with carbon and is extremely resistant to thermal and chemical attack and has a high melting point.

Diatomic halogen molecules

The halogens form homo nuclear diatomic molecules (not proven for astatine). Due to relatively weak intermolecular forces, chlorine and fluorine form part of the group known as "elemental gases". The elements become less reactive and have higher melting points as the atomic number increases. The higher melting points are caused by stronger London dispersion forces resulting from more electrons.

Hydrogen halides All of the halogens have been observed to react with hydrogen to form hydrogen halides. For fluorine, chlorine, and bromine, this reaction is in the form of:



However, hydrogen iodide and hydrogen astatide can split back into their constituent elements

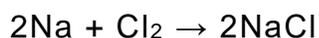
The hydrogen-halogen reactions get gradually less reactive toward the heavier halogens. A fluorine-hydrogen reaction is explosive even when it is dark and cold. A chlorine-hydrogen reaction is also explosive, but only in the presence of light and heat. A bromine-hydrogen reaction is even less explosive; it is explosive only when exposed to flames. Iodine and astatine only partially react with hydrogen, forming equilibria.

All halogens form binary compounds with hydrogen known as the hydrogen halides: hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen bromide (HBr), hydrogen iodide (HI), and hydrogen astatide (HAt). All of these compounds form acids when mixed with water. Hydrogen fluoride is the only hydrogen halide that forms hydrogen bonds. Hydrochloric acid, hydrobromic acid, hydroiodic acid, and hydroastatic acid are all strong acids, but hydrofluoric acid is a weak acid.

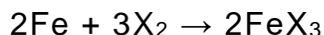
All of the hydrogen halides are irritants. Hydrogen fluoride and hydrogen chloride are highly acidic. Hydrogen fluoride is used as an industrial chemical, and is highly toxic, causing pulmonary edema and damaging cells. Hydrogen chloride is also a dangerous chemical. Breathing in gas with more than fifty parts per million of hydrogen chloride can cause death in humans. Hydrogen bromide is even more toxic and irritating than hydrogen chloride. Breathing in gas with more than thirty parts per million of hydrogen bromide can be lethal to humans. Hydrogen iodide, like other hydrogen halides, is toxic.

Metal halides

All the halogens are known to react with sodium to form sodium fluoride, sodium chloride, sodium bromide, sodium iodide, and sodium astatide. Heated sodium's reaction with halogens produces bright-orange flames. Sodium's reaction with chlorine is in the form of:



Iron reacts with fluorine, chlorine, and bromine to form Iron(III) halides. These reactions are in the form of:



However, when iron reacts with iodine, it forms only iron(II) iodide.

Iron wool can react rapidly with fluorine to form the white compound iron(III) fluoride even in cold temperatures. When chlorine comes into contact with heated iron, they react to form the black iron (III) chloride. However, if the reaction conditions are moist, this reaction will instead result in a reddish-brown product. Iron can also react with bromine to form iron(III) bromide. This compound is reddish-brown in dry conditions. Iron's reaction with bromine is less reactive than its reaction with fluorine or chlorine. Hot iron can also react with iodine, but it forms iron(II) iodide. This compound may be gray, but the reaction is always contaminated with excess iodine, so it is not known for sure. Iron's reaction with iodine is less vigorous than its reaction with the lighter halogens

Interhalogen compounds

Interhalogen compounds are in the form of XY_n where X and Y are halogens and n is one, three, five, or seven. Interhalogen compounds contain at most two different halogens. Large interhalogens, such as ClF_3 can be produced by a reaction of a pure halogen with a smaller interhalogen such as ClF. All interhalogens except IF_7 can be produced by directly combining pure halogens in various conditions.

Interhalogens are typically more reactive than all diatomic halogen molecules except F_2 because interhalogen bonds are weaker. However, the chemical properties of interhalogens are still roughly the same as those of diatomic halogens. Many interhalogens consist of one or more atoms of fluorine bonding to a heavier halogen. Chlorine can bond with up to 3 fluorine atoms, bromine can bond with up to five fluorine atoms, and iodine can bond with up to seven fluorine atoms. Most interhalogen compounds are covalent gases. However, there are some interhalogens that are liquids, such as BrF_3 , and many iodine-containing interhalogens are solids.

Organohalogen compounds

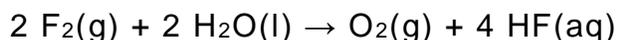
Many synthetic organic compounds such as plastic polymers, and a few natural ones, contain halogen atoms; these are known as halogenated compounds or organic halides. Chlorine is by far the most abundant of the halogens in seawater, and the only one needed in relatively large amounts (as chloride ions) by humans. For example, chloride ions play a key role in brain function by mediating the action of the inhibitory transmitter GABA and are also used by the body to produce stomach acid. Iodine is needed in trace amounts for the production of thyroid hormones such as thyroxine. Organohalogens are also synthesized through the nucleophilic abstraction reaction.

Polyhalogenated compounds

Polyhalogenated compounds are industrially created compounds substituted with multiple halogens. Many of them are very toxic and bioaccumulate in humans, and have a very wide application range. They include PCBs, PBDEs, and perfluorinated compounds (PFCs), as well as numerous other compounds.

Reactions with water

Fluorine reacts vigorously with water to produce oxygen (O₂) and hydrogen fluoride (HF):



Chlorine has maximum solubility of ca. 7.1 g Cl₂ per kg of water at ambient temperature (21 °C). Dissolved chlorine reacts to form hydrochloric acid (HCl) and hypochlorous acid, a solution that can be used as a disinfectant or bleach:



Bromine has a solubility of 3.41 g per 100 g of water, but it slowly reacts to form hydrogen bromide (HBr) and hypobromous acid (HBrO):



Iodine, however, is minimally soluble in water (0.03 g/100 g water at 20 °C) and does not react with it. However, iodine will form an aqueous solution in

the presence of iodide ion, such as by addition of potassium iodide (KI), because the triiodide ion is formed.

Isotopes

Fluorine has one stable and naturally occurring isotope, fluorine-19. However, there are trace amounts in nature of the radioactive isotope fluorine-23, which occurs via cluster decay of protactinium-231. A total of eighteen isotopes of fluorine have been discovered, with atomic masses ranging from 14 to 31. Chlorine has two stable and naturally occurring isotopes, chlorine-35 and chlorine-37. However, there are trace amounts in nature of the isotope chlorine-36, which occurs via spallation of argon-36. A total of 24 isotopes of chlorine have been discovered, with atomic masses ranging from 28 to 51.

There are two stable and naturally occurring isotopes of bromine, bromine-79 and bromine-81. A total of 32 isotopes of bromine have been discovered, with atomic masses ranging 67 to 98. There is one stable and naturally occurring isotope of iodine, iodine-127. However, there are trace amounts in nature of the radioactive isotope iodine-129, which occurs via spallation and from the radioactive decay of uranium in ores. Several other radioactive isotopes of iodine have also been created naturally via the decay of uranium. A total of 38 isotopes of iodine have been discovered, with atomic masses ranging from 108 to 145.

There are no stable isotopes of astatine. However, there are three naturally occurring radioactive isotopes of astatine produced via radioactive decay of uranium, neptunium, and plutonium. These isotopes are astatine-215, astatine-217, and astatine-219. A total of 31 isotopes of astatine have been discovered, with atomic masses ranging from 193 to 223.

Group 17: General Properties of Halogens

The halogens are located on the left of the noble gases on the periodic table. These five toxic, non-metallic elements make up Group 17 of the periodic table and consist of: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Although astatine is radioactive and only has short-lived isotopes, it behaves similar to iodine and is often included in the halogen group. Because the halogen elements have seven valence electrons, they only require one additional electron to form a full octet. This characteristic makes them more reactive than other non-metal groups.

Introduction

Halogens form diatomic molecules (of the form X_2 , where X denotes a halogen atom) in their elemental states. The bonds in these diatomic molecules are non-polar covalent single bonds. However, halogens readily combine with most elements and are never seen uncombined in nature. As a general rule, fluorine is the most reactive halogen and astatine is the least reactive. All halogens form Group 1 salts with similar properties. In these compounds, halogens are present as halide anions with charge of -1 (e.g. Cl^- , Br^- , etc.). Replacing the -ine ending with an -ide ending indicates the presence of halide anions; for example, Cl^- is named "chloride." In addition, halogens act as oxidizing agents—they exhibit the property to oxidize metals. Therefore, most of the chemical reactions that involve halogens are oxidation-reduction reactions in aqueous solution. The halogens often form single bonds, when in the -1 oxidation state, with carbon or nitrogen in organic compounds. When a halogen atom is substituted for a covalently-bonded hydrogen atom in an organic compound, the prefix halo- can be used in a general sense, or the prefixes fluoro-, chloro-, bromo-, or iodo- can be used for specific halogen substitutions. Halogen elements can cross-link to form diatomic molecules with polar covalent single bonds.

Chlorine (Cl_2) was the first halogen to be discovered in 1774, followed by iodine (I_2), bromine (Br_2), fluorine (F_2), and astatine (At, discovered last in 1940). The name "halogen" is derived from the Greek roots hal- ("salt") and -gen ("to form"). Together these words combine to mean "salt former", referencing the fact that halogens form salts when they react with metals. Halite is the mineral name for rock salt, a natural mineral consisting essentially of sodium chloride (NaCl). Lastly, the halogens are also relevant in daily life, whether it be the fluoride that goes in toothpaste, the chlorine that disinfects drinking water, or the iodine that facilitates the production of thyroid hormones in one's body.

Elements

A. **Fluorine** - Fluorine has an atomic number of 9 and is denoted by the symbol F. Elemental fluorine was first discovered in 1886 by isolating it from hydrofluoric acid. Fluorine exists as a diatomic molecule in its free state (F_2) and is the most abundant halogen found in the Earth's crust. Fluorine is the most electronegative element in the periodic table. It appears as a pale yellow gas at room temperature. Fluorine also has a relatively small atomic radius. Its oxidation state is always -1 except in its elemental, diatomic state (in which its oxidation state is zero). Fluorine is extremely reactive and reacts directly with all elements except helium (He), neon (Ne) and argon (Ar). In H_2O solution, hydrofluoric acid (HF) is a weak acid. Although fluorine is highly electronegative, its electronegativity does not determine its acidity; HF is a weak acid due to the fact that the fluoride ion is basic ($\text{pH} > 7$). In addition, fluorine produces very powerful oxidants. For example, fluorine can react with the noble gas xenon and form the strong oxidizing agent Xenon Difluoride (XeF_2). There are many uses for fluorine, which will be discussed in Part VI of this article.

B. **Chlorine** - Chlorine has the atomic number 17 and the chemical symbol Cl. Chlorine was discovered in 1774 by extracting it from hydrochloric acid. In its elemental state, it forms the diatomic molecule Cl₂. Chlorine exhibits multiple oxidation states, such as -1, +1, 3, 5, and 7. At room temperature it appears as a light green gas. Since the bond that forms between the two chlorine atoms is weak, the Cl₂ molecule is very reactive. Chlorine reacts with metals to produce salts called chlorides. Chloride ions are the most abundant ions that dissolve in the ocean. Chlorine also has two isotopes: ³⁵Cl and ³⁷Cl. Sodium chloride is the most prevalent compound of the chlorides.

C. **Bromine** - Bromine has an atomic number of 35 with a symbol of Br. It was first discovered in 1826. In its elemental form, it is the diatomic molecule Br₂. At room temperature, bromine is a reddish- brown liquid. Its oxidation states vary from -1, +1, 3, 4 and 5. Bromine is more reactive than iodine, but not as reactive as chlorine. Also, bromine has two isotopes: ⁷⁹Br and ⁸¹Br. Bromine consists of bromide salts, which have been found in the sea. The world production of bromide has increased significantly over the years, due to its access and longer existence. Like all of the other halogens, bromine is an oxidizing agent, and is very toxic.

D. **Iodine** - Iodine has the atomic number 53 and symbol I. Iodine has oxidation states -1, +1, 5 and 7. Iodine exists as a diatomic molecule, I₂, in its elemental state. At room temperature, it appears as a violet solid. Iodine has one stable isotope: ¹²⁷I. It was first discovered in 1811 through the use of seaweed and sulfuric acid. Currently, iodide ions can be isolated in seawater. Although iodine is not very soluble in water, the solubility may increase if particular iodides are mixed in the solution. Iodine has many important roles in life, including thyroid hormone production. This will be discussed in Part VI of the text.

E. **Astatine** - Astatine is a radioactive element with an atomic number of 85 and symbol At. Its possible oxidation states include: -1, +1, 3, 5 and 7. It is the only halogen that is not a diatomic molecule and it appears as a black, metallic solid at room temperature. Astatine is a very rare element, so there is not that much known about this element. In addition, astatine has a very short radioactive half-life, no longer than a couple of hours. It was discovered in 1940 by synthesis. Also, it is thought that astatine is similar to iodine. However, these two elements are assumed to differ by their metallic character.

F.

Halogen	Electronic Configuration
Fluorine	$1s^2 2s^2 2p^5$
Chlorine	$[\text{Ne}]3s^2 3p^5$
Bromine	$[\text{Ar}]3d^{10} 4s^2 4p^5$
Iodine	$[\text{Kr}]4d^{10} 5s^2 5p^5$
Astatine	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^5$

Melting and Boiling Points: increases down the group

The melting and boiling points increase down the group because of the van der Waals forces. The size of the molecules increases down the group. This increase in size means an increase in the strength of the van der Waals forces.

$F < Cl < Br < I < At$

Melting and Boiling Points of Halogens		
Halogen	Melting Point (°C)	Boiling Point (°C)
Fluorine	-220	-188
Chlorine	-101	-35
Bromine	-7.2	58.8
Iodine	114	184
Astatine	302	337

Atomic Radius: increases down the group

The size of the nucleus increases down a group (F < Cl < Br < I < At) because the numbers of protons and neutrons increase. In addition, more energy levels are added with each period. This results in a larger orbital, and therefore a longer atomic radius.

Halogen	Covalent Radius (pm)	Ionic (X ⁻) radius (pm)
Fluorine	71	133
Chlorine	99	181
Bromine	114	196
Iodine	133	220
Astatine	150	

Ionization Energy: decreases down the group

If the outer valence electrons are not near the nucleus, it does not take as much energy to remove them. Therefore, the energy required to pull off the outermost electron is not as high for the elements at the bottom of the group since there are more energy levels. Also, the high ionization energy makes

the element appear non-metallic. Iodine and astatine display metallic properties, so ionization energy decreases down the group (At < I < Br < Cl < F).

Halogen	First Ionization Energy (kJ/mol)
Fluorine	1681
Chlorine	1251
Bromine	1140
Iodine	1008
Astatine	890±40

Electronegativity: decreases down the group

The number of valence electrons in an atom increases down the group due to the increase in energy levels at progressively lower levels. The electrons are progressively further from the nucleus; therefore, the nucleus and the electrons are not as attracted to each other. An increase in shielding is observed. Electronegativity therefore decreases down the group (At < I < Br < Cl < F).

Halogen	Electronegativity
Fluorine	4.0
Chlorine	3.0
Bromine	2.8
Iodine	2.5
Astatine	2.2

Electron Affinity: decreases down the group

Since the atomic size increases down the group, electron affinity generally decreases (At < I < Br < F < Cl). An electron will not be as attracted to the nucleus, resulting in a low electron affinity. However, fluorine has a lower

electron affinity than chlorine. This can be explained by the small size of fluorine, compared to chlorine.

Halogen	Electron Affinity (kJ/mol)
Fluorine	-328.0
Chlorine	-349.0
Bromine	-324.6
Iodine	-295.2

Reactivity of Elements: decreases down the group

The reactivities of the halogens decrease down the group ($\text{At} < \text{I} < \text{Br} < \text{Cl} < \text{F}$). This is due to the fact that atomic radius increases in size with an increase of electronic energy levels. This lessens the attraction for valence electrons of other atoms, decreasing reactivity. This decrease also occurs because electronegativity decreases down a group; therefore, there is less electron "pulling." In addition, there is a decrease in oxidizing ability down the group.

Hydrogen Halides and Halogen Oxoacids

Hydrogen Halides

A halide is formed when a halogen reacts with another, less electronegative element to form a binary compound. Hydrogen, for example, reacts with halogens to form halides of the form HX:

- Hydrogen Fluoride: HF
- Hydrogen Chloride: HCl

- Hydrogen Bromide: HBr
- Hydrogen Iodide: HI

Hydrogen halides readily dissolve in water to form hydrohalic (hydrofluoric, hydrochloric, hydrobromic, hydroiodic) acids. The properties of these acids are given below:

- The acids are formed by the following reaction: $\text{HX (aq)} + \text{H}_2\text{O (l)} \rightarrow \text{X}^- \text{(aq)} + \text{H}_3\text{O}^+ \text{(aq)}$
- All hydrogen halides form strong acids, except HF
- The acidity of the hydrohalic acids increases as follows: $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$

Hydrofluoric acid can etch glass and certain inorganic fluorides over a long period of time.

It may seem counterintuitive to say that HF is the weakest hydrohalic acid because fluorine has the highest electronegativity. However, the H-F bond is very strong; if the H-X bond is strong, the resulting acid is weak. A strong bond is determined by a short bond length and a large bond dissociation energy. Of all the hydrogen halides, HF has the shortest bond length and largest bond dissociation energy.

Halogen Oxoacids A halogen oxoacid is an acid with hydrogen, oxygen, and halogen atoms. The acidity of an oxoacid can be determined through analysis of the compound's structure. The halogen oxoacids are given below:

- Hypochlorous Acid: HOCl
- Chlorous Acid: HClO₂
- Chloric Acid: HClO₃
- Perchloric Acid: HClO₄
- Hypobromous Acid: HOBr
- Bromic Acid: HBrO₃
- Perbromic Acid: HBrO₄
- Hypoiodous Acid: HOI
- Iodic Acid: HIO₃
- Metaperiodic Acid: HIO₄; H₅IO₆

In each of these acids, the proton is bonded to an oxygen atom; therefore, comparing proton bond lengths is not useful in this case. Instead, electronegativity is the dominant factor in the oxoacid's acidity. Acidic strength increases with more oxygen atoms bound to the central atom.

V. Oxidation States of Halogens in Compounds

As a general rule, halogens usually have an oxidation state of -1. However, if the halogen is bonded to oxygen or to another halogen, it can adopt different states: the -2 rule for oxygen takes precedence over this rule; in the case of

two different halogens bonded together, the more electronegative atom takes precedence and adopts the -1 oxidation state.

Example 1.1: Iodine Chloride (ICl)

Chlorine has an oxidation state of -1, and iodine will have an oxidation of +1. Chlorine is more electronegative than iodine, therefore giving it the -1 oxidation state.

Example 1.2: Perbromic Acid (HBrO₄)

Oxygen has a total oxidation state of -8 (-2 charge x 4 atoms = -8 total charge). Hydrogen has a total oxidation state of +1. Adding both of these values together, the total oxidation state of the compound so far is -7. Since the final oxidation state of the compound must be 0, bromine's oxidation state is +7.

One third exception to the rule is this: if a halogen exists in its elemental form (X₂), its oxidation state is zero.

Oxidation States of Halogens	
Halogen	Oxidation States in <u>Compounds</u>
Fluorine	(always) -1*
Chlorine	-1, +1, +3, +5, +7
Bromine	-1, +1, +3, +4, +5
Iodine	-1, +1, +5, +7
Astatine	-1, +1, +3, +5, +7

Applications of Halogens : Fluorine: Although fluorine is very reactive, it serves many industrial purposes. For example, it is a key component of the plastic

ticpolytetrafluoroethylene (called Teflon-TFE by the DuPont company) and certain other polymers, often referred to as fluoropolymers. Chlorofluorocarbons (CFCs) are organic chemicals that were used as refrigerants and propellants in aerosols before growing concerns about their possible environmental impact led to their discontinued use. Hydrochlorofluorocarbons (HFCs) are now used instead. Fluoride is also added to toothpaste and drinking water to help reduce tooth decay. Fluorine also exists in the clay used in some ceramics. Fluorine is associated with generating nuclear power as well. In addition, it is used to produce fluoroquinolones, which are antibiotics. Below is a list of some of fluorine's important inorganic compounds.

Compound	Uses
Na_3AlF_6	Manufacture of aluminum
BF_3	Catalyst
CaF_2	Optical components, manufacture of HF, metallurgical flux
ClF_3	Fluorinating agent, reprocessing nuclear fuels
HF	Manufacture of F_2 , AlF_3 , Na_3AlF_6 , and fluorocarbons
LiF	Ceramics manufacture, welding, and soldering
NaF	Fluoridating water, dental prophylaxis, insecticide
SF_6	Insulating gas for high-voltage electrical equipment
SnF_2	Manufacture of toothpaste
UF_6	Manufacture of uranium fuel for nuclear reactors

Chlorine: Chlorine has many industrial uses. It is used to disinfect drinking water and swimming pools. Sodium hypochlorite (NaClO) is the main component of bleach. Hydrochloric acid, sometimes called muriatic acid, is a commonly used acid in industry and laboratories. Chlorine is also present in polyvinyl chloride (PVC), and several other polymers. PVC is used in wire insulation, pipes, and electronics. In addition, chlorine is very useful in the pharmaceutical industry. Medicinal products containing chlorine are used to

treat infections, allergies, and diabetes. The neutralized form of hydrochloride is a component of many medications. Chlorine is also used to sterilize hospital machinery and limit infection growth. In agriculture, chlorine is a component of many commercial pesticides: DDT (dichlorodiphenyltrichloroethane) was used as an agricultural insecticide, but its use was discontinued.

Bromine: Bromine is used in flame retardants because of its fire-resistant properties. It also found in the pesticide methyl bromide, which facilitates the storage of crops and eliminates the spread of bacteria. However, the excessive use of methyl bromide has been discontinued due to its impact on the ozone layer. Bromine is involved in gasoline production as well. Other uses of bromine include the production of photography film, the content in fire extinguishers, and drugs treating pneumonia and Alzheimer's disease.

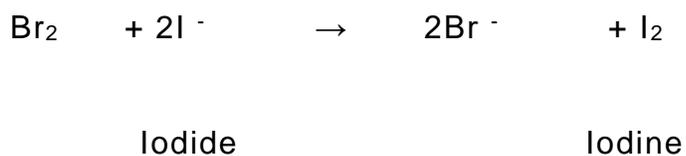
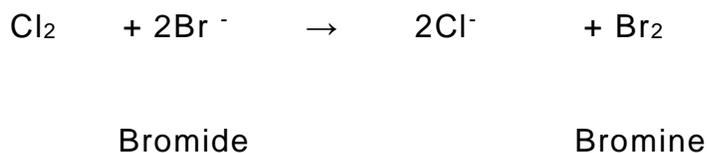
Iodine: Iodine is important in the proper functioning of the thyroid gland of the body. If the body does not receive adequate iodine, a goiter (enlarged thyroid gland) will form. Table salt now contains iodine to help promote proper functioning of the thyroid hormones. Iodine is also used as an antiseptic. Solutions used to clean open wounds likely contain iodine, and it is commonly found in disinfectant sprays. In addition, silver iodide is important for photography development.

Astatine: Because astatine is radioactive and rare, there are no proven uses for this halogen element. However, there is speculation that this element could aid iodine in regulating the thyroid hormones. Also, ^{211}At has been used in mice to aid the study of cancer.

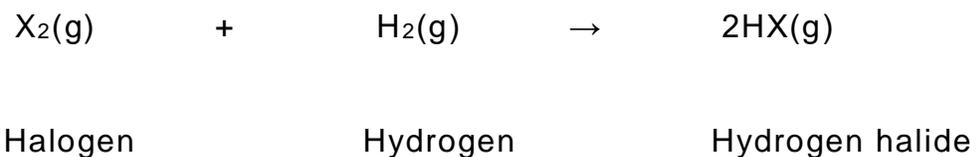
Chemical Properties Group -17 elements are more reactive than all other elements in the periodic table. They react with metals and non-metals to form halides. The reactivity of these elements decreases down the group.

All these elements are ready to accept an electron from other elements. Hence, they are all good oxidising agents. The oxidising capacity of these elements decreases down the group. So fluorine is the strongest oxidising agent among them.

Fluorine oxidises other halide ions. In general, a halogen oxidises higher halides to their respective halogens.



When these elements react with hydrogen gives hydrogen halides.





Hydrogen

Water

Hydrogen acid X = F, Cl, Br, I

These hydrogen halides react with water to give hydrohalic acids.

The acidic strength and bond lengths of these halides increases and bond dissociation energy decrease from top to bottom.

The melting and boiling points of these halides gradually increase from top to bottom except for hydrogen fluoride due to the high electro-negativity and small atomic size of fluorine.

Halogens form many oxides with oxygen. The stability of these oxides increases down the group.

Fluorine forms only two oxides - OF_2 and O_2F_2 . These two are thermally stable at room temperature, and both are fluorinating agents due to the high electro-negativity of fluorine. Chlorine forms the oxides Cl_2O , ClO_2 , Cl_2O_6 and Cl_2O_7 . All these are powerful bleaching agents. ClO_2 is used as a bleaching agent in the wood pulp, water purification and paper industries.

Bromine forms the oxides Br_2O , and BrO_2 . All these are less stable, exist at very low temperatures and act as powerful oxidising agents.

Iodine forms I_2O_4 , I_2O_5 and I_2O_7 . All these are solids and are insoluble in water. Among these, I_2O_5 is a good oxidising agent.

Halogens react with metals to give metal halides.

Ex: Chlorine reacts with Calcium to give calcium chloride. All these metal halides are ionic in nature. The ionic nature of monovalent metal halides decreases from fluorine to iodine.

Due to electro-negative difference and atomic size variations, these halogens combine amongst themselves to form complexes known as inter-halogen compounds of the type AX, AX₃, AX₅ and AX₇.

Inter halogen Compounds			
AX	AX ₃	AX ₅	AX ₇
ClF	ClF ₃	ClF ₅	-
BrF, BrCl	BrF ₃	BrF ₅	-
ICl	ICl ₃	ICl ₅	ICl ₇

Anomalous behaviour of fluorine:

The anomalous behaviour in properties like ionisation energy, electro-negativity, bond dissociation energy, electrode potentials, electron-gaining enthalpy, ionic and covalent radii, melting point, and boiling point is due to the high electro-negativity, small atomic size, low bond dissociation energy and no availability of d-orbitals in the valence shell of Fluorine.

Trends in Properties of Group 17 (VIIA) Elements

- All Group 17 (VIIA) elements have 7 valence electrons (7 electrons in the highest energy level).
- Atomic radius increases down the Group as successive 'electron shells' (energy levels) are filled.

- Electronegativity (the relative tendency shown by a bonded atom to attract electrons to itself) decreases down the group as the elements become more metallic in nature. (Typically, metals have low electronegativity, little ability to attract electrons, while non-metals have high electronegativity, greater ability to attract electrons). The reactivity of Group 17 (VIIA) elements is related to the element's ability to attract electrons, so the greater the electronegativity, the more reactive the Halogen. So, chemical reactivity of Group 17 (VIIA) elements decreases down the Group, from the most reactive (Fluorine) to the least reactive (Iodine).
- Down the Group, first ionization energy (the energy required to remove 1 electron from the gaseous atom) decreases. As the atomic radius increases and the electron is further from the nucleus it is less attracted to the nucleus (electron is said to be 'shielded').
- Melting point and boiling point increase down the Group as the elements become more metallic in nature.
- There is a gradation in color going down the group, the elements become darker in colour as they become more metallic in nature. Similarly there is a gradation in physical appearance at STP, from gas to liquid to solid, as the elements become more metallic in nature.

Interhalogen Compounds

Interhalogen compounds are compounds formed when halogen group elements react with each other. In other words it is a molecule which consists of two or more different elements of group 17. There are four types of interhalogen compounds:

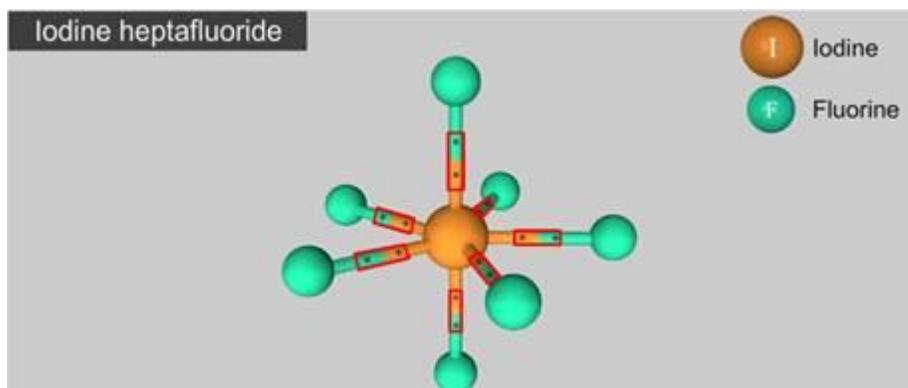
- Diatomic interhalogens (AX)

- Tetratomic interhalogens (AX_3)
- Hexatomicinterhalogens(AX_5)
- Octatomicinterhalogens (AX_7)

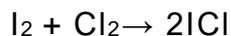
A halogen with large size and high electropositivity reacts with an element of group 17 with small size and lower electropositivity. As the ratio of radius of larger and smaller halogen increases, the number of atoms in a molecule also increases.

Preparation of Interhalogen compounds:

These molecules are formed due to the direct combination or by the action of a group 17 element with a lower interhalogen compound under specific conditions. For example: At 437K, chlorine reacts with fluorine of equal volume to form ClF. This method is widely used in the production of group 17 fluorides.



Interhalogen Compounds



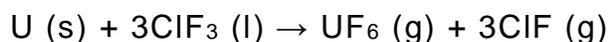
Properties of Interhalogen Compounds:

- These molecules are covalent and diamagnetic in nature.
- The bonds formed between these compounds are more reactive than diatomic halogen bonds.
- The physical properties of these molecules are transitional between its constituents.
- The molecular structure of AX_3 molecules is bent T shaped, an AX_5 molecule is square or pyramidal and the structure of AX_7 is bipyramidal or pentagonal.
- The bond length depends upon the size of the constituent halogens.
- The molecule which consists of lighter group 17 elements is fairly colourless but one which is made up of higher halogens is deeper in colour which is due to the rise in the molecular weight.

Uses of Interhalogen Compounds:

- These are used as non-aqueous solvents.
- They are used as a catalyst in few reactions.

- UF₆ which is used in the enrichment of ²³⁵U is produced by using ClF₃ and BrF₃.



- These are used as fluorinating compounds.

Valence-shell electron-pair repulsion theory, VSEPR

The premise of the VSEPR is that the valence electron pairs surrounding an atom mutually repel each other, and will therefore adopt an arrangement that minimizes this repulsion, thus determining the molecular geometry. The number of electron pairs surrounding an atom, both bonding and nonbonding, is called its steric number. The VSEPR theory thus provides a simple model for predicting the shapes of such species, in particular for main group compounds. The model combines original ideas of Sidgwick and Powell (1940's) with extensions developed by Nyholm and Gillespie (1950's).

- Each valence shell electron pair of the central atom E in a molecule EX_n containing E-X single bonds is stereochemically significant, and repulsions between them determine the molecular shape.
- Electron-electron repulsions decrease in the sequence: lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair.
- Where the central atom E is involved in multiple bond formation to atoms X, electron-electron repulsions decrease in the order: triple bond-single bond > double bond-single bond > single bond-single bond.

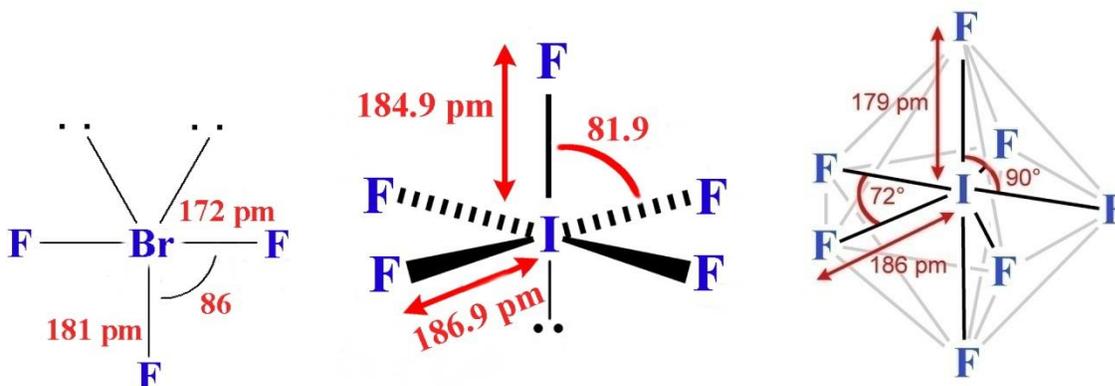
- Repulsions between the bonding pairs in EX_n depend on the difference between the electronegativities of E and X; electron-electron repulsions are less the more the E.X bonding electron density is drawn away from the central atom E.

The VSEPR theory works best for simple halides of the p-block elements, but may also be applied to species with other substituents. However, the model does not take steric factors (i.e. the relative sizes of substituents) into account

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs
2	linear			
3	trigonal planar	bent		
4	tetrahedral	trigonal pyramid	bent	
5	trigonalbipyramid	seesaw	T-shaped	linear
6	octahedral	square pyramid	square planar	
7	pentagonal bipyramid	pentagonal pyramid		

Structure of the Interhalogens

The structures found for the various interhalogens conform to what would be expected based on the VSEPR model. For XY_3 the shape can be described as T-shaped with 2 lone pairs sitting in equatorial positions of a trigonalbipyramid. For XY_5 the shape is a square pyramid with the unpaired electrons sitting in an axial position of an octahedral and XY_7 is a pentagonal bipyramid.

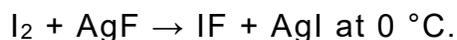
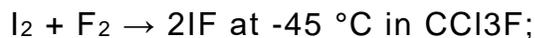


XY diatomic interhalogens

The interhalogens with formula XY have physical properties intermediate between those of the two parent halogens. The covalent bond between the two atoms has some ionic character, the larger element, X, becoming oxidised and having a partial positive charge. Most combinations of F, Cl, Br and I are known, but not all are stable.

- Chlorine monofluoride (ClF), the lightest interhalogen, is a colorless gas with a boiling point of 173 °K.
- Bromine monofluoride (BrF) has not been obtained pure - it dissociates into the trifluoride and free bromine. Similarly, iodine monofluoride is unstable - iodine reacts with fluorine to form a pentafluoride.
- Iodine monofluoride (IF) is unstable and disproportionates rapidly and irreversibly at room temperature: $5\text{IF} \rightarrow 2\text{I}_2 + \text{IF}_5$. However, its molecular properties have been determined by spectroscopy: the iodine-fluorine distance is 190.9 pm and the I-F bond dissociation energy is around 277 kJ mol⁻¹. $\Delta\text{Hf}^\circ = -95.4 \text{ kJ mol}^{-1}$ and $\Delta\text{Gf}^\circ = -117.6 \text{ kJ mol}^{-1}$, both at 298 K.

IF can be generated, by the following reactions:



- Bromine monochloride (BrCl) is an unstable red-brown gas with a boiling point of 5 °C.

- Iodine monochloride (ICl) consists of red transparent crystals which melt at 27.2 °C to form a choking brownish liquid (similar in appearance and weight to bromine). It reacts with HCl to form the strong acid HICl₂. The crystal structure of iodine monochloride consists of puckered zig-zag chains, with strong interactions between the chains.

- Iodine monobromide (IBr) is made by direct combination of the elements to form a dark red crystalline solid. It melts at 42 °C and boils at 116 °C to form a partially dissociated vapor.

XY₃ interhalogens

- Chlorine trifluoride (ClF₃) is a Colorless gas that condenses to a green liquid, and freezes to a white solid. It is made by reacting chlorine with an excess of fluorine at 250° C in a nickel tube. It reacts more violently than fluorine, often explosively. The molecule is planar and T-shaped.

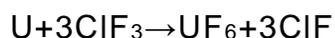
- Bromine trifluoride (BrF₃) is a yellow green liquid that conducts electricity - it ionises to form [BrF₂⁺] + [BrF₄⁻]. It reacts with many metals and metal oxides

to form similar ionised entities; with some others it forms the metal fluoride plus free bromine and oxygen. It is used in organic chemistry as a fluorinating agent. It has the same molecular shape as chlorine trifluoride.

- Iodine trifluoride (IF₃) is a yellow solid which decomposes above -28 °C. It can be synthesised from the elements, but care must be taken to avoid the formation of IF₅. F₂ attacks I₂ to yield IF₃ at -45 °C in CCl₃F. Alternatively, at low temperatures, the fluorination reaction $I_2 + 3XeF_2 \rightarrow 2IF_3 + 3Xe$ can be used. Not much is known about iodine trifluoride as it is so unstable.

- Iodine trichloride (ICl₃) forms lemon yellow crystals which can be melted under pressure to a brown liquid. It can be made from the elements at low temperature, or from iodine pentoxide and hydrogen chloride. It reacts with many metal chlorides to form tetrachloriodides, and hydrolyses in water. The molecule is a planar dimer, with each iodine atom surrounded by four chlorine atoms.

Chlorine trifluoride, ClF₃ was first reported in 1931 and it is primarily used for the manufacture of uranium hexafluoride, UF₆ as part of nuclear fuel processing and reprocessing, by the reaction:



U isotope separation is difficult because the two isotopes have very nearly identical chemical properties, and can only be separated gradually using small mass differences. (235U is only 1.26% lighter than 238U.) A cascade of identical stages produces successively higher concentrations of 235U. Each stage passes a slightly more concentrated product to the next stage and returns a slightly less concentrated residue to the previous stage.

There are currently two generic commercial methods employed internationally for enrichment: gaseous diffusion (referred to as first generation) and gas centrifuge (second generation) which consumes only 6% as much energy as gaseous diffusion. These both make use of the volatility of UF_6 . ClF_3 has been investigated as a high-performance storable oxidizer in rocket propellant systems. Handling concerns, however, prevented its use.

XY_5 interhalogens

- Chlorine pentafluoride (ClF_5) is a Colorless gas, made by reacting chlorine trifluoride with fluorine at high temperatures and high pressures. It reacts violently with water and most metals and nonmetals.

- Bromine pentafluoride (BrF_5) is a Colorless fuming liquid, made by reacting bromine trifluoride with fluorine at 200°C . It is physically stable, but reacts violently with water and most metals and nonmetals.

- Iodine pentafluoride (IF_5) is a Colorless liquid, made by reacting iodine pentoxide with fluorine, or iodine with silver fluoride. It is highly reactive, even slowly with glass. It reacts with elements, oxides and carbon halides. The molecule has the form of a tetragonal pyramid.

XY_7 interhalogens

- Iodine heptafluoride (IF_7) is a Colorless gas. It is made by reacting the pentafluoride with fluorine. IF_7 is chemically inert, having no lone pair of electrons in the valency shell; in this it resembles sulfur hexafluoride. The molecule is a pentagonal bipyramid. This compound is the only interhalogen compound possible where the larger atom is carrying seven of the smaller atoms.

- All attempts to form bromine heptafluoride have met with failure; instead, bromine pentafluoride and fluorine gas are produced.

Diatomic Interhalogens (AX)

The interhalogens of form XY have physical properties intermediate between those of the two parent halogens. The covalent bond between the two atoms has some ionic character, the less electronegative element, X, being oxidised and having a partial positive charge. Most combinations of F, Cl, Br and I are known, but not all are stable.

- Chlorine monofluoride (ClF): The lightest interhalogen compound, ClF is a colorless gas with a normal boiling point of $-100\text{ }^{\circ}\text{C}$.

- Bromine monofluoride (BrF): BrF has not been obtained pure and dissociates into the trifluoride and free bromine.

- Iodine monofluoride (IF): IF is unstable and decomposes at $0\text{ }^{\circ}\text{C}$, disproportionating into elemental iodine and iodine pentafluoride.

- Bromine monochloride (BrCl): A red-brown gas with a boiling point of $5\text{ }^{\circ}\text{C}$.

- Iodine monochloride (ICl): Red transparent crystals which melt at $27.2\text{ }^{\circ}\text{C}$ to form a choking brownish liquid (similar in appearance and weight to bromine). It reacts with HCl to form the strong acid HICl_2 . The crystal structure of iodine monochloride consists of puckered zig-zag chains, with strong interactions between the chains.

•Iodine monobromide (IBr): Made by direct combination of the elements to form a dark red crystalline solid. It melts at 42 °C and boils at 116 °C to form a partially dissociated vapor.

Tetra-atomic Interhalogens (AX₃)

•Chlorine trifluoride (ClF₃) is a colorless gas which condenses to a green liquid, and freezes to a white solid. It is made by reacting chlorine with an excess of fluorine at 250 °C in a nickel tube. It reacts more violently than fluorine, often explosively. The molecule is planar and T-shaped. It is used in the manufacture of uranium hexafluoride.

•Bromine trifluoride (BrF₃) is a yellow green liquid which conducts electricity and ionizes to form [BrF₂⁺] + [BrF₄⁻]. It reacts with many metals and metal oxides to form similar ionized entities; with some others it forms the metal fluoride plus free bromine and oxygen . It is used in organic chemistry as a fluorinating agent. It has the same molecular shape as chlorine trifluoride.

•Iodine trifluoride (IF₃) is a yellow solid which decomposes above -28 °C. It can be synthesized from the elements, but care must be taken to avoid the formation of IF₅. F₂ attacks I₂ to yield IF₃ at -45 °C in CCl₃F. Alternatively, at low temperatures, the fluorination reaction $I_2 + 3XeF_2 \rightarrow 2IF_3 + 3Xe$ can be used. Not much is known about iodine trifluoride as it is so unstable.

•Iodine trichloride (ICl₃) forms lemon yellow crystals which can be melted under pressure to a brown liquid. It can be made from the elements at low temperature, or from iodine pentoxide and hydrogen chloride. It reacts with many metal chlorides to form tetrachloriodides, and hydrolyses in water. The molecule is a planar dimer, with each iodine atom surrounded by four chlorine atoms.

Hexa-atomic Interhalogens (AX₅)

- Chlorine pentafluoride (ClF₅) is a colorless gas, made by reacting chlorine trifluoride with fluorine at high temperatures and high pressures. It reacts violently with water and most metals and nonmetals.

- Bromine pentafluoride (BrF₅) is a colorless fuming liquid, made by reacting bromine trifluoride with fluorine at 200 Å C. It is physically stable, but reacts violently with water and most metals and nonmetals.

- Iodine pentafluoride (IF₅) is a colorless liquid, made by reacting iodine pentoxide with fluorine, or iodine with silver fluoride. It is highly reactive, even slowly with glass. It reacts with elements, oxides and carbon halides. The molecule has the form of a tetragonal pyramid.

Octa-atomic interhalogens (AX₇)

- Iodine heptafluoride (IF₇) is a colourless gas. It is made by reacting the pentafluoride with fluorine. IF₇ is chemically inert, having no lone pair of electrons in the valency shell; in this it resembles sulfur hexafluoride. The molecule is a pentagonal bipyramid. This compound is the only interhalogen compound possible where the larger atom is carrying seven of the smaller atoms

- All attempts to form bromine heptafluoride (BrF₇) have failed and instead produce bromine pentafluoride (BrF₅) gas.

Group 18: Properties of Nobel Gases The noble gases (Group 18) are located in the far right of the periodic table and were previously referred to as the "inert gases" due to the fact that their filled valence shells (octets)

make them extremely nonreactive. The noble gases were characterized relatively late compared to other element groups.

The History

The first person to discover the noble gases was Henry Cavendish in the late 18th century. Cavendish distinguished these elements by chemically removing all oxygen and nitrogen from a container of air. The nitrogen was oxidized to NO_2

by electric discharges and absorbed by a sodium hydroxide solution. The remaining oxygen was then removed from the mixture with an absorber. The experiment revealed that 1/120 of the gas volume remained un-reacted in the receptacle. The second person to isolate, but not typify, them was William Francis (1855-1925). Francis noted the formation of gas while dissolving uranium minerals in acid.

Argon

In 1894, John William Strutt discovered that chemically-obtained pure nitrogen was less dense than the nitrogen isolated from air samples. From this breakthrough, he concluded that another, unknown gas was present in the air. With the aid of William Ramsay, Strutt managed to replicate and modify Cavendish's experiment to better understand the inert component of air in his original experiment. The researchers' procedure differed from the Cavendish procedure: they removed the oxygen by reacting it with copper, and removed the nitrogen in a reaction with magnesium. The remaining gas was properly characterized and the new element was named "argon," which originates from the Greek word for "inert."

Helium

Helium was first discovered in 1868, manifesting itself in the solar spectrum as a bright yellow line with a wavelength of 587.49 nanometers. This discovery was made by Pierre Jansen. Jansen initially assumed it was a sodium line. However, later studies by Sir William Ramsay (who isolated helium on Earth by treating a variety of rare elements with acids) confirmed that the bright yellow line from his experiment matched up with that in the spectrum of the sun. From this, British physicist William Crookes identified the element as helium.

Neon, Krypton, Xenon

These three noble gases were discovered by Morris W. Travers and Sir William Ramsay in 1898. Ramsay discovered neon by chilling a sample of the air to a liquid phase, warming the liquid, and capturing the gases as they boiled off. Krypton and xenon were also discovered through this process.

Radon

In 1900, while studying the decay chain of radium, Friedrich Earns Dorn discovered the last gas in Group 18: radon. In his experiments, Dorn noticed that radium compounds emanated radioactive gas. This gas was originally named niton after the Latin word for shining, "nitens". In 1923, the International Committee for Chemical Elements and International Union of Pure Applied Chemistry (IUPAC) decided to name the element radon. All isotopes of radon are radioactive. Radon-222 has the longest half-life at less than 4 days, and is an alpha-decay product of Radium-226 (part of the U-238 to Pb-206 radioactive decay chain).

The Electron Configurations for Noble Gases

- Helium $1s^2$
- Neon $[\text{He}] 2s^2 2p^6$
- Argon $[\text{Ne}] 3s^2 3p^6$
- Krypton $[\text{Ar}] 3d^{10} 4s^2 4p^6$
- Xenon $[\text{Kr}] 4d^{10} 5s^2 5p^6$
- Radon $[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^6$

Table 1: Trends within Group 18

	Atomic #	Atomic mass	Boiling point (K)	Melting point (K)	1 st Ionization (E/kJ mol ⁻¹)	Density (g/dm ³)	Atomic radius (pm)
He	2	4.003	4.216	0.95	2372.3	0.1786	31
Ne	10	20.18	27.1	24.7	2080.6	0.9002	38
Ar	18	39.948	87.29	83.6	1520.4	1.7818	71
Kr	36	83.3	120.85	115.8	1350.7	3.708	88
Xe	54	131.29	166.1	161.7	1170.4	5.851	108
Rn	86	222.1	211.5	202.2	1037.1	9.97	120

The Atomic and Physical Properties

- Atomic mass, boiling point, and atomic radii INCREASE down a group in the periodic table.
- The first ionization energy DECREASES down a group in the periodic table.
- The noble gases have the largest ionization energies, reflecting their chemical inertness.

- Down Group 18, atomic radius and interatomic forces INCREASE resulting in an INCREASED melting point, boiling point, enthalpy of vaporization, and solubility.

- The INCREASE in density down the group is correlated with the INCREASE in atomic mass.

- Because the atoms INCREASE in atomic size down the group, the electron clouds of these non polar atoms become increasingly polarized, which leads to weak van Der Waals forces among the atoms. Thus, the formation of liquids and solids is more easily attainable for these heavier elements because of their melting and boiling points.

- Because noble gases' outer shells are full, they are extremely stable, tending not to form chemical bonds and having a small tendency to gain or lose electrons.

- Under standard conditions all members of the noble gas group behave similarly.

- All are monatomic gases under standard conditions.

- Noble gas atoms, like the atoms in other groups, INCREASE steadily in atomic radius from one period to the next due to the INCREASING number of electrons.

- The size of the atom is positively correlated to several properties of noble gases. The ionization potential DECREASES with an INCREASING radius, because the valence electrons in the larger noble gases are further away from the nucleus; they are therefore held less tightly by the atom.

- The attractive force INCREASES with the size of the atom as a result of an INCREASE in polarizability and thus a DECREASE in ionization potential.

- Overall, noble gases have weak interatomic forces, and therefore very low boiling and melting points compared with elements of other groups.

For covalently-bonded diatomic and polyatomic gases, heat capacity arises from possible translational, rotational, and vibrational motions. Because monatomic gases have no bonds, they cannot absorb heat as bond vibrations. Because the center of mass of monatomic gases is at the nucleus of the atom, and the mass of the electrons is negligible compared to the nucleus, the kinetic energy due to rotation is negligible compared to the kinetic energy of translation (unlike in di- or polyatomic molecules where rotation of nuclei around the center of mass of the molecule contributes significantly to the heat capacity). Therefore, the internal energy per mole of a monatomic noble gas equals its translational contribution, $3/2RT$

, where R is the universal gas constant and T

is the absolute temperature.

For monatomic gases at a given temperature, the average kinetic energy due to translation is practically equal regardless of the element. Therefore at a given temperature, the heavier the atom, the more slowly its gaseous atoms move. The mean velocity of a monatomic gas decreases with increasing molecular mass, and given the simplified heat capacity situation, noble gaseous thermal conductivity decreases with increasing molecular mass.

Applications of Noble Gases

Helium

Helium is used as a component of breathing gases due to its low solubility in fluids or lipids. This is important because other gases are absorbed by the blood and body tissues when under pressure during scuba diving. Because of its reduced solubility, little helium is taken into cell membranes; when it replaces part of the breathing mixture, helium causes a decrease in the narcotic effect of the gas at far depths. The reduced amount of dissolved gas in the body means fewer gas bubbles form, decreasing the pressure of the ascent. Helium and Argon are used to shield welding arcs and the surrounding base metal from the atmosphere.

Helium is used in very low temperature cryogenics, particularly for maintaining superconductors (useful for creating strong magnetic fields) at a very low temperatures. Helium is also the most common carrier gas in gas chromatography.

Neon

Neon has many common and familiar applications: neon lights, fog lights, TV cine-scopes, lasers, voltage detectors, luminous warnings, and advertising signs. The most popular application of neon is the neon tubing used in advertising and elaborate decorations. These tubes are filled with neon and helium or argon under low pressure and submitted to electrical discharges. The color of emitted light is depends on the composition of the gaseous mixture and on the color of the glass of the tube. Pure Neon within a colorless tube absorbs red light and reflects blue light, as shown in the figure below. This reflected light is known as fluorescent light.

Argon

Argon has a large number of applications in electronics, lighting, glass, and metal fabrications. Argon is used in electronics to provide a protective heat transfer medium for ultra-pure silicon crystal semiconductors and for growing germanium. Argon can also fill fluorescent and incandescent light bulbs, creating the blue light found in "neon lamps." By utilizing argon's low thermal conductivity, window manufacturers provide a gas barrier needed to produce double-pane insulated windows. This insulation barrier improves the windows' energy efficiencies. Argon also creates an inert gas shield during welding, flushes out melted metals to eliminate porosity in casting, and provides an oxygen- and nitrogen-free environment for annealing and rolling metals and alloys.

Similarly to argon, krypton can be found in energy efficient windows. Because of its superior thermal efficiency, krypton is sometimes chosen over argon for insulation. It is estimated that 30% of energy efficient windows sold in Germany and England are filled with krypton; approximately 1.8 liters of krypton are used in these countries. Krypton is also found in fuel sources, lasers and headlights. In lasers, krypton functions as a control for a desired optic wavelength. It is usually mixed with a halogen (most likely fluorine) to produce excimer lasers. Halogen sealed beam headlights containing krypton produce up to double the light output of standard headlights. In addition, Krypton is used for high performance light bulbs, which have higher color temperatures and efficiency because the krypton reduces the rate of evaporation of the filament.

Xenon

Xenon has various applications in incandescent lighting, x-ray development, plasma display panels (PDPs), and more. Incandescent lighting uses xenon

because less energy can be used to obtain the same light output as a normal incandescent lamp. Xenon has also made it possible to obtain better x-rays with reduced amounts of radiation. When mixed with oxygen, it can enhance the contrast in CT imaging. These applications have had great impact on the health care industries. Plasma display panels (PDPs) using xenon as one of the fill gases may one day replace the large picture tubes in television and computer screens.

Nuclear fission products may include several radioactive isotopes of xenon, which absorb neutrons in nuclear reactor cores. The formation and elimination of radioactive xenon decay products are factors in nuclear reactor control.

Radon

Radon is reported as the second most frequent cause of lung cancer, after cigarette smoking. However, it also has beneficial applications in radiotherapy, arthritis treatment, and bathing. In radiotherapy, radon has been used in implantable seeds, made of glass or gold, primarily used to treat cancers. It has been said that exposure to radon mitigates auto-immune diseases such as arthritis. Some arthritis sufferers have sought limited exposure to radioactive mine water and radon to relieve their pain. "Radon Spas" such as Bad Gastein in Austria and Onsen in Japan offer a therapy in which people sit for minutes to hours in a high-radon atmosphere, believing that low doses of radiation will boost up their energy.

Neon, like all noble gases, has a full valence shell. Noble gases have eight electrons in their outermost shell, except in the case of helium, which has two.

Configuration

Like other groups, the members of this family show patterns in its electron configuration, especially the outermost shells resulting in trends in chemical behavior:

<u>Z</u>	<u>Element</u>	<u>No. of electrons/shell</u>
2	<u>helium</u>	2
10	<u>neon</u>	2, 8
18	<u>argon</u>	2, 8, 8
36	<u>krypton</u>	2, 8, 18, 8
54	<u>xenon</u>	2, 8, 18, 18, 8
86	<u>radon</u>	2, 8, 18, 32, 18, 8

The noble gases have full valence electron shells. Valence electrons are the outermost electrons of an atom and are normally the only electrons that participate in chemical bonding. Atoms with full valence electron shells are extremely stable and therefore do not tend to form chemical bonds and have little tendency to gain or lose electrons. However, heavier noble gases such as radon are held less firmly together by electromagnetic force than lighter noble gases such as helium, making it easier to remove outer electrons from heavy noble gases.

As a result of a full shell, the noble gases can be used in conjunction with the electron configuration notation to form the noble gas notation. To do this, the nearest noble gas that precedes the element in question is written first, and then the electron configuration is continued from that point forward. For example, the electron notation of phosphorus is $1s^2 2s^2 2p^6 3s^2 3p^3$, while the noble gas notation is $[\text{Ne}] 3s^2 3p^3$. This more compact notation makes it easier to identify elements, and is shorter than writing out the full notation of atomic orbitals.

Structure of XeF

The noble gases show extremely low chemical reactivity; consequently, only a few hundred noble gas compounds have been formed. Neutral compounds in which helium and neon are involved in chemical bonds have not been formed (although there is some theoretical evidence for a few helium compounds), while xenon, krypton, and argon have shown only minor reactivity. The reactivity follows the order $\text{Ne} < \text{He} < \text{Ar} < \text{Kr} < \text{Xe} < \text{Rn}$. and kinetically unstable.

Xenon compounds are the most numerous of the noble gas compounds that have been formed. Most of them have the xenon atom in the oxidation state of +2, +4, +6, or +8 bonded to highly electronegative atoms such as fluorine or oxygen, as in xenon difluoride (XeF_2)

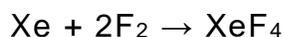
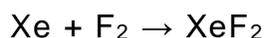
2), xenon tetrafluoride (XeF_4)

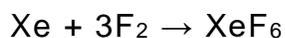
4), xenon hexafluoride (XeF_6)

6), xenon tetroxide (XeO_4)

4), and sodium perxenate (Na_4XeO_6)

6). Xenon reacts with fluorine to form numerous xenon fluorides according to the following equations:



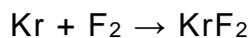


Some of these compounds have found use in chemical synthesis as oxidizing agents; XeF

2, in particular, is commercially available and can be used as a fluorinating agent. As of 2007, about five hundred compounds of xenon bonded to other elements have been identified, including organoxenon compounds (containing xenon bonded to carbon), and xenon bonded to nitrogen, chlorine, gold, mercury, and xenon itself. Compounds of xenon bound to boron, hydrogen, bromine, iodine, beryllium, sulphur, titanium, copper, and silver have also been observed but only at low temperatures in noble gas matrices, or in supersonic noble gas jets.

In theory, radon is more reactive than xenon, and therefore should form chemical bonds more easily than xenon does. However, due to the high radioactivity and short half-life of radon isotopes, only a few fluorides and oxides of radon have been formed in practice.

Krypton is less reactive than xenon, but several compounds have been reported with krypton in the oxidation state of +2. Krypton difluoride is the most notable and easily characterized. Under extreme conditions, krypton reacts with fluorine to form KrF₂ according to the following equation:



Compounds in which krypton forms a single bond to nitrogen and oxygen have also been characterized, but are only stable below -60 °C (-76 °F) and -90 °C (-130 °F) respectively.

Krypton atoms chemically bound to other nonmetals (hydrogen, chlorine, carbon) as well as some late transition metals (copper, silver, gold) have also been observed, but only either at low temperatures in noble gas matrices, or in supersonic noble gas jets. Similar conditions were used to obtain the first few compounds of argon in 2000, such as argon fluorohydride (HArF), and some bound to the late transition metals copper, silver, and gold. As of 2007, no stable neutral molecules involving covalently bound helium or neon are known.

The noble gases—including helium—can form stable molecular ions in the gas phase. The simplest is the helium hydride molecular ion, HeH^+ , discovered in 1925. Because it is composed of the two most abundant elements in the universe, hydrogen and helium, it is believed to occur naturally in the interstellar medium, although it has not been detected yet. In addition to these ions, there are many known neutral excimers of the noble gases. These are compounds such as ArF and KrF that are stable only when in an excited electronic state; some of them find application in excimer lasers.

In addition to the compounds where a noble gas atom is involved in a covalent bond, noble gases also form non-covalent compounds. The clathrates, first described in 1949, consist of a noble gas atom trapped within cavities of crystal lattices of certain organic and inorganic substances. The essential condition for their formation is that the guest (noble gas) atoms must be of appropriate size to fit in the cavities of the host crystal lattice. For instance, argon, krypton, and xenon form clathrates with hydroquinone, but helium and neon do not because they are too small or insufficiently polarizable to be retained. Neon, argon, krypton, and xenon also form clathrate hydrates, where the noble gas is trapped in ice.

Applications

1) Noble gases have very low boiling and melting points, which makes them useful as cryogenic refrigerants.[63] In particular, liquid helium, which boils at 4.2 K ($-268.95\text{ }^{\circ}\text{C}$; $-452.11\text{ }^{\circ}\text{F}$), is used for superconducting magnets, such as those needed in nuclear magnetic resonance imaging and nuclear magnetic resonance. Liquid neon, although it does not reach temperatures as low as liquid helium, also finds use in cryogenics because it has over 40 times more refrigerating capacity than liquid helium and over three times more than liquid hydrogen.

Helium is used as a component of breathing gases to replace nitrogen, due to its low solubility in fluids, especially in lipids. Gases are absorbed by the blood and body tissues when under pressure like in scuba diving, which causes an anesthetic effect known as nitrogen narcosis. Due to its reduced solubility, little helium is taken into cell membranes, and when helium is used to replace part of the breathing mixtures, such as in trimix or heliox, a decrease in the narcotic effect of the gas at depth is obtained. Helium's reduced solubility offers further advantages for the condition known as decompression sickness, or the bends. The reduced amount of dissolved gas in the body means that fewer gas bubbles form during the decrease in pressure of the ascent. Another noble gas, argon, is considered the best option for use as a drysuit inflation gas for scuba diving. Helium is also used as filling gas in nuclear fuel rods for nuclear reactors.

2) In many applications, the noble gases are used to provide an inert atmosphere. Argon is used in the synthesis of air-sensitive compounds that are sensitive to nitrogen. Solid argon is also used for the study of very unstable compounds, such as reactive intermediates, by trapping them in an inert matrix at very low temperatures. Helium is used as the carrier medium in gas chromatography, as a filler gas for thermometers, and in devices for

measuring radiation, such as the Geiger counter and the bubble chamber. Helium and argon are both commonly used to shield welding arcs and the surrounding base metal from the atmosphere during welding and cutting, as well as in other metallurgical processes and in the production of silicon for the semiconductor industry.

3) Noble gases are commonly used in lighting because of their lack of chemical reactivity. Argon, mixed with nitrogen, is used as a filler gas for incandescent light bulbs. Krypton is used in high-performance light bulbs, which have higher colour.

