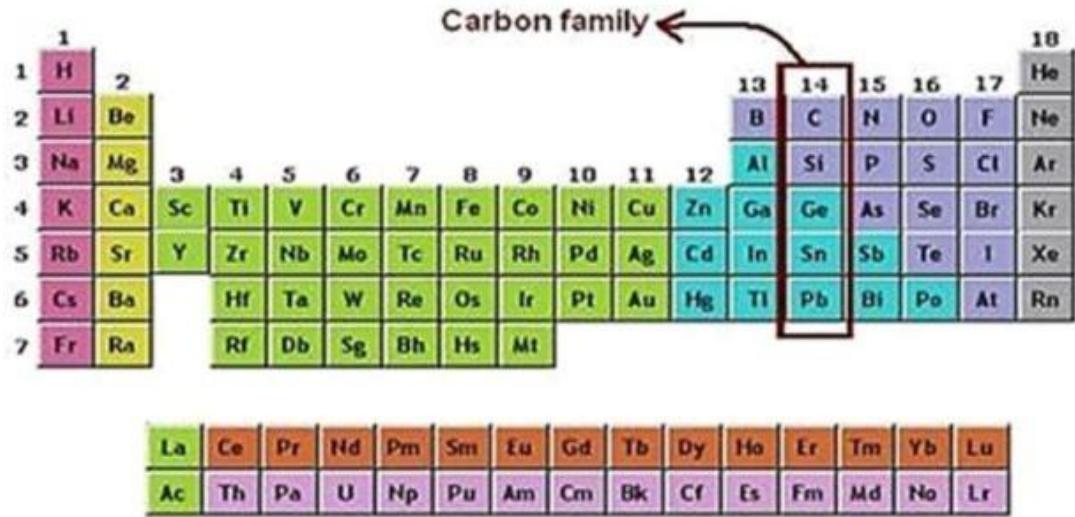


Chemistry of Gr 14



Element	Atomic number	Electronic configuration
C	6	[He]2s ² 2p ²
Si	14	[Ne]3s ² 3p ²
Ge	32	[Ar]3d ¹⁰ 4s ² 4p ²
Sn	50	[Kr]4d ¹⁰ 5s ² 5p ²
Pb	82	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ²

Catenation

The ability of an element to form long chains or ring structures by linking its atoms with one another through covalent bonds is called catenation. On moving down the group, the catenation tendency decreases. The variation of the tendency for catenation in going from carbon to lead follows the order.



The atomic size increases and hence the strength of the element -element bond, i.e., the bond dissociation enthalpy decreases steadily. Consequently the tendency for catenation decreases down the group with increasing atomic number.

Exception of catenation property is found in group-15 and group -16 in the periodic table. The catenation property of phosphorus is higher than that of nitrogen. This is due to the higher bond strength of P-P bond as compared to N-N bond. The weakness of N-N bond is due to repulsion between the lone pairs present on the two nitrogen atoms. But N₂ molecule is stable due to triple bond.

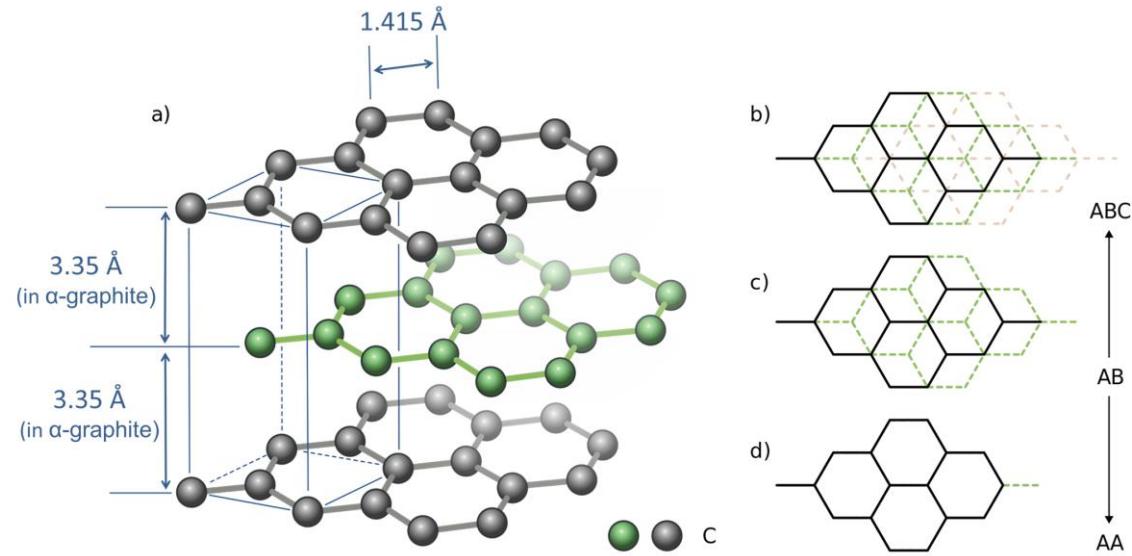
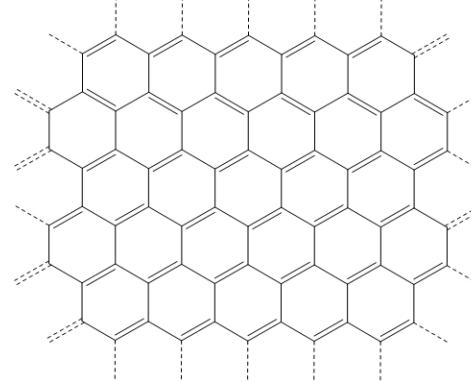
Phosphorus also contains lone pairs but due to longer bond length, the lone pairs exert less repulsion. Also the vacant d-orbitals on phosphorus involved in lone pair delocalization.

The catenation property of sulphur is also higher than that of oxygen due to above mentioned reason

As elements, carbon's ability to form strong multiple bonds enables it to form many allotropes while the remaining elements are network covalent or metallic solids.

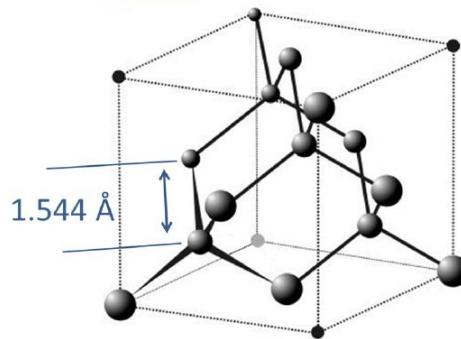
Carbon forms a wider variety of allotropes than the other group 14 elements. Specifically, carbon's ability to form strong π bonds enables it to form delocalized sheet-like structures in the form of graphite and graphene (planar sheets) and nanotubes and fullerenes, which may be considered as sheets wrapped over to form tubes and ball-like structures

α - and β -Graphite: The α form of graphite is the most stable carbon allotrope. It is formed naturally through the decomposition of carbonaceous material in sediments but may also be made synthetically by vaporizing the Si out of SiC.



Graphene: Individual graphene sheets have been the subject of intense experimental and theoretical investigation as a 2D nanomaterial.

Diamond: When subjected to extremes of heat and pressure, graphite converts to its more dense diamond allotrope, in which all the carbons are tetrahedral and held together by sigma bonds. In this structure all the carbons are tetrahedral and connected in chair conformation rings. As might be expected from such a tightly interconnected, diamond is extremely hard,, all- σ structure, it is a poor electrical conductor and the 1.544 Å C-C bond length in diamond is longer than the 1.415 Å C-C bond length in graphite

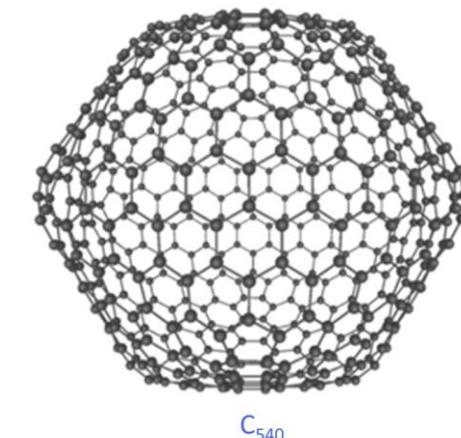
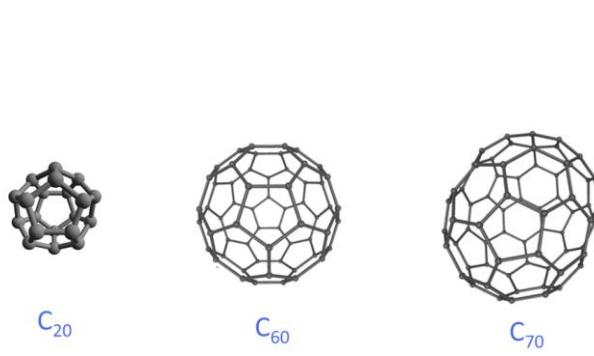


Fullerenes. Since the late 1980s discovery of the sixty-carbon European football (soccer ball) shaped buckminsterfullerene shown in Figure. It is recognized that such molecules have long been present in soot, carbon black, and related materials. Produced today by electrolytic or laser ablation or pyrolysis, a large number of such structures have been produced

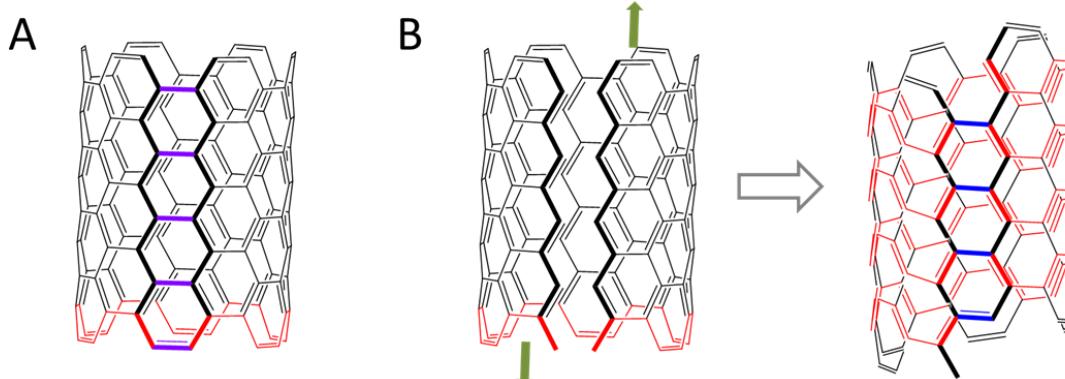
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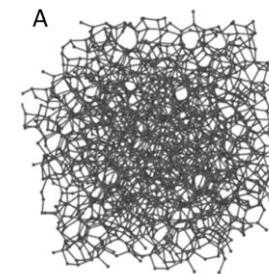
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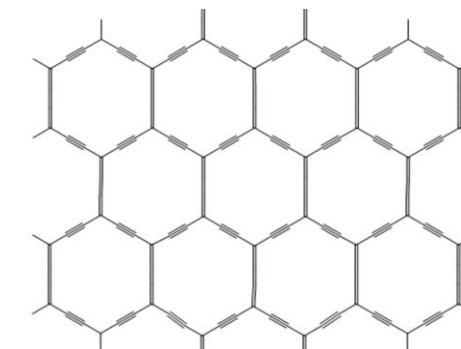
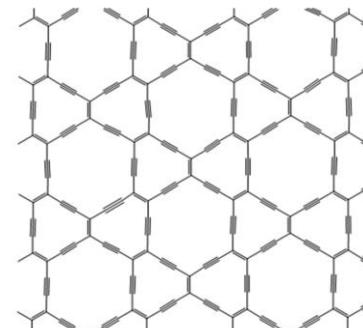
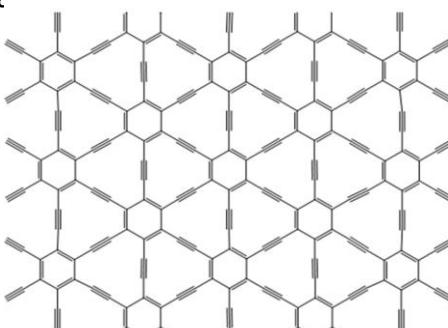
carbon nanotubes are relatively linear.



High-carbon content amorphous materials. These are technically not a single form or a pure allotrope but rather a family of high-carbon content materials that include amorphous carbon, carbon black, soot, pyrolyzed coal, coal, and charcoal.



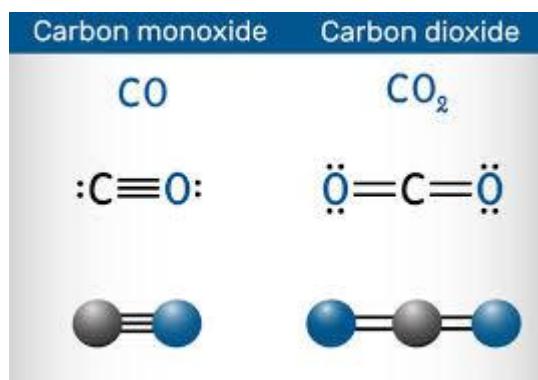
Graphyne - a possible future carbon allotrope? The discovery of fullerene and carbon nanotube structures held together exclusively by interconnected C-C and C=C bonds raises the issue of whether it might be possible to construct forms of carbon that include or are even primarily comprised of C≡C bonds. These materials, called graphynes, by analogy with the double bonded structure of graphene, are predicted to be theoretically stable but as yet have been neither observed in nature or made experimentally.



Compounds (Oxides of Carbon)

CO₂ (Carbon dioxide)

- Formed when organic matter burns in the a plentiful source of air and when animals exhale
- CO₂ is always present in air but the burning of fossil fuels is increasing the amount of CO₂ in the air which is then in-turn leading to global warming
- CO₂ is an acid anhydride of carbonic acid
$$\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$$
- Carbonated beverages have high partial pressures of CO₂ to drive the equilibrium to H₂CO₃ when the beverage is opened the equilibrium shifts to produce CO₂



CO (Carbon monoxide)

- Formed when carbon burns in the a limited source of air
- This happens in cigarettes and badly tuned automobile engines
- CO is the formula anhydride to formic acid (HCOOH)
- CO can be produced in the laboratory by the dehydration of formic acid with hot, concentrated sulfuric acid
$$\text{HCOOH(l)} \xrightarrow{150^\circ \text{C}, \text{H}_2\text{SO}_4} \text{CO(g)} + \text{H}_2\text{O(l)}$$
- CO is a reducing agent and is used in the production of a number of metals, most notably iron in blast furnaces

Properties:

Colorless
Odorless
Flammable
Almost Insoluble
Toxic Gas

Water gas is a combustion fuel containing carbon monoxide (CO) and hydrogen gas (H₂).

The principle of water gas production is straightforward. Steam is forced over red-hot carbon-based fuel, producing the following reaction:

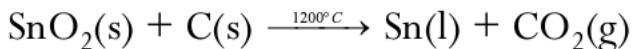


Si, Ge, Sn and Pb

- Second most abundant atom in the earth's crust
- Occurs widely in rocks as silicates (compounds containing the silicate ion, SiO_3^{2-})
- Pure silicon is obtained by reduction of quartzite (a granular form of quartz) with high purity carbon in an electric arc furnace

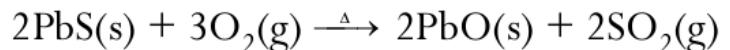


- Germanium is recovered from the flue dust of industrial plants processing zinc ores (it occurs as an impurity in zinc).
- Germanium is mainly used in the semiconductor industry.
- Tin is easily obtained from its ore (cassiterite (SnO_2)) by reduction with carbon.



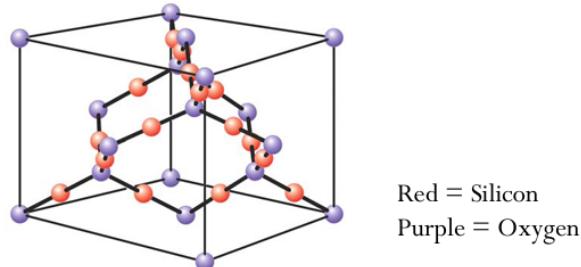
- Tin is expensive and not very strong but it is resistant to corrosion. Its main use is in tin plating and used in alloys such as bronze.

- Lead is also easily obtained from its ore (galena (PbS)) and converted to its oxide and then reduced with coke (form of carbon)



SiO_2 (Silica)

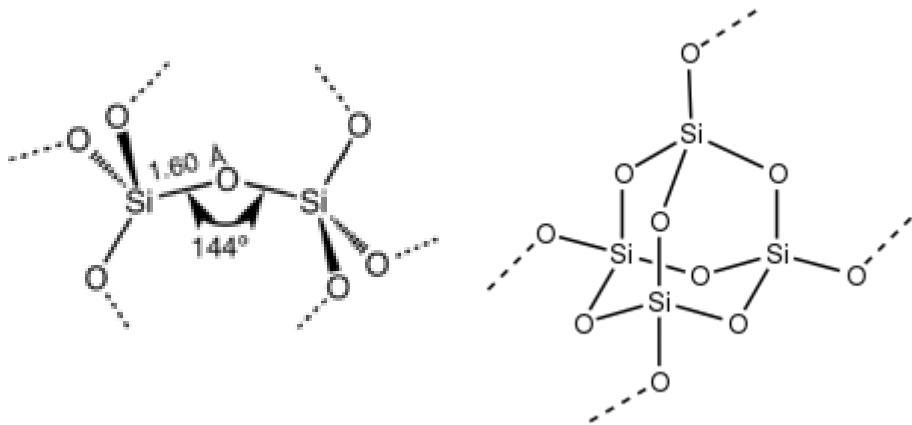
- Occurs naturally in quartz,
- Sand is usually small fragments of quartz. The golden brown color is caused by iron oxide impurities
- Silica gets its strength from its covalent bonding network structure.



- Silicates can be viewed as various arrangements of tetrahedral oxoanions (an anion of an acid that contains oxygen) of silicon in which each Si-O bond has considerable covalent character
- Differences in the internal structure of these highly regular network solids lead to a wide array of materials, ranging from gemstones to fibers

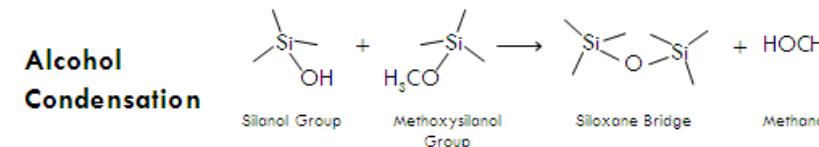
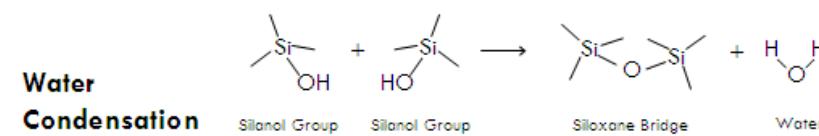
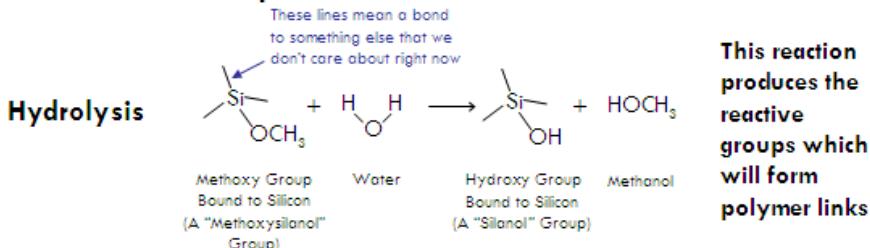
Properties:

Hard
Rigid network solid
Insoluble in water



quartz

The Three Primary Reactions in Silica Gel Formation via the Alkoxide Technique



This reaction produces the reactive groups which will form polymer links

Once silanol groups form, they can condense through two different reactions to form connective silicon-oxygen-silicon bridges

ZnSiO_4 (Zircon) Used as a substitute for diamonds in costume jewelry

$\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_11)_2(\text{OH})_2$ (Tremolite or Asbestos) Fibrous material which can withstand extreme heat (once widely used for insulation in buildings) however fibers can lodge in lung tissue where fibrous scar tissue forms leading to lung cancer

This is quite similar to diamond, although it alternates silicon (grey) with oxygen (red) instead of being all carbon atoms. The silicon atoms bond to the four oxygen atoms in a way which is also similar to carbon in diamond, a tetrahedral (triangular-based pyramid) structure. However, the proportion of silicon to oxygen is actually 1:2, hence the empirical formula SiO_2 .

Silicones

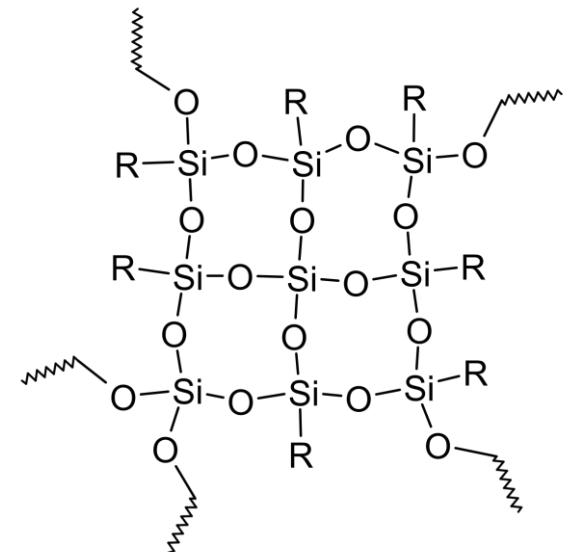
- Synthetic materials that consist of long -O-Si-O-Si- chains with the remaining silicon bonding positions occupied by organic groups such as the methyl group (-CH₃)
- Silicones are used to waterproof fabric because their oxygen atoms attach to the fabric, leaving the hydrophobic methyl groups like tiny inside out umbrellas sticking out of the fabrics surface

Most common are materials based on polydimethylsiloxane, which is derived by hydrolysis of dimethyldichlorosilane. This dichloride reacts with water as follows:



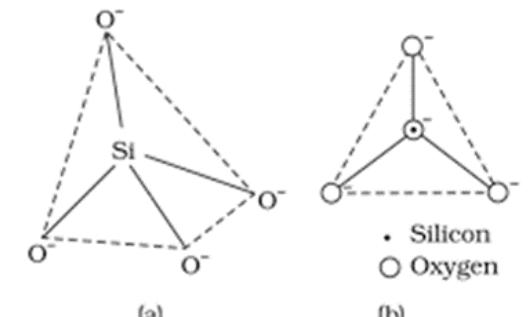
The polymerization typically produces linear chains capped with Si-Cl or Si-OH (silanol) groups. Under different conditions, the polymer is a cyclic, not a chain

Silicones have a number of medical applications because they are chemically inert. Medical devices composed of silicone may be approved by the FDA for permanent or temporary implantation. Catheters, tubing, gastric bags, drains, and endoscopic windows are examples of consumable medical devices that are often molded from silicone.



The most common type of **silicate** is $(\text{SiO}_4)^{4-}$.

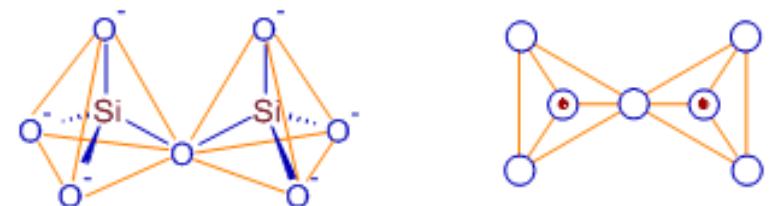
Orthosilicates are minerals consisting of only single SiO_4^{4-} units. The cations are some other metals. For example, the following minerals are orthosilicates: The Be and Zn ions are tetrahedrally bonded to the oxygen of the silicate in these two minerals: phenacite, Be_2SiO_4 and willemite, Zn_2SiO_4 . In olivine, $(\text{Fe}, \text{Mg})_2\text{SiO}_4$, the cations are either Fe^{2+} or Mg^{2+} .



(a) Tetrahedral structure of SiO_4^{4-} anion; (b) Representation of SiO_4^{4-} unit

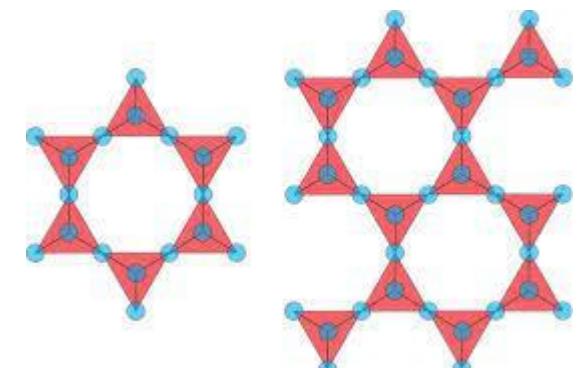
Pyrosilicates

When two SiO_4^{4-} units are linked together, they form the pyrosilicate group, $\text{Si}_2\text{O}_7^{6-}$. For example, thortveitite, $\text{Sc}_2\text{Si}_2\text{O}_7$ is a pyrosilicate.



Ring and chain silicates

When two oxygen of SiO_4^{4-} units share with other SiO_4^{4-} units, the silicates form a ring or an infinite chain. The stoichiometry of the silicates becomes $(\text{SiO}_3)_n^{2n-}$. Benitoite $\text{BaTi}(\text{SiO}_3)_3$ contain three silica rings, but these are relaxed 6-atom rings



Silicon, Silica, Silicates and Silicone

People get confused about the differences between silicon, silicate, silica and even silicone. What is it exactly that we collect, cut and polish?? Silicon is a chemical element, one of the 97 natural building blocks from which our minerals are formed. A chemical element is a substance that can't be subdivided into simple substances without splitting atoms. Silicon is the second most abundant element in the earth's crust, making up about 27% of the average rock. Silicon links up with oxygen (which makes up 55% of the earth's crust) to form the most common suite of minerals, called the silicates. Quartz, feldspars, olivine, micas, thomsonite, jadeite, and prehnite are all silicates. There is so much oxygen around that pure native silicon is almost never found naturally. Silica is a bit trickier concept. It refers the combination of silicon plus oxygen. The mineral quartz is silica. But so are the minerals tridymite, coesite, cristobalite and stishovite which are mineral forms of silica that are stable at high temperatures and pressures. All these minerals are also silicates. In other words, quartz is a silicate made of pure silica. But feldspars contain sodium, aluminum, potassium and calcium in addition to silicon and oxygen. Thus feldspars are silicates but they aren't pure silica. Geochemists also use the term "silica" to refer to the overall silicon and oxygen content of rocks. This is confusing, but stems from the fact that in rock analysis a sample is dissolved, the solution treated, and the amount of silicon present is determined by precipitating it as silica.

So a geologist may say "This rock is 48% silica". A rockhound will look at the rock and say "How can that be? I don't see any quartz in it!" Both are right. The rock will not have the mineral quartz because the silicon and oxygen are tied up with other elements to make silicate minerals like feldspar. Its a bit like looking at a cake and saying "I don't see any eggs in there!" The eggs are cake ingredients but are present now in different forms. Now, what is silicone? Its a synthetic polymer of silicon with carbon and oxygen that could be in solid, liquid or gel form. It has all kinds of medical uses, such as in antacids, artificial joints, pacemakers and implants of various notoriety, but is not, as far as anyone knows, found in rocks. Can pure silicon be found in Nature? Yes, rarely. Recently Russian geologists were sampling gasses from Kudriavy volcano on the Kamchatka Peninsula. Here they drove quartz tubes into vents jetting out gases of over 900 degrees C. Their tubes filled with minerals precipitating from this gas. Among them were pure silicon metal embedded in masses of salts such as halite. The silicon formed crystals up to 0.3 mm across.

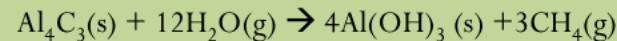
It was associated with pure aluminum metal, Si-Al alloys and other rare minerals. This find was unusual enough to warrant a note in the prestigious science journal, Nature. So unless you are in Russia sampling hot volcanic gases, you can be sure that what you are finding are silica and silicates, but not silicon or silicone.

Korzhinsky, M.A., et al., 1995, "Native Al and Si Formation", Nature, vol. 375, p. 544.

A carbide is a compound composed of carbon and a less electronegative element, usually a metal or a metal oxide. Carbides can be generally classified by chemical bonding type as follows:

Salt-like or ionic carbides - Having discrete carbon anions of the forms C^{4-} , sometimes called methanides, C_2^{2-} carbides are acetylides

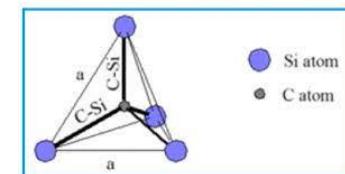
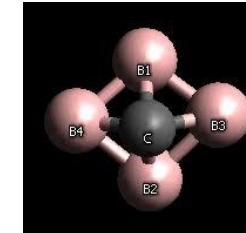
Example:



- The methide ions are very strong Bronstead bases

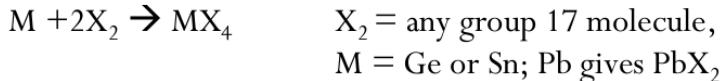
Acetylides react with water to produce ethyne (C_2H_2) and the corresponding hydroxide CaC_2 (calcium carbide) is the most common saline carbide.

Covalent compounds - Two carbides that are considered completely covalent; they are formed with the two elements that are most similar to carbon in size and electronegativity, boron and silicon

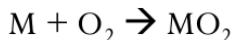


Interstitial compounds - Characterized by extreme hardness but also extreme brittleness. Interstitial carbides are the compounds formed by the direct reaction of a d-block metal and carbon at temperature above 2000 deg C.

Reaction with Halogens



Reactions with O

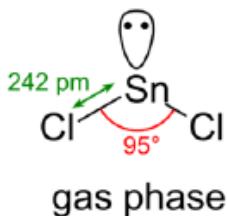


Reactions with the ions

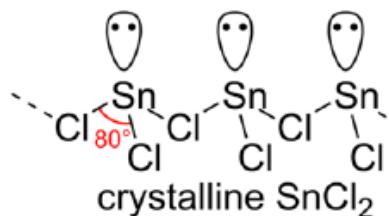


The inert pair of electrons exerts structural effects.

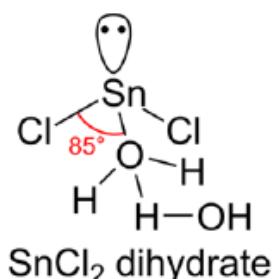
Regardless of the origin of the inert pair effect, the inert pair of electrons influences the structure of compounds in the $(n-2)^+$ oxidation state. Electron pairs that do this by altering the observed geometry of compounds are said to be stereochemically active inert pairs. The lone pairs of Sn(II)Cl_2 are the classic example. Gas phase Sn(II)Cl_2 exhibits an AX_2E VSEPR geometry while its in the solid state, hydrates, and salts all exhibit AX_3E geometries, consistent with the influence of a lone pair of electrons.



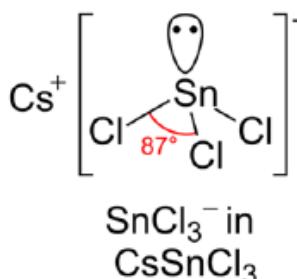
gas phase



crystalline SnCl_2



SnCl_2 dihydrate



SnCl_3^- in
 CsSnCl_3

Gr-15 chemistry

Nitrogen

- Electron configurations ns^2np^3 (n is the period number)
 - Oxidation states that range from -3 to +5
 - The metallic character of the group increases down the group

- Rare in the Earth's crust but elemental nitrogen (N_2) is the principal component of our atmosphere (76% by mass)
 - N≡N triple bond strength is $944 \text{ kJ}\cdot\text{mol}^{-1}$ making it almost as inert as the noble gases
 - Nitrogen is used in medicines, fertilizers, explosives, and plastics
 - The biggest commercial use for elemental nitrogen gas is for the formation of ammonia in the Haber process
 - N is very electronegative and it is the only group 15 element that can form hydrides capable of hydrogen bonding
 - N has a wide range of oxidation numbers. Nitrogen compounds are known to have every whole number oxidation number from -3 to +5. In addition, some fractional oxidation numbers are known to exist.



Small amounts of N₂ can be prepared by thermal decomposition of sodium azide or by reaction. The latter should be carried out cautiously because of the risk of explosion. Ammonium nitrite (NH₄NO₂) is potentially explosive, as is ammonium nitrate which is a powerful oxidant and a component of dynamite. In car airbags, the decomposition of NaN₃ is initiated by an electrical impulse.

Phosphorous

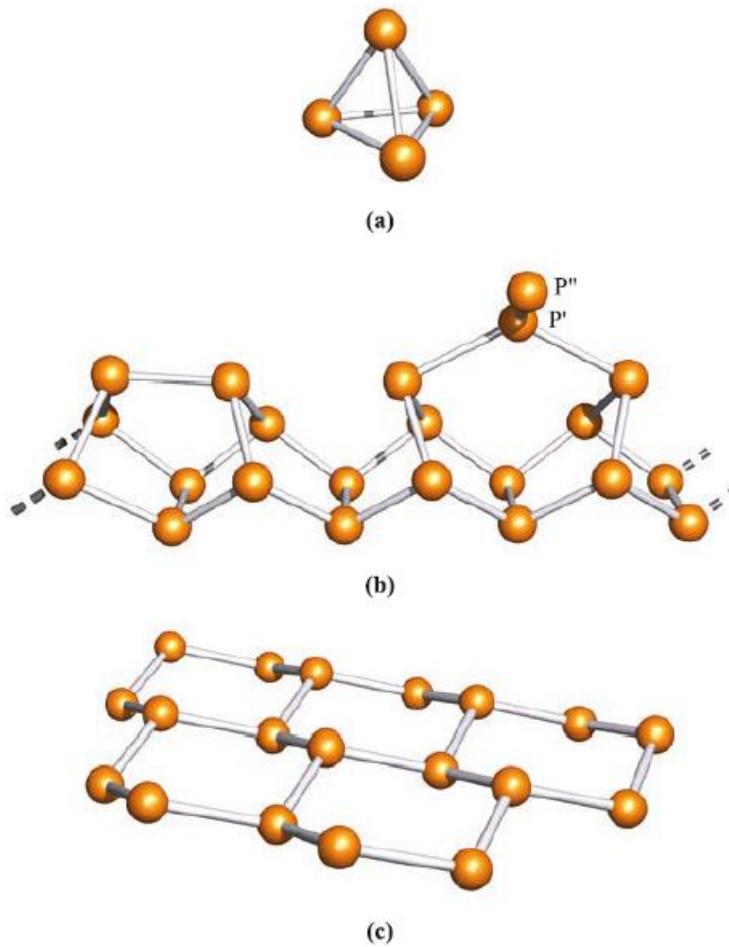
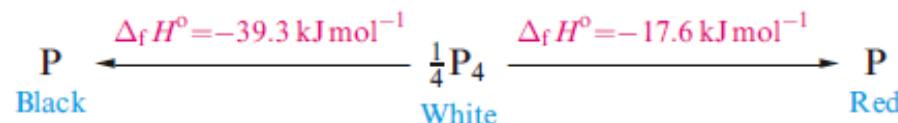


Fig. 15.3 (a) The tetrahedral P_4 molecule found in white phosphorus. (b) Part of one of the chain-like arrays of atoms present in the infinite lattice of Hittorf's phosphorus; the repeat unit contains 21 atoms, and atoms P' and P'' are equivalent atoms in adjacent chains, with chains connected through $P'-P''$ bonds. The same chains are also present in fibrous red phosphorus. (c) Part of one layer of puckered 6-membered rings present in black phosphorus and in the rhombohedral allotropes of arsenic, antimony and bismuth.

Phosphorus exhibits complicated allotropy; 12 forms have been reported, and these include both crystalline and amorphous forms. Crystalline white phosphorus contains tetrahedral P_4 molecules in which the P-P distances (221 pm) are used to define $r_{\text{cov}} = 110$ pm for a single bond. White phosphorus is defined as the standard state of the element, but is actually metastable. The lower stability of the white form probably originates in strain associated with the 60 deg bond angles.

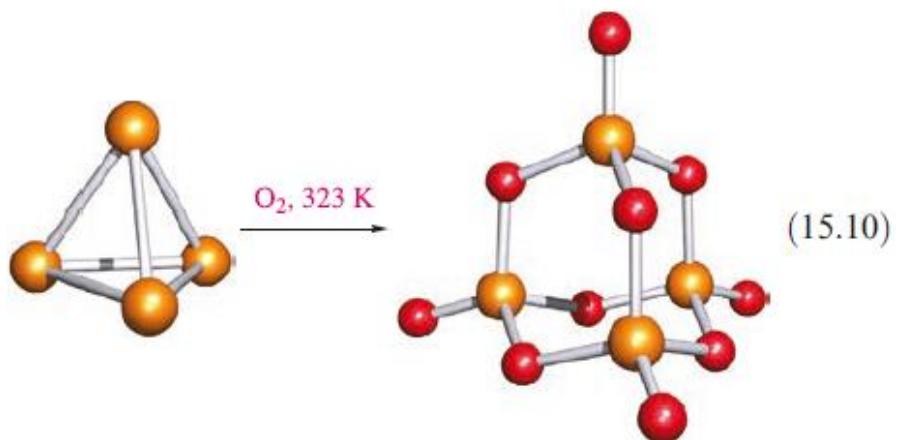


White phosphorus is manufactured by reaction, and heating this allotrope in an inert atmosphere at 540K produces red phosphorus.

On melting, all allotropes give a liquid containing P_4 molecules, and these are also present in the vapour. Above 1070K or at high pressures, P_4 is in equilibrium with P_2

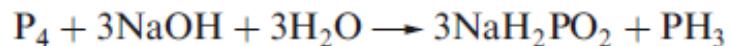


In moist air, white P undergoes chemiluminescent oxidation, emitting a green glow and slowly forming P_4O_8 and some O_3 ; the chain reaction involved is extremely complicated.



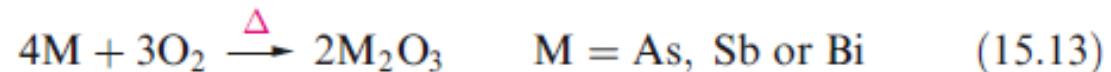
Above 323 K, white phosphorus inflames, yielding phosphorus(V) oxide (eq. 15.10); in a limited supply of air, P₄O₆ may form.

White phosphorus combines violently with all of the halogens, giving PX₃ (X = F, Cl, Br, I) or PX₅ (X = F, Cl, Br) depending on the relative amounts of P₄ and X₂. Concentrated HNO₃ oxidizes P₄ to H₃PO₄, and with hot aqueous NaOH, reaction occurs, some H₂ and P₂H₄ also being formed.

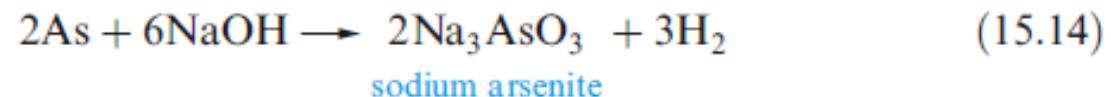


As, Sb, Bi

Arsenic, antimony and bismuth burn in air (eq. 15.13) and combine with halogens (see Section 15.7).



The elements are not attacked by non-oxidizing acids but react with concentrated HNO₃ to give H₃AsO₄ (hydrated As₂O₅), hydrated Sb₂O₅ and Bi(NO₃)₃ respectively, and with concentrated H₂SO₄ to produce As₄O₆, Sb₂(SO₄)₃ and Bi₂(SO₄)₃ respectively. None of the elements reacts with aqueous alkali, but As is attacked by fused NaOH (eq. 15.14).



Oxides

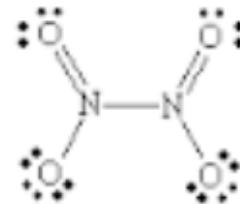
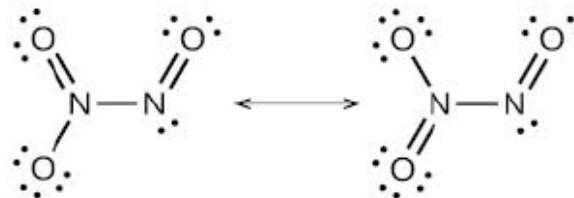
- Nitrogen: N_2O , NO , N_2O_3 ,
 NO_2 , N_2O_4 , N_2O_5 ;

- Phosphorus: P_4O_6 & P_4O_{10} ;

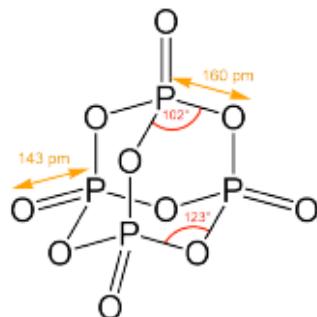
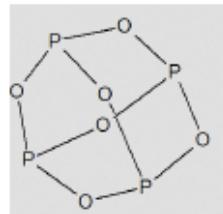
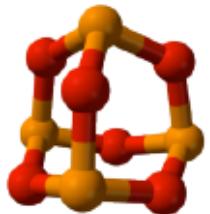
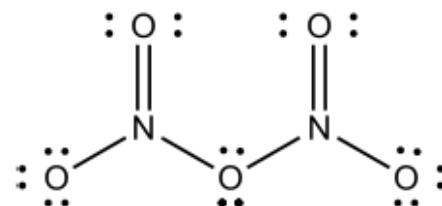
- Arsenic: As_2O_3 (As_4O_6) & As_2O_5 ;

- Antimony: Sb_2O_3 & Sb_2O_5

- Bismuth: Bi_2O_3 & Bi_2O_5



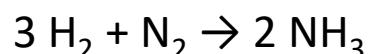
Dinitrogen tetroxide, N_2O_4



phosphorus in orange, oxygen in red

Hydrides of Gr.15:

Ammonia: To produce the desired end-product ammonia, the hydrogen is then catalytically reacted with nitrogen (derived from process air) to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop (also referred to as the Haber-Bosch process):

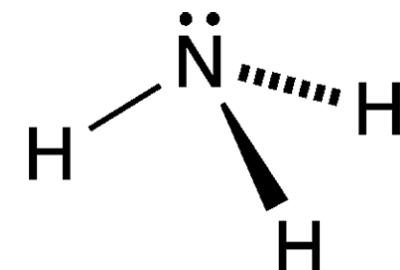
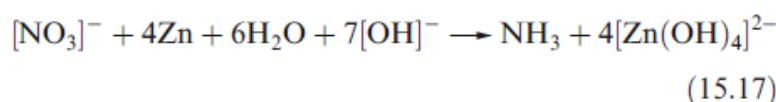
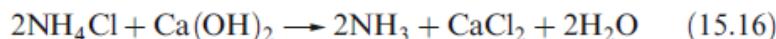


Frank–Caro process

Adolph Frank and Nikodem Caro found that N₂ could be fixed by calcium carbide to form calcium-cyanamide, which could then be divided with water to form ammonia. The method was developed between 1895 and 1899.



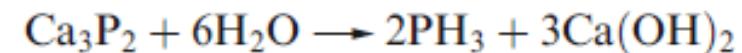
Ammonia is obtained by the action of H₂O on the nitrides of Li or Mg (eq. 15.15), by heating [NH₄]⁺ salts with base (e.g. reaction 15.16), or by reducing a nitrate or nitrite in alkaline solution with Zn or Al (e.g. reaction 15.17).



Obnoxious smell

Aqueous ammonia is also called ammonium hydroxide, but that molecule cannot be isolated. Ammonia is used as a ligand in coordination complexes.

Phosphine synthesis

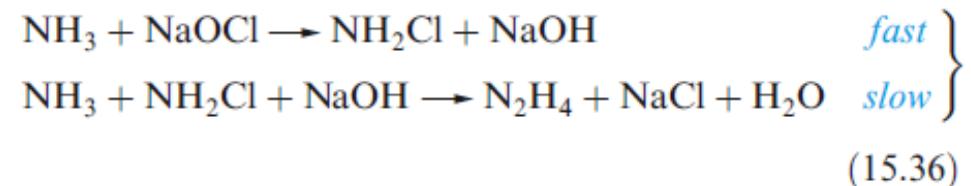


Hydrides E₂H₄ (E = N, P, As)

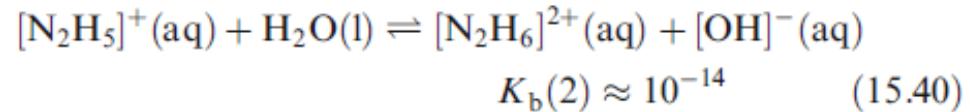
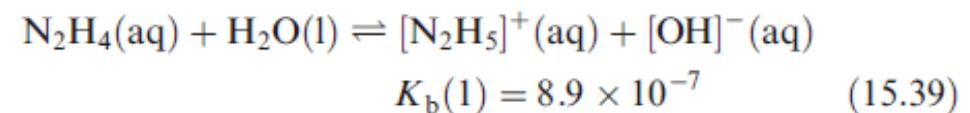
Hydrazine, N₂H₄, is a colourless liquid (mp 275 K, bp 386 K), miscible with water and with a range of organic solvents, and is corrosive and toxic. Its vapour forms explosive mixtures with air. Although $\Delta_f H^\circ(N_2H_4, 298\text{ K}) = +50.6\text{ kJ mol}^{-1}$, N₂H₄ at ambient temperatures is *kinetically* stable with respect to N₂ and H₂. Alkyl derivatives of hydrazine (see eq. 15.44) have been used as rocket fuels, e.g. combined with N₂O₄ in the *Apollo* missions.[†] N₂H₄ has uses in the agricultural and plastics industries, and in the removal of O₂ from industrial water boilers to minimize corrosion (eq. 15.35).



Hydrazine is obtained by the Raschig reaction (the basis for the industrial synthesis) which involves the partial oxidation of NH₃ (eq. 15.36). Glue or gelatine is added to inhibit side-reaction 15.37 which otherwise consumes the N₂H₄ as it is formed; the additive removes traces of metal ions that catalyse reaction 15.37.



In aqueous solution, N₂H₄ usually forms [N₂H₅]⁺ (hydrazinium) salts, but some salts of [N₂H₆]²⁺ have been isolated, e.g. [N₂H₆][SO₄]. The pK_b values for hydrazine are given in eqs. 15.39 and 15.40, and the first step shows N₂H₄ to be a weaker base than NH₃ (eq. 15.24).



Both N₂H₄ and [N₂H₅]⁺ are reducing agents, and reaction 15.41 is used for the determination of hydrazine.



Hydrogen azide and azide salts

Sodium azide, NaN_3 , is obtained from molten sodium amide by reaction 15.50 (or by reacting NaNH_2 with NaNO_3 at 450 K), and treatment of NaN_3 with H_2SO_4 yields hydrogen azide, HN_3 .

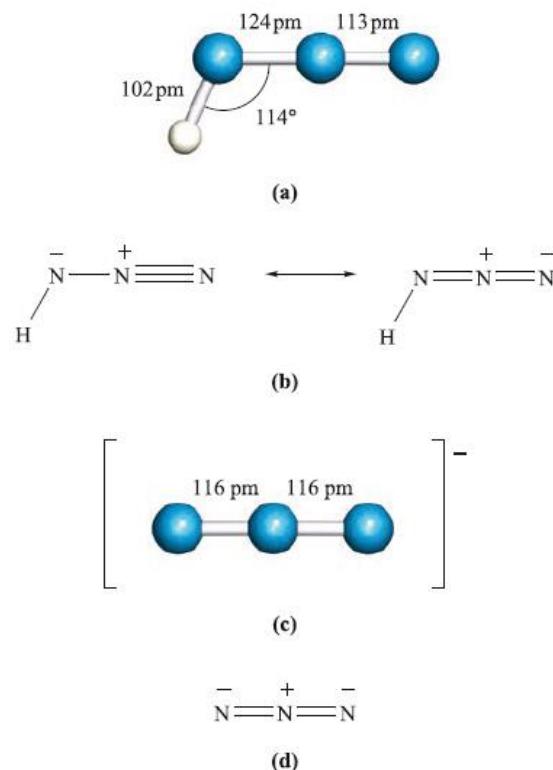
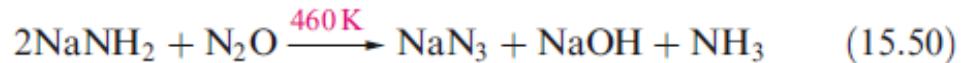
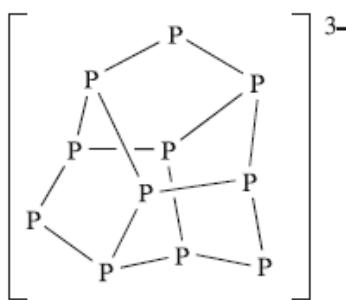
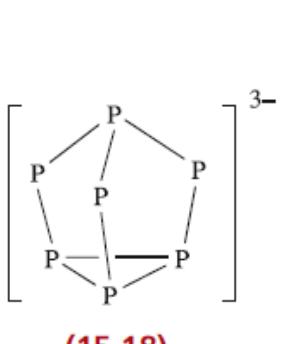


Fig. 15.7 (a) Structure of HN_3 , (b) the major contributing resonance forms of HN_3 , (c) the structure of the azide ion (the ion is symmetrical but bond distances vary slightly in different salts), and (d) the principal resonance structure of $[\text{N}_3]^-$. Colour code: N, blue; H, white.

Phosphides

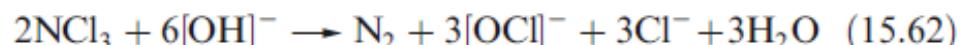
Most elements combine with phosphorus to give solid state binary phosphides; exceptions are Hg, Pb, Sb and Te.

The group 1 and 2 metals form compounds M_3P and M_3P_2 respectively, which are hydrolysed by water and can be considered to be ionic. The alkali metals also form phosphides which contain groups of P atoms forming chains or cages, the cages being either $[\text{P}_7]^{3-}$ (15.18) or $[\text{P}_{11}]^{3-}$ (15.19). Lithium phosphide of stoichiometry LiP consists of helical chains and is better formulated as $\text{Li}_n[\text{P}_n]$, the $[\text{P}_n]^{n-}$ chains being isoelectronic with S_n (see Box 1.1). The P-P distances in the chains are 221 ppm, consistent with single bonds ($r_{\text{cov}} = 110$ pm). K_4P_3 contains $[\text{P}_3]^{4-}$ chains, Rb_4P_6 has planar $[\text{P}_6]^{4-}$ rings, Cs_3P_7 contains $[\text{P}_7]^{3-}$ cages, and Na_3P_{11} features $[\text{P}_{11}]^{3-}$ cages. Ba_3P_{14} and Sr_3P_{14} also contain $[\text{P}_7]^{3-}$ cages. The phosphides BaP_{10} , CuP_7 , Ag_3P_{11} , MP_4 (e.g. M = Mn, Tc, Re, Fe, Ru, Os) and TiP_5 contain more extended arrays of P atoms, two examples (15.9 and 15.10) of which have already been mentioned.

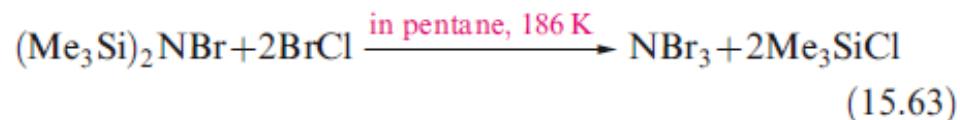


Halides of Nitrogen

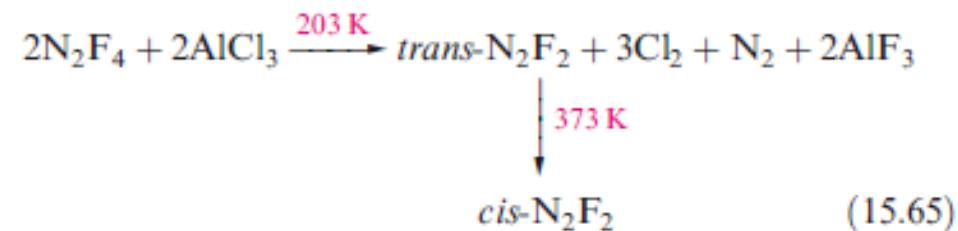
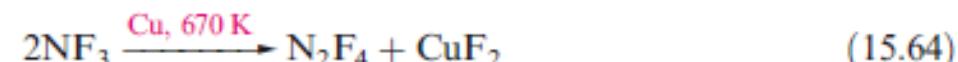
Nitrogen trichloride is an oily, yellow liquid at 289 K, but it is highly endothermic and dangerously explosive (Table 15.5). The difference in stabilities of NF_3 and NCl_3 lies in the relative bond strengths of N–F over N–Cl, and of Cl_2 over F_2 . Nitrogen trichloride can be prepared by reaction 15.61, with the equilibrium being drawn to the right-hand side by extracting NCl_3 into a suitable organic solvent. Diluted with air, NCl_3 is used for bleaching flour since hydrolysis by moisture forms HOCl (see Section 17.9). Alkalies hydrolyse NCl_3 according to eq. 15.62.



Nitrogen tribromide is more reactive than NCl_3 , and explodes at temperatures as low as 175 K. It can be prepared by reaction 15.63, attempts to make it by treating NCl_3 with Br_2 being unsuccessful.



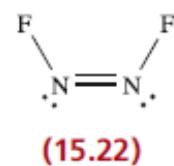
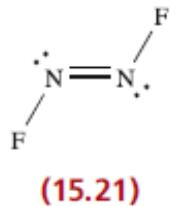
The nitrogen fluorides N_2F_4 and N_2F_2 can be obtained from reactions 15.64 and 15.65. Properties of these fluorides are listed in Table 15.5, and both compounds are explosive.



The structure of N_2F_4 resembles that of hydrazine, except that both the *gauche* and *trans* (staggered) conformers (Fig. 15.4) are present in the liquid and gas phases. At temperatures above 298 K, N_2F_4 reversibly dissociates into blue NF_2^+ radicals which undergo a wide range of reactions (e.g. eqs 15.66–15.68).

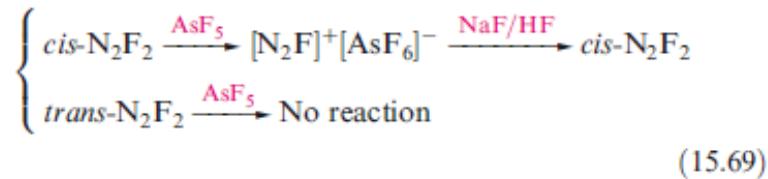


Phosphorous halides

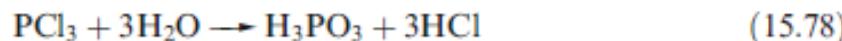
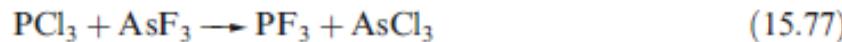
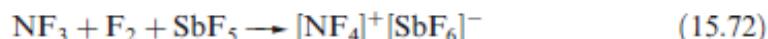
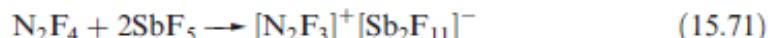


Dinitrogen difluoride, N_2F_2 , exists in both the *trans*- and *cis*-forms (15.21 and 15.22), with the *cis*-isomer being thermodynamically the more stable of the two but also the more reactive. Reaction 15.65 gives a selective method of preparing *trans*- N_2F_2 . Isomerization by heating gives a mixture of isomers from which *cis*- N_2F_2 can be isolated by treatment with AsF_5 (reaction 15.69).

Mixture of isomers:

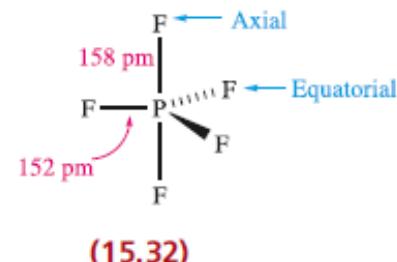
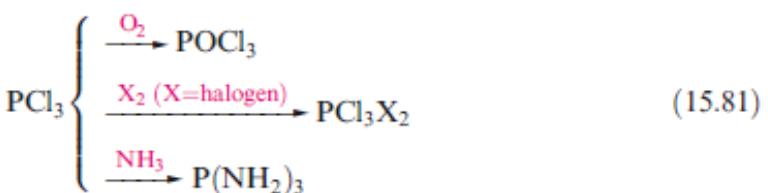


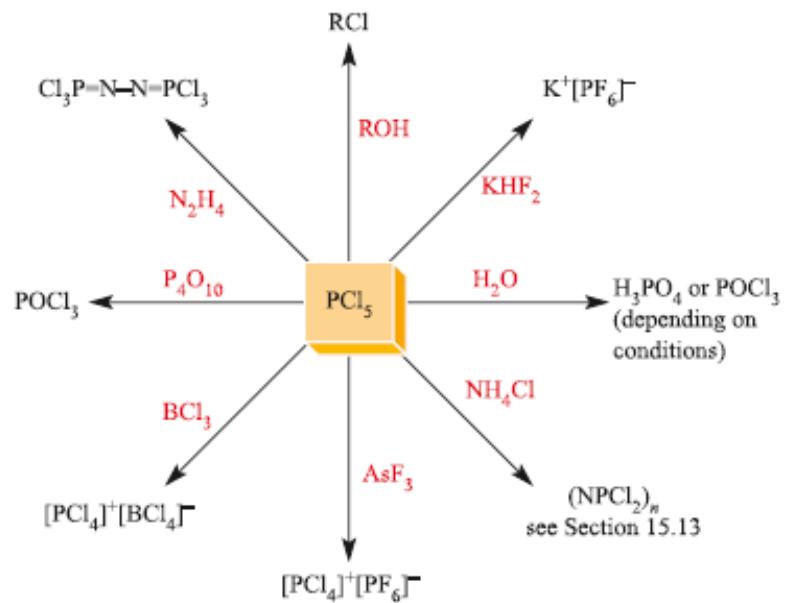
Reaction 15.69 illustrates the ability of N_2F_2 to donate F^- to *strong* acceptors such as AsF_5 and SbF_5 , a reaction type shared by N_2F_4 (eqs. 15.70 and 15.71). The cation $[\text{NF}_4]^+$ is formed in reaction 15.72. We return to the properties of AsF_5 and SbF_5 later.



X	a / pm	α / °
F	156	96.5
Cl	204	100
Br	222	101
I	243	102

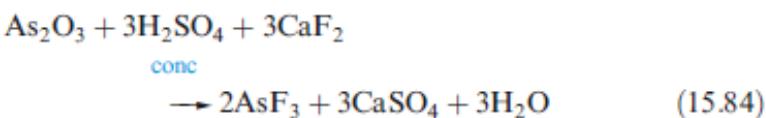
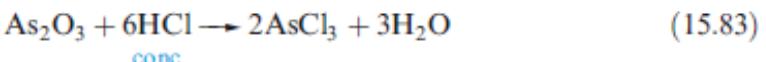
Phosphorus trichloride is a colourless liquid (mp 179.5 K, bp 349 K) which fumes in moist air (eq. 15.78) and is toxic. Its reactions include those in scheme 15.81.



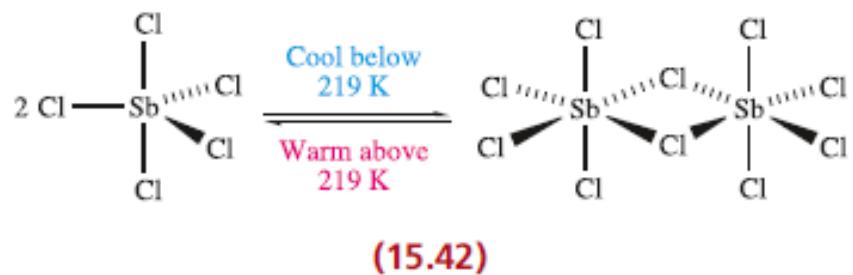


Arsenic and antimony halides

Arsenic forms the halides AsX_3 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) and AsX_5 ($X = \text{F}, \text{Cl}$). The trihalides AsCl_3 , AsBr_3 and AsI_3 can be made by direct combination of the elements, and reaction 15.83 is another route to AsCl_3 . Reaction 15.84 is used to prepare AsF_3 (mp 267 K, bp 330 K) despite the fact that AsF_3 (like the other trihalides) is hydrolysed by water; the H_2O formed in the reaction is removed with excess H_2SO_4 . Glass containers are not practical for AsF_3 as it reacts with silica in the presence of moisture.

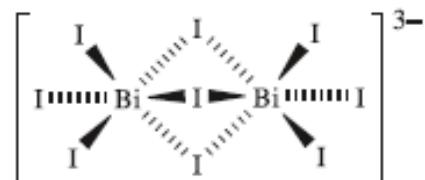
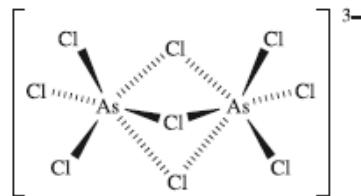


AsF_5 is a strong F⁻ acceptor and many complexes containing the octahedral $[\text{AsF}_6]^-$ ion are known.



Like PCl_5 and AsCl_5 , the axial bonds in SbCl_5 are longer than the equatorial bonds (233 and 227 pm for the solid at 243 K). Below 219 K, the solid undergoes a reversible change involving dimerization of the SbCl_5 molecules.

The reaction of AsCl_3 with Me_2NH and excess HCl in aqueous solution gives $[\text{Me}_2\text{NH}_2]_3[\text{As}_2\text{Cl}_9]$ containing anion 15.36.[†]



Reactions of Oxides and Chlorides

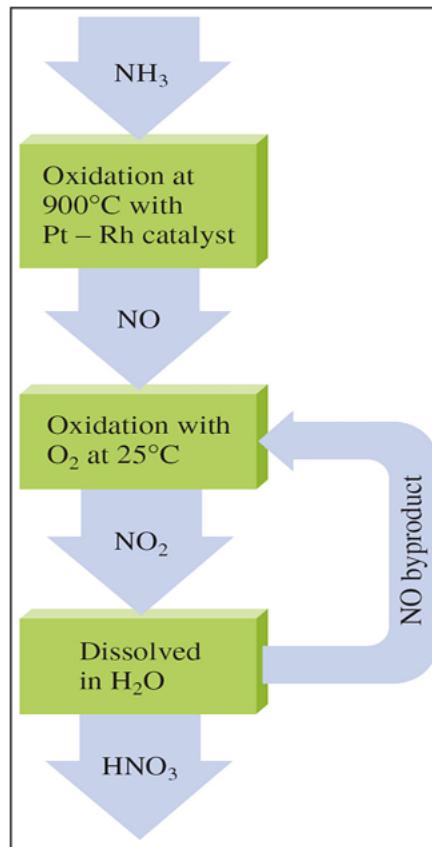
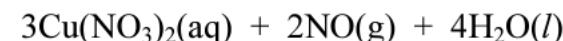
- $3\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(aq) + \text{NO}(g);$
- $\text{N}_2\text{O}_5(g) + \text{H}_2\text{O}(l) \rightarrow 2\text{HNO}_3(aq)$
- $\text{P}_4\text{O}_{10}(s) + 6\text{H}_2\text{O}(l) \rightarrow 4\text{H}_3\text{PO}_4(aq);$
- $\text{As}_2\text{O}_5(s) + 3\text{H}_2\text{O}(l) \rightarrow 2\text{H}_3\text{AsO}_4(aq);$
- $\text{PCl}_5(s) + 4\text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{PO}_4(aq) + 5\text{HCl}(aq);$
- $\text{AsCl}_5(s) + 4\text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{AsO}_4(aq) + 5\text{HCl}(aq);$
- $2\text{SbCl}_5(s) + 5\text{H}_2\text{O}(l) \rightarrow \text{Sb}_2\text{O}_5(s) + 10\text{HCl}(aq);$

- NH_2OH (-1), N_2H_4 (-2), and NH_3 (-3)
- Many reactions involving nitrogen gas are endothermic and compounds containing nitrogen decompose exothermically to the elements.
- $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \quad \Delta H^\circ = 180 \text{ kJ}$
- $2\text{NO}_2(g) \rightarrow \text{N}_2(g) + \text{O}_2(g); \quad \Delta H^\circ = -68 \text{ kJ}$
 $\text{N}_2\text{H}_4(g) \rightarrow \text{N}_2(g) + 2\text{H}_2(g); \quad \Delta H^\circ = -95 \text{ kJ}$

Production of HNO₃ Oswald Process:

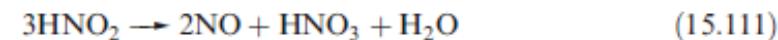
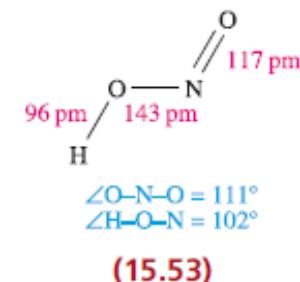
1. NH₃(g) + O₂(g) → NO(g) + H₂O(g)
2. 2NO(g) + O₂(g) → NO₂(g)
3. 3NO₂(g) + H₂O(l) → 2HNO₃(aq) + NO(g)

- HNO₃ - a strong acid and an oxidizing agent;
- Reactions with metals **does not produce H₂**



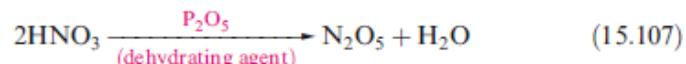
Nitrous acid, HNO₂

Nitrous acid is known only in solution and in the vapour phase. In the latter, it has structure 15.53. It is a weak acid ($\text{pK}_a = 3.37$), but is unstable with respect to disproportionation in solution (eq. 15.111). It may be prepared *in situ* by reaction 15.112, the water-soluble reagents being chosen so as to give an insoluble metal salt (BaSO_4) as a product. AgNO_2 is insoluble but other metal nitrites are soluble in water.



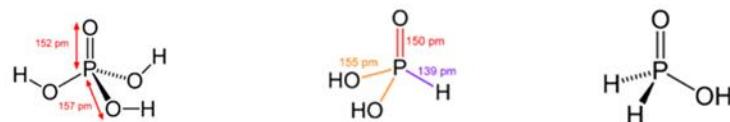
Dinitrogen pentoxide, N₂O₅

Dinitrogen pentoxide (Table 15.6 and Fig. 15.15) is the acid anhydride of HNO₃ and is prepared by reaction 15.107.

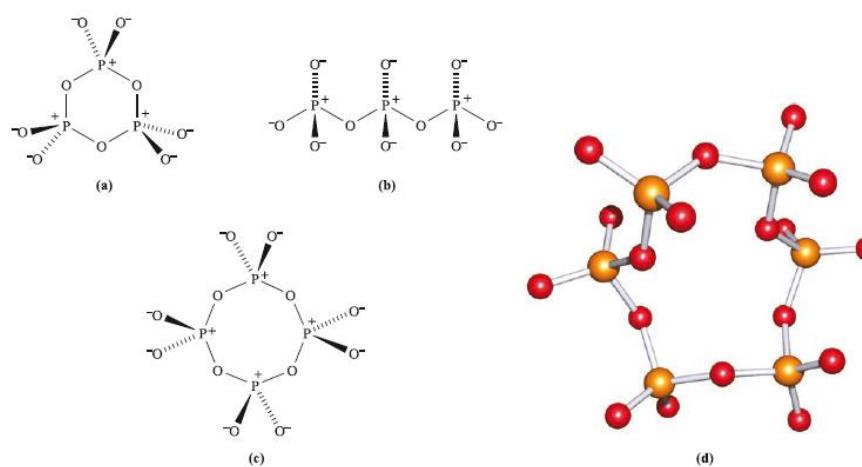
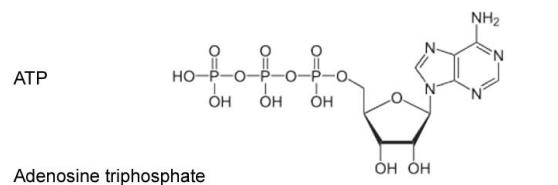


Oxyacids of Phosphorus

- Phosphoric acid, H_3PO_4 - triprotic
- Phosphorous acid, H_3PO_3 - diprotic
- Hypophosphorous acid, H_3PO_2 - monoprotic



H_3PO_2	Phosphinic acid (hypophosphorous acid)		$\text{pK}_a = 1.24$
H_3PO_3	Phosphonic acid (phosphorous acid)		$\text{pK}_a(1) = 2.00; \text{pK}_a(2) = 6.59$
H_3PO_4	Phosphoric acid (orthophosphoric acid)		$\text{pK}_a(1) = 2.21; \text{pK}_a(2) = 7.21; \text{pK}_a(3) = 12.67$
$\text{H}_4\text{P}_2\text{O}_6$	Hypophosphoric acid		$\text{pK}_a(1) = 2.2; \text{pK}_a(2) = 2.8; \text{pK}_a(3) = 7.3; \text{pK}_a(4) = 10.0$
$\text{H}_4\text{P}_2\text{O}_7$	Diphosphoric acid (pyrophosphoric acid)		$\text{pK}_a(1) = 0.85; \text{pK}_a(2) = 1.49; \text{pK}_a(3) = 5.77; \text{pK}_a(4) = 8.22$
$\text{H}_5\text{P}_3\text{O}_{10}$	Triphosphoric acid		$\text{pK}_a(1) \leq 0; \text{pK}_a(2) = 0.89; \text{pK}_a(3) = 4.09; \text{pK}_a(4) = 6.98; \text{pK}_a(5) = 9.93$



Phosphazene

Phosphazenes are a group of P(V)/N(III) compounds featuring chain or cyclic structures, and are oligomers of the hypothetical NPR_2 . The reaction of PCl_5 with NH_4Cl in a chlorinated solvent (e.g. $\text{C}_6\text{H}_5\text{Cl}$) gives a mixture of colourless solids of formula $(\text{NPCl}_2)_n$ in which the predominant species have $n \geq 3$ or 4. The compounds $(\text{NPCl}_2)_3$ and $(\text{NPCl}_2)_4$ are readily separated by distillation under reduced pressure. Although eq. 15.144 summarizes the overall reaction, the mechanism is complicated. There is some evidence to support the scheme in Fig. 15.22 which illustrates the formation of the trimer.

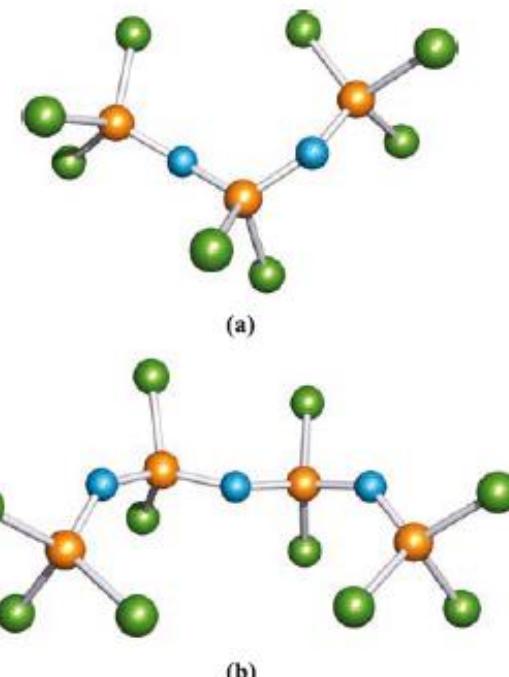
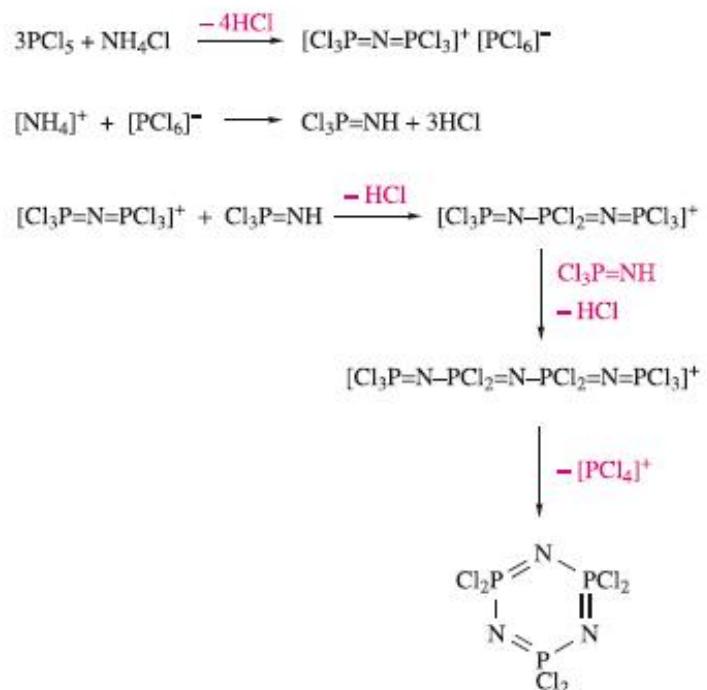
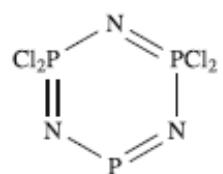
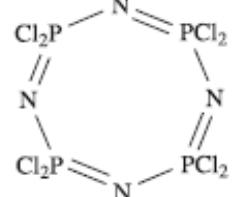


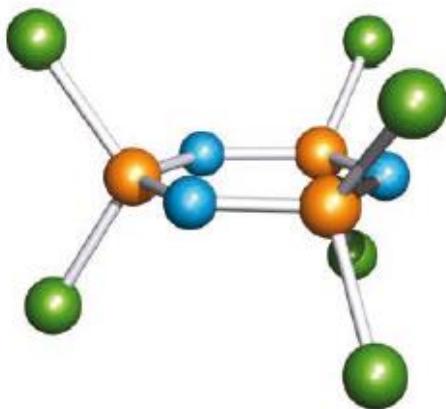
Fig. 15.22 Proposed reaction scheme for the formation of the cyclic phosphazene $(\text{NPCl}_2)_3$, and the structures of (a) $[\text{Cl}_3\text{P}=\text{N}-\text{PCl}_2=\text{N}=\text{PCl}_3]^+$ and (b) $[\text{Cl}_3\text{P}=\text{N}-(\text{PCl}_2=\text{N})_2=\text{PCl}_3]^+$. Both were determined by X-ray diffraction for the chloride salts [E. Rivard *et al.* (2004) *Inorg. Chem.*, vol. 43, p. 2765]. Colour code: P, orange; N, blue; Cl, green.



(15.69)

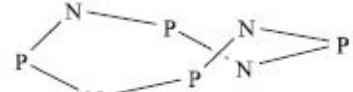


(15.70)

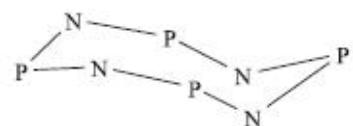


(a)

X = Cl	X = F
P—N / pm	158
P—X / pm	199
∠ P—N—P / deg	121
∠ N—P—N / deg	118
∠ X—P—X / deg	102



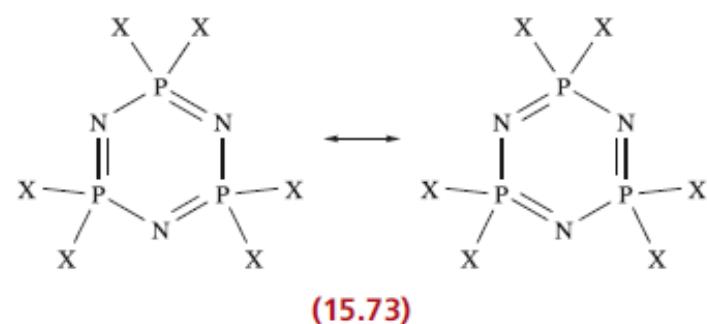
Saddle



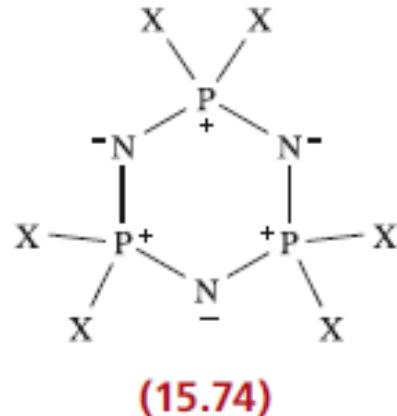
Chair

(b)

Fig. 15.23 (a) Structural parameters for the phosphazenes $(\text{NPX}_2)_3$ ($\text{X} = \text{Cl}$ or F); colour code: P, orange, N, blue; X, green.
 (b) Schematic representations of the P_4N_4 ring conformations in $(\text{NPF}_2)_4$ (saddle conformation only) and $(\text{NPCl}_2)_4$ (saddle and chair conformations).



Traditional bonding descriptions for the 6-membered rings have involved $\text{N}(2p)-\text{P}(3d)$ overlap, both in and perpendicular to the plane of the P_3N_3 -ring. However, this model is not consistent with current opinion that phosphorus makes little or no use of its $3d$ orbitals. Structure 15.74 provides another resonance form for a 6-membered cyclophosphazene, and is consistent with the observed $\text{P}-\text{N}$ bond equivalence, as well as the observation that the N and P atoms are subject to attack by electrophiles and nucleophiles, respectively. Theoretical results are consistent with highly polarized $\text{P}^{\delta+}-\text{N}^{\delta-}$ bonds and the absence of aromatic character in the P_3N_3 -ring.[†] As for the linear polyphosphazenes, both ionic bonding and negative hyperconjugation appear to contribute to the bonding in cyclic phosphazenes.



Sulphides and selenides of Phosphorus

The terminal PS bonds are shorter than those in the cage (e.g. 191 versus 208 pm in P₄S₁₀), and this can be rationalized in terms of a greater ionic contribution to the terminal bonds. Only some of the sulfides are prepared by direct combination of the elements.

Above 570 K, white phosphorus combines with sulfur to give P₄S₁₀ which is the most useful of the phosphorus sulfides. It is a thiating agent (i.e. one that introduces sulfur into a system) in organic reactions, and is a precursor to organothiophosphorus compounds. The reaction of red phosphorus with sulfur above 450K yields P₄S₃, and P₄S₇ can also be made by direct combination under appropriate conditions.

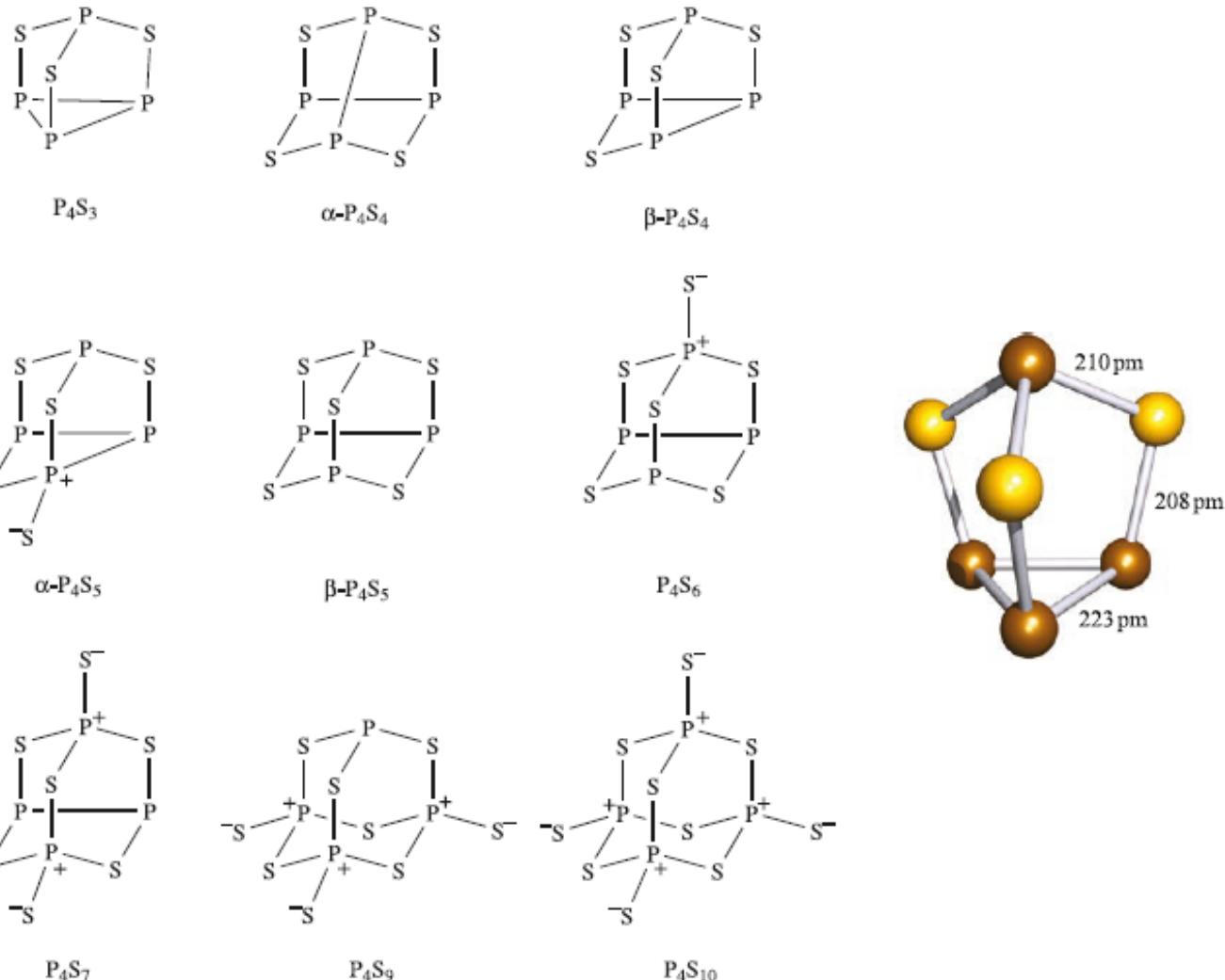
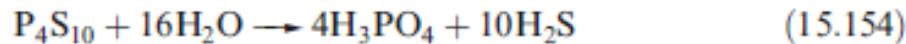
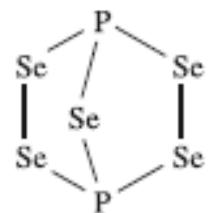


Fig. 15.24 Schematic representations of the molecular structures of phosphorus sulfides, and the structure (X-ray diffraction) of P₄S₃ [L.Y. Goh *et al.* (1995) *Organometallics*, vol. 14, p. 3886]. Colour code: S, yellow; P, brown.

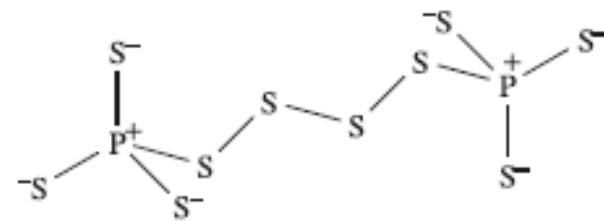
Phosphorus sulfides ignite easily, and P_4S_3 is used in ‘strike anywhere’ matches; it is combined with $KClO_3$, and the compounds inflame when subjected to friction. (In safety matches, the head of the match contains $KClO_3$ and this reacts with red phosphorus which is combined with glass powder on the side of the match box; see end-of-chapter problem 15.42). Whereas P_4S_3 does not react with water, other phosphorus sulfides are slowly hydrolysed (e.g. reaction 15.154).



We have already noted (Section 15.10) that, although sometimes referred to as ‘phosphorus pentoxide’, phosphorus(V) oxide does not exist as P_2O_5 molecules. In contrast, the vapour of phosphorus(V) sulfide contains some P_2S_5 molecules (although decomposition of the vapour to S, P_4S_7 and P_4S_3 also occurs). The phosphorus selenides P_2Se_5 and P_4Se_{10} are distinct species. Both can be made by direct combination of P and Se under appropriate conditions; P_2Se_5 is also formed by the decomposition of P_3Se_4I , and P_4Se_{10} from the reaction of P_4Se_3 and selenium at 620 K. Structure 15.77 has been confirmed by X-ray diffraction for P_2Se_5 ; P_4Se_{10} is isostructural with P_4S_{10} and P_4O_{10} .



(15.77)



(15.78)

When P_2S_5 is heated under vacuum with Cs_2S and sulfur in a 1:2:7 molar ratio, $Cs_4P_2S_{10}$ is formed. This contains discrete $[P_2S_{10}]^{4-}$ ions (15.78), the terminal P–S bonds in which are shorter (201 pm) than the two in the central chain (219 pm).

Group 16: The Oxygen Family

The Element

A periodic table showing the elements of Group 16 (Oxygen Family). The group includes Hydrogen (H), Helium (He), and the chalcogens: Boron (B), Nitrogen (N), Phosphorus (P), Sulphur (S), Selenium (Se), and Tellurium (Te). A blue bracket groups the chalcogens (B, N, P, S, Se, Te) together.

1	2	13/III	14/IV	15/V	16/VI	17/VII	18/VIII
Li	Be	B	C	N	O	F	Ne
			P	S	Cl		
			As	Se	Br		
			Sb	Te	I		
			Bi	Po	At		

- Electron configurations $ns^2 np^4$ (n is the period number)
- Elements become increasingly more nonmetallic toward the right-hand side of the periodic table
- The elements of the group are collectively called the chalcogens

Valence-shell configuration: $ns^2 np^4$

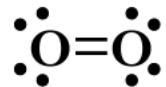
O, S, Se, Te, Po

None of the Group 6A elements behaves as a typical metal.

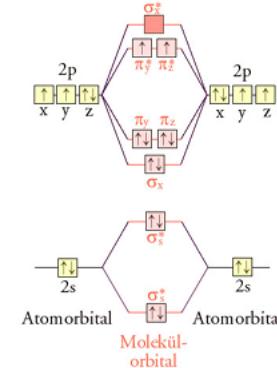
Elements form covalent bonds with other nonmetals.

- The most common form of elemental oxygen is O_2 .

Lewis Structure



Molecular Orbital Diagram

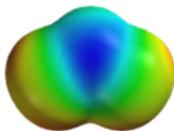
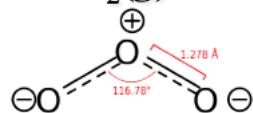
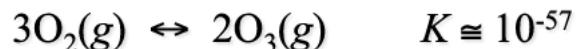


- O_2 has been shown to be paramagnetic therefore it behaves like the molecular orbital diagram predicts instead of the Lewis structure

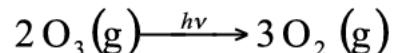
Oxygen

- O₂ makes up 21% of the Earth's atmosphere.
- O₃ (ozone) exists naturally in the upper atmosphere (the stratosphere) of the Earth.

Ozone – forming at electric discharges - pale blue gas

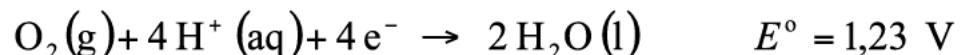


- Ozone layer absorbs UV light and acts as a screen to block most uv-radiation from reaching the Earth's surface.



- We now know that Freons (CFCs = chloro-fluorocarbons) are promoting destruction of ozone layer.

Strong oxidizing agent



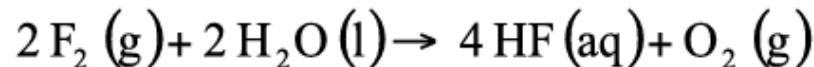
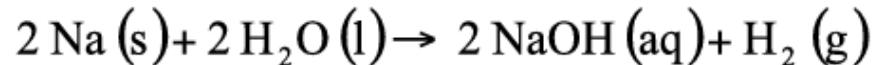
Various Forms of Oxides

- Metal oxides (ionic)
 1. Nonconductor – example: MgO
 2. Semiconductor – example: NiO
 3. Conductor – example: ReO₃
 4. Superconductor – example: YBa₂Cu₃O₇
- Nonmetal oxides (covalent):
 - Molecular oxides – examples: CO₂, NO, NO₂, N₂O, SO₂, P₄O₁₀, etc.
 - Covalent network oxide – SiO₂

Characteristics of Oxides

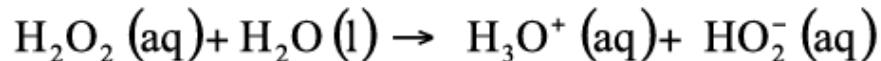
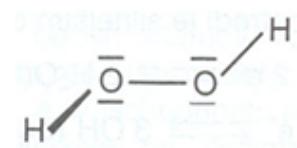
- Metallic oxides – basic or amphoteric
 - Examples: Na₂O (basic); Al₂O₃ (amphoteric)
- Semi-metallic oxides – mild to weakly acidic
 - Example: B₂O₃
- Nonmetallic oxides – weak to strong acids
 - Examples:
 1. SO₂(g) + H₂O(l) → H₂SO₃(aq) (weak acid);
 2. SO₃(g) + H₂O(l) → H₂SO₄(aq) (strong acid);

Redox properties of water



Hydrogen peroxide

weak acid

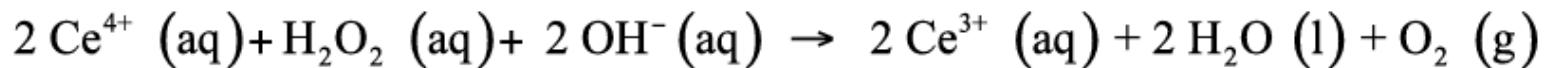
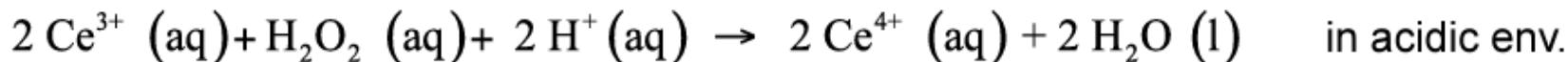


$$\text{p}K_{a1} = 12$$

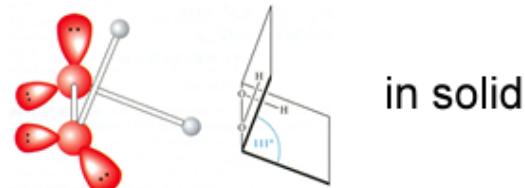
disproportionation



Redox properties



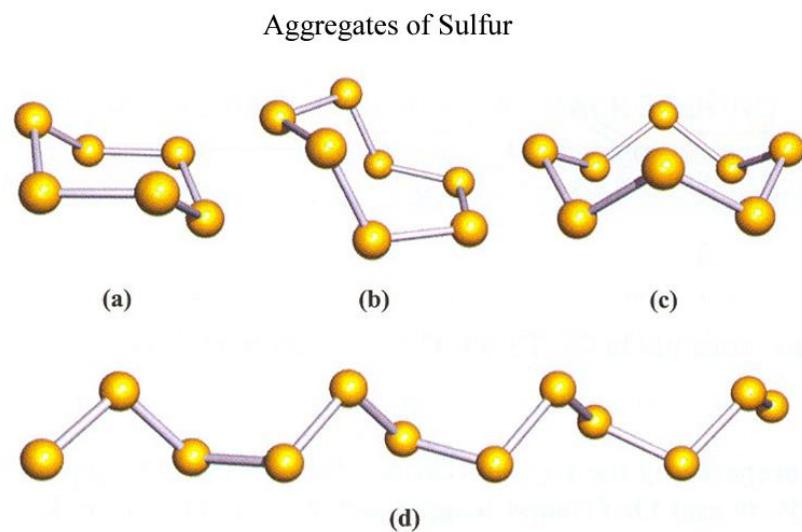
in basic env.



in solid

Sulfur

- Sulfur is found in nature both in large deposits of the free element and in ores such as:
- Galena = PbS,
- Cinnabar = HgS,
- Pyrite = FeS₂,
- Gypsum = CaSO₄·2H₂O,
- Epsomite = MgSO₄·7H₂O, and
- Glauberite = Na₂Ca(SO₄)₂

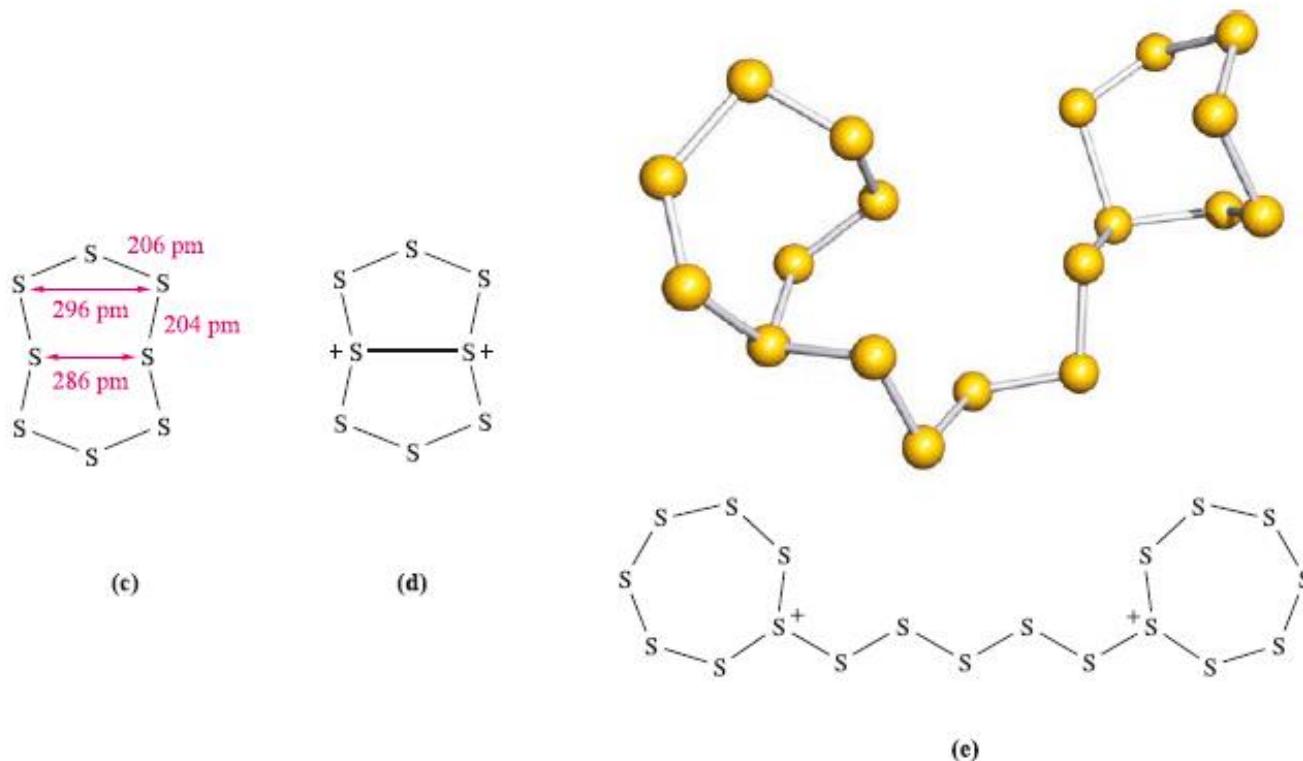
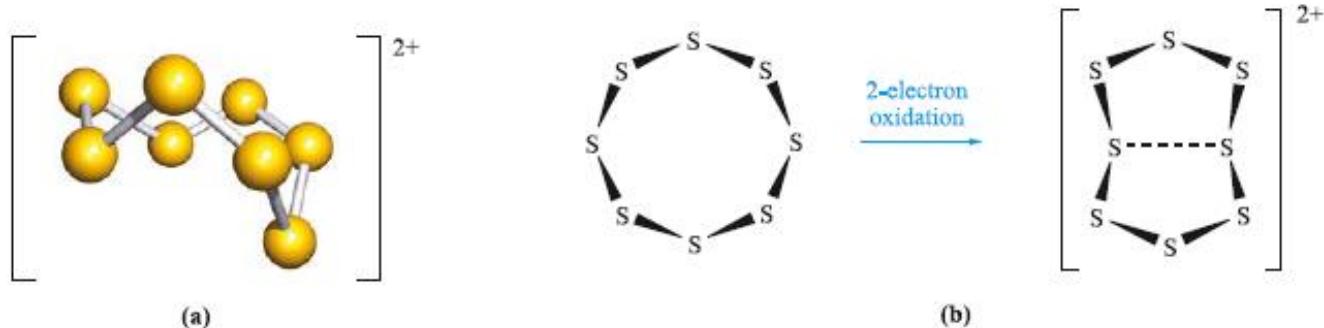


 **Fig. 15.6** Schematic representations of the structures of some allotropes of sulfur: (a) S₆, (b) S₇, (c) S₈ and (d) catena-S_∞ (the chain continues at each end).

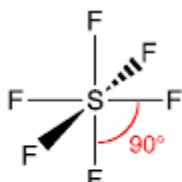
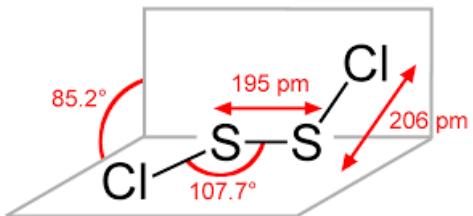
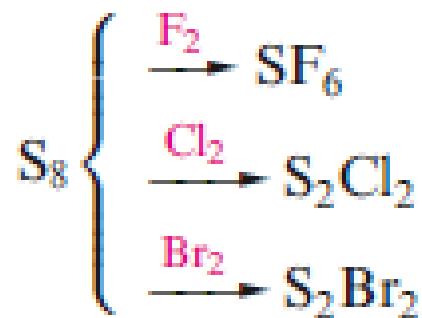
The allotropy of sulfur is complicated, and we describe only the best-established species. The tendency for catenation (see Section 14.3) by sulfur is high and leads to the formation of both rings of varying sizes and chains. Allotropes of known structure include cyclic S₆, S₇, S₈, S₉, S₁₀, S₁₁, S₁₂, S₁₈ and S₂₀ (all with puckered rings, e.g. Figs. 16.6a–c) and fibrous sulfur (*catena*-S_∞, Figs. 16.6d and 3.20a). In most of these, the S–S bond distances are 206 ± 1 pm, indicative of single bond character; the S–S–S bond angles lie in the range 102–108°. The ring conformations of S₆ (chair) and S₈ (crown) are readily envisaged but other rings have more complicated conformations. The structure of S₇ (Fig. 16.6b) is noteworthy because of the wide range of S–S bond lengths (199–218 pm) and angles (101.5–107.5°). The energies of interconversion between the cyclic forms are very small.

The most stable allotrope is orthorhombic sulfur (the α -form and standard state of the element) and it occurs naturally as large yellow crystals in volcanic areas. At 367.2 K, the α -form transforms reversibly into monoclinic sulfur (β -form). Both the α - and β -forms contain S₈ rings; the density of the α -form is 2.07 g cm^{-3} , compared with 1.94 g cm^{-3} for the β -form in which the packing of the rings is less efficient. However, if single crystals of the α -form are rapidly heated to 385 K, they melt before the $\alpha \rightarrow \beta$ transformation occurs. If crystallization takes place at 373 K, the S₈ rings adopt the structure of the β -form, but the crystals must be cooled rapidly to 298 K. On standing at 298 K, a $\beta \rightarrow \alpha$ transition occurs within a few weeks. β -Sulfur melts at 401 K, but this is not a true melting point, since some breakdown of S₈ rings takes place, causing the melting point to be depressed.

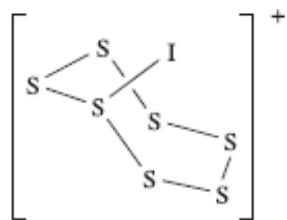
Rhombohedral sulfur (the ρ -form) comprises S₆ rings and is obtained by the ring closure reaction 16.18. It decomposes in light to S₈ and S₁₂.



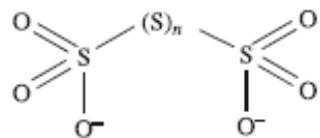
 **Fig. 16.8** (a) Schematic representation of the structure of $[S_8]^{2+}$. (b) The change in conformation of the ring during oxidation of S_8 to $[S_8]^{2+}$. (c) Structural parameters for $[S_8]^{2+}$ from the $[AsF_6]^-$ salt. (d) One resonance structure that accounts for the transannular interaction in $[S_8]^{2+}$. (e) The structure of the $[S_{19}]^{2+}$ cation, determined by X-ray diffraction for the $[AsF_6]^-$ salt [R.C. Burns *et al.* (1980) *Inorg. Chem.*, vol. 19, p. 1423], and a schematic representation showing the localization of positive charge.



Sulfur does not react directly with I_2 , but in the presence of AsF_5 or SbF_5 in liquid SO_2 , the salts $[S_7I][EF_6]$ ($E = As$ or Sb) are produced which contain the $[S_7I]^+$ cation (16.11). If an excess of I_2 is used, the products are $[S_2I_4][EF_6]_2$ ($E = As$ or Sb). The $[S_2I_4]^{2+}$ cation has the ‘open-book’ structure shown in Fig. 16.7. The bonding can be considered in terms of S_2 interacting with two $[I_2]^+$ ions by means of donation of the unpaired electron in the π^* MO of each $[I_2]^+$ into a vacant MO of S_2 . On the basis of the short S–S bond, stretching mode at 734 cm^{-1} , and theoretical investigations, it is proposed that the S–S bond order lies between 2.2 and 2.4. When treated with hot aqueous alkali, sulfur forms a mixture of polysulfides, $[S_x]^{2-}$, and polythionates (16.12), while oxidizing agents convert it to H_2SO_4 .



(16.11)



(16.12)

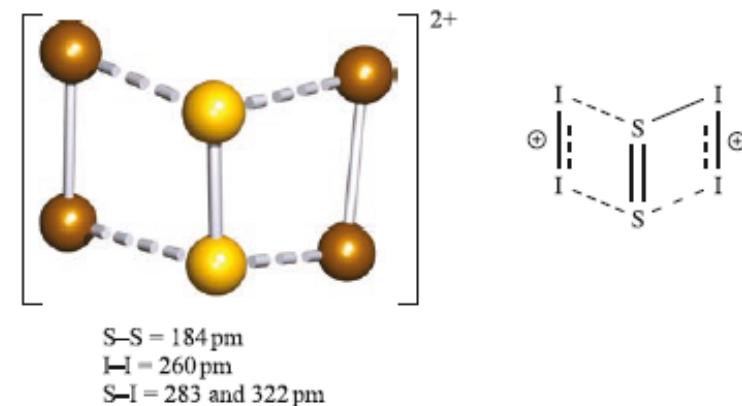
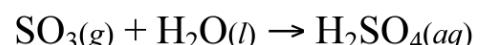
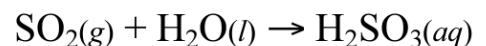
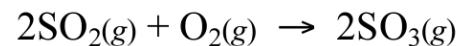


Fig. 16.7 The structure of $[S_2I_4]^{2+}$ determined by X-ray diffraction at low temperature for the $[AsF_6]^-$ salt [S. Brownridge *et al.* (2005) *Inorg. Chem.*, vol. 44, p. 1660], and a representation of the bonding in terms of S_2 interacting with two $[I_2]^+$. Colour code: S, yellow; I, brown.

Sulfur Oxides and Oxyacids



- H_2SO_3 – diprotic; weak acid
- H_2SO_4 – diprotic; strong acid

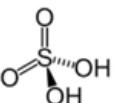
Sulfuric Acid

Productions:

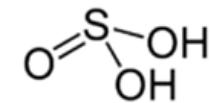
1. $S_8(s) + 8 O_2(g) \rightarrow 8SO_2(g);$
2. $2H_2S(g) + 3 O_2(g) \rightarrow 2SO_2(g) + 2H_2O(l);$
3. $FeS_2(s) + 11 O_2(g) \rightarrow Fe_2O_3(s) + 8SO_2(g);$
4. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g); (V_2O_5/K_2O \text{ catalyst})$
5. $2SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l);$
6. $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l);$

Oxyacids of sulfur

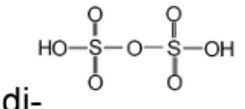
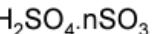
Sulfuric acid



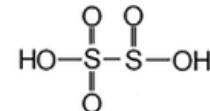
Sulfurous acid



Polysulfuric acids



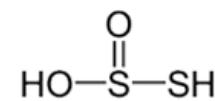
Disulfurous acid



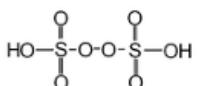
Peroxymonosulfuric acid



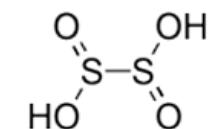
Thiosulfurous acid



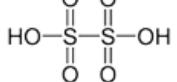
Peroxydisulfuric acid



Dithionous acid

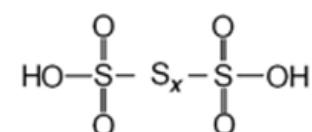
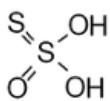


Dithionic acid



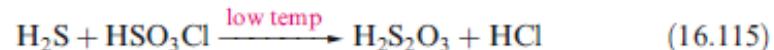
Polythionic acids

Thiosulfuric acid

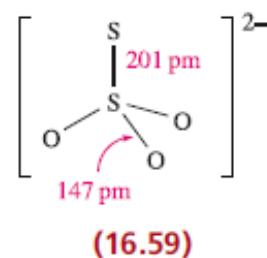


Thiosulfuric acid, H₂S₂O₃, and polythionates

Thiosulfuric acid may be prepared under *anhydrous* conditions by reaction 16.115, or by treatment of lead thiosulfate (PbS₂O₃) with H₂S, or sodium thiosulfate with HCl. The free acid is very unstable, decomposing at 243 K or upon contact with water.



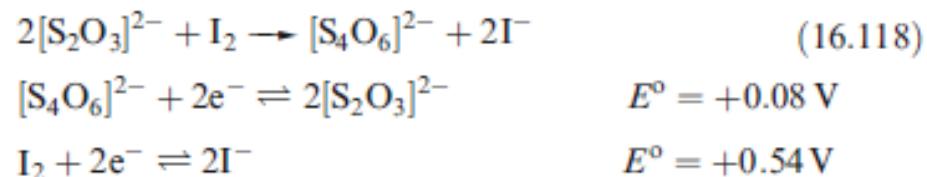
A representation of the structure of thiosulfuric acid is given in Table 16.8, but the conditions of reaction 16.115 may suggest protonation at sulfur, i.e. (HO)(HS)SO₂. Thiosulfate salts are far more important than the acid. Crystallization of the aqueous solution from reaction 16.116 yields Na₂S₂O₃·5H₂O.



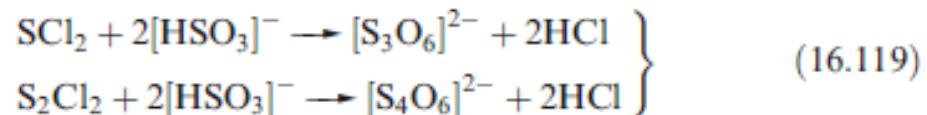
The thiosulfate ion, 16.59, is a very good complexing agent for Ag⁺, and Na₂S₂O₃ is used in photography for removing unchanged AgBr from exposed photographic film (eq. 16.117) although this use is in decline as a result of the huge growth in digital photography. In [Ag(S₂O₃)₃]⁵⁻, each thiosulfate ion coordinates to Ag⁺ through a sulfur donor atom.



Most oxidizing agents (including Cl₂ and Br₂) slowly oxidize [S₂O₃]²⁻ to [SO₄]²⁻, and Na₂S₂O₃ is used to remove excess Cl₂ in bleaching processes. In contrast, I₂ rapidly oxidizes [S₂O₃]²⁻ to tetrathionate; reaction 16.118 is of importance in titrimetric analysis.



Polythionates contain ions of type [S_nO₆]²⁻ and may be prepared by condensation reactions such as those in scheme 16.119, but some ions must be made by specific routes. Polythionate ions are structurally similar and have two {SO₃}⁻ groups connected by a sulfur chain (16.60 shows [S₅O₆]²⁻). Solid state structures for a number of salts show chain conformations are variable. In aqueous solution, polythionates slowly decompose to H₂SO₄, SO₂ and sulfur.

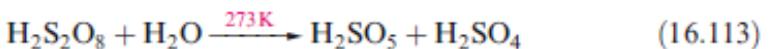
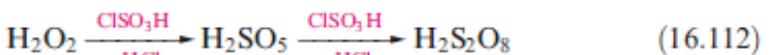
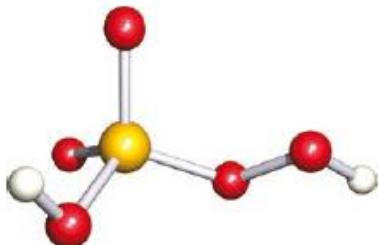


Fluoro- and chlorosulfonic acids, HSO_3F and HSO_3Cl

Fluoro- and chlorosulfonic acids, HSO_3F and HSO_3Cl , are obtained as shown in scheme 16.95, and their structures are related to that of H_2SO_4 with one OH group replaced by F or Cl. Both are colourless liquids at 298 K, and fume in moist air. HSO_3Cl reacts explosively with water. Both acids are commercially available. HSO_3F has wide applications in *superacid* systems (see Section 9.9) and as a fluorinating agent, while HSO_3Cl is used as a chlorosulfonating agent.

Peroxysulfuric acids, $\text{H}_2\text{S}_2\text{O}_8$ and H_2SO_5

The reaction between cold, anhydrous H_2O_2 and chlorosulfonic acid yields peroxysulfuric acid, H_2SO_5 , and peroxydisulfuric acid, $\text{H}_2\text{S}_2\text{O}_8$ (eq. 16.112). However, $\text{H}_2\text{S}_2\text{O}_8$ (Table 16.8) is readily hydrolysed to H_2SO_5 (16.58) (eq. 16.113).



Both H_2SO_5 and $\text{H}_2\text{S}_2\text{O}_8$ are crystalline solids at 298 K. Few salts of H_2SO_5 are known, but those of $\text{H}_2\text{S}_2\text{O}_8$ are easily made by anodic oxidation of the corresponding sulfates in acidic solution at low temperatures and high current densities. Peroxydisulfates are strong oxidizing agents (eq. 16.114), and oxidations are often catalysed by Ag^+ , with $\text{Ag}(\text{II})$ species being formed as intermediates. In acidic solutions, $[\text{S}_2\text{O}_8]^{2-}$ oxidizes Mn^{2+} to $[\text{MnO}_4]^-$, and Cr^{3+} to $[\text{Cr}_2\text{O}_7]^{2-}$.



Peroxydisulfuric acid smells of ozone, and when $\text{K}_2\text{S}_2\text{O}_8$ is heated, a mixture of O_2 and O_3 is produced.

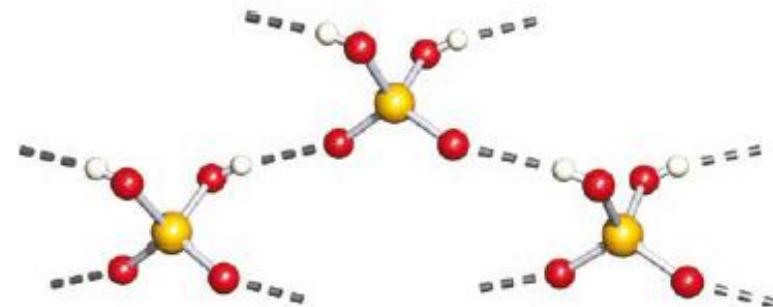
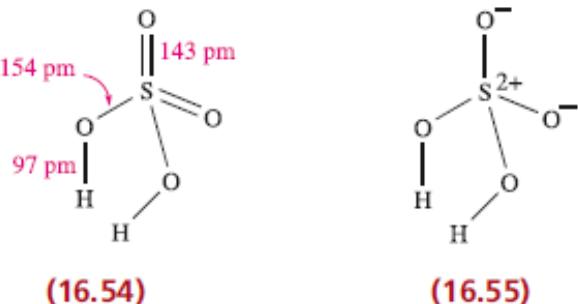


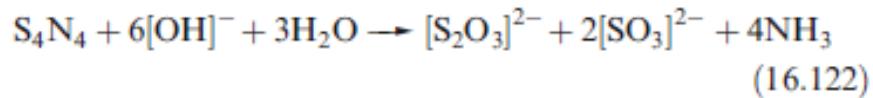
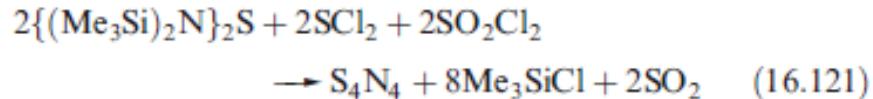
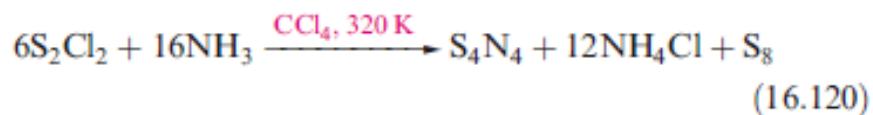
Fig. 16.19 Part of the 3-dimensional, hydrogen-bonded network of H_2SO_4 molecules in crystalline sulfuric acid. The structure was determined by X-ray diffraction at 113 K [E. Kemnitz *et al.* (1996) *Acta Crystallogr., Sect. C*, vol. 52, p. 2665]. Colour code: S, yellow; O, red; H, white.

Important Compounds of Sulfur

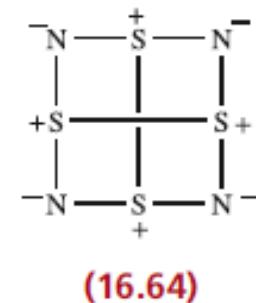
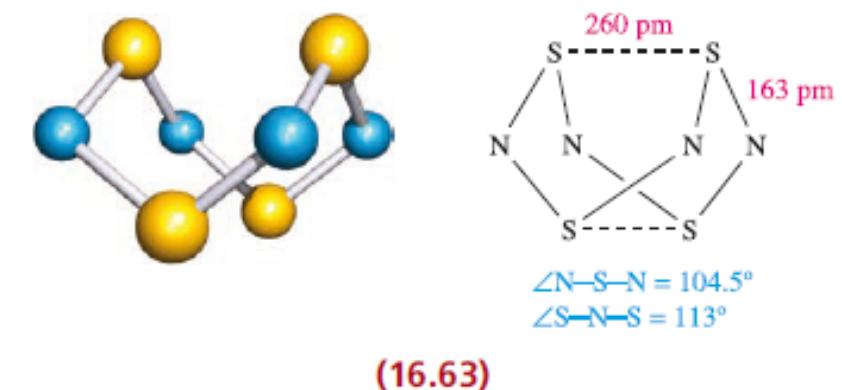
- H_2SO_4 – most important compound, for manufacture of fertilizer, soap, detergents, metal and textile processing, sugar refinery, and organic syntheses;
- SF_4 – for fluoridation
- SF_6 – as insulating and inert blanket
- $\text{Na}_2\text{S}_2\text{O}_3$ – as reducing agent and complexing agent for Ag^+ in photography (called “hypo”);
- P_4S_3 – in “strike-anywhere” match heads

Sulphur-Nitrogen compounds

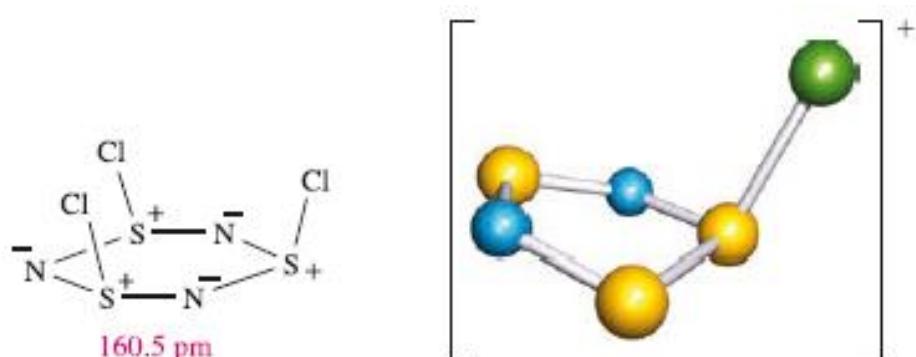
Sulfur–nitrogen chemistry is an area that has seen major developments over the last few decades, in part because of the conductivity of the polymer $(SN)_x$. The following discussion is necessarily selective, and more detailed accounts are listed at the end of the chapter. Probably the best known of the sulfur–nitrogen compounds is tetrasulfur tetranitride, S_4N_4 . It has traditionally been obtained using reaction 16.120, but a more convenient method is reaction 16.121. Tetrasulfur tetranitride is a diamagnetic orange solid ($mp\ 451\ K$) which explodes when heated or struck. Pure samples are very sensitive. It is hydrolysed slowly by water (in which it is insoluble) and rapidly by warm alkali (eq. 16.122).



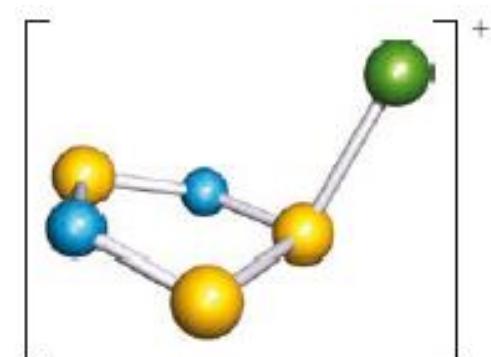
The structure of S_4N_4 , 16.63, is a cradle-like ring in which pairs of S atoms are brought within weak bonding distance of one another (compare with $[S_8]^{2+}$, Fig. 16.8). The S–N bond distances in S_4N_4 indicate delocalized bonding with π -contributions (compare the S–N distances of 163 pm with the sum of the S and N covalent radii of 178 pm). Transfer of charge from S to N occurs giving $S^{\delta+}$ – $N^{\delta-}$ polar bonds. A resonance structure for S_4N_4 that illustrates the cross-cage S–S bonding interactions is shown in 16.64.



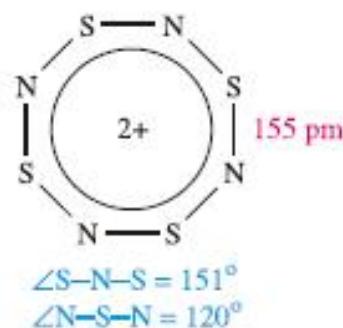
Halogenation of S_4N_4 (at S) may degrade the ring depending on X_2 or the conditions (Fig. 16.20). The ring in $S_4N_4F_4$ has a puckered conformation quite different from that in $S_4N_4H_4$. Fluorination of S_4N_4 under appropriate conditions (Fig. 16.20) yields thiazyl fluoride, NSF, 16.65, or thiazyl trifluoride NSF_3 , 16.66, which contain $S\equiv N$ triple bonds (see end-of-chapter problem 16.29a). Both are pungent gases at room temperature, and NSF slowly trimerizes to $S_3N_3F_3$; note that $S_4N_4F_4$ is not made from the monomer. The structures of $S_3N_3Cl_3$ (16.67) and $S_3N_3F_3$ are similar. The rings exhibit only slight puckering and the S–N bond distances are equal in $S_3N_3Cl_3$ and approximately equal in the fluoro analogue. The salt $[S_3N_2Cl]^+Cl^-$ (made by heating a mixture of S_2Cl_2 , sulfur and NH_4Cl) contains cation 16.68. Oxidation of S_4N_4 with AsF_5 or SbF_5 gives $[S_4N_4][EF_6]_2$ ($E = As$ or Sb) containing $[S_4N_4]^{2+}$. This has the planar structure 16.69 in many of its salts, but $[S_4N_4]^{2+}$ can also adopt a planar structure with alternating bond distances, or a puckered conformation. The $[S_4N_3]^+$ cation (prepared as shown in Fig. 16.20) has the planar structure 16.70 with delocalized bonding.



(16.67)



(16.68)



(16.69)

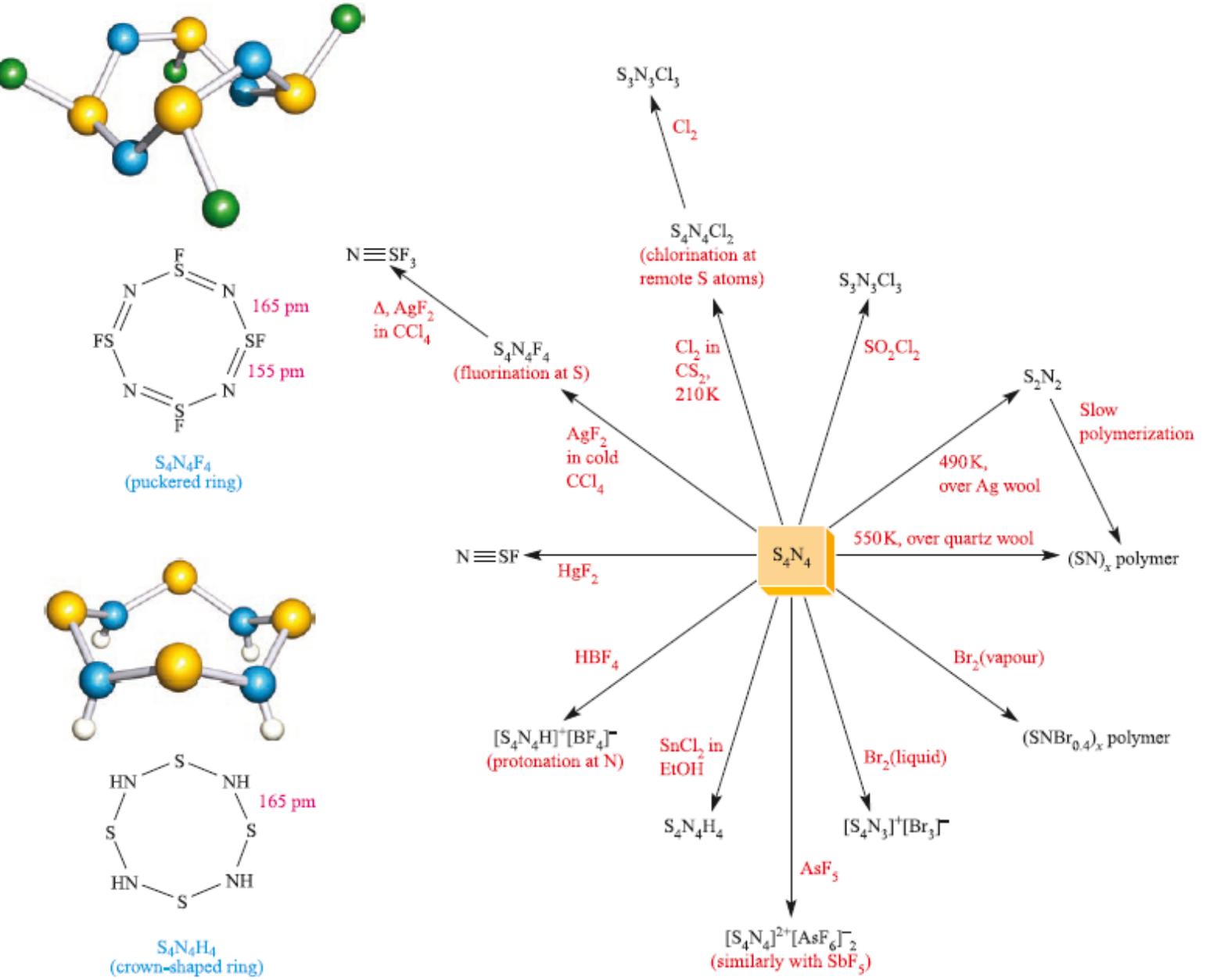
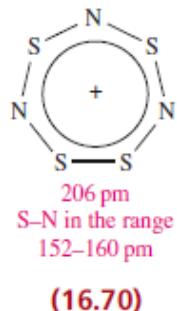
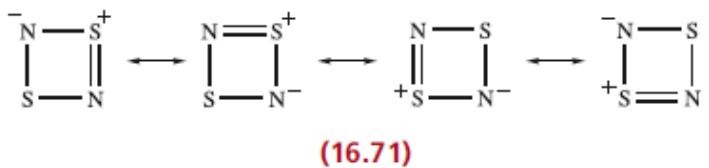


Fig. 16.20 Selected reactions of S_4N_4 ; the rings in $\text{S}_4\text{N}_4\text{H}_4$ and $\text{S}_4\text{N}_4\text{F}_4$ are non-planar.

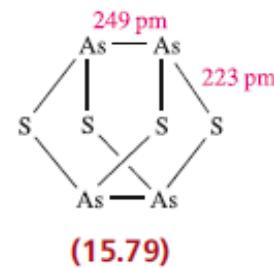


The S_4N_4 cage can be degraded to S_2N_2 (Fig. 16.20) which is isoelectronic with $[\text{S}_4]^{2+}$ (see Section 16.4). S_2N_2 is planar with delocalized bonding ($\text{S}-\text{N} = 165 \text{ pm}$), and resonance structures are shown in 16.71. At room temperature, this converts to the lustrous golden-yellow, fibrous polymer $(\text{SN})_x$, which can also be prepared from S_4N_4 . The polymer decomposes explosively at 520 K, but can be sublimed *in vacuo* at $\approx 410 \text{ K}$. It is a remarkable material, being covalently bonded but showing metallic properties:

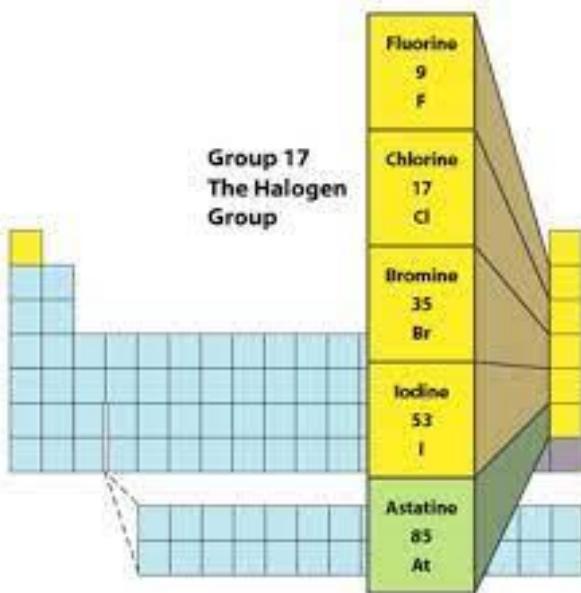
a 1-dimensional pseudo-metal. It has an electrical conductance about one-quarter of that of mercury in the direction of the polymer chains, and at 0.3 K it becomes a superconductor. However, the explosive nature of S_4N_4 and S_2N_2 limits commercial production of $(\text{SN})_x$. In the solid state, X-ray diffraction data indicate that the $\text{S}-\text{N}$ bond lengths in $(\text{SN})_x$ alternate (159 and 163 pm) but highly precise data are still not available; the closest interchain distances are non-bonding $\text{S}-\text{S}$ contacts of 350 pm. Structure 16.72 gives a representation of the polymer chain and the conductivity can be considered to arise from the unpaired electrons on sulfur occupying a half-filled conduction band (see Section 6.8).



The sulfides As_4S_3 (*dimorphite*), As_4S_4 (*realgar*) and As_2S_3 (*orpiment*) occur naturally; the last two are red and golden-yellow respectively and were used as pigments in early times.[†] The arsenic sulfides As_4S_3 , $\alpha\text{-As}_4\text{S}_4$, $\beta\text{-As}_4\text{S}_4$ and $\beta\text{-As}_4\text{S}_5$ are structural analogues of the phosphorus sulfides in Fig. 15.24, but As_4S_6 is structurally related to P_4O_6 and As_4O_6 rather than to P_4S_6 . The bond distances in $\alpha\text{-As}_4\text{S}_4$ (15.79) are consistent with As–As and As–S single bonds, and this view of the cage allows a comparison with S_4N_4 (see Section 16.10).

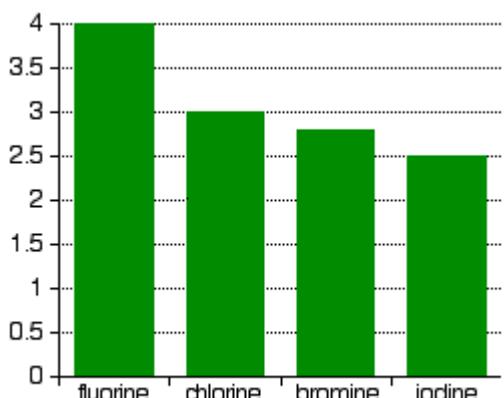


Group 17 elements

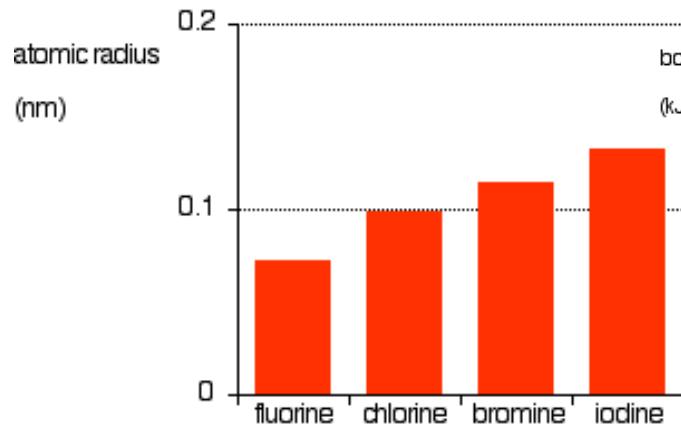


Chlorine (Cl_2) was the first halogen to be discovered in 1774, followed by iodine (I_2), bromine (Br_2), fluorine (F_2), and astatine (At, discovered last in 1940). The name "halogen" is derived from the Greek roots hal- ("salt") and -gen ("to form"). Together these words combine to mean "salt former", 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.

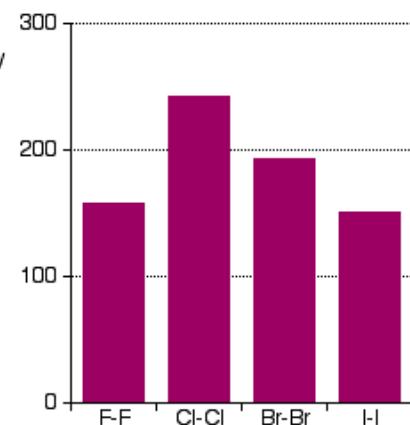
Electronegativity trend



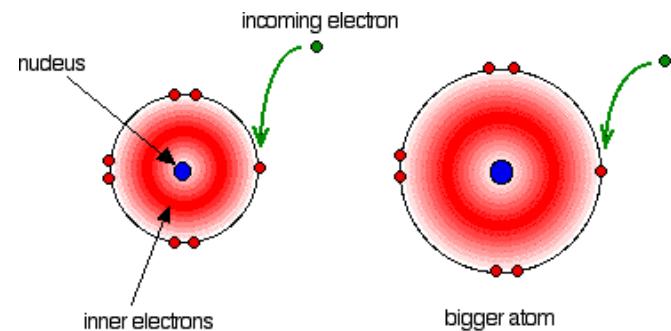
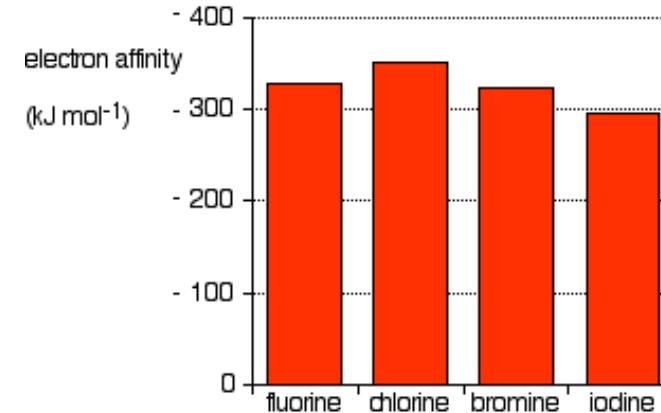
Atomic radii of the Group 7 elements



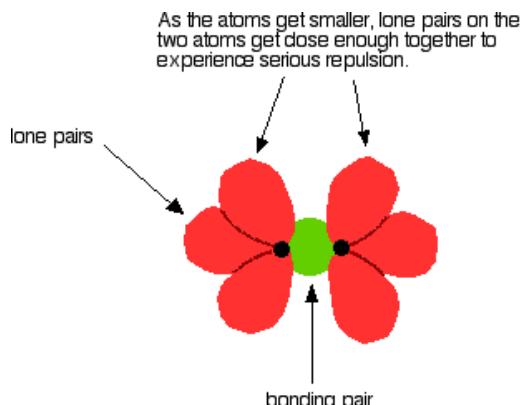
Bond enthalpies



Electron affinity trend

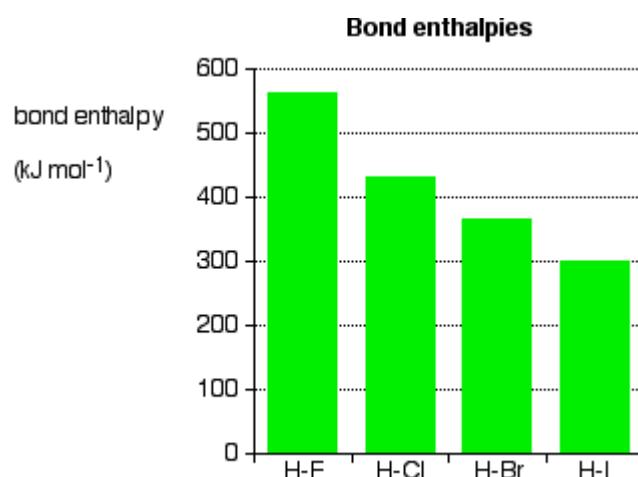


Fluorine small size



Bond enthalpies in the hydrogen halides, HX(g)

If the halogen atom is attached to a hydrogen atom, this does not occur; there are no lone pairs on a hydrogen atom. Bond enthalpies for halogen-hydrogen bonds are given below:



As larger halogens are involved, the bonding pair is more distant from the nucleus. The attraction is lessened, and the bond should be weaker; this is supported by the data, without exception. This fact has significant implications for the thermal stability of the hydrogen halides— they are easily broken into hydrogen and the halogen on heating.

Hydrogen fluoride and hydrogen chloride are thermally very stable under typical laboratory conditions. Hydrogen bromide breaks down to some extent into hydrogen and bromine on heating, and hydrogen iodide is even less stable when heated. Weaker bonds are more easily broken.

The halogens other than fluorine form stable compounds corresponding to nearly all values of the oxidation number from -1 to $+7$, as shown in the accompanying chart.

$\begin{array}{c} \text{+7} \\ \\ \text{+6} \\ \\ \text{+5} \\ \\ \text{+4} \\ \\ \text{+3} \\ \\ \text{+2} \\ \\ \text{+1} \\ \\ \text{0} \\ \\ -1 \end{array}$	$\text{HClO}_4, \text{Cl}_2\text{O}_7$ Cl_2O_6 HClO_3 ClO_2 HClO_2 F_2 HF, F^-	HBrO_3 BrO_2 $\text{HBrO}, \text{Br}_2\text{O}$ Cl_2 HCl, Cl^-	H_5IO_6 $\text{HIO}_3, \text{I}_2\text{O}_5$ IO_2 HIO I_2 HI, I^-
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States of Matter at Room Temperature

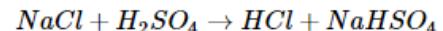
Table 1.7: States of Matter and Appearance of Halogens

States of Matter (at Room Temperature)	Halogen	Appearance
Solid	Iodine	Violet
	Astatine	Black/Metallic [Assumed]
Liquid	Bromine	Reddish-Brown
Gas	Fluorine	Pale Yellow-Brown
	Chlorine	Pale Green

Halides as reducing agents

Concentrated sulfuric acid acting as an acid

The concentrated sulfuric acid transfers a proton to the halide ion to produce a gaseous hydrogen halide, which immediately escapes from the system. If the hydrogen halide is exposed to moist air, steam fumes are formed. For example, concentrated sulfuric acid reacts with solid sodium chloride at low temperatures produce hydrogen chloride and sodium bisulfate, as in the following equation:



All the halide ions behave similarly.

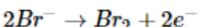
Concentrated sulfuric acid acting as an oxidizing agent

With fluoride or chloride

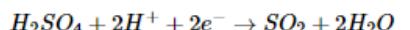
Concentrated sulfuric acid is not a strong enough oxidizing agent to oxidize fluoride or chloride. In those cases, only the steamy fumes of the hydrogen halide—hydrogen fluoride or hydrogen chloride—are produced. In terms of the halide ions, fluoride and chloride are not strong enough reducing agents to reduce the sulfuric acid. This is not the case for bromides and iodides.

With bromide

Bromide is a strong enough reducing agent to reduce sulfuric acid. Bromide is oxidized to bromine in the process, as in the half-equation below:



Bromide reduces sulfuric acid to sulfur dioxide gas, decreasing the oxidation state of sulfur from +6 to +4. The half-equation for this transition is as follows:



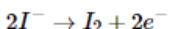
These two half-equations can be combined into the overall ionic equation for the reaction:



In practice, this reaction is confirmed by the steamy fumes of hydrogen bromide contaminated with the brown color of bromine vapor. The sulfur dioxide is a colorless gas, its presence cannot be directly observed.

With Iodide

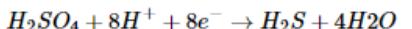
Iodide is a stronger reducing agent than bromide, and it is oxidized to iodine by the sulfuric acid:



The reduction of the sulfuric acid is more complicated than with bromide. Iodide is powerful enough to reduce it in three steps:

- sulfuric acid to sulfur dioxide (sulfur oxidation state = +4)
- sulfur dioxide to elemental sulfur (oxidation state = 0)
- sulfur to hydrogen sulfide (sulfur oxidation state = -2).

The most abundant product is hydrogen sulfide. The half-equation for its formation is as follows:



Combining these two half-equations gives the following net ionic equation:



This is confirmed by a trace of steamy fumes of hydrogen iodide, and a large amount of iodine. The reaction is exothermic: purple iodine vapor is formed, with gray solid iodine condensing around the top of the reaction vessel. There is also a red color where the iodine comes into contact with solid iodide salts. The red color is due to the I_3^- ion formed by reaction between I_2 molecules and I^- ions. Hydrogen sulfide gas can be detected by its "rotten egg" smell, but this gas is intensely poisonous.

Summary

- Fluoride and chloride cannot reduce concentrated sulfuric acid.
- Bromide reduces sulfuric acid to sulfur dioxide. In the process, bromide ions are oxidized to bromine.
- Iodide reduces sulfuric acid to a mixture of products including hydrogen sulfide. Iodide ions are oxidized to iodine.
- The reducing ability of halide ions increases down the group.

Halogen as oxidizing agents

Basic facts

Consider a situation in which one halogen (chlorine, for example) is reacted with the ions of another (iodide, perhaps) from a salt solution. In the chlorine and iodide ion case, the reaction is as follows:



- The iodide ions lose electrons to form iodine molecules. In other words, they are oxidized.
- The chlorine molecules gain electrons to form chloride ions— they are reduced.

This is therefore a redox reaction in which chlorine acts as an oxidizing agent.

Fluorine

Fluorine must be excluded from this discussion because its oxidizing abilities are too strong. Fluorine oxidizes water to oxygen, as in the equation below, and so it is impossible to carry out reactions with it in aqueous solution.



Chlorine, Bromine and Iodine

In each case, a halogen higher in the group can oxidize the ions of one lower down. For example, chlorine can oxidize bromide ions to bromine:



The bromine forms an orange solution. As shown below, chlorine can also oxidize iodide ions to iodine:



The iodine appears either as a red solution if little chlorine is used, or as a dark gray precipitate if the chlorine is in excess.

Bromine can only oxidize iodide ions, and is not a strong enough oxidizing agent to convert chloride ions into chlorine. A red solution of iodine is formed (see the note above) until the bromine is in excess. Then a dark gray precipitate is formed.



Iodine won't oxidize any of the other halide ions, except possibly the extremely radioactive and rare astatide ions.

Summary

Oxidation is the loss of electrons. Each of the elements (for example, chlorine) could potentially take electrons from something else and are subsequently ionized (e.g. Cl^-). This means that they are all potential oxidizing agents.

Fluorine is such a powerful oxidizing agent that solution reactions are unfeasible.

Chlorine has the ability to take electrons from both bromide ions and iodide ions. Bromine and iodine cannot reclaim those electrons from the chloride ions formed.

This indicates that chlorine is a more powerful oxidizing agent than either bromine or iodine.

Similarly, bromine is a more powerful oxidizing agent than iodine. Bromine can remove electrons from iodide ions, producing iodine; iodine cannot reclaim those electrons from the resulting bromide ions.

In short, oxidizing ability decreases down the group.

Interhalogens

The halogens react with each other to form interhalogen compounds. The general formula of most interhalogen compounds is XY_n , where $n = 1, 3, 5$ or 7 , and X is the less electronegative of the two halogens between X and Y . The compounds which are formed by the union of two different halogens are called inter halogen compounds. There are never more than two types of halogen atoms in an interhalogen molecule. There are of four general types:

AX-type : ClF, BrF, BrCl, ICl, IBr,

AX₃-type: ClF₃, BrF₃, (ICl₃)₂,

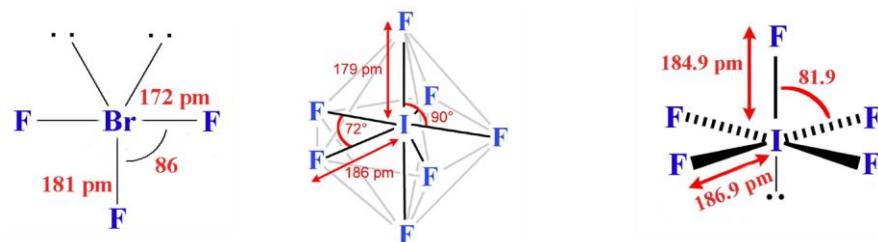
AX₅-type: ClF₅, BrF₅, IF₅,

AX₇-type: IF₇.

The interhalogen compounds of type AX and AX₃ are formed between the halogen having very low electronegative difference (e.g., ClF, ClF₃). The interhalogen compounds of type AX₅ and AX₇ are formed by larger atoms having low electronegativity with the smaller atoms having high electronegativity. This is because it is possible to fit the greater number of smaller atom around a larger one (e.g. BrF₅, IF₇).

Interhalogen are all prone to hydrolysis and ionize to give rise to polyatomic ions. The inter halogens are generally more reactive than halogens except F. This is because A-X bonds in interhalogens are weaker than the X-X bonds in dihalogen molecules. Reaction of inter halogens are similar to halogens. Hydrolysis of interhalogen compounds give halogen acid and oxy-acid.

The structures found for the various interhalogens conform to what would be expected based on the VSEPR model. For XY₃ the shape can be described as T-shaped with 2 lone pairs sitting in equatorial positions of a trigonal bipyramidal. For XY₅ the shape is a square pyramid with the unpaired electrons sitting in an axial position of an octahedral and XY₇ is a pentagonal bipyramidal



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.

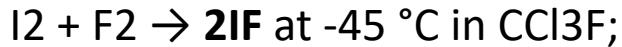
Chlorine monofluoride (ClF), the lightest interhalogen, is a colorless gas with a boiling point of 173 °K.

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. $\Delta\text{H}_f^\circ = -95.4$ kJ mol⁻¹ and $\Delta\text{G}_f^\circ = -117.6$ kJ mol⁻¹, both at 298 K.

IF can be generated, by the following reactions:



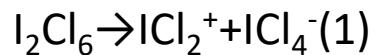
XY₃ interhalogens

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 I₂ + 3XeF₂ → 2IF₃ + 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. In the melt it is conductive, which may indicate dissociation:



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:



XY5 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.

XY7 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.

Summary

All Interhalogens are volatile at room temperature.

All are polar due to difference in their electronegativity.

These are usually covalent liquids or gases due to small electronegativity difference among them.

Some compounds partially ionize in solution.

For example:



Interhalogen compounds are more reactive than normal halogens except fluorine.