CHM 121 (INORGANIC CHEMISTRY)

GROUPS VI AND VII

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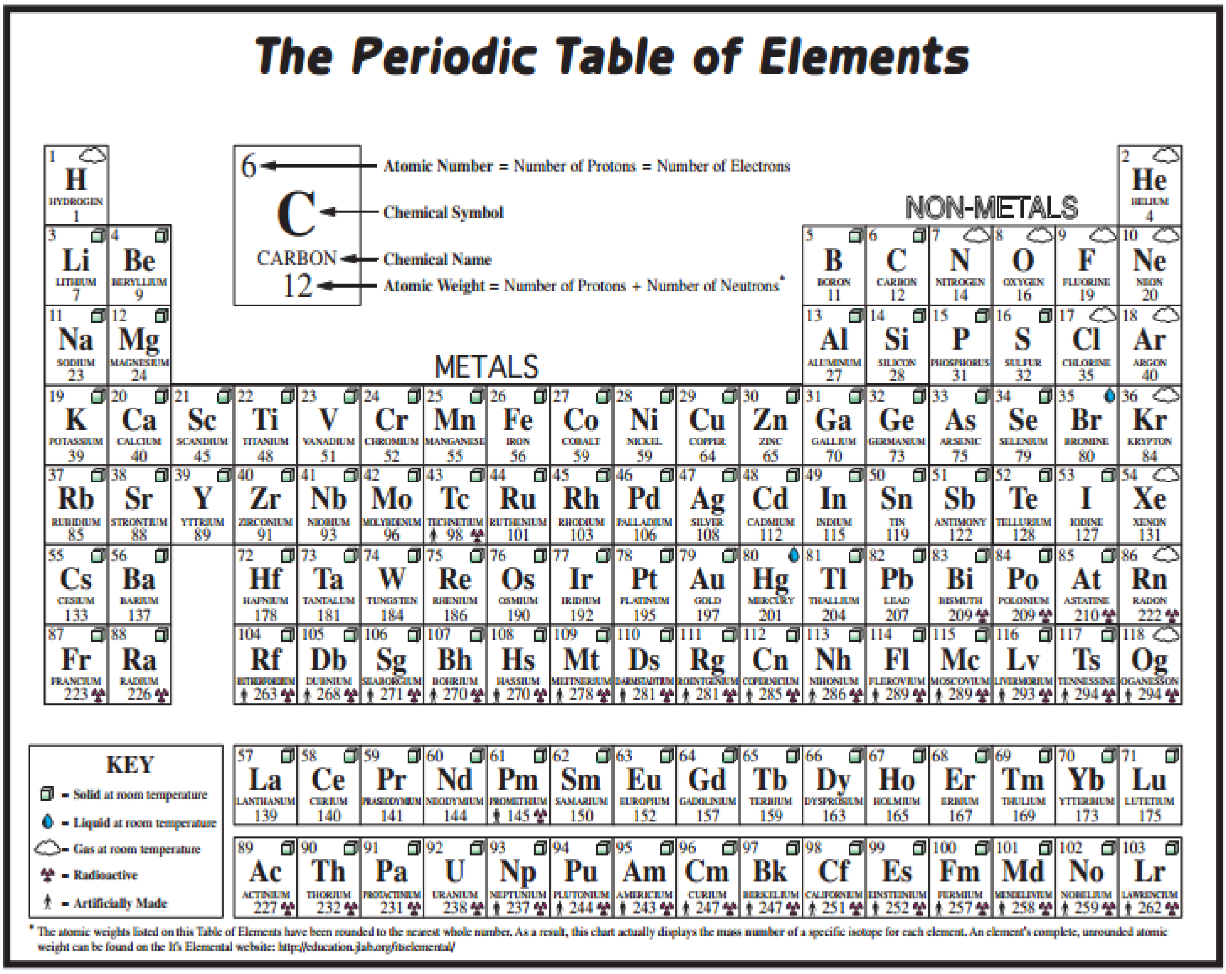
PERIODIC TABLE



The Periodic Table of Elements

6 ← Atomic Number = Number of Protons = Number of Electrons
C ← Chemical Symbol
CARBON ← Chemical Name
12 ← Atomic Weight = Number of Protons + Number of Neutrons*

NON-METALS

METALS

1 H HYDROGEN 1																	2 He HELIUM 4
3 Li LITHIUM 7	4 Be BERYLLIUM 9											5 B BORON 11	6 C CARBON 12	7 N NITROGEN 14	8 O OXYGEN 16	9 F FLUORINE 19	10 Ne NEON 20
11 Na SODIUM 23	12 Mg MAGNESIUM 24											13 Al ALUMINUM 27	14 Si SILICON 28	15 P PHOSPHORUS 31	16 S SULFUR 32	17 Cl CHLORINE 35	18 Ar ARGON 40
19 K POTASSIUM 39	20 Ca CALCIUM 40	21 Sc SCANDIUM 45	22 Ti TITANIUM 48	23 V VANADIUM 51	24 Cr CHROMIUM 52	25 Mn MANGANESE 55	26 Fe IRON 56	27 Co COBALT 59	28 Ni NICKEL 59	29 Cu COPPER 64	30 Zn ZINC 65	31 Ga GALLIUM 70	32 Ge GERMANIUM 73	33 As ARSENIC 75	34 Se SELENIUM 79	35 Br BROMINE 80	36 Kr KRYPTON 84
37 Rb RUBIDIUM 85	38 Sr STRONTIUM 88	39 Y YTTRIUM 89	40 Zr ZIRCONIUM 91	41 Nb NIOBIUM 93	42 Mo MOLYBDENUM 96	43 Tc TECHNETIUM 98	44 Ru RUTHENIUM 101	45 Rh RHODIUM 103	46 Pd PALLADIUM 106	47 Ag SILVER 108	48 Cd CADMIUM 112	49 In INDIUM 115	50 Sn TIN 119	51 Sb ANTIMONY 122	52 Te TELLURIUM 128	53 I IODINE 127	54 Xe XENON 131
55 Cs CESIUM 133	56 Ba BARIUM 137		72 Hf HAFNIUM 178	73 Ta TANTALUM 181	74 W TUNGSTEN 184	75 Re RHENIUM 186	76 Os OSMIUM 190	77 Ir IRIDIUM 192	78 Pt PLATINUM 195	79 Au GOLD 197	80 Hg MERCURY 201	81 Tl THALLIUM 204	82 Pb LEAD 207	83 Bi BISMUTH 209	84 Po POLONIUM 209	85 At ASTATINE 210	86 Rn RADON 222
87 Fr FRANCIUM 223	88 Ra RADIUM 226		104 Rf RUTHERFORDIUM 263	105 Db DUBNIUM 268	106 Sg SEABORGIUM 271	107 Bh BOHRIUM 270	108 Hs HASSIUM 270	109 Mt MEITNERIUM 278	110 Ds DARMSTADTIUM 281	111 Rg ROENTGENIUM 281	112 Cn COPERNICIUM 285	113 Nh NIHONIUM 286	114 Fl FLEROVIUM 289	115 Mc MOSCOVIUM 289	116 Lv LIVERMORIUM 293	117 Ts TENNESSINE 294	118 Og OGANESSON 294

57 La LANTHANUM 139	58 Ce CERIUM 140	59 Pr PRASEODYMIUM 141	60 Nd NEODYMIUM 144	61 Pm PROMETHIUM 145	62 Sm SAMARIUM 150	63 Eu EUROPIUM 152	64 Gd GADOLINIUM 157	65 Tb TERBIUM 159	66 Dy DYSPROSIUM 163	67 Ho HOLMIUM 165	68 Er ERBIUM 167	69 Tm THULIUM 169	70 Yb YTTERBIUM 173	71 Lu LUTETIUM 175
89 Ac ACTINIUM 227	90 Th THORIUM 232	91 Pa PROTACTINIUM 231	92 U URANIUM 238	93 Np NEPTUNIUM 237	94 Pu PLUTONIUM 244	95 Am AMERICIUM 243	96 Cm CURIUM 247	97 Bk BERKELIUM 247	98 Cf CALIFORNIUM 251	99 Es EINSTEINIUM 252	100 Fm FERMIUM 257	101 Md MENDELEVIUM 258	102 No NOBELIUM 259	103 Lr LAWRENCIUM 262

KEY
- Solid at room temperature
- Liquid at room temperature
- Gas at room temperature
- Radioactive
- Artificially Made

* The atomic weights listed on this Table of Elements have been rounded to the nearest whole number. As a result, this chart actually displays the mass number of a specific isotope for each element. An element's complete, unrounded atomic weight can be found on the It's Elemental website: http://education.jlab.org/itselemental/

http://education.jlab.org/

Last revised on June 8, 2016

GROUP VI

The group 6A elements show the usual graduation from non-metallic to metallic properties with increasing atomic number that occurs in any periodic group. Oxygen and sulphur are non-metals, selenium and tellurium are semi-conductors and polonium is metallic.

Sulphur, selenium and tellurium are collectively known as the **chalcogens**. They form so compounds similar to those of oxygen, but show many differences characteristic of other nonmetal groups.

Electronic Configuration

O : 2, 6
$1s^2 2s^2 2p^4$

S : 2.8.6
$1s^2 2s^2 2p^6 3s^2 3p^4$

Se : 2.8.18.6
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$

Te : 2.8.18.18.6
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^4$

Po : 2.8.18.32.18.6
$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^65d^{10}6s^26p^4$

Physical Data of Group 6A Elements

symbol	Atomic number	Atomic Radius/nm	Ionic radius/nm X^{2-}	Melting point/°C	Boiling point/°C
O	8	0.074	0.140	-218	-183
S	16	0.104	0.184	119[a]	445
Se	34	0.117	0.198	217[b]	685
Te	52	0.137	0.221	450	990
Po	84	0.137		254	960

Group Trends

There are great differences between the chemistry of oxygen and that of sulphur, with more gradual variations through the sequences S, Se, Te, Po. Differences from oxygen are attributable, among other things, to the following:

1. The lower electronegativities of S–Po elements lessens the ionic character of those of their compounds that are formally analogous to those of oxygen, alters the relative stabilities of various kinds of bonds, and drastically lessens the importance of hydrogen bonding, although weak S…H–S bonds do indeed exist.
2. The maximum coordination number is not limited to four nor is the valence limited to two, as in the case of oxygen, since *d* orbitals may be utilized in bonding. Thus sulphur forms several hexacoordinate compounds, for example, SF_6, and for tellurium six is the characteristic coordination number.
3. Sulphur has a strong tendency to catenation, so that it forms compounds having no oxygen, selenium, or tellurium analogs. For example, polysulphide ions, S_n^{2-}; sulphanes, XS_nX (where X may be H, halogen, –CN or $–NR_2$); and the polysulphuric acids, $HO_3SS_nSO_3H$ and their salts. Although selemium and tellurium have a smaller tendency to catenation, they form rings and long chains in their elemental forms. The chains are linear, because the valence is two.

Gradual changes of properties are evident with increasing size, decreasing electronegativity, etc., such as:

1. Decreasing thermal stability of the H_2X compounds. Thus, H_2Te is considerably endothermic.
2. Increasing metallic character of the elements.
3. Increasing tendency to form anionic complexes such as $SeBr_6^{2-}$, $TeBr_6^{2-}$, PoI_6^{2-}.
4. Decreasing stability of compounds in higher formal positive oxidation states.
5. Emergence of cationic properties of Po and, very marginally, for Te. Thus, TeO_2 and PoO_2 appear to have ionic lattices and they react with hydrohalic acids to give Te (IV) and Po (IV) halides, and PoO_2, forms a hydroxide $Po(OH)_4$.

OXYGEN

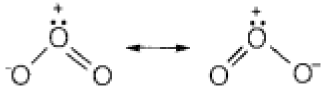
Oxygen is the second most electronegative element after fluorine, and forms thermodynamically stable compounds with nearly all elements. It rivals fluorine in the ability to stabilize the highest known oxidation states of many elements.

Oxidation reactions with oxygen are often slow, because of the strength of the O=O double bond (490 kJ mol^{-1}).

Oxygen is the most abundant element on Earth, making around 46% of the Earth's crust by mass.
The commonest minerals are complex oxides such as silicates and carbonates. Oxygen is also a constituent of water, and of nearly all biological molecules. Atmospheric O_2 comes almost entirely from photosynthesis by green plants, and is not found on other known planets. Reactions involving dioxygen, both in photosynthesis and in respiration by air-breathing animals, are important in biological chemistry.

Oxygen can be extracted from the atmosphere by liquefaction and fractional distillation. The liquid boils at -183°C (90 K) and is dangerous when mixed with combustible materials.

Oxygen has two allotropes, the normal dioxygen O_2 form and ozone O_3, formed by subjecting O_2 to an electric discharge. Ozone is a trace constituent of the atmosphere, where it plays an important role as an absorber of UV radiation.



Physical Properties

1. Oxygen is a colourless and odourless diatomic gas.
2. It is neutral to litmus paper.
3. It is slightly soluble in water.
4. It is liquefies at -183 ^oC, freezes at -218 ^oC and solidifies at -225 ^oC.

Chemical Properties

Chemically, oxygen is very reactive, forming compounds with all other elements except the noble gases and, apart from the halogens and some unreactive metals these can be made to combine directly with oxygen under the right conditions.

1. **Reaction with metals**: Most metal react with oxygen to form basic oxides. The oxides of very electropositive metals like potassium, sodium and calcium dissolve in water to form alkalis.

$$4K_{(s)} + O_{2(g)} \rightarrow 2K_2O_{(s)}$$
$$2K_2O_{(s)} + 2H_2O_{(l)} \rightarrow 4KOH_{(aq)}$$

2. **Reaction with non-metals**: Non-metals like sulphur, carbon and phosphorus burn in oxygen to form acidic oxides. These can also be called acid anhydrides. They dissolve in water to form acids.

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$
$$SO_{2(g)} + H_2O_{(l)} \rightarrow H_2SO_{3(aq)}$$
$$P_{4(s)} + 3O_{2(g)} \rightarrow P_4O_{6(g)}$$
$$P_4O_{6(g)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{3(aq)}$$
$$P_{4(s)} + 5O_{2(g)} \rightarrow P_4O_{10(g)}$$
$$P_4O_{10(g)} + 6H_2O_{(l)} \rightarrow 4H_3PO_{4(aq)}$$
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$
$$CO_{2(g)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$$

3. **Combustion of organic compounds:**

$$C_2H_5OH + 3O_{2(g)} \rightarrow 3CO_{2(g)} + 3H_2O_{(l)}$$

Compounds of Oxygen

Oxides

Oxides are formed when elements combine with oxygen. They can be classified as:

1. Basic oxides
2. Acidic oxides
3. Amphoteric oxides
4. Neutral oxides
5. Peroxides and Superoxides

Basic Oxides

These are oxides of metals. They react with acids to form salt and water only. Examples are: Na_2O, K_2O, CaO, MgO, FeO, Fe_2O_3, CuO, etc

$$Na_2O_{(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)}) + H_2O_{(l)}$$
$$PbO_{(s)} + 2HNO_{3(aq)} \rightarrow Pb(NO_3)_{2(aq)} + H_2O_{(l)}$$

Acidic Oxides

These are oxides of non-metals. They react with water to form acids. They also react with alkalis to form salt and water only e.g. SO_3, CO_2, SO_2, SiO_2, N_2O_5, etc

$$CO_{2(g)} + 2NaOH_{(aq)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$
$$SO_{3(g)} + 2KOH_{(aq)} \rightarrow K_2SO_{4(aq)} + H_2O_{(l)}$$

Amphoteric Oxides

These are oxides which can behave both as basic oxides and acidic oxides. Examples are: Al_2O_3 and ZnO and H_2O, etc

$$ZnO_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_2O_{(l)}$$
$$ZnO_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \rightarrow Na_2Zn(OH)_{4(aq)}$$

Neutral Oxides

Neutral oxides are neither acidic nor basic oxides. They are neutral to litmus. Examples are: H_2O, N_2O, CO and NO, etc

Peroxides and Superoxide

Peroxides are oxides containing higher presentation of oxygen than the ordinary oxides. Adding one or two electrons to dioxygen gives the superoxide, O_2^- and peroxide ions, O_2^{2-}. Examples are: Na_2O_2, CaO_2 and BaO_2.

Other Compounds

Water

H_2O is the most abundant molecular substance on Earth. It is highly polar, with physical properties dominated by hydrogen bonding, and an excellent solvent for ionic substances and reactions.

Hydrated Salts

Many hydrated salts are known (e.g. $CuSO_4.5H_2O$), which contain water bound by coordination to metal ions and/or hydrogen bonding to anions. Autoprotolysis gives the ions

H_3O^+ and OH^-, which are also known in solid salts, H_3O^+ with anions of strong acids (e.g. $[H_3O]^+[NO_3]^-$; hydrated species such as $[H_5O_2]^+$ are also known), and OH^- in hydroxides, which are formed by many metals.

Ozonides

The interaction of O_3 with hydroxides of K, Rb, Cs has long been known to give materials that are neither peroxides nor superoxides. These are ozonides.

$$3KOH_{(s)} + 2O_{3(g)} \rightarrow 2KO_{3(s)} + KOH.H_2O_{(s)} + \frac{1}{2}O_{2(g)}$$

The ozonide ion is paramagnetic with one unpaired electron

N.B: NH_4O_3 has also been reported

Uses of Oxygen

1. Oxygen is used for respiration and combustion process
2. It is used in oxyacetylene welding and cutting (i.e oxy-ethyne flame).
3. It is used in the manufacture of many metals particularly steel. It is used in steel industry for the removal of carbon, sulphur and phosphorus impurities from iron.
4. It is used for highly altitude flying and mountaineering
5. It is used for manufacture of chemical compounds like tetraoxosulphate (VI) acid, trioxonitrate (V) acid and ethonoic acid.

Sulphur

Sulphur occurs in combination with many metals as sulphides, if they are insoluble in water, e.g. the sulphides of zinc, lead, copper and mercury.

As sulphur (IV) oxide, it is recovered as a by-product during extraction of these metals from their sulphide ores.

Other important sources of sulphur are crude oil and natural gas, from which it is extracted as hydrogen sulphide.

Sulphur occurs in the Free State in Japan, and underground in Texas and Louisiana, where it was discovered by Frasch in 1867.

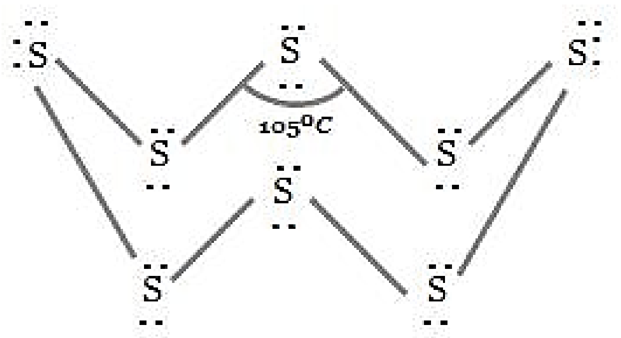
Sulphur is widespread in the Earth's crust, occurring as metal sulphides, sulphates, and native or elemental sulfur formed by bacterial oxidation of sulphides.

Many less electropositive metals known as chalcophiles are found commonly as sulphide minerals; some important examples are pyrites (FeS_2), sphalerite (zinc blende, ZnS), molybdenite (MoS_2), cinnabar (HgS) and galena (PbS). Volatile sulfur compounds such as H_2S and organic compounds are also found in petroleum and natural gas.

The element is used in large amounts for the manufacture of sulphuric acid. Selenium and tellurium are much rarer, found as minor components of sulfide minerals.

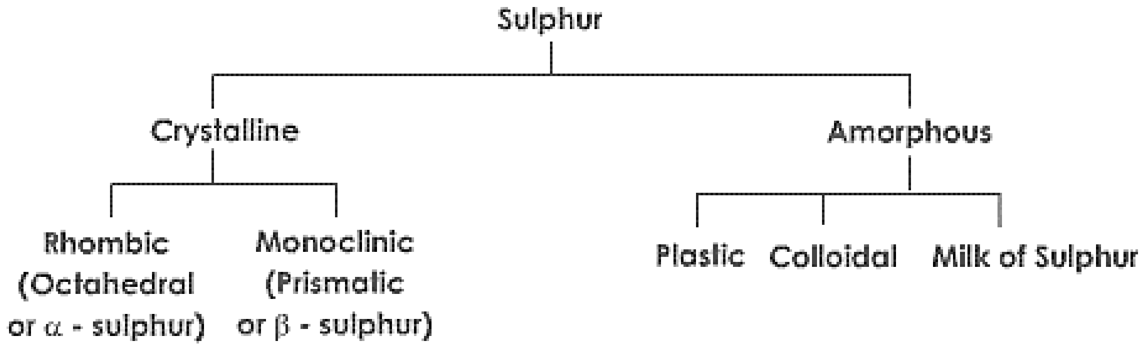
The Allotropy of Sulphur

Unlike oxygen, which is a discrete molecule, two atoms being united by a double bond, sulphur atom shows a marked reluctance to double bond with themselves and the two main allotropes of sulphur contain S_8 molecules, in which single bounds unite sulphur atoms in a puckered octagonal ring. The high relative molecular mass of these S_8 structural units explains why sulphur, unlike oxygen, is a solid. The bond angles of 105^o are consistent with the simple theory of electron pair repulsion.



The structure of the S_8 molecule

There are five forms of allotropes of sulphur
1. Rhombic sulphur (α – sulphur)
2. Monoclinic sulphur (β - sulphur)
3. Plastic sulphur
4. Colloidal sulphur
5. Milk of sulphur



Rhombic Sulphur (Octahedral or Alpha Sulphur)
This is the form of sulphur normally encountered and consists of S_8 structure unites packed together to give crystals with octahedral shape. It is the only state allotropes of sulphur at temperature below 96^0C. Fairly large crystals can be obtained by allowing a saturated solution of sulphur in carbon (IV) sulphide to evaporate slowly. They are bright yellow, transparent and have a density of 2.06g/cm^3.

Monoclinic Sulphur (Prismatic or Beta Sulphur)
This form of sulphur is formed when molten sulphur is allowed to crystalize above 95.6^0C. Like rhombic sulphur, it consists of S_8 structure units but these are arranged differently in the crystal lattice. The crystals are long, thin and needled shaped. The temperature of 95.6^0C is the transition temperature for sulphur. Below this temperature, rhombic sulphur is the more stable allotrope and above it, monoclinic sulphur is the more stable allotrope of the two forms. This type of allotropy, in which a definite transition point exists where two forms become equally stable, is called enantiotropy.

$$\text{Rhombic sulphur} \xrightarrow{95.6\ ^{o}C} \text{monoclinic sulphur}$$

Crystals of monoclinic sulphur are amber in colour and have density of 1.96g/cm^3. As they gradually change over into rhombic sulphur below 95.6^{0}C, each crystal retains its overall shape but changes into mass of small rhombic crystals.

Plastic Sulphur

This is obtained, as an amber-brown soft and elastic solid, by pouring nearly boiling sulphur into cold water. It consists of a complete random arrangement of chains of sulphur atoms which, when stretched, align themselves parallel to each other. On standing sulphur, it slowly changes over into rhombic sulphur, as the chains of sulphur atoms break and reform the S_8 cyclic units.

Colloidal Sulphur

This type of sulphur is prepared by passing hydrogen sulphide through a cooled saturated solution of sulphur dioxide in water, or by adding a solution of sulphur and alcohol in water. Colloidal sulphur is soluble in carbon disulphide. It is used in medicine.

Milk of Sulphur

Milk of sulphur is prepared by the action of dilute hydrochloric acid on ammonium sulphide. Milk of sulphur is also prepared by boiling roll sulphur with an aqueous solution of calcium hydroxide. The mixture is then filtered and dilute hydrochloric acid is added to the filtrate to get milk of sulphur. Milk of sulphur is non-crystalline and white in colour. It is soluble in carbon disulphide. When heated, it changes to the ordinary yellow variety of sulphur. It is used in medicine.

Physical Properties

1. Sulphur is a yellow solid
2. It is insoluble in water but soluble in carbon (IV) sulphide and methyl benzene
3. It is a bad conductor of heat and electricity
4. It has a melting point of 119 ^{o}C and boiling point of 445 ^{o}C.

N.B:

- Both rhombic and monoclinic sulphur melt to a yellow liquid. Owing to the conversion of rhombic to monoclinic sulphur, and also to possible variations in the percentage of allotropes of liquid sulphur formed, the melting points are sharp; rhombic sulphur melts at approximately 113 ^{o}C and monoclinic sulphur at approximately 119 ^{o}C.
- As the temperature rises the colour of the liquid darkens until it is nearly black, and it becomes viscous. At about 200 ^{o}C the viscosity begins to fall and at its boiling point of 445 ^{o}C the liquid is again mobile.
- When sulphur vapour comes in contact with a cool surface it sublimes to give pale yellow solid.

Chemical Properties

1. **Reaction with metals**: Sulphur combines directly with many metals to form sulphides when heated in the absence of air.

$$Mg_{(s)} + S_{(s)} \rightarrow MgS_{(s)}$$
$$Fe_{(S)} + S_{(s)} \rightarrow FeS_{(S)}$$
$$2Cu + S_{(s)} \rightarrow Cu_2S_{(s)}$$

2. **Reaction with non-metals**: Non-metals that combine with sulphur directly include fluorine, chlorine, oxygen and carbon; hydrogen combines reversibly to a slight extent when passed through molten sulphur near its boiling point.

$$S_{(s)} + 3F_{2(g)} \rightarrow SF_{6(g)}$$
$$2s_{(s)} + Cl_{2(g)} \rightarrow S_2Cl_{2(l)}$$
$$S_{(s)} + C_{(s)} \rightarrow CS_{2(l)}$$
$$H_{2(g)} + S_{(l)} \leftrightarrows H_2S_{(g)}$$
$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$$

NOTE: when sulphur is heated in a plentiful supply of air, it burns with a bright blue flame to form sulphur (IV) oxide and a small amount of Sulphur (VI) oxide.

3. **Reaction with concentrated acid**: Sulphur is oxidized when warmed with concentrated tetraoxosulphate (VI) acid to form sulphur (IV) oxide. When warmed with concentrated trioxosulphate (V) acid, using bromine as a catalyst, it is oxidized to tetraoxosulphate (VI) acid. It is oxidized by hot concentrated solutions of alkalis to form a sulphide and a sulphite when react with more sulphur to form polysulphides and a thiosulphide respectively.

$$S_{(s)} + 6HNO_{3(aq)} \rightarrow 2H_2O_{(l)} + H_2SO_{4(aq)} + 6NO_{2(g)}$$
$$S_{(s)} + 2H_2SO_{4(l)} \rightarrow 2H_2O_{(aq)} + 3SO_{2(g)}$$
$$3S_{(s)} + 6OH^-_{(aq)} \rightarrow 2S^{2-}_{(aq)} + SO_3^{2-} + 3H_2O_{(l)}$$

Hydrogen Sulphide

Hydrogen sulphide occurs in great quantities in the natural gas deposits of France and Canada and these sources are of major importance to the sulphuric acid industry. Very small quantities of the gas are released from bad eggs.

It is usually prepared in the laboratory by the action of dilute hydrochloric acid in ion (II) sulphide in a Kipp's apparatus.

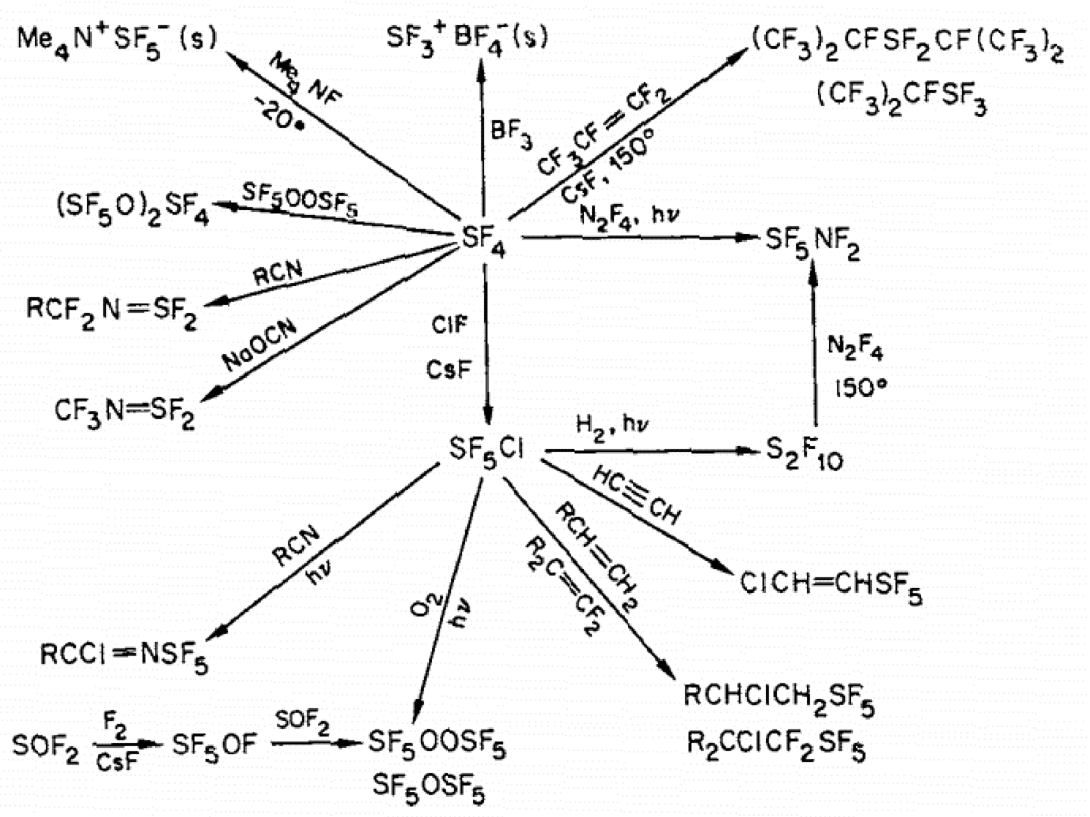
$$FeS_{(s)} + 2H^+_{(aq)} + 2Cl^-_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2Cl^-_{(aq)} + H_2S_{(g)}$$

Since iron (II) sulphide always contains uncombined iron, the gas is contaminated with free hydrogen. A pure gas can be obtained by warming antimony (II) sulphide with concentrated hydrochloric acid.

$$Sb_2S_{3(s)} + 6HCl_{(aq)} \rightarrow 2SbCl_3 + 3H_2S_{(g)}$$

Unlike water, hydrogen sulphide is a gas, since electronegativity of the sulphur atom is insufficient to allow it to participate in hydrogen bonding. However, as should be expected, its molecule has an angular structure with the two lone pair and two bonding pair electron taking up an approximately tetrahedral position.

It is an extremely poisonous substance (as little as 1 part per 1000 parts of air is fatal), but fortunately its smell becomes intolerable long before the fatal concentration is released.



Some Reactions of Sulphur–Fluorine Compounds

Uses of Sulphur

1. Sulphate is use to produce sulphur (IV) oxide for manufacturing tetraoxosulphate (VI) acid
2. Sulphur is use in the vulcanization of rubber
3. It is used as fungicides and insecticides for spraying crops.
4. It is used as bleaching agent in the pulp and paper industry
5. It is used for production of skin ointments and dyes.

GROUP VII^A

The halogen group (7^A or 17) is the most electronegative in the periodic table, and all elements readily form halide ions, X^-. Trends in chemistry resemble those found in other groups.

The elements form diatomic molecules, F_2 and Cl_2, being gases at normal temperature and pressure, Br_2 liquid and I_2 solid.

Fluorine is limited to an octet of valence electrons. It is the most electronegative and reactive of all elements and often (as with oxygen) brings out the highest oxidation state in other elements. Fluorine is different from other halogen because of its inability to exhibit oxidation state other than -1 in its compounds, the relatively small size of its atom and ion and its low dissociation energy.

Occurrence

F and Cl are moderately abundant elements, principal sources being **fluorite** or fluorspar**,** CaF_2 and **halite,** NaCl, from which the very electronegative elements are obtained by electrolysis. Other sources of F are cryolite, $Na_3[AlF_6]$ and fluorapatite $Ca_5F(PO_4)_3$. Bromine is mainly obtained by oxidation of Br^- found in salt water; iodine occurs as iodates such as $Ca(IO_3)_2$. Astatine is radioactive and only minute amounts are found in nature. Chlorine is used as ClO^- and ClO_2 in bleaches and is an important industrial chemical, other major uses (as with all the halogens) being in the manufacture of halogenated organic compounds.

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Electronic Configuration

F : 2, 7
$1s^22s^22p^5$
Cl : 2.8.7
$1s^22s^22p^63s^23p^5$
Br : 2.8.18.7
$1s^22s^22p^63s^23p^63d^{10}4s^24p^5$
I : 2.8.18.18.7
$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^5$
At : 2.8.18.32.18.7
$1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^65d^{10}6s^26p^5$

Physical Data of Group 7^A Elements

Name	Symbol	Atomic No.	Atomic radius (Ionic radius)	Mp °C	Bp °C
Fluorine	F	9	0.072 (0.136)	-220	-188
Chlorine	Cl	17	0.099 (0.181)	-101	-34.7
Bromine	Br	35	0.114 (0.195)	-7.2	58.8
Iodine	I	53	0.133 (0.216)	114	184
Astatine	At	85			

General Properties

1. All halogens exist as diatomic molecules linked by a covalent bond.
2. F and Cl exist as gases, bromine as liquid and iodine as solid. They are all non-metallic, although there is the usual increase in metallic character with increasing atomic number

e.g. dipyridine iodine nitrate can be written as $[I(pyridine)_2]^+NO_3^-$ containing I^+ ion as part of the complex.

3. Their melting point and boiling point increasing down the group while the volatility decreases down the group. This is due to the increasing strength of Van der Waal's forces with increasing relative molar mass.
4. They are all coloured, the depth of the colour increasing with increase in atomic number.

   Fluorine = pale yellow
   Chlorine = pale green
   Bromine = red brown
   Iodine = Shiny black

5. All halogens except fluorine dissolve slightly in water and colour it. Fluorine is a strong oxidizing agent that converts water to oxygen. Halogens are non-polar simple molecules, hence are more soluble in organic solvents e.g. in tetrachloromethane [Cl is colourless, Br is red and I is violet].

6. They react with metals to form ionic compounds containing halide ion (X^-). With nonmetals and some metals with high oxidation states, they tend to form simple molecular compounds with covalent bond (X_n).

7. They act as strong oxidizing agents. The order of decreasing power as oxidizing agents is $F_2 > Cl_2 > Br_2 > I_2$

Chlorine

Chlorine is the most important element of Halogens. It does not occur free in nature, because it is too reactive instead it is usually find in the combined state as chlorines.

Physical Properties

1. Chlorine is a greenish-yellow gas with an unpleasant chocking smell
2. It is moderately soluble in water
3. It is about 2.5 times denser than air
4. It can easily be liquefied under a pressure of about 6 atmosphere.
5. It is poisonous

Chemical Properties

1. Direct combination with other elements

With metal

Metal react readily with chlorine especially when heated to form corresponding chlorides.

$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$
$$Zn_{(s)} + Cl_{2(g)} \rightarrow ZnCl_{2(s)}$$
$$2Fe_{(s)} + 3Cl_{2(g)} \rightarrow 2FeCl_{2(s)}$$

With non-metals

With the exception of noble gas, oxygen, nitrogen and carbon, all other non-metals burn in chlorine to produce the corresponding chlorides.

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$$

2. With Hydrocarbons

$$C_{10}H_{16} + 8Cl_{2(g)} \rightarrow 10C_{(s)} + 16HCl_{(s)}$$

Or

$$CH_{4(g)} + Cl_{2(g)} \rightarrow CH_3Cl + HCl_{(g)}$$

3. With Ammonia

Chlorine will remove hydrogen from ammonia with the formation of nitrogen and hydrogen chloride.

$$2NH_{3(g)} + 3Cl_{2(g)} \rightarrow N_{2(g)} + 6HCl_{(g)}$$
$$6HCl_{(g)} + 6NH_{3(g)} \rightarrow 6NH_4Cl_{(s)}$$

4. With Hydrogen sulphide

A yellow deposit of sulphur is formed as a result of the oxidation sulphide by chlorine.

$$H_2S_{(g)} + Cl_{(g)} \rightarrow 2HCl_{(g)} + S_{(s)}$$

5. With Water: Chlorine water gives off oxygen when exposed to sunlight.

$$Cl_{2(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + HOCl_{(aq)}$$
$$2HOCl_{(aq)} \xrightarrow{sunlight} 2HCl_{(aq)} + O_{2(g)}$$

6. As a bleaching agent

It bleaches most dyes and inks in the pressure of water.

$$HOCl_{(aq)} \rightarrow HCl_{(aq)} + [O]$$
$$\underset{\text{Coloured}}{\text{Dye}} + [O] \rightarrow \underset{\text{Colourless}}{[\text{Dye} + O]}$$

7. With concentrated alkalis solutions

If chlorine is bubbled through a hot concentrated solution of sodium hydroxide, a mixture of trioxochlorate (V) is formed.

$$3Cl_{2(g)} + 6NaOH_{(aq)} \rightarrow NaClO_{3(aq)} + 5NaCl_{(aq)} + 3H_2O_{(l)}$$

Uses of Chlorine

1. It is used in the sterilization of water for domestic and industrial use and in the treatment of sewage.
2. It is used as a bleaching agent for cotton, linen and wood-pulp.
3. It is used as a domestic antiseptic e.g. acidified sodium oxochlorate (I) solution.
4. It is used in the manufacturing of important organic solvent such as $CHCl_3$, CCl_4, C_2HCl_3 etc
5. It is used in the manufacture of plastics and polyvinyl chloride (PVC)

Fluorine

The most important naturally occurring compound of fluorine is fluorspar (calcium fluoride), CaF_2; cryolite (Na_3AlF_6) is of importance in the extraction of aluminium.

Physical Properties

1. Fluorine is a pale yellow with an irritating smell; it is extremely poisonous. It liquefies at -188^oC and freezes at $-220\ ^oC$
2. Most metals catch fire in fluorine.

3. It is the most reactive element found on earth

Chemical Properties

1. Reaction with water

   It dissolves readily in water to form hydrofluoric acid

$$2H_2O_{(l)} + 2F_{2(g)} \rightarrow 4HF_{(l)} + O_{2(g)}$$

Fluorine is the most electronegative element; it displaces other halogens from aqueous solution of their compound.

2. Reaction with Xenon

$$Xe_{(g)} + 2F_{2(g)} \rightarrow XeF_{4(s)}$$

Uses of Fluorine

1. Fluorine and hydrogen fluoride are used to make uranium hexafluoride which is used in separating the isotopes of uranium.
2. Hydrofluoric acid is used in etching glass and in cleaning steel
3. Its compounds are also used as a refrigerator, anesthetic, non-stick agent, insulator and so on.

Compounds

1. Halides

Stability

Nearly all elements form thermodynamically stable halides. The normal stability sequence is F>Cl>Br>I, which in covalent compounds, follows the expected order of bond strengths, and in ionic compounds that of lattice energies.

The thermodynamic stability of fluorides (and the kinetic reactivity of F_2) is also aided by the weak F-F bond.

Volatility

Most nonmetallic elements form simple **molecular compounds** in which each halogen atom has a single bond to the other element. This is true also for metals in high oxidation states (e.g. $TiCl_4$ and UF_6). The compounds may be solids, liquids or gases, with volatility in the order F>Cl>Br>I as expected from the strength of van der Waals' forces. In hydrogen halides, HF is exceptional, because of strong hydrogen bonding. HF is a weak acid in water, the other HX compounds being strong acids.

Polymeric Nature

Covalent halides are less often polymeric in structure than oxides, a difference partly caused by the different stoichiometries (e.g. SiF_4 versus SiO_2), which provide a higher coordination number in the monomeric molecular halides. However, the halides of some metals (e.g. beryllium) may be better regarded as polymeric than ionic. Some molecular halides of both metallic and nonmetallic elements form halogen-bridged dimers and higher oligomers (e.g. Al_2Cl_6).

Polarizability

Most metallic elements form solid halides with structures expected for **ionic solids**. Structural differences often occur with MX_2 and MX_3, fluorides more often having rutile, fluorite or rhenium trioxide structures, and the heavier halides layer structures. These differences reflect the more ionic nature of fluorides, and the higher polarizability of the larger halide ions.

Solubility

Many halides are very soluble in water, but low solubilities are often found with fluorides of M2+ and M3+ ions (e.g. CaF2, AlF3), and with heavier halides of less electropositive metals (e.g. AgCl, TlCl). These differences are related to lattice energy trends.

2. Halide Complexes

Many halides of metals and nonmetals are good Lewis acids. Such compounds are often hydrolyzed by water, and also form halide complexes (e.g. $\mathrm{AlCl_4^{2-}}$, $\mathrm{PF_6^-}$), which can make useful counterions in solids with large or strongly oxidizing cations.

3. Oxides and oxoacids

I_2O_5 is the only halogen oxide of moderate thermodynamic stability. Other compounds include X_2O (not I), X_2O_2 (F and Cl), the odd-electron XO_2 (Cl and Br), and Cl_2O_7.

Most of these compounds are strongly oxidizing, have low thermal stability and can decompose explosively. ClO_2 is used as a bleaching agent. Except for fluorine, the elements have extensive oxoacid chemistry.

The sharp trend in oxidizing power of the elements (X_2/X^- potential) can be seen. As expected from Pauling's rules, the **hypohalous acids** X(OH) and **chlorous acid** ClO(OH) are weak acids, but the **halic acids** $XO_2(OH)$ and especially **perchloric acid** $ClO_3(OH)$ and perbromic acid are strong. **Periodic acid** is exceptional, as, although periodates containing the tetrahedral ion are known, the predominant form in water is the octahedral $IO(OH)_5$, which, as expected, is a weak acid.

4. Interhalogen and Polyhalogen Compounds

Binary compounds known as **interhalogen compounds** with stoichiometry XY_n are found between every pair of halogens. For neutral molecules, *n* is an odd number and when *n*>1, the terminal atom Y is always the lighter element. The maximum *n* found with a given pair increases with the difference in period number, some examples being IBr, ICl_3, BrF_5 and IF_7. Most interhalogen compounds are obtained by direct reaction. They are strongly oxidizing and the fluorides are good fluorinating agents.

Many interhalogen and polyhalogen anions and cations are also known, some forming easily. For example, aqueous solutions containing I^- dissolve I_2 to form I_3^- . In liquid BrF3 the following equilibrium occurs:

$$2\mathrm{BrF_3} \leftrightharpoons \mathrm{BrF_2^+} + \mathrm{BrF_4^-}$$