NITROSYL CHLORIDE

[2696-92-6]
Formula: ClNO; MW 65.459
Structure: Cl—N=O. bent molecule, N—O bond distance 1.139Å and N—Cl bond distance 1.975Å

Uses

Nitrosyl chloride is an important component of aqua regia. It is an oxidizing agent in organic synthesis. It also is used as a catalyst.

Physical Properties

Yellow gas; heavier than air, density 2.3 (air=1); gas density 2.872 g/L; liquefies at –5.55°C; liquid density 1.273 g/mL; freezes at –59.4°C; critical temperature 167°C; reacts with water; soluble in fuming sulfuric acid.

Thermochemical Properties

$\Delta H_f°$	12.37 kcal/mol
$\Delta G_f°$	15.81 kcal/mol
$S°$	62.55 cal/degree mol
C_ρ	10.68 cal/degree mol
ΔH_{vap}	6.16 kcal/mol

Preparation

Nitrosyl chloride can be prepared by the reaction of nitric oxide with chlorine:

$$2NO + Cl_2 \rightarrow 2ClNO$$
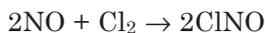
Also, nitrosyl chloride is produced by the action of chlorine on sodium nitrate; or by the reaction of nitrosyl sulfuric acid with hydrochloric acid:

$$NaNO_3 + Cl_2 \rightarrow ClNO + NaClO_2$$

$$ONHSO_4 + HCl \rightarrow ClNO + H_2 SO_4$$
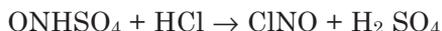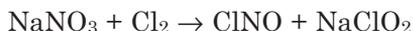
Nitrosyl chloride also is obtained as a byproduct in the manufacture of potassium nitrate from potassium chloride and nitric acid:

$$3KCl + 4HNO_3 \xrightarrow{\text{elevated temperature}} 3KNO_3 + Cl_2 + ClNO + 2H_2O$$
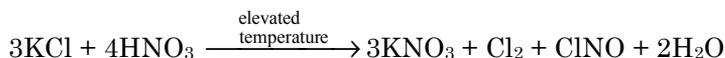
In the above preparative method, nitrosyl chloride must be separated from nitric acid; otherwise, in the presence of pure and excess nitric acid, it can decompose to nitrogen dioxide and chlorine:

$$2ClNO + HNO_3 \rightarrow 6NO_2 + Cl_2 + 2H_2O$$
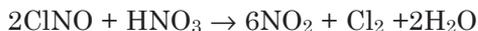
Also, nitrosyl chloride can be synthesized from its elements by heating nitrogen, oxygen and chlorine gas at 400°C:

$$N_2 + O_2 + Cl_2 \rightarrow 2ClNO$$

Faraday obtained nitrosyl chloride by dissolving palladium in a mixture of hydrochloric and nitric acids (Faraday, M. *Trans. Roy. Soc.* (London), Vol. 136, pp. 48, 1846):
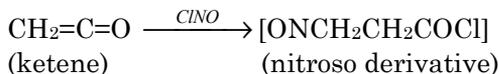
$$Pd + HNO_3 + 3HCl \rightarrow PdCl_2 + ClNO + 2H_2O$$
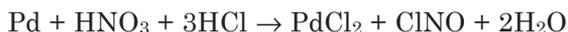
Reactions

Nitrosyl chloride undergoes addition reactions with many unsaturated organic compounds. It adds to olefinic double bond as follows:

$$—HC=CH— + Cl—N=O \rightarrow —ClCH—CHNO$$
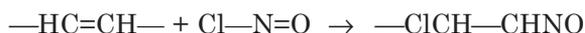
For example, it reacts with ketone to yield a nitroso derivative:

$$CH_2=C=O \xrightarrow{\;ClNO\;} [ONCH_2CH_2COCl]$$
(ketene)   (nitroso derivative)

Propylene oxide undergoes electrophilic addition, giving a nitroso derivative, $CH_3CH(—ON=O)CH_2Cl$:

$$CH_3—CH—CH_2 + ONCl \rightarrow CH_3CH(—ON=O)CH_2Cl$$
$$\diagdown \quad \diagup$$
$$O$$
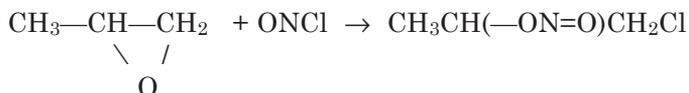
Reaction with a cyclic amine in the presence of a base and at ambient temperature forms alkene. Thus, nitrosyl chloride reacts with aziridine to form ethylene and nitrous oxide:

$$
\begin{array}{l}
CH_2 \\
\diagdown \\
\bigg| \quad \quad NH + ClNO \xrightarrow{\;base\;} CH_2=CH_2 + N_2O + HCl \\
\diagup \\
CH_2
\end{array}
$$
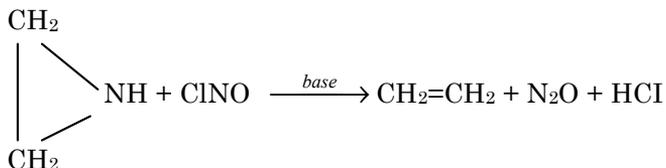
Nitrosyl chloride is oxidized by nitric acid to yield nitrogen dioxide, chlorine and water.

$$2ClNO + 4HNO_3 \rightarrow 6NO_2 + Cl_2 + 2H_2O$$
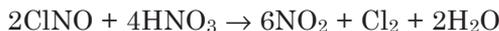
Reaction with sulfuric acid forms nitrosyl sulfuric acid:

$$H_2SO_4 + ClNO \rightarrow ONHSO_4 + HCl$$

Nitrosyl chloride reacts with cyclohexane in the presence of UV light to form cyclohexanone oxime hydrochloride:
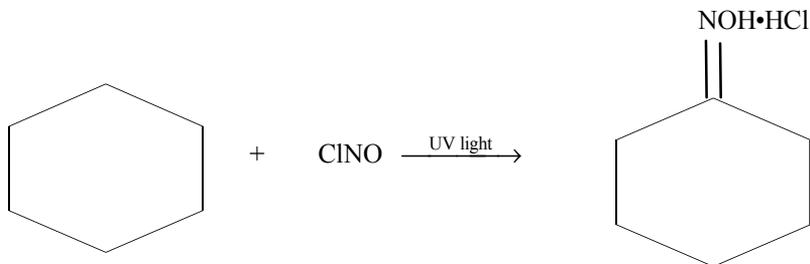
Nitrosyl chloride in carbon tetrachloride reacts with silver thiocyanate to form silver chloride and nitrosyl thiocyanate:

$$ClNO + AgSCN \rightarrow AgCl + ONSCN$$
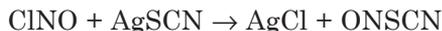
Analysis

Elemental composition: Cl 54.16%, N 21.40%, O 24.44%. The compound can be identified by its color and other physical properties. Analysis may be done by GC/MS using a diluent gas such as helium. Alternatively, it may be added to an olefinic double bond and the derivatives identified by physical properties, IR, and mass spectra. (See Reactions.)

Toxicity

Nitrosyl chloride is a toxic gas and a severe irritant to eyes, skin, and mucous membranes. Inhalation can result in pulmonary edema and hemorrhage.

NITROSYL FLUORIDE

[7789-25-5]
Formula: FNO; MW 49.00;
Structure: F—N=O
Synonym: nitrogen oxyfluoride

Uses

Nitrosyl fluoride is an oxidizer in rocket propellants. Other applications are in organic synthesis where it is a fluorinating agent. The compound also is a stabilizer for liquid sulfur trioxide.

Physical Properties

Colorless gas when pure; often appears bluish because of impurities; density 2.176 g/L; liquefies at –56°C; density of liquid 1.326g/mL at its boiling point; solidifies at –134°C; density of solid 1.719 g/cm^3; reacts with water.
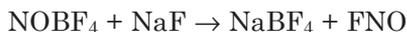
Thermochemical Properties

$\Delta H_f°$	–15.9 kcal/mol
$\Delta G_f°$	–12.2 kcal/mol
$S°$	59.5 cal/degree mol
C_ρ	9.88 cal/degree mol

Preparation

Nitrosyl fluoride may be prepared by the reaction of fluorine with nitric oxide:

$$F_2 + 2NO \rightarrow 2FNO$$
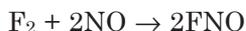
Nitrosyl fluoride also can be obtained by heating nitrosyl fluborate, $NOBF_4$, and sodium fluoride:

$$NOBF_4 + NaF \rightarrow NaBF_4 + FNO$$

Nitrosyl fluoborate required for the above preparation may be obtained by dissolving boric acid in 40% HF, concentrating the solution till it fumes, and purifying the $NOBF_4$ formed by sublimation in a vacuum.

Nitrosyl fluoride also can be produced by the action of nitrosyl chloride with silver fluoride:

$$NOCl + AgF \rightarrow FNO + AgCl$$
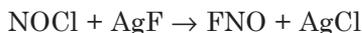
All preparations must be done in complete absence of water.

Reactions

Nitrosyl fluoride decomposes in water forming nitrous acid, nitric acid, nitric oxide and HF:

$$FNO + H_2O \rightarrow HNO_2 + HF$$

$$2FNO + HNO_2 + H_2O \rightarrow HNO_3 + 2NO + 2HF$$
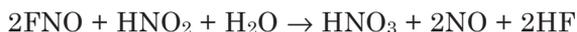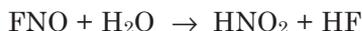
Reaction with iridium hexafluoride forms trifluoroamine oxide, NF_3O, and nitrosyl iridium hexafluoride, $NOIrF_6$:

$$3FNO + 2IrF_6 \rightarrow NF_3O + 2NOIrF_6$$
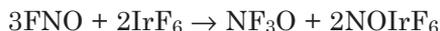
Nitrosyl fluoride reacts slowly with silica when heated at 150°C forming silicon tetrafluoride, SiF_4 and dinitrogen trioxide, N_2O_3:

$$4FNO + SiO_2 \rightarrow SiF_4 + 2N_2O_3$$
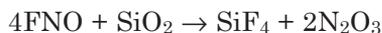
Hazard

Nitrosyl fluoride is a dangerous irritant to the eyes, skin, and mucous membranes. Explosive reactions can occur with alkenes.

NITROSYLSULFURIC ACID

[7782-78-7]
Formula: HSO_4NO; MW 127.08
Structure:

$$HO-S-O-N=O$$
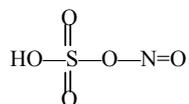
Synonyms: nitrosyl sulfate; chamber crystals; nitroxylsulfuric acid; nitrososulfuric acid; nitrosyl hydrogen sulfate

Uses

Nitrosylsulfuric acid is used in making caprolactam from benzoic acid and in preparing many disperse azo dyes. Other applications are bleaching, maturing, dough-conditioning cereal products, and in preparing crystalline diazonium sulfates.

Physical Properties

Colorless crystalline solid; rhombohedral structure; decomposes at 73.5°C; decomposes in water; soluble in sulfuric acid.

Preparation

Nitrosylsulfuric acid is produced as an intermediate in the manufacture of sulfuric acid using the lead chamber process by the reaction of sulfur dioxide, nitrogen dioxide, oxygen, and water.

Nitrosylsulfuric acid also is made from absorption of nitrogen oxides (NO_x) in oleum (fuming sulfuric acid):

$$N_2O_3 + 2H_2SO_4 \rightarrow 2ONSO_4H + H_2O$$
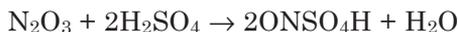
or by the reaction of nitrosyl chloride with concentrated sulfuric acid:

$$ClNO + H_2SO_4 \rightarrow ONSO_4H + HCl$$

Another method of preparation involves the reaction of nitrosyl bromide with silver bisulfate:

$$AgHSO_4 + BrNO \rightarrow ONHSO_4 + AgBr$$
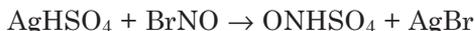
In making disperse azo dyes, nitrosylsulfuric acid is produced by the addition of sodium nitrite, $NaNO_2$, to concentrated sulfuric acid (1g $NaNO_2$ per 13 g H_2SO_4)

Reactions

The compound decomposes in moist air forming nitric and sulfuric acids.

$$2ONHSO_4 + O_2 + 2H_2O \rightarrow 2HNO_3 + 2H_2SO_4$$

However, above 50°C decomposition in moist air forms nitric oxide, nitrogen dioxide, and sulfuric acid:

$$2ONHSO_4 + H_2O \rightarrow NO + NO_2 + 2H_2SO_4$$
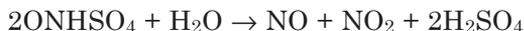
Nitrosylsulfuric acid hydrolyzes in water forming sulfuric acid and oxides of nitrogen as shown above.

Nitrosylsulfuric acid reacts with cyclohexane carboxylic acid to form caprolactam. The starting material in such large-scale production of caprolactam is benzoic acid. The reactions are:

$$C_6H_5COOH \xrightarrow[Pd]{H_2} \qquad C_6H_{11}COOH \qquad \xrightarrow{ONHSO_4}$$

(benzoic acid)   (cyclohexane carboxylic acid)

$$cyclo—(C_6H_{10}NH){=}O \ + \ CO_2 \ + \ H_2SO_4$$
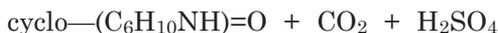
(caprolactam)

Analysis

Elemental composition: S 25.23%, H 0.79%, N 11.02, O 62.95%. Nitrosylsulfuric acid may be analysed by IR, NMR and mass spectrometry, as well as by elemental microanalysis. Wet analysis involves hydrolyzing the compound in the presence of excess NaOH and measuring excess base by potentiometric titration.

NITROUS ACID

[7782-77-6]
Formula: HNO_2; MW 47.014; exists only in solution and has not been isolated.

Uses

Nitrous acid is a diazotizing agent. The acid diazotizes primary aromatic

amines to diazo derivatives in manufacturing azo dyes.

Physical Properties

Pale blue solution; stable only in solution; weak acid, Ka 4.5×10^{-4}.

Thermochemical Properties

$\Delta H_f°$ (gas)	−19.00 kcal/mol
$\Delta G_f°$ (gas)	−10.99 kcal/mol
S° (gas)	60.73 cal/degree mol
C_ρ	10.90 cal/degree mol

Preparation

Nitrous acid may be obtained in solution by adding a strong acid to nitrite; e.g., adding hydrochloric acid to sodium nitrite solution:

$$H^+ + NO_2^- \rightarrow HNO_2$$
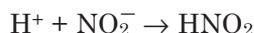
Reactions

Nitrous acid is unstable. It decomposes to form nitric acid and nitric oxide:

$$3HNO_2 \rightarrow NO_3^- + H_3O^+ + 2NO$$
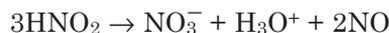
Strong oxidizing agents, such as permanganate, readily oxidize nitrous acid to nitric acid.

Nitrous acid is an effective oxidizing agent. It oxidizes hydrogen sulfide to sulfur forming either nitric oxide or ammonia, depending on the acidity of the solution:

$$2HNO_2 + H_2S \rightarrow S + 2NO + 2H_2O$$

$$HNO_2 + 3H_2S \rightarrow 3S + NH_3 + 2H_2O$$
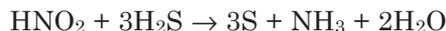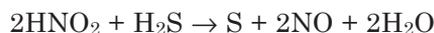
In acid medium it oxidizes iodide ion to iodine:

$$HNO_2 + I^- + 6H^+ \rightarrow 3I_2 + NH_3 + 2H_2O$$

Analysis

Nitrous acid in solution can be analysed by measuring the nitrite ion, NO_2^-, by ion chromatography, or a colorimetric method. The colorimetric test sees the reddish purple azo dye produced at pH 2.0 to 2.5 by coupling diazotized sulfanilamide with N-(1-naphthyl)ethylenediaminedihydrochloride (APHA, AWWA and WEF. 1998. *Standard methods for the Examination of Water and Wastewater*, 20th ed. Washington, DC: American Public Health Association). In addition to tests for nitrite ion, other tests should confirm that the NO_2^- is from nitrous acid and not any metal nitrite. This can be done by oxidizing iodide ion in acid medium and measuring the liberated iodide by titrating against a standard solution of sodium thiosulfate using starch indicator, and

also by measuring ammonia liberated with an ammonium ion selective electrode. (See Reactions).

NITROUS OXIDE

[10024-97-2]
Formula: N_2O; MW 44.013; a diamagnetic molecule.
Synonyms: dinitrogen oxide; nitrogen monoxide; dinitrogen monoxide; hyponitrous acid anhydride; laughing gas.

History and Uses
Nitrous oxide was discovered by Priestley. It is found in the atmosphere in trace concentrations. The gas is used as an anesthetic, especially in dentistry and minor surgery. It produces mild hysteria and laughter preceding the anesthetic effect, for which reason it also is called "laughing gas." It is used as an aerosol propellant, an aerating agent for whipped cream, and an oxidizing agent at high temperatures. Nitrous oxide also is used in the preparation of nitrites and as a flame gas in flame atomic absorption spectrometry of metals.

Physical Properties
Colorless gas with faint sweet odor and taste; heavier than air, density in air 1.53 (air=1); gas density 1.977 g/L at 0°C; noncombustible gas; supports combustion; liquefies to a colorless liquid at –88.5°C; liquid density 1.226 g/mL at –89°C; freezes to a cubic crystalline solid at –90.8°C; dipole moment 0.166 ; critical temperature 36.5°C; critical pressure 71.7 atm; solubility in water: 130 mL gas dissolves in 100mL water at 0°C and 56.7 mL in 100 mL water at 25°C; soluble in alcohol, ether and sulfuric acid.

Thermochemical Properties
$\Delta H_f°$	19.61 kcal/mol
$\Delta G_f°$	24.90 kcal/mol
$S°$	52.52 cal/degree mol
C_ρ	9.19 cal/degree mol

Preparation
Nitrous oxide may be prepared by heating molten ammonium nitrate carefully. Rapid and strong heating can cause explosion:

$$NH_4NO_3 \xrightarrow{\quad 250°C \quad} N_2O\uparrow + 2H_2O$$

Any nitric oxide produced in small amounts may be removed by passage through $FeSO_4$ solution.

Alternatively, the gas may be obtained by warming a solution of ammonium nitrate in nitric acid containing a small amount of hydrochloric acid.

Pure nitrous oxide may be prepared by treating a solution of sodium nitrite, $NaNO_2$ with that of hydroxyl amine hydrochloride, $NH_2OH \cdot HCl$:

$$NH_3OH^+ + NO_2^- \rightarrow N_2O\uparrow + 2H_2O$$
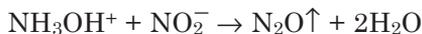
Reactions

Nitrous oxide at ambient temperature is chemically unreactive to most substances. It is not readily oxidized or reduced, unlike other oxides of nitrogen. When passed over heated metals such as iron, copper, and lead, nitrous oxide decomposes to nitrogen and oxygen, exothermically:

$$N_2O \rightarrow N_2 + \tfrac{1}{2}\ O_2$$

Because of its ability to release oxygen at high temperatures, nitrous oxide supports combustion only at high temperatures. Once the reaction initiates, the substances burn in oxygen liberated from nitrous oxide. Thus, nitrous oxide can oxidize many nonmetals, such as sulfur and phosphorus at high temperatures:

$$2N_2O + S \rightarrow SO_2 + 2N_2$$

$$5N_2O + 2P \rightarrow P_2O_5 + 5N_2$$
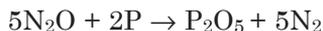
When passed over molten sodium amide, nitrous oxide yields sodium azide:

$$N_2O + 2NaNH_2 \rightarrow NaN_3 + NaOH + NH_3$$

Nitrous oxide reacts with dioxygen difluoride at ordinary temperatures forming various fluorinated products, such as FNO, FNO_2, and $FONO_2$:

$$N_2O + O_2F_2 \rightarrow FNO + FNO_2$$

$$FNO_2 + O_2F_2 \rightarrow FONO_2 + F_2$$
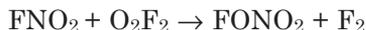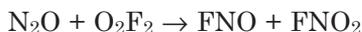
Analysis

Nitrous oxide can be analyzed by GC on a molecular sieve column using a thermal conductivity detector and helium as carrier gas. It may be identified by GC/MS from its mass spectra. The molecular ion is 44. Also, it can be oxidized to NO and identified by the brown-ring test, using $FeSO_4$ solution. (see Nitric Oxide.)

NITRYL CHLORIDE

[13444-90-1]
Formula: NO_2Cl; MW 81.47; planar structure;
Cl—N bond distance 1.84Å; N—O distance 1.202Å; O—N—O bond angle 130.6°

Uses

Nitryl chloride is used as a nitrating agent in organic synthesis. For example, benzene may be converted to nitrobenzene. The compound also is a chlorinating agent in many preparative reactions.

Physical Properties

Colorless gas; chlorine-like odor; gas density 2.81 g/L at 100°C; liquefies to a pale-yellow liquid at –14.3°C; density of the liquid 1.33 g/mL; solidifies at –145°C; decomposes above 120°C; reacts with water.

Preparation

Nitryl chloride is prepared most conveniently by reacting chlorosulfonic acid with anhydrous nitric acid at 0°C:

$$ClSO_3H + HNO_3 \xrightarrow{\;0^\circ C\;} NO_2Cl + H_2SO_4$$
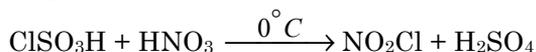
An older preparation method involves passing dry chlorine gas slowly over dry silver nitrate heated to about 100°C. The gaseous reaction products are allowed to cool to low temperature. After several hours, nitryl chloride condenses to a pale yellowish-brown liquid. Chlorine is removed by purging with CO_2.

$$2AgNO_3 + 2Cl_2 \rightarrow 2NO_2Cl + 2AgCl + O_2$$

Reactions

Nitryl chloride hydrolyzes in water forming nitric acid and hydrochloric acid:

$$NO_2Cl + H_2O \rightarrow HNO_3 + HCl$$
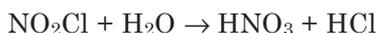
The compound decomposes readily to nitrogen dioxide and chlorine on heating; slow decomposition can occur at ordinary temperatures:

$$2\ NO_2Cl \rightarrow 2NO_2 + Cl_2$$
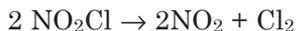
Reaction with sodium hydroxide forms sodium nitrite and sodium hypochlorite:

$$2NaOH + NO_2Cl \rightarrow NaNO_2 + NaOCl + H_2O$$

Nitryl chloride is a strong oxidizing agent. It reacts explosively with reducing agents. It readily attacks many metals.

Nitryl chloride reacts with many organics forming their nitro derivatives. Such Friedel-Crafts nitration is catalyzed by a Lewis acid, such as $AlCl_3$. An example is nitration of benzene to nitrobenzene:

$$C_6H_6 + NO_2Cl \xrightarrow{\;AlCl_3\;} C_6H_5NO_2 + HCl$$
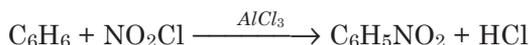
Nitration also may be achieved noncatalytically without using $AlCl_3$. For example, sodium tetrafluoroborate may be added to benzene to yield nitroben-

zene:

$$C_6H_6 + NaBF_4 + NO_2Cl \rightarrow C_6C_5NO_2 + NaCl + HF + BF_3$$

Nitryl chloride reacts with acetic anhydride forming acetyl chloride and acetyl nitrate:

$$(CH_3CO)_2O + NO_2Cl \rightarrow CH_3COCl + CH_3\ CONO_3$$

Analysis
Nitryl chloride may be identified by its mass spectra. The characteristic mass ions are 81, 83, 46, 35, and 37. Alternatively, nitryl chloride may be identified from its physical and chemical properties (See Reactions). The wet analytical method involves treatment with an excess solution of NaOH and titrating the excess NaOH with a standard solution of H_2SO_4. Alternatively, nitryl chloride is decomposed in water, and the acids HNO_3 and HCl formed are measured by titration or the NO_3^- and Cl^- determined by ion specific electrodes or ion chromatography.

Hazard
Nitryl chloride is a strong oxidizing agent. Contact with strong reducing agents can cause explosion. The gas is highly corrosive and a strong irritant to eyes, nose and lungs. Exposure to high concentration can be fatal.

NITRYL FLUORIDE

[10022-50-1]
Formula: NO_2F; MW 65.00; planar structure; F—N distance 1.35Å; N—O distance 1.23Å; O—N—O angle 125°C (estimated).

Uses
Nitryl fluoride is an oxidizer in rocket propellants. It also is a fluorinating and nitrating agent in organic synthesis.

Physical Properties
Colorless gas; pungent odor; density 2.90 g/L; heavier than air, density in air 2.24 (air=1); liquefies to a colorless liquid at –63.5°C; solidifies at –139°C; decomposes in water; also decomposes in alcohol, ether and chloroform.

Preparation
Nitryl fluoride is obtained by reacting fluorine with nitrogen dioxide or nitric oxide:

$$N_2O_4 + F_2 \rightarrow 2NO_2F$$

$$4NO + F_2 \rightarrow 2NO_2F + N_2$$
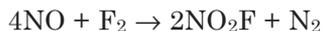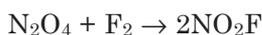
Using nitrogen dioxide provides an easier preparation than nitric oxide.

A convenient method of preparing nitryl fluoride is to heat dinitrogen tetroxide with cobalt(III) fluoride at 300°C:

$$N_2O_4 + CoF_3 \xrightarrow{\;300^\circ C\;} 2NO_2F + 2CoF_2$$
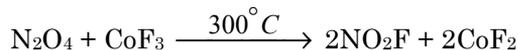
Reactions

Nitryl fluoride is a strong oxidizing agent. Most reactions are similar to those of nitryl chloride, NO_2Cl (See Nitryl Chloride Reactions). Nitryl fluoride hydrolyzes rapidly in water forming nitric acid and hydrofluoric acid:

$$NO_2F + H_2O \rightarrow HNO_3 + HF$$
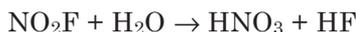
Reaction with ethanol produces ethyl nitrate:

$$NO_2F + C_2H_5OH \rightarrow C_2H_5NO_3 + HF$$
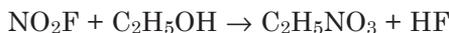
Reactions with reducing agents can be explosive. The compound attacks most metals almost as vigorously as fluorine. It spontaneously ignites boron, silicon, phosphorus, arsenic, antimony, and iodine at ordinary temperatures.

Nitryl fluoride can add a nitrate group to many organics forming their nitro derivatives:

$$C_6H_6 + NO_2F \rightarrow C_6H_5NO_2 + HF$$
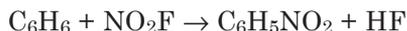
Analysis

Nitryl fluoride may be identified from its physical and chemical properties. Its hydrolysis products, nitric and hydrofluoric acids, may be measured by selective ion electrodes or by ion chromatography. The gas, diluted in helium or hydrogen (in cold), may be identified by GC/MS.

NOBELIUM

[10028-14-5]
Symbol: No; atomic number 102; atomic weight 259; an actinide series, transuranium, synthetic radioactive element; electron configuration $[Rn]5f^{14}7s^2$; valence states +2, +3.

The element was discovered independently by several groups nearly simultaneously. In 1958, Ghiorso, Sikkeland, Walton, and Seaborg at Berkeley, California, synthesized an isotope of this new element by bombardment of a mixture of curium isotopes containing 95% Cm-244 and 4.5% Cm-246 with carbon-12 ions. This new element was named nobelium in honor of Alfred Nobel, discoverer of dynamite.

Prior to this, in 1957, two other groups also reported making isotopes of ele-

ment 102. One team consisting of investigators from the USA, England, and Sweden irradiated Cm-244, –246, and –248 target with C-13 ions generated in the heavy ion cyclotron and produced an isotope of element 102 with mass 254. The other group, working at Dubna Institute in the USSR, bombarded plutonium-239 and –241 with oxygen-16 in the heavy ion cyclotron.

Nobelium may be synthesized by several methods involving irradiation of isotopes of curium, plutonium, and fermium in the form of thin targets with heavy ions of boron, carbon, and oxygen using double-recoil technique. The nuclear reaction in the synthesis of No-254 carried out by Ghiorso and his group is as follows:

$$_{96}^{246} Cm + _{96}^{246} C \xrightarrow{\text{8.5 MeV}} _{88}^{227} No + 4 \, _{2}^{4} n$$
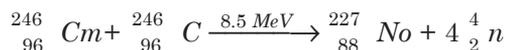
Eleven isotopes of nobelium are known at present. Their masses range from 250 to 262. The longest-lived isotope is No-259 with a half life of 58 minutes.

OSMIUM

[7440-04-2]
Symbol: Os; atomic number 76; atomic weight 190.23; a Group VIII B (Group 8) transition metal element; a noble metal of platinum group; electron configuration $[Xe]4f^{14}5d^66s^2$; valence states +1, +2, +3, +4, +5, +6, +7, +8; most common states +3, +4, +6; seven natural isotopes: Os-184 (0.02%), Os-186 (1.58%), Os-187 (1.61%), Os-188 (13.32%), Os-189 (16.13%), Os-190 (26.44%), Os-192 (41.03%); twenty-eight radioactive isotopes in the mass range 162–183, 185, 191 and 193-196; longest-lived radioisotope, Os-194 ($t_{1/2}$ 6.0 year).

History, Occurrence, and Uses

Osmium was discovered by English chemist Smithson Tennant in 1804. The element was named osmium after the Greek word, *osme*, which means a smell, because of the pungent and peculiar odor of its volatile oxide.

Osmium occurs in nature, always associated with other platinum group metals. It usually is found in lesser abundance than other noble metals. Its most important mineral is osmiridium (or iridosmine), a naturally occurring mineral alloyed with iridium.

The commercial applications of osmium are limited and considerably fewer than other platinum group metals. Its alloys are very hard and are used to make tips of fountain-pen nibs, phonograph needles, and pivots. The metal also exhibits effective catalytic properties in hydrogenation and other organic reactions. Such catalytic applications, however, are limited and osmium fails to replace other noble metals, particularly palladium and platinum, which are more effective as catalysts and cost less.

Physical Properties

Bluish-white lustrous metal; brittle and fairly hard; close-packed hexago-

nal crystal system; density 22.48 g/cm^3; Moh's hardness 7.0; melts at about 3,050°C; vaporizes above 5,300°C; electrical resistivity 8.12 microhms-cm at 0°C; Young's modulus 4.0x10^4 tons/in^2; magnetic susceptibility 0.052x10^{-6} cm^3/g; thermal neutron absorption coefficient 15 barns; insoluble in water; insoluble in HCl and H$_2$SO$_4$; slightly soluble in nitric acid and aqua regia; insoluble in ammonia; solubilized by fusion with caustic soda and sodium peroxide or caustic soda and potassium chlorate and the mass dissolved in water.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	189.0 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	178.89 kcal/mol
S° (cry)	7.8 cal/degree mol
S° (gas)	46.00 cal/degree mol
C$_\rho$ (cry)	5.90 cal/degree mol
C$_\rho$ (gas)	4.97 cal/degree mol
Coefficient of linear expansion, at 20°C	6.1x10^{-6}/°C

Production

Osmium is recovered from platinum group minerals or certain ores of nickel and copper.

When recovered from the mineral osmiridium, the mineral is fused with zinc to convert it into a zinc alloy. The alloy is then treated with hydrochloric acid to dissolve the zinc away leaving a finely divided material. This finely divided solid then is fused with sodium peroxide and caustic soda to convert osmium and ruthenium into their water-soluble sodium salts, sodium osmate and sodium iridate, respectively. While osmium is fully converted to osmate salt, most ruthernium and a small part of iridium are converted to ruthenate and iridate, respectively. The fused mass is leached with water to separate metals from solid residues.

To separate osmium from ruthenium, the aqueous solution is acidified with nitric acid. While nitric acid oxidizes osmate ion to volatile osmium tetroxide, OsO$_4$, it converts ruthenium to a nitric oxide complex. Osmium tetroxide is removed from the solution by distillation in air and collected in an aqueous solution of caustic soda containing ethanol. Osmium tetroxide solution is heated with ammonium chloride, upon which osmium precipitates out as a complex chloride, OsO$_2$(NH$_3$)$_4$Cl$_2$. The precipitate is filtered, washed and decomposed by ignition with hydrogen to yield osmium metal.

The mineral osmiridium may alternatively be chlorinated at elevated temperatures on a bed of sodium chloride. Osmium is converted to water-soluble sodium chloroosmate. Iridium and ruthenium also are converted into water-soluble sodium chloroiridate and chlororuthenate. The insoluble residues are filtered out. Osmium is recovered from this solution in several steps as mentioned above.

Osmium and other precious metals also may be recovered from sludges generated at the anode from electrolytic refining of nickel and copper from

certain nickel-copper ores. After removal of all nonplatinum group metals by a combination of various methods, the residual sludge is digested with aqua regia to solubilize osmium and other precious metals.

Reactions

Osmium in finely divided form reacts slowly with oxygen or air at ambient temperatures to form osmium tetroxide.

$$Os + 2O_2 \rightarrow OsO_4$$
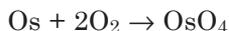
The bulk metal is stable in oxygen at ordinary temperatures but reacts at 200°C, forming osmium tetroxide. When further heated to 800 to 1,500°C in air or oxygen, the tetroxide converts to volatile trioxide, OsO_3. When the metal is heated in a stream of OsO_4 vapor, osmium dioxide is produced:

$$Os + OsO_4 \rightarrow 2OsO_2$$

The metal converts to its fluoride, OsF_6 when heated with fluorine at 300°C. The reaction also yields the tetrafluoride, OsF_4, as a minor product. A similar reaction occurs with chlorine, but at much higher temperatures of 650 to 700°C, forming both the trichloride, $OsCl_3$, and the tetrachloride, $OsCl_4$. Formation of the tetrachloride is favored at higher temperatures.

Osmium is stable in mineral acids even under boiling conditions. The metal, however, is attacked by fused alkalies, such as caustic soda and caustic potash, particularly in the presence of an oxidizing agent such as sodium peroxide, sodium hypochlorite, or sodium nitrite, forming osmates.

Osmium is oxidized by nitric acid to form osmium tetroxide, OsO_4.

Analysis

Osmium in trace quantities can be determined by flame AA method using nitrous oxide-acetylane flame at wavelength 290.9 nm. The metal or its insoluble compounds can be solubilized by fusion with caustic soda and potassium perchlorate and dissolving the fused mass in water.

OSMIUM TETROXIDE

[20816-12-0]
Formula: OsO_4; MW 254.23
Synonym: osmium(VIII) oxide.

Uses

Osmium tetroxide is an intermediate in the separation of osmium from other platinum group metals. It is used as an oxidizing agent and also an oxidation catalyst in organic synthesis. It is used for hydroxylation of organic compounds at double bonds, such as conversions of olefins to glycols. The oxide also is used for fixing and staining biological materials for microscopic

examination.

Physical Properties

Pale, yellow crystalline solid; chlorine-like acrid odor; monoclinic crystals having terahedral structure; density 5.1 g/cm³; melts at 40.6°C; vaporizes at 129.7°C; sublimation begins below its boiling point; vapor pressure 11 torr at 27°C; critical temperature 405°C; critical pressure 170 atm; moderately soluble in water, 7.24 g/100mL at 25°C; soluble in most organic solvents.

Thermochemical Properties

$\Delta H_f°$ (cry)	–94.19 kcal/mol
$\Delta H_f°$ (gas)	–80.59 kcal/mol
$\Delta G_f°$ (cry)	–72.87 kcal/mol
$\Delta G_f°$ (gas)	–69.98 kcal/mol
$S°$ (cry)	34.39 cal/degree mol
$S°$ (gas)	70.22 cal/degree mol
C_ρ (gas)	17.71 cal/degree mol
ΔH_{fus}	2.34 kcal/mol

Preparation

Osmium tetroxide is obtained as an intermediate during recovery of osmium metal from osmiridium or other noble metal minerals (See Osmium). In general, oxidation of an aqueous solution of an osmium salt or complex, such as sodium osmate with nitric acid, yields the volatile tetroxide which may be distilled out from the solution. In the laboratory, the compound can be prepared by oxidation of the osmium tetrachloride, $OsCl_4$, or other halide solutions with sodium hypochlorite followed by distillation.

Osmium tetroxide may also be produced by heating finely divided osmium metal in a stream of oxygen or air at 300 to 400°C.

Reactions

Heating osmium tetroxide with osmium metal forms osmium dioxide:

$$OsO_4 + Os \rightarrow 2OsO_2$$

Reaction with sodium or potassium hydroxide forms *trans*-osmate ion, *trans*-$[OsO_4(OH)_2]^{2-}$, which is reduced by ethanol to form dark purple $[Os^{VI}(O)_2(OH)_4]^{2-}$. On the other hand, reaction of osmium tetroxide with rubidium or cesium hydroxide in stoichiometric ratios usually form the ions, $[OsO_4(OH)]^-$ and $[OsO(\mu\text{-}OH)OsO_4]$ in addition to *trans*-$[OsO_4(OH)_2]^{2-}$.

Reaction with fluoride ion forms the adduct oxofluoro ion, $[OsO_4F_2]^{2-}$. For example, osmium tetroxide reacts with sodium fluoride to form an oxofluoro salt of sodium:

$$OsO_4 + 2NaF \rightarrow Na_2[OsO_4F_2]$$
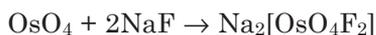
Osmium tetroxide forms various complexes with donor molecules under varying conditions. For example, with pyridine(*py*) it forms a bridged complex, $[(py)OsO_2(\mu–O)]_2$.

Reaction with ammonia in aqueous potassium hydroxide yields orange red crystalline "osmiamate", $K[N{\equiv}OsO_3]$.

Osmium tetroxide reacts with amines, undergoing partial substitution of NR^{2-} (where R=alkyl group) with O^{2-} to form compounds such as OsO_3 (NR) and $OsO(NR)_3$.

Osmium tetroxide reacts with phenyl Grignard reagent to produce a reactive intermediate, serving as a synthetic route to prepare polyphenyl osmium complexes. For example, reaction with *o*-tolyl magnesium bromide, *o*-tolMgBr, forms a purple, tetracoordinated osmium *ortho*-tolyl complex, $Os(o\text{-}tol)_4$, which reacts with trimethylphosphine or carbon monoxide to yield osmium π-aryl complexes.

Osmium tetroxide forms several thiolate complexes from interaction with thiols and triphenyl- or trialkylphosphines:

$$OSO_4 \xrightarrow[PPh_3]{CH_3SH} OS^{IV}(SCH_3)_4(PPh_3)_3$$

Osmium tetroxide forms halide complex ions, hexachloroosmates, such as $[OsCl_6]^-$, $[OsCl_6]^{2-}$, and $[OsCl_6]^{3-}$. The former ion $[OsCl_6]^-$ is obtained by reaction of the tetroxide with sulfur dichloride and chlorine at ambient temperature:

$$OsO_4 + SCl_2 + Cl_2 \rightarrow [SCl_3]^+ + [OsCl_6]^-$$
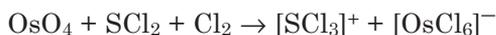
The ions, $[OsCl_6]^{2-}$ and $[OsCl_6]^{3-}$ are obtained by reducing OsO_4 in HCl with Fe^{2+}.

Analysis

Elemental composition: Os 74.82%, O 25.18%. The compound can be identified by its physical properties, such as, odor, color, density, melting-, and boiling points. Its acrid odor is perceptib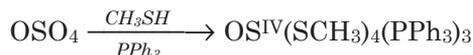le at concentrations of 0.02 mg/liter in air. The oxide also produces an orange color when a small amount of the compound or its aqueous solution is mixed with an aqueous solution of ammonia in KOH (see Reactions). Aqueous solution of the tetroxide may be analyzed for osmium by AA or ICP spectrometry (see Osmium). Vapors of the tetroxide may be purged from an aqueous solution by helium, adsorbed over a trap, and desorbed thermally by helium onto a GC. Alternatively, a benzene or carbon tetrachloride solution may be injected onto the GC and the compound peak identified by mass spectrometry. The characteristic mass ions for its identification should be 190 and 254.

Toxicity

Osmium tetroxide is poisonous by all routes of exposure. The vapor is an

eye irritant and can produce tears and damage. The vapor also can cause upper respiratory tract irritation.

> LD_{50} oral (mouse): 162 mg/kg
>
> LC_{LO} inhalation (mouse): 40 ppm (104 mg/m^3)/4 hr.

OXYGEN

[7782-44-7]

Symbol: O; atomic number 8; atomic weight 15.9994; a Group VI A (Group 16) nonmetallic element; electron configuration [He]$2s^2 2p^4$, ; valence states –2, –1; occurs as a diatomic molecule; bond length 1.48Å; electronegativity 3.5 (the second most electronegative element after fluorine); atomic radius 0.73Å; ionic radius 1.40Å (as O^{2-}). The element occurs in three stable isotopes; most stable isotope, O-16 [14797-70-7], natural abundance 99.76%; the other two isotopes are O-17 [13968-48-4] (0.038%) and O-18 [14797-71-8] (0.20%).

History, Occurrence, and Uses

The discovery of oxygen, its role in respiration and combustion processes, the synthesis and understanding of some of its most important compounds undoubtedly established the foundation of modern chemistry. Most of these pioneering works were done independently during the 1770's by Scheele, Priestley, Lavoisier, and Cavendish. While Scheele was first to prepare oxygen in 1772 by heating a mixture of silver carbonate and mercury carbonate, and later on heating oxides of different metals, his results were not published until 1777. Priestley, in 1774, prepared oxygen independently by heating mercuric oxide and is usually credited for discovering oxygen. Both Scheele and Priestley recognized that oxygen was a component of air that supported combustion and respiration. Priestley's discovery was tested and extended by Lavoisier who, in 1775, meticulously established a correct theory of combustion. Cavendish synthesized water by sparking a mixture of hydrogen and air or oxygen. He also made nitric oxide and nitrogen dioxide by sparking an air-oxygen mixture, and later produced sulfur dioxide from burning sulfur in oxygen.

Oxygen takes its name from the two words 'ox' meaning 'sharp (taste)' and 'gen', which means 'to form'. The element was named oxygen by Lavoisier, who mistakenly assumed that it was a component of all acids.

Oxygen is the most abundant and most widely distributed element on earth. More than 50% of the earth's mass constitutes oxygen. Oxygen is a component of the earth's crust, mantle, rocks, minerals, hydrosphere and the atmosphere. It occurs in all oxides and in a large number of minerals containing phosphates, sulfates, carbonates, nitrates and hydroxides. The oxygen content of the earth's oceans is   about 88.7% by mass. Oxygen is a component of innumerable inorganic and organic compounds that include water, carbon dioxide, nitrogen oxides, sulfur oxides, oxo acids, most bases, alcohols, aldehydes, ketones, esters, carboxylic acids, lactones, sugars and carbohydrates. Oxygen is a major constituent of air, being the second most abundant gas of

the earth's atmosphere constituting 20.8% of atmosphere. While the oxygen in the lower atmosphere essentially is diatomic O_2 molecule, at about 30 to 45 km height, a triatomic form of oxygen, ozone (O_3), coexists with O_2 at varying but significant concentrations. Atomic oxygen, O, is found with molecular oxygen in the upper atmosphere.

Elemental oxygen also is present in the sun in less than 1% mass composition, as a fusion product of carbon-12, and helium-4. No planet or its moon in the solar system, other than the earth is known to contain molecular oxygen in its atmosphere, although CO_2 is a major component of many planetary atmospheres.

Oxygen is present in all living organisms and is vital for sustenance of life in the animal kingdom. The animal respiration process provides energy for tissues, produced by oxidation of carbohydrates with oxygen. The process in all vertebrates and some invertebrates involves transport of oxygen through blood where oxygen binds to hemoglobin, forming oxyhemoglobin. Despite consumption of oxygen by animals, there is no depletion of its content in air, because carbon dioxide generated in such combustion is used by plants in photosynthesis, releasing oxygen.

Oxygen has numerous industrial applications. Most oxygen manufactured today is consumed in refining iron in the steel industry. Oxygen is used for removing carbon, silicon, sulfur, phosphorus, manganese, and other impurities from liquid iron in steel making. In nonferrous metallurgy, oxygen is used to enrich fuel-air flame in furnaces in producing copper and nickel from sulfide ores.

Oxygen also is a component of oxy-hydrogen flame and oxy-acetylene flame for welding and glass blowing.

Oxygen has major uses in the chemical industry too. It is used to oxidize methane, ethylene, and other hydrocarbons. Oxidation of methane produces synthesis gas. Ethylene oxidation yields products such as ethylene oxide, acetaldehyde, and acetic acid. Oxygen also is used in making many commercial inorganic compounds including various metal oxides, oxoacids, and oxosalts.

Oxygen is used in all breathing masks and life support devices; in space vehicles, high altitude flying, fire fighting, underground mining, submarines, and underwater operations. In medicine, oxygen is used in respirators, incubators, and life support devices. It is given to patients under hypoxia, respiratory distress, impaired respiratory function, and asthmatic attack. It also is administered to treat cyanosis and for poisoning by carbon monoxide and other toxicants that can bind to hemoglobin in the blood. Oxygen also is a component of most anesthetic mixtures.

Oxygen also is used in fermentation, bleaching wood chips, odor control, and as a flame-enhancing agent.

Physical Properties

Colorless, odorless, tasteless gas; gas density 1.429 g/L at 0°C and 1.309 g/L at 25°C; liquefies at –182.96°C; liquid density 1.149 g/mL at –183°C; solidifies at –218.4°C; density of the solid oxygen at –252.4°C 1.426 g/cm^3; critical tem-

perature –118.56°C; critical pressure 49.77 atm; critical volume 73 cm^3/mol; viscosity of gas at 25°C and 1 atm 0.192 centipoise; diffusion coefficient into air at STP 0.178 cm^2/sec; velocity of sound in oxygen at 25°C and 1 atm 330m/sec; thermal neutron absorption cross section < 0.0002 barn; solubility in water, 0.0310 mL O$_2$ at STP per 1mL water at 20°C or 4.34 mg/100 g water at 20°C and 1 atm (760 torr = pressure of oxygen + water vapor pressure); solubility in water at 0°C 0.0489 mL O$_2$ measured at STP or 6.945 mg/100 g at 0°C and 1 atm (pressure of gas + water vapor).

Thermochemical Properties

$\Delta H_f°$	0.0
$\Delta G_f°$	0.0
$S°$	49.0 cal/degree mol
C_ρ	7.016 cal/degree mol
ΔH_{diss}	119.11 kcal/mol

Production

Most commercial oxygen at present is obtained from air by cryogenic separation processes. Although design of oxygen manufacturing plants and process conditions may vary depending on production capacity, purity desired, and cost, basic steps are similar.

Air first is filtered to remove dust particles. Water and carbon dioxide and most trace impurities are removed by silica gel (or other effective adsorbent) at a temperature slightly above 0°C. Acetylene and other hydrocarbons also can be removed by such adsorption processes. Alternatively, clean air is compressed and cooled to freeze out water and carbon dioxide, which can be trapped and removed in reversing exchangers. Compression and cooling of air is a critical step in its liquefaction. When cooled compressed air is allowed to expand it cools further (Joule-Thomson effect), converting the gaseous air to liquid air at about –196°C. Liquefied air is subjected to fractional distillation. More volatile argon and nitrogen distill out on warming, leaving behind oxygen with trace quantities of hydrogen, helium, and other inert gases.

Oxygen may be produced by electrolysis of water. In such electrolytic procedure, small amounts of H$_2$SO$_4$ or NaOH may be added to water. Electrolysis methods, however, are not used as much commercially as are air liquefaction processes which cost less. However, in making hydrogen from water by electrolysis, oxygen is obtained as a by-product.

In the laboratory oxygen may be prepared by several chemical methods that involve thermal decomposition of solid oxides or oxo salts. The most convenient method of preparing oxygen is to heat potassium chlorate in the presence of manganese dioxide catalyst:

$$2KClO_3 \xrightarrow[MnO_2]{heat} 2KCl + 3O_2$$
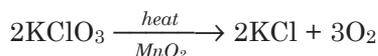
Early preparation of oxygen involved thermal dissociation of metal oxides, notably mercury(II) oxide, which was used independently by both Priestley

and Scheele. Also, oxides of lead, silver, and barium or potassium nitrate and permanganate were used by these and later investigators to prepare oxygen. Some reactions that yield oxygen by thermal decomposition of metal oxides and metal oxo salts, are highlighted below:
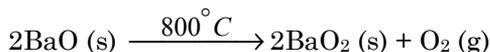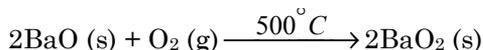
$$2HgO \text{ (s)} \rightarrow 2Hg \text{ (l)} + O_2 \text{ (g)}$$

$$2BaO_2 \text{ (s)} \rightarrow 2BaO \text{ (s)} + O_2 \text{ (g)}$$

$$2PbO_2 \text{ (s)} \rightarrow 2PbO \text{ (s)} + O_2 \text{ (g)}$$

$$2KNO_3 \text{ (s)} \rightarrow 2KNO_2 \text{ (s)} + O_2 \text{ (g)}$$

$$2Ag_2O \text{ (s)} \rightarrow 4Ag \text{ (s)} + O_2 \text{ (g)}$$

$$2KMnO_4 \text{ (s)} \rightarrow K_2MnO_4 \text{ (s)} + MnO_2 \text{ (s)} + O_2 \text{ (g)}$$

$$2K_2S_2O_8 \text{ (s)} \rightarrow 2K_2SO_4 \text{ (s)} + 2SO_2 \text{ (g)} + O_2 \text{ (g)}$$

Barium peroxide was used in commercial production of oxygen in the past. Heating barium oxide in air at 500°C forms barium peroxide, which decomposes at 800°C to yield oxygen:

$$2BaO \text{ (s)} + O_2 \text{ (g)} \xrightarrow{\;500^\circ C\;} 2BaO_2 \text{ (s)}$$

$$2BaO \text{ (s)} \xrightarrow{\;800^\circ C\;} 2BaO_2 \text{ (s)} + O_2 \text{ (g)}$$

Oxygen can be prepared chemically at ordinary temperatures. Several reactions in solution are known that may produce small quantities of oxygen at room temperatures. One such convenient method of producing oxygen is to slowly add water to sodium peroxide. The reaction is exothermic; therefore, the addition of water must be done cautiously.

$$2Na_2O_2 \text{ (s)} + 2H_2O \text{ (l)} \rightarrow 4NaOH \text{ (aq)} + O_2 \text{ (g)}$$
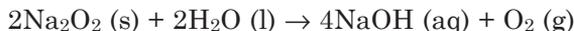
Oxygen also is liberated when an acidified solution of potassium permangnate, acidified with sulfuric acid, is treated with a solution of hydrogen peroxide:

$$2MnO_4^- \text{ (aq)} + 5H_2O_2 \text{ (aq)} + 6H^+ \text{ (aq)} \rightarrow 2Mn^{2+} \text{ (aq)} + 8H_2O \text{ (l)} + 5O_2 \;\; \text{(g)}$$

Reactions

Oxygen reacts with practically all elements, a number of inorganic salts, and all organics under various conditions including elevated temperatures, pressures, and the presence of a catalyst. While certain reactive metals, such as sodium, potassium and calcium react vigorously at ordinary temperatures,

most other metals react with oxygen at elevated temperatures. Among alkali metals, lithium, sodium, and potassium form the oxide, Li_2O; peroxide, Na_2O_2; the peroxide K_2O_2, and superoxide, KO_2, respectively. Alkaline earth metals form oxides, such as CaO and MgO. Transition metals combine with oxygen to form three oxides at different oxidation states, e.g., FeO, Fe_2O_3, Fe_3O_4. Rate of oxidation at ambient temperatures depends on the nature of the metal and its surface area. Most metals are pyrophoric in their finely divided state, but react very slowly in bulk form. Often metal surfaces are passivated by formation of a protective oxide film. Noble and coinage metals react extremely slowly with oxygen at ordinary temperatures.

All nonmetals except helium, neon, and argon react with oxygen. Nitrogen forms five oxides, N_2O, NO, NO_2 (N_2O_4), N_2O_3, and N_2O_5; sulfur yields SO_2 and SO_3; carbon forms CO and CO_2; phosphorus forms P_2O_3 and P_2O_5; hydrogen forms H_2O and H_2O_2; and halogens form various oxides, including OF_2, ClO, and ClO_2. Inert gases, krypton and xenon, are known to form oxides.

All organic compounds undergo combustion reactions when heated with oxygen. Hydrocarbons and compounds containing C, H, and O yield carbon dioxide and water as products, while nitrogen-containing organics also form NO_x. A few reactions are shown below:

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$$

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$4C_6H_5N + 33O_2 \rightarrow 24CO_2 + 10H_2O + 4NO_2$$

Many organics also undergo oxidation of a noncombustion nature to form various commercial products. Such reactions are mostly catalytic and include production of synthesis gas, a mixture of CO and H_2, conversion of ethylene to ethylene oxide, and cumene to phenol and acetone.

$$CH_4 + \tfrac{1}{2}O_2 \xrightarrow{\text{catalyst}} CO + 2H_2$$

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow{\text{catalyst}} C_2H_4O$$

(ethylene)   (ethylene oxide)

$$C_6H_5{-}CH(CH_3)_2 + O_2 \xrightarrow{\text{UV light 350 nm}}$$

(cumene)

$$C_6H_5C(CH_3)_2COOH \longrightarrow C_6H_5OH + (CH_3)_2CO$$

(cumene hydroperoxide)   (phenol)   (acetone)

Certain classes of organic compounds containing oxygen atoms, such as aldehydes and ethers, may react with oxygen to form peroxy derivatives:

$$CH_3CHO + O_2 \quad \rightarrow \quad CH_3C(=O)OOH$$
(acetaldehyde)   (peracetic acid)

Analysis

Oxygen may be identified because it supports combustion. Thus, a glowing splinter will burst into flame when exposed to oxygen. Also, it combines readily with nitric oxide forming brown nitrogen dioxide. Oxygen may be identified by GC/MS using a suitable capillary GC column, preferably under cryogenic conditions. The characteristic mass for O_2 is 32.

OXYGEN DIFLUORIDE

[7783-41-7]
Formula OF_2 ; MW 54:00 ; a bent molecule with FOF angle 104° and O–F distance 0.14 nm.
Synonyms: fluorine monoxide; fluorine oxide.

Uses

Commercial applications of oxygen difluoride are limited. It is used in organic synthesis to prepare fluoropropylenes and acylfluorides. It is used as an oxidizing and fluorinating agent in many preparative reactions and as a monomer in diolefin copolymerization.

Physical Properties

Colorless gas with a characteristic odor; unstable in the presence of moisture, otherwise stable up to 250°C; gas density 2.21g/L at 25°C; liquefies to a yellowish-brown liquid at –144.8°C; density of the liquid 1.90g/ml at –223.8°C; solidifies at –223.8°C; slightly soluble in water, decomposing very slowly; solubility 68ml gas per liter of water at 0°C; slightly soluble in acids and alkali.

Thermochemical Properties

$\Delta H_f°$	7.60 kcal/mol
ΔH_{vap}	9.11 kcal/mol

Preparation

Oxygen difluoride may be prepared by passing fluorine gas slowly through a dilute solution of caustic soda. Usually a 2% solution of NaOH is suitable for the preparation:

$$2F_2 + 2\ Na\ OH \rightarrow 2NaF + OF_2 + H_2O$$
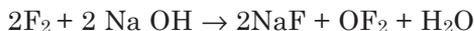
At a higher alkali concentration, oxygen is formed:

$$2F_2 + 4NaOH \rightarrow 4NaF + 2H_2O + O_2$$

Oxygen difluoride can be produced by electrolysis of an aqueous solution of HF or, alternatively, electroylzing molten potassium hydrogen difluoride, KHF_2, in the presence of water.
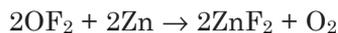
Reactions

Oxygen difluoride decomposes slowly in water forming oxygen and fluorine:

$$2OF_2 \xrightarrow{\ H_2O\ } O_2 + 2F_2$$
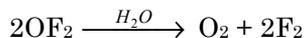
Such decomposition also occurs in dilute alkali solutions. The reaction, however, is slow:

$$OF_2 + 2OH^- \rightarrow O_2 + 2F^- + H_2O$$
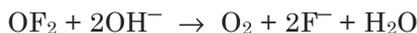
Oxygen difluoride reacts with many common metals forming fluorides. The reaction stops when the metal surface is covered with a protective layer of fluoride:

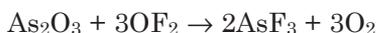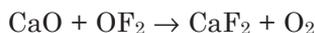$$2OF_2 + 2Zn \rightarrow 2ZnF_2 + O_2$$

Reactions with certain metals, especially metalloid type elements, yield metal fluorides and oxyfluorides. Such metals include B, Si, Ge, As, Sb, Se, and Te:

$$Sb + 2OF_2 \rightarrow SbF_3 + SbOF$$
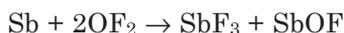
Oxygen difluoride reacts with nonmetals, such as sulfur and phosphorus, forming fluorides and oxyfluorides:

$$6OF_2 + 4S \rightarrow SF_6 + 3SO_2F_2$$
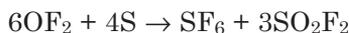
Metal oxides react with oxygen difluoride forming fluorides:

$$CaO + OF_2 \rightarrow CaF_2 + O_2$$

$$As_2O_3 + 3OF_2 \rightarrow 2AsF_3 + 3O_2$$

Oxygen difluoride is a strong oxiding agent. When mixed with hydrogen, carbon monoxide, methane or carbon, and ignited with an electrical shock, the mixture explodes forming various products. It catches fire in contact with nitric oxide.
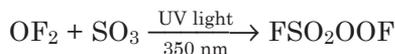
Oxygen difluoride oxidizes sulfur dioxide to sulfur trioxide:

$$OF_2 + SO_2 \rightarrow SO_3 + F_2$$
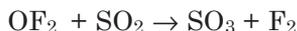
However, in the presence of UV radiation the products are sulfuryl fluoride, SO_2F_2, and pyrosulfuryl fluoride, $S_2O_5F_2$:

$$OF_2 + 2SO_2 \xrightarrow{\text{UV radiation}} S_2O_5F_2$$
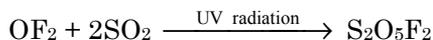
Photochemical reaction with sulfur trioxide in the presence of UV light forms a peroxy compound, FSO_2OOF:

$$OF_2 + SO_3 \xrightarrow[\text{350 nm}]{\text{UV light}} FSO_2OOF$$

Oxygen difluoride oxidizes hydrochloric, hydrobromic, and hydriodic acids in aqueons solutions, liberating chlorine, bromine, and iodine, respectively:

$$OF_2 + 4HCl \rightarrow 2\ Cl_2 + 2HF + H_2O$$

$$OF_2 + 4HBr \rightarrow 2\ Br_2 + 2HF + H_2O$$

In aqueous solutions, halide salts (Cl^-, Br^- and I^-) are similarly oxidized to free halogens.

Oxygen difluoride reacts with carbonyl fluoride, COF_2, in the presence of a catalyst, cesium fluoride, to form bis(trifluorylmethyl)trioxide, CF_3OOOCF_3 (Solomon, Irvine J. 1980. *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Vol. 3, pp 773-75. New York: John Wiley & Sons). The overall reaction is as follows:

$$OF_2 + 2COF_2 \xrightarrow{\text{CsF}} CF_3OOOCF_3$$

Oxygen difluoride oxidizes a number of organic compounds of the type, alcohols, aldehydes, amines and aromatics. Olefins yield fluorinated products. Reactions with ethylene under controlled conditions form fluoroethane, C_2H_5F, and 1, 2- difluoroethane, FCH_2CH_2F. Tetrafluoroethylene readily combines with oxygen difluoride, forming hexafluoroethane, C_2F_6 and carbonyl fluoride, COF_2. The overall reaction is:

$$3\ F_2C{=}CF_2 + 2OF_2 \rightarrow 2F_3CCF_3 + 2COF_2$$
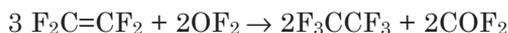
Reaction with benzene produces quinone and hydroquinone.
Lower aliphatic alcohols are readily oxidized to carboxylic acids:

$$CH_3CH_2OH + 2OF_2 \rightarrow CH_3COOH + H_2O + 2F_2$$

Oxygen difluoride reacts with primany amines in fluorocarbon solvents under very cold conditions to form nitroso compounds:

$$CH^3CH_2NH_2 + OF_2 \xrightarrow[\text{fluorocarbons}]{-42°\ C} CH_3CH_2N{=}O + 2HF$$
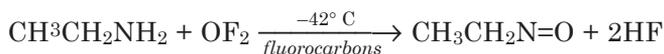
At ambient temperatures, these primary amines decompose.

Analysis

Oxygen difluoride may be analyzed by GC, GC/MS, IR, and NMR methods. The compound may be identified by GC/MS, the characteristic mass ions are 54, 38 and 35. The compound can be measured quantitatively by wet methods based on its strong oxidizing ability (see Reactions). It liberates I_2 from an acidified solution of potassium iodide and the liberated I_2 can be measured by iodometric titration using $Na_2S_2O_3$ titrant and starch indicator. Alternatively, the compound may be treated with a measured amount of excess NaOH and the unreacted excess NaOH measured by titrating against a standard solution of HCl. Also, the fluoride ion, F^-, may be measured by fluoride selective electrode.

Hazard

Oxygen difluoride is a highly toxic gas that attacks lungs, manifesting delayed symptoms. It causes irritation of eyes, lungs, and skin. Chronic exposure can lead to pulminary edema and congestion in lungs. Inhalation also can cause systemic toxic effects in humans. LC_{50} inhalation (rat): 136ppm/1 hr

The compound is a very powerful oxidizing agent. Contact with reducing agents can cause explosion.

OZONE

[10028-15-6]
Formula: O_3; MW 47.998; an allotrope of oxygen; O—O bond length 1.28Å; O—O—O bond angle 117°.

History, Occurrence, and Uses

Ozone was discovered in 1785 by the Dutch chemist Van Marum. He observed that when an electric spark passed through oxygen, a product was formed that had a peculiar, irritating odor and that tarnished mercury. Schonbein confirmed Van Marum's observation in 1840 and determined the oxidizing properties of this "irritating odor" gas. He named it ozone from the Greek word *ozo*, which means "smelling."

Ozone occurs in the stratosphere at an altitude of 20 to 40 km, known as ozonosphere, having maximum concentrations at about 25km. It is formed in the atmosphere by the decomposition of oxygen by short wavelength UV radiation (~185 nm or shorter). The stratospheric ozone layer is vital for sustenance of life on earth. It protects the earth by absorbing the harmful ultraviolet radiation from the sun of wavelengths 220 to 290 nm, which can cause skin cancer and cataracts. Certain substances, such as chloroflurocarbons used as refrigerants for air-conditioners, aerosol propellants and reagents for plastic foam, release reactive chlorine atoms that deplete ozone in the stratosphere. On a clear, sunny day, ozone also is found in the lower atmosphere (the troposphere, the air at ground level), at concentrations ranging between 0.02 to 0.05 ppm. The concentration may vary with location and may change at different times of day, being highest in summer mid-afternoons.

Ozone has many industrial applications. It is a sterilizing and deodorizing agent. It is used for disinfection of filtered drinking water and to purify wastewaters. It also is used in water treatment plants for removal of metal impurities by oxidizing them into insoluble compounds. This removes undesired taste, odor, and color from the water. Ozone also is used for odor control.

Ozone is used in the food industry to inhibit growth of bacterias and mold in fruits, vegetables, and meat products. In paper and textile industries, ozone is used as a bleaching agent on wet paper pulp and cloth.

Probably the biggest use of ozone is in chemical industries where it is a strong oxidizing agent. It is heavily used in organic synthesis (see Reactions). It readily attacks most kinds of double bonds.

Physical Properties

Pale blue gas (in undiluted form); irritating odor above a concentration of 0.15 ppm, but the odor may be pleasant and refreshing at about 0.05 ppm; density of gas 2.144g/L at 0ºC; liquefies at –111.9ºC to a dark blue liquid; density of liquid ozone 1.614 g/L at –195.4ºC; refractive index of liquid 1.2226; freezes at –192.7º C to a bluish-black solid; critical temperature –12.05°C; critical pressure 54.98 atm; critical volume 89cm^3/mol; slightly soluble in water.

Thermochemical Properties

|	
$\Delta H_f°$	34.1 kcal/mol
$\Delta G_f°$	39.0 kcal/mol
$S°$	57.08 cal/degree mol
C_ρ	9.37 cal/degree mol

Production

Ozone is generated from oxygen by passing an electric spark or silent electrical discharge through dry, and pure oxygen. This electrical discharge may be applied between two glass surfaces between which oxygen is passed. Many types of ozonizers (ozone generating apparatus) are known and commercially available for small-scale production of this gas for various uses.

Ozone may be produced by electrolysis of chilled dilute sulfuric acid (e.g. 2.5N H_2SO_4) or perchloric acid at high current density (higher than that required to produce oxygen alone). A mixture of oxygen and ozone evolve at the anode.
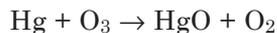
Reactions

The most important reactions of ozone are in oxidation. It is a stronger oxidizing agent than oxygen and in acid solution it is a very powerful oxidizing agent. The standard electrode potential, E°, for the half reaction $O_3(g) + 2H^+$ (aq) $+ 2e^- \rightarrow O_2$ (g) $+ H_2O$ (l) is $+ 2.07$ V. At ordinary temperatures ozone oxidizes metals such as silver and mercury to form their oxides. It oxidizes halides to halogens, nitrogen oxides to higher oxides of nitrogen, sulfur dioxide to sulfur trioxide, ferrous to ferric salts, and sulfides to sulfates. Some typical reactions are illustrated below.

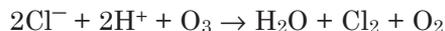Oxidation of silver gives a black oxide, which probably is the AgO:

$$Ag + O_3 \rightarrow AgO + O_2$$
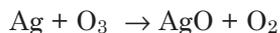
Mercury forms mercury(II) oxide:

$$Hg + O_3 \rightarrow HgO + O_2$$

The product mixture consists of mercury (II) oxide and mercury:

$$2Hg + O_3 \rightarrow (Hg + HgO) + O_2$$

Ozone oxidizes halides in acidified aqueous solutions, liberating halogens:

$$2Cl^- + 2H^+ + O_3 \rightarrow H_2O + Cl_2 + O_2$$
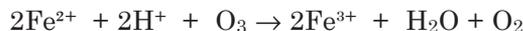
Iodine similarly is liberated from an acidified solution of potassium iodide. The reaction is used to measure ozone quantitatively:

$$2I^- + 2H^+ + O_3 \rightarrow H_2O + I_2 + O_2$$

Ozone converts black lead sulfide to white lead sulfate:

$$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$$
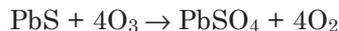
Ozone oxidizes ferrous to ferric ion in aqueous acidic solution:

$$2Fe^{2+} + 2H^+ + O_3 \rightarrow 2Fe^{3+} + H_2O + O_2$$

When an oxygen-ozone mixture containing 3.5% ozone is passed through a solution of cobalt sulfate, cobalt (III) hydroxide precipitates. This precipitation is quantitative within the pH range 1.8 to 2.5. The overall reaction is

$$2CoSO_4 + O_3 + 5H_2O \rightarrow 2Co(OH)_3 + 2H_2SO_4 + O_2$$
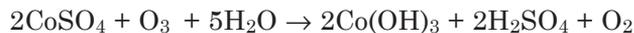
Ozone reacts with nitric oxide forming nitrogen dioxide:

$$NO + O_3 \rightarrow NO_2 + O_2$$

Smog formation in the atmosphere is caused by such reaction. Nitrogen dioxide is rapidly oxidized by ozone to form nitrogen pentoxide:

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$
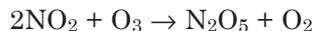
Ozone decomposes readily to oxygen in the presence of a catalyst, such as manganese dioxide or other metal oxides. It also decomposes in the presence of chlorine or bromiae vapor. Such decomposition also occurs slowly noncat-

alytically at ordinary temperatures as well as in aqueous solution. Ozone can decompose explosively on heating.

Ozone forms red-brown potassium ozonide, KO_3, by reacting with dry potassium hydroxide. Ozonide is obtained by passing oxygen-ozone mixture containing 6 to 8% ozone over dry KOH at –10 to –15°C for several hours, followed by extraction with liquid ammonia at –60°C. Evaporation of the red solution forms red-brown needles of KO_3.

Ozone reacts with organics, attacking most kinds of double bonds. It reacts with ethylene forming ethylene ozonide, a cyclic compound containing three oxygen atoms:

$$H_2C=CH_2 + O_3 \quad \rightarrow \quad \begin{array}{c} H_2C{-}{-}CH_2 \\ | \quad\quad | \\ O \quad\quad O \\ \diagdown \quad \diagup \\ O \end{array}$$
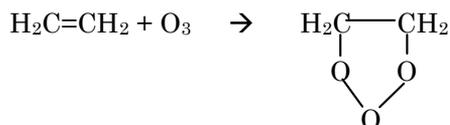
Ozone attacks C=C in unsaturated compounds including olefins, cycloolefins, pinenes, aromatics, and polybutadienes (for example, causing rubber to crack).

Analysis

Many portable ozone detectors equipped with metal oxide semiconductor-type sensors are available commercially for detecting ozone, particularly for checking ozone leaks and monitoring ozone concentration in air. In the laboratory, ozone may be measured quantitatively by reaction with an aqueous solution of potassium iodide and measuring iodine liberated by titration with a standard solution of sodium thiosulfate or phenyl arsine oxide, using starch as colorimetric indicator. The reaction may be carried out in neutral solution because in acid solution other oxidizing agents can liberate iodine, too. Several other reactions may be applied to measure ozone (see Reactions). Alternatively, ozone may be separated from oxygen, nitrogen, argon, and other gases by passing the gaseous mixture over cooled silica gel, desorbing it thermally, and analyzing by GC using a TCD. It may be confirmed by mass spectrometry. The characteristic masses are $48(O_3)$, $32(O_2)$, and $16(O)$; 32 being the primary mass and the abundance of the mass 48 may range between 20 to 30% of mass 32 (depending on the MS conditions).

Ozone can be measured by UV and IR spectroscopy. It forms an intense band at 290nm.

Hazard

Ozone is a highly toxic gas. Inhalation can cause death in a short time. A 1-hour exposure to 100ppm can be lethal to humans. Chronic exposure can cause pulmonary disease.

LC_{50} inhalation (rat): 50ppm/4 hr. (Patnaik, P. 1999. *A Comprehensive Guide to the Hazardous Properties of Chemical Substances*, 2nd ed. New York: John Wiley & Sons)

A concentrated solution of ozone or the liquefied gas can explode on

warming. Mixing liquid ozone with oxidizable organics can cause explosion. Low molecular weight ozonides formed with unsaturated organics are unstable and may cause explosive decomposition.

PALLADIUM

[7440-05-3]
Symbol: Pd; atomic number 46; atomic weight 106.42; a Group VIII (Group 10) platinum-group metal; electron configuration $[Kr]4d^{10}$; atomic radius 1.375Å; ionic radius, Pd^{2+} (coordination number 4, square planar) 0.64Å; valence states +2, +3, +4; most common valence state +2; six natural isotopes: Pd-102 (1.02%), Pd-104 (11.15%), Pd-105 (22.34%), Pd-106 (27.33%), Pd-108 (26.47%), Pd-110 (11.73%); twenty-one radioactive isotopes in the mass range 94–101, 103, 107, 109, 111–120; longest-lived radioisotope Pd-107, $t_{1/2}$ $6.5\mathsf{x}0^6$ year; shortest half-life Pd-120, $t_{1/2}$ 0.5 sec

History, Occurrence, and Uses

Palladium was discovered in 1803 by W.H. Wollaston during refining and purification of platinum metal. This new metal was found in the aqua regia extract of native platinum and was detected in solution after platinum was precipitated. It was removed as ammonium chloroplatinate. Treating this solution with mercurous cyanide precipitated a yellow palladium complex salt. The precipitate was washed and ignited to form palladium metal. Wollaston named the element palladium after the newly discovered asteroid *Pallas.*

Palladium in nature is always associated with other platinum group metals. Its abundance in earth's crust is estimated at 0.015 mg/kg, about three times more abundant than platinum. Palladium is used mostly in alloys and the majority of its alloys are used for electronics and telecommunications. They are contacts in electrical relays and automatic switching gear. Palladium-gold alloys are applied widely in dentistry and medicine. They are in devices for replacement of damaged bones and joints and as support in porcelain-overlay bridgework. Palladium alloys are used in decoration and jewelry as a substitute for gold. They are used in gems, watch cases and brooches.

One of the most important applications of palladium is to catalyze hydrogenation, dehydrogenation, and petroleum cracking. Such reactions are widely employed in organic syntheses and petroleum refining. Palladium and platinum are installed in catalytic converters in automobiles to cut down the emission of unsaturated hydrocarbon gasses.

Physical Properties

Silvery-white metal; face-centered cubic crystalline structure; density 12.02 g/cm³; Vickers hardness, annealed 37-39; melts at 1,554°C; vaporizes at 2,970°C; electrical resistivity 9.93 microhm-cm at 0°C; Poisson's ratio 0.39; magnetic susceptibility $5.231\mathsf{x}10^{-6}$ cm³/g; thermal neutron cross section 8

barns; insoluble in water; dissolves in aqua regia, hot nitric acid and boiling sulfuric acid.

Thermochemical Properties

$\Delta H_f°$ (cry)	0.0
$\Delta H_f°$ (gas)	90.2 kcal/mol
$\Delta G_f°$ (cry)	0.0
$\Delta G_f°$ (gas)	81.2 kcal/mol
S° (cry)	8.98 cal/deg mol
S° (gas)	39.9 cal/deg mol
C_ρ (cry)	6.21 cal/deg mol
C_ρ (gas)	4.97 cal/deg mol
Thermal conductivity	75.3 W/(m.K)
Coefficient of thermal expansion, at 20°C	11.1×10^{-6}/°C

Reactions

Among the platinum group metals, palladium is the least noble metal, exhibiting greater reactivity than other metals of the group. The metal forms mostly bivalent compounds, although a small number of tetravalent and a fewer trivalent compounds are known. Palladium exhibits a strong tendency to form complexes, most of which are four-coordinated square planar complexes of the metal in +2 oxidation state. When heated in air or oxygen above 350°C, palladium forms a black oxide, PdO coated over its surface. On further heating to over 790°C, the oxide decomposes back to the metal. Palladium dissolves more oxygen in molten state than in solid form.

Palladium reacts with fluorine and chlorine at 500°C forming its halides, the black PdF_3 and the red deliquescent solid $PdCl_2$.

Palladium is attacked by concentrated nitric acid, particularly in the presence of nitrogen oxides. The reaction is slow in dilute nitric acid. Finely divided palladium metal reacts with warm nitric acid forming palladium(II) nitrate, $Pd(NO_3)_2$. Hydrochloric acid has no affect on the metal. Reaction with boiling sulfuric acid yields palladium sulfate, $PdSO_4$, and sulfur dioxide.

Palladium readily dissolves in aqua regia forming chloropalladic acid, H_2PdCl_6. Evaporation of this solution yields palladium(II) chloride, $PdCl_2$.

Palladium absorbs hydrogen over 800 times its own volume over a range of temperature. By doing so, the metal swells, becoming brittle and cracked. Such absorption of hydrogen decreases the electrical conductivity of the metal. Also, such absorption activates molecular hydrogen, dissociating it to atomic hydrogen.

Production

The initial steps are similar to any other mineral extraction process. This involves crushing mineral, froth flotation, gravity concentration and other steps to obtain platinum metal concentrates that may contain about 30 to 40 wt% of platinum group metals. The concentrate is treated with aqua regia to separate soluble metals, gold, platinum, and palladium from other noble metals such as ruthenium, rhodium, iridium, osmium, and silver that remain in

the insoluble residues. The solution is filtered and the filtrate consists of gold, platinum, and palladium as $HAuCl_4$, H_2PtCl_6 and H_2PdCl_4. Gold is removed by precipitation with dibutyl carbitol. Platinum is precipitated by treatment with ammonium chloride which forms an insoluble complex, ammonium chloroplatinate, $(NH_4)_2PtCl_6$. To the filtrate containing H_2PdCl_4, ammonia is added in excess, followed by hydrochloric acid. Palladium precipitates as palladium diamine dichloride, $Pd(NH_3)_2Cl_2$. The complex is purified by dissolving in excess ammonia and reprecipitating with HCl. The purified palladium complex is ignited to give a sponge of palladium metal at 99.99% purity. Alternatively, the palladium complex is heated with formic acid to obtain palladium black which on ignition yields palladium sponge.

Analysis

Palladium metal is digested in aqua regia, evaporated to near dryness. This is followed by addition of concentrated HCl and distilled water and the solution is warmed until dissolution is complete. The solution is aspirated directly into an air-acetylene flame. Palladium is detected by flame-AA spectrophotometry. Other instrumental techniques such as ICP/AES, x-ray fluorescence, and neutron activation analysis are used also.

PALLADIUM DICHLORIDE

[7647-10-1]
Formula $PdCl_2$; MW 177.33; forms a stable dihydrate, $PdCl_2 \cdot 2H_2O$.
Synonyms: palladium(II) chloride; palladous chloride.

Uses

Palladium dichloride is a starting material for preparing several palladium compounds. It also is used for detection of carbon monoxide. For such detection, a paper is soaked in very dilute solution of $PdCl_2$ which is decolorized by CO, methane and other reducing substances. It also is used in toning and electroplating solutions and in photography for porcelain pictures.

Physical Properties

Red rhombohedral crystal; hygroscopic; density $4.0 g/cm^3$; melts at 679°C; dissolves slowly in water; also soluble in ethanol and acetone; dissolves rapidly in hydrochloric acid.
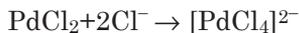
Preparation

Palladium dichloride is prepared by dissolving palladium metal in aqua regia or hydrochloric acid in the presence of chlorine. Alternatively, it may be prepared by heating palladium sponge with chlorine gas at 500°C

Reactions

Palladium dichloride dissolves in HCl forming tetrachloropalladate

ion, $[PdCl_4]^{2-}$:

$$PdCl_2 + 2Cl^- \rightarrow [PdCl_4]^{2-}$$

The complex ion catalyzes various types of organic reactions including oxidation of ethylene to acetaldehyde in aqueous solution (the Wacker Process):

$$PdCl_4^{2-} + C_2H_4 + H_2O \rightarrow CH_3CHO + Pd + 2HCl + 2Cl^-$$

Palladium dichloride forms polymeric carbonyl complexes when the dry chloride is heated in a stream of carbon monoxide charged with methane vapor. Such complexes include $[PdCl_2(CO)_n]$ and $[PdCl(CO)_2]_n$. The reaction also occurs in aqueous phase resulting in decolorization of the solution.

When H_2S is passed through palladium dichloride solution, it yields a brown-black precipitate of palladium monosulfide, PdS.

When heated with sulfur at 450 to 500°C, palladium dichloride forms palladium disulfide, PdS_2, a grey-black crystalline compound, insoluble in strong acids but soluble in aqua regia, and which converts to monosulfide, PdS, on heating at 600°C.

When ammonia gas is passed through an aqueous solution of $PdCl_2$, the product is tetrammine palladium(II) chloride, $Pd(NH_4)_2Cl_2$. The same product also is obtained in dry state by passing ammonia gas over anhydrous $PdCl_2$.

Analysis

Elemental composition: Pd 60.01%, Cl 39.99%. Palladium may be analyzed in aqueous solution by flame AA spectrophotometry. Its reddish solution is decolorized by reducing gases, such as, CO and CH_4. The compound also may be determined from its precipitation reactions (see Reactions).

PALLADIUM NITRATE

[10102-05-3]
Formula $Pd(NO_3)_2$; MW 230.43
Synonyms: palladium(II) nitrate; palladous nitrate.

Uses

Palladium nitrate is a catalyst in many organic synthesis.

Physical Properties

Brown crystalline solid; deliquesces; decomposes on heating; moderately soluble in water, forming a turbid solution; hydrolyzes in excess water forming a brown basic salt; soluble in dilute nitric acid.

Preparation

Palladirm nitrate may be prepared by dissolving palladium oxide hydrate in dilute nitric acid followed by crystallization. The nitrate crystallizes as yel-

low-brown deliquescent prisms. Alternatively, the compound may be obtained by reacting palladium metal with nitric acid.

Analysis

Elemental composition: Pd 46.18%, N 12.16%, O 41.66%. The compound may be characterized by x-ray diffraction. Its solution in dilute nitric acid may be analyzed for palladium by AA or ICP spectrophotometry.

PALLADIUM OXIDE

[1314-08-5]
Formula PdO; MW 122.42
Synonyms: palladium (II) oxide; palladium monoxide; palladous oxide

Uses

Palladium oxide is used to prepare palladium catalyst for hydrogenation. The oxide is readily reduced by hydrogen to metal.

Physcial Properties

Greenish black tetragonal crystals; density 8.3 g/cm^3; decomposes to Pd metal at 750°C; insoluble in water and acids; slightly soluble in aqua regia.

Thermochemical Properties

ΔH_f° (cry)	–20.4 cal/mol
ΔH_f° (gas)	83.4 kcal/mol
ΔG_f° (gas)	77.9 kcal/mol
S° (gas)	52.1 cal/deg mol
C_ρ (cry)	7.50 cal/deg mol

Preparation

Palladium oxide is prepared by heating palladium sponge in oxygen at 350°C. The oxide is obtained as a black powder. The oxide also may be prepared specially for catalytic use by heating a mixture of palladium chloride and potassium nitrate at 600°C and then leaching out water-soluble residue. A hydrated form of the oxide, which is acid soluble can be prepared by precipitation from solution, for example, by hydrolysis of palladium nitrate. The brown hydrated oxide converts to black anhydrous oxide on heating. Its solubility in acids decreases with lowering of water content.

Analysis

Elemental composition: Pd 86.93%. O 13.07%. The oxide may be identified by x-ray diffraction. The oxide readily can be reduced with hydrogen and the water formed can be measured by gravitmetry or other wet methods. Also, palladium metal obtained from reduction of the oxide may be digested in aqua

regia, diluted, and analyzed by AA or ICP spectrometry.

PHOSGENE

[75-44-5]
Formula $COCl_2$; MW 98.92; planar molecule; Cl—C—Cl bond angle 117°; the C—Cl bond distance 1.68Å and C=O bond distance 1.28Å.
Synonyms: carbonyl chloride; carbon oxychloride; chloroformyl chloride; carbonic dichloride

History, Occurrence, and Uses
Phosgene was prepared first in 1812 by reacting carbon monoxide with chlorine. Phosgene was used historically as a military gas in warfare. At present, it is used extensively to make polyurethanes. These urethane polymers produce polycarbonates and chloroformates for making pesticides and pharmaceuticals.

Physical Properties
Colorless gas; density 4.34 g/L; heavier than air, density in air 3.41 (air=1); liquefies at 8.3°C; liquid density 1.432 g/mL; freezes at –118°C; slightly soluble in water with slow decomposition; also decomposed by alcohol and acids; soluble in benzene, toluene and acetic acid; critical temperature 182°C; critical pressure 56.04 atm; critical volume 190 cm^3/mol.

Thermochemical Properties
$\Delta H_f^°$	–52.3 kcal/mol
$\Delta G_f^°$	–48.9 kcal/mol
$S°$	67.74 cal/ deg mol
C_ρ	13.78 cal/deg mol
ΔH_{vap}	5.75 kcal/mol

Production
Phosgene is manufactured from carbon monoxide and chlorine:

$$CO + Cl_2 \rightarrow COCl_2$$
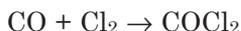
To obtain high-purity phosgene, starting materials must be pure and free from moisture. Equimolar amounts of chlorine and carbon monoxide are mixed in a reactor in the presence of a catalyst, activated charcoal. The reaction is exothermic. Heat exchangers are used to remove excess heat; otherwise the product may decompose back to carbon monoxide and chlorine. Product gases are passed into a condenser where phosgene is collected in liquid form. The gaseous mixture containing phosgene that is not condensed is passed through caustic soda solution to destroy any uncondensed phosgene. Phosgene also can be obtained by the reaction of nickel tetracarbonyl with
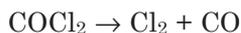
chlorine gas:

$$Ni(CO)_4 + 4Cl_2 \rightarrow 4COCl_2 + NiCl_2$$

Phosgene is a highly toxic gas. All safety precautions must be followed during its preparation and handling. It is stored and shipped in leak-free steel cylinders in the complete absence of any water (or moisture).

Reactions

Phosgene decomposes on heating at 300°C forming chlorine and carbon monoxide:

$$COCl_2 \rightarrow Cl_2 + CO$$

Phosgene readily reacts with water at ordinary temperatures forming hydrogen chloride and carbon dioxide:

$$COCl_2 + H_2O \rightarrow 2HCl + CO_2$$
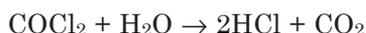
Metal oxides decompose phosgene at elevated temperatures, forming their chlorides and carbon dioxide

$$COCl_2 + CdO \rightarrow CdCl_2 + CO_2$$

$$COCl_2 + Fe_2O_3 \rightarrow 2FeCl_3 + 3CO_2$$
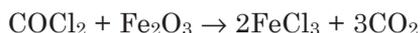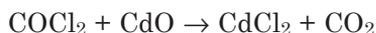
Similar decomposition occurs when phosgene is heated with metal sulfide; the products are usually the metal chloride and carbonyl sulfide:

$$COCl_2 + ZnS \rightarrow ZnCl_2 + COS$$
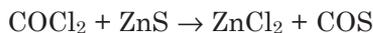
Analysis

The gas is adsorbed over activated charcoal by sampling air. It is then desorbed out from charcoal with hexane or toluene and analyzed by GC-FID or GC/MS. Characteristic masses are 98, 100, 102, 63, 65.

Toxicity

Highly poisonous gas. It manifests delayed effects. Initial symptoms may be mild, but severe congestion of lungs occurs within 6 to 24 hours after exposure. Symptoms are dry burning of the throat, choking, chest pain, vomiting, labored breathing, and cyanosis.

PHOSPHINE

[7803-51-2]
Formula PH_3; MW 34.00; molecular geometry: trigonal pyramidal.
Synonyms: phosphorus trihydride; hydrogen phosphide

Occurrence and Uses

Phosphine is produced naturally in small amounts in marshy lands, especially in damp graveyards, resulting from bacterial decay of animal and vegetable matter containing phosphorus. The atmospheric oxidation of impure phosphine (containing trace amounts of diphosphine, P_2H_4) emits pale flickering lights, the so-called "Will o' the wisps" or "corpse candles" seen on dark nights.

The compound has very little commercial application. It is used to prepare phosphonium salts, which also can be made by other processes.

Physical Propertie

Colorless gas with an odor of decaying fish; flammable; burns with a luminous flame; density 1.492 g/L; liquefies at –87.7°C; solidifies at –133°C; critical temperature 51.35°C; critical pressure 64.55 atm; slightly soluble in water; the solution is weakly basic.

Preparation

Phosphine, unlike ammonia, is not made by direct union of elements. However, phosphine is prepared from other phosphorus compounds by several methods.

Phosphine can be prepared by alkaline hydrolysis of white phosphorus. Thus, a strong aqueous solution of caustic potash when boiled with white phosphorus yields hypophosphite with liberation of phosphine:

$$P_4 + 3KOH + 3H_2O \rightarrow 3KH_2PO_2 + PH_3\uparrow$$
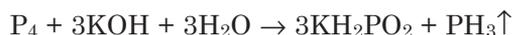
Caustic soda or barium hydroxide can be used instead of caustic potash. The apparatus should be free from air. Either hydrogen or natural gas may be passed through the generator to purge out all residual oxygen out from the flask to prevent any explosion. A small amount of diphosphine, P_2H_4 also is produced in the reaction. The latter inflames spontaneously in air. Diphosphine, which is an unstable liquid at 20°C, may be removed by condensation in a tube immersed in a freezing mixture; or by passing through concentrated hydrochloric acid; or slowly by photochemical decomposition by exposing to light.

Phosphine also is prepared by reduction of a solution of phosphorus trichloride with lithium aluminum hydride in dry ether under warm conditions. The solution of the latter is added from a dropping funnel to phosphorus trichloride solution in dry ether placed in a water bath.

$$4\ PCl_3 + 3LiAlH_4\ \rightarrow\ 3\ LiCl\ \ +\ 3AlCl_3 + 4PH_3\uparrow$$

The flask is connected to a reflux condenser to condense down solvent ether back into the flask. Phosphine is collected over water as a moist gas. Dry phosphine may alternatively be condensed in a U-tube placed in freezing mixture.

Phosphine may be produced by mixing a solution of phosphonium iodide with potassium hydroxide:

$$PH_4I + KOH \rightarrow KI + H_2O + PH_3\uparrow$$

Another preparation method involves treating metallic phosphide with dilute acids:

$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + 2PH_3\uparrow$$
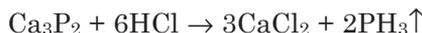
This method was applied earlier to produce floating signal flares at sea. Floating cans of calcium phosphide were punctuated to admit sea water to generate phosphine, which ignited spontaneously to emit flares. The flares could not be extinguished by wind or water.

Reactions

Phosphine is slightly soluble in water forming the phosphonium ion, PH_4^+ in very low yield:

$$PH_3 + H_2O \leftrightarrow PH_4^+ + OH^-$$

Phosphine ignites in air at 150°C. Impure phosphine containing diphosphine ignites at a lower temperature. Phosphoric acid is produced from oxidation of phosphine:

$$PH_3 + 2O_2 \rightarrow H_3PO_4$$

If phosphine is bubbled through water into air, the bubbles ignite at the surface of the water forming beautiful smoke rings.

Phosphine is a strong reducing agent. It inflames in chlorine at ordinary temperatures forming phosphorus trichloride and hydrogen chloride:

$$PH_3 + 3Cl_2 \rightarrow PCl_3 + 3HCl$$
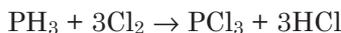
When passed through a solution of gold chloride, phosphine reduces gold chloride, forming colloidal gold of very small particle size:

$$2AuCl_3 + PH_3 \rightarrow Au + PCl_3 + 3HCl$$

It reduces copper, silver and gold salts in solutions, precipitating metal phosphides or the metals themselves:

$$PH_3 + 3CuSO_4 + 3H_2O \rightarrow Cu_3P + H_3PO_3 + 3H_2SO_4$$
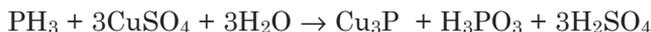
The phosphide produced above can decompose slowly on standing or rapidly on boiling to form the metal.

Phosphine combines with dry hydrogen iodide to yield crystalline phosphonium iodide, PH_4I:

$$PH_3 + HI \rightarrow PH_4I$$

The product cannot be made in aqueous solution as it readily hydrolyzes. The corresponding chloride salt, PH_4Cl, can be prepared from phosphine and anhydrous hydrogen chloride at –40°C or at room temperature under a pressure of 20 atm.

Phosphine forms complexes, such as, *cis*-$Cr(CO)_3(PH_3)_3$ with many transition metals.

Phosphine reacts with formaldehyde in hydrochloric acid solution to form a methanol derivative of phophonium chloride, $[P(CH_2OH)_4{}^+]Cl^-$:

$$PH_3 + 4CH_2O + HCl \rightarrow [P(CH_2OH)^+]Cl^-$$

Analysis

Phosphine can be analyzed by GC using a NPD detector in phosphorus mode or by GC/MS. The mass ion for its identification is 34. It can be identified also from its odor and formation of smoke ring and other chemical reactions (see Reactions).

Hazard

Phosphine is a highly toxic and flammable gas. Acute effects are irritation, tightness of chest, painful breathing, and lung damage. High concentration can be fatal. A fire hazard.

PHOSPHONIUM IODIDE

[12125-09-6]
Formula PH_4I; MW 161.91
Synonym: iodophosphonium

Uses

Phosphonium iodide is used to prepare phosphine

Physical Properties

Colorless tetragonal crystal; deliquesces; density 2.86 g/cm^3; sublimes at ordinary temperatures; vapor pressure 50 torr at 20°C, 760 torr at 61.8°C; melts at 18.5°C under its own vapor pressure; boils at 80°C; decomposes in water; soluble in acids and alkalies with decomposition; decomposes in ethanol.

Thermochemical Properties

ΔH_f°	–16.7 kcal/mol
S°	29.4 cal/deg mol
C_ρ	26.2 cal/deg mol
ΔH_{fus}	12.68 kcal/mol

Preparation

Phosphonium iodide may be prepared by the action of phosphine with dry hydrogen iodide:

$$PH_3 + HI \rightarrow PH_4I$$

Solid phosphonium iodide may be produced in the laboratory by slowly and very cautiously adding water to an intimate mixture of white phosphorus and iodine. Also, this phosphorus-iodine mixture may be obtained by mixing solutions in carbon disulfide and carefully evaporating the solvent in a stream of inert gas:

$$P_4 + I + H_2O \rightarrow PH_4I + H_3PO_4$$

$$2P + I_2 + 4H_2O \rightarrow PH_4I + H_3PO_4 + HI$$
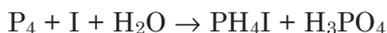
Also, the compound can be prepared by hydrolysis of a mixture of diphosphorus tetraiodide and white phosphorus:

$$P_2I_4 + P + H_2O \rightarrow PH_4I + H_3PO_4$$
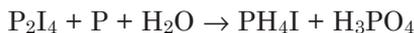
Reactions

Phosphonium iodide dissociates to phosphine and hydrogen iodide when heated at 60°C:

$$PH_4I \rightarrow PH_3 + HI$$

The compound decomposes in water evolving phosphine:

$$PH_4I + H_2O \rightarrow PH_3 + H_3O^+ + I^-$$

Reaction with alkali hydroxide in the cold liberates phosphine:

$$PH_4I + KOH \rightarrow PH_3 + KI + H_2O$$

Analysis

Elemental composition: P 19.13%, I 78.38%, H 2.49%. The compound may be decomposed cautiously in water and the iodide ion measured by ion chromatography or electrode method (see Iodine, Analysis). Liberated phosphine may be diluted with helium and analyzed by GC/MS (see Phosphine, Analysis).

PH_4I alternatively may be dissociated in the dry state by slow and cautious heating, and decomposition products may be analyzed as above.

Hazard

Phosphonium iodide detonates on rapid heating. It dissociates by water, alcohol or heat, evolving toxic phosphine gas.