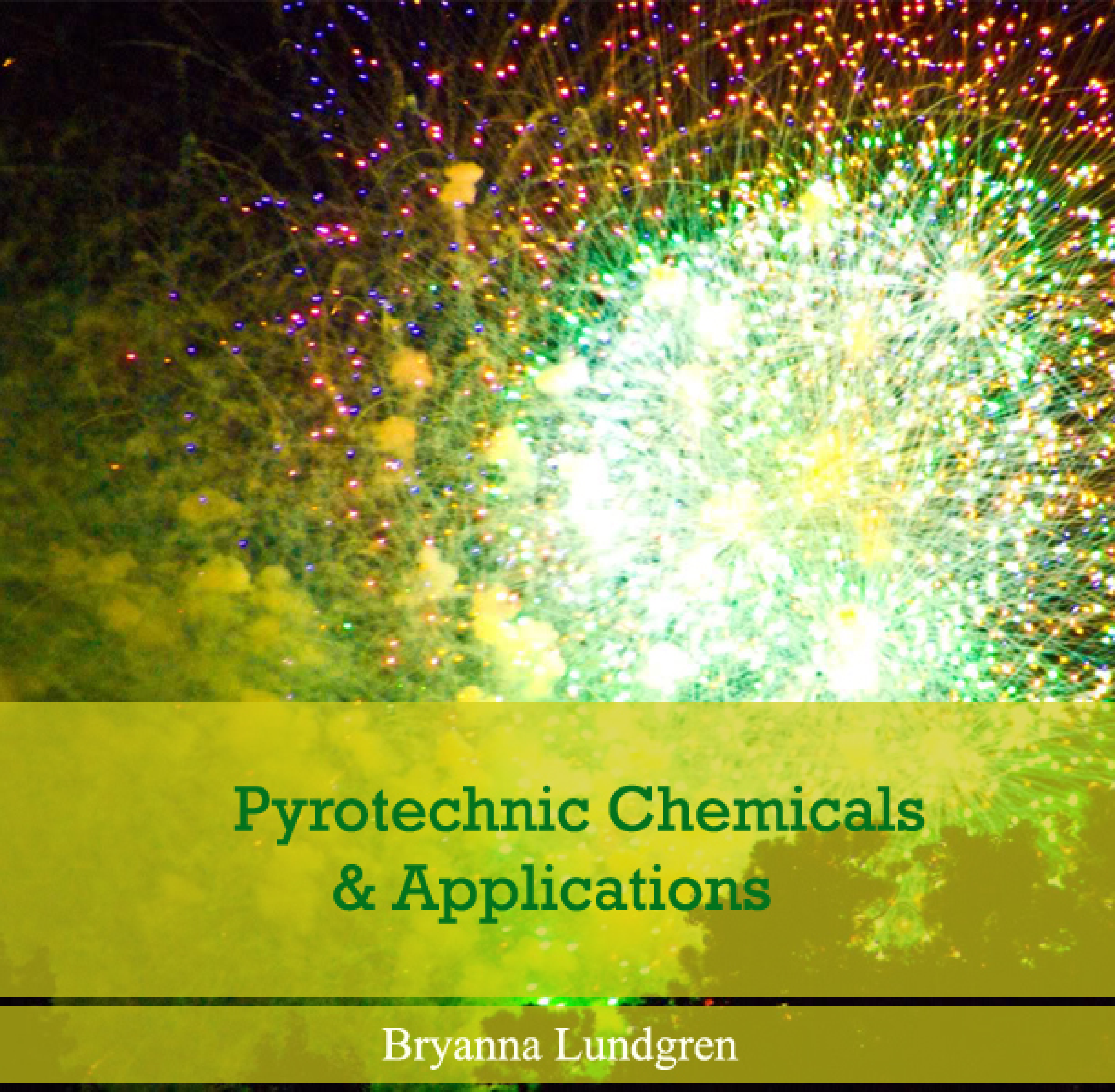

Pyrotechnic Chemicals & Applications

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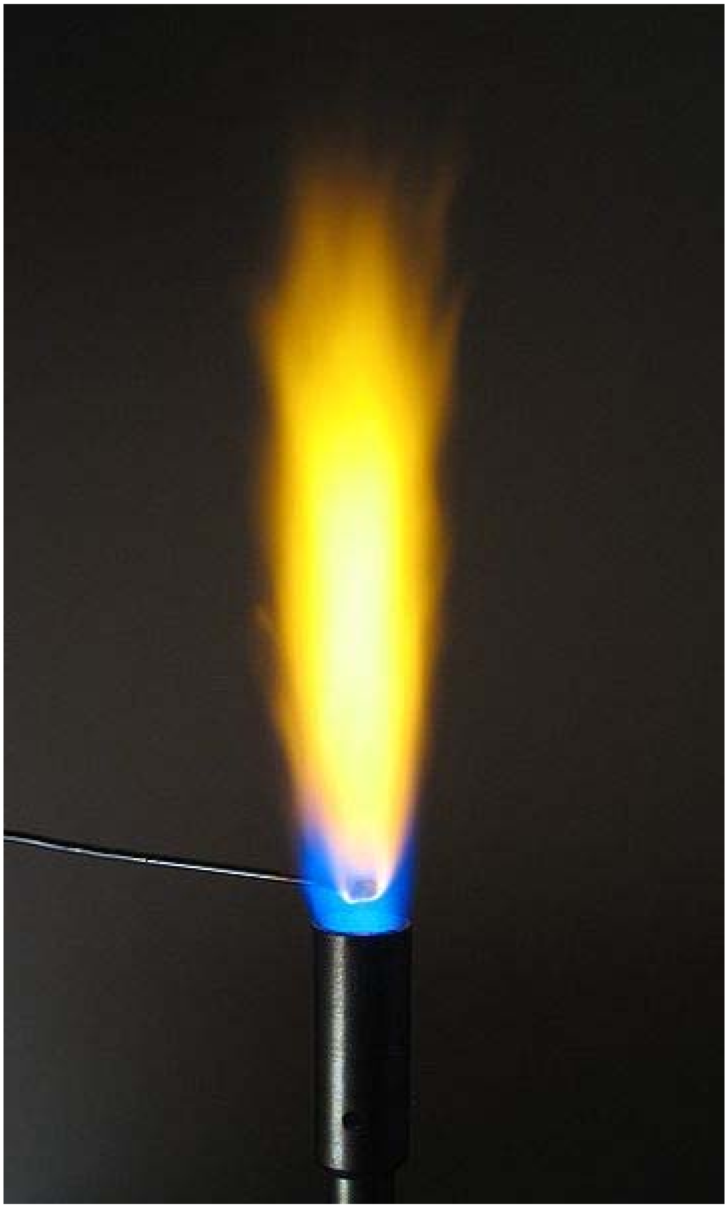
Pyrotechnic Colorant

The red lithium flame leads to lithium's use in flares and pyrotechnics

Copper compounds glow green or blue-green in a flame.

Calcium compounds glow orange in a flame.



Sodium compounds glow yellow in a flame.

A **pyrotechnic colorant** is a chemical compound which causes a flame to burn with a particular color. These are used to create the colors in pyrotechnic compositions like fireworks and colored fires. The color-producing species are usually created from other chemicals during the reaction. Metal salts are commonly used; elemental metals are used rarely (e.g. copper for blue flames).

The color of the flame is dependent on the metal cation; the anion of the salt has very little direct influence. The anions however influence the flame temperature, both by increasing it (e.g. nitrates, chlorates) and decreasing it (e.g. carbonates, oxalates), indirectly influencing the flame brightness and brilliancy. For temperature-decreasing additives, the limit of colorant may be about 10–20 wt.% of the composition.

Some common examples are:

Color	Compound name	Chemical formula	Notes
Red	Strontium nitrate	$Sr(NO_3)_2$	Common. Used with chlorine donors. Excellent red, especially with metal fuels. Used in many compositions including road flares.
Red	Strontium carbonate	$SrCO_3$	Common. Produces good red. Slows burning of compositions, decomposes yielding carbon dioxide. Fire retardant in gunpowders. Inexpensive, non-hygroscopic, neutralizes acids. Superior over strontium oxalate in absence of magnesium.
Red	Strontium oxalate	SrC_2O_4	Decomposes yielding carbon dioxide and carbon monoxide. In presence of magnesium fuel, carbon monoxide reduces particles of magnesium oxide, yielding gaseous magnesium and eliminating the black body radiation of the MgO particles, resulting in clearer color.
Red	Strontium sulfate	$SrSO_4$	High-temperature oxidizer. Used in strobe mixtures and some metal-based red compositions.
Orange	Calcium carbonate	$CaCO_3$	Produces orange flame. Yields carbon dioxide on decomposition. Often used in toy fireworks as a substitute for strontium.
Orange	Calcium chloride	$CaCl_2$	
Orange	Calcium sulfate	$CaSO_4$	High-temperature oxidizer. Excellent orange source in strobe compositions.
Orange	Hydrated calcium sulfate	$CaSO_4(H_2O)_{x^*}$	
Gold/Yellow	Charcoal	C	

	powder		
Gold/Yellow	Iron powder with oxygen based carbon OC12	Fe+C	
Yellow	Sodium bicarbonate	$NaHCO_3$	Compatible with potassium chlorate. Less burning rate decrease than sodium carbonate. Incompatible with magnesium and aluminium, reacts evolving hydrogen gas.
Yellow	Sodium carbonate	Na_2CO_3	Hygroscopic. Significantly decreases burning rate, decomposes evolving carbon dioxide. Strongly alkaline. Very effective colorant, can be used in small amounts. Corrodes magnesium and aluminium, incompatible with them.
Yellow	Sodium chloride	$NaCl$	Loses hygroscopicity on heating. Corrodes metals.
Yellow	Sodium oxalate	$Na_2C_2O_4$	Non-hygroscopic. Slightly reacts with magnesium, no reaction with aluminium.
Yellow	Sodium nitrate	$NaNO_3$	Also acts as oxidizer. Bright flame, used for illumination.
Yellow	Cryolite	Na_3AlF_6	One of the few sodium salts that is nonhygroscopic and insoluble in water.
Green	Barium chloride	$BaCl_2$	
Green	Barium chlorate	$Ba(ClO_3)_2$	Sensitive to shock and friction. Oxidizer.
Green	Barium carbonate	$BaCO_3$	Pretty color when ammonium perchlorate is used as oxidizer.
Green	Barium nitrate	$Ba(NO_3)_2$	Not too strong effect. With chlorine donors yields green color, without chlorine burns white. In green compositions usually used with perchlorates.
Green	Barium oxalate	BaC_2O_4	

Blue	Copper(I) chloride	$CuCl$	Richest blue flame. Almost insoluble in water.
Blue	Copper(I) oxide	Cu_2O	
Blue	Copper(II) oxide	CuO	Used with chlorine donors. Excellent in composite stars.
Blue	Copper carbonate	$CuCO_3$	Best when used with ammonium perchlorate.
Blue	Basic copper carbonate	$CuCO_3 \cdot Cu(OH)_2$, $2\ CuCO_3 \cdot Cu(OH)_2$	Occurs naturally as malachite and azurite. Good with ammonium perchlorate and for high-temperature flames with presence of hydrogen chloride. Not easily airborne, less poisonous than Paris Green.
Blue	Copper oxychloride	$3CuO \cdot CuCl_2$	Used in cheap compositions. Not common anymore due to need for mercury(II) chloride to bring out the color.
Blue	Paris Green	$Cu(CH_3COO)_2.3Cu(AsO_2)_2$	Copper acetoarsenite, Emerald Green. Toxic. With potassium perchlorate produces the best blue colors. Non-hygroscopic. Fine powder readily becomes airborne; toxic inhalation hazard. Used in majority of Japanese blue compositions as it gives very pretty color.
Blue	Copper arsenite	$CuHAsO_3$	Almost non-hygroscopic. Almost as good colorant as copper acetoarsenite. Toxic. Can be used with chlorate oxidizers.
Blue	Copper sulfate	$CuSO_4 \cdot 5\ H_2O$	Can be used with nitrates and perchlorates. Acidic, incompatible with chlorates. With red phosphorus in presence of moisture liberates heat, may spontaneously ignite. Less expensive than copper acetoarsenite. Anhydrous copper sulfate is hygroscopic, can be used as a desiccant. With ammonium perchlorate produces almost as pretty blue

			color as achievable with copper acetoarsenite.
Blue	Copper metal	Cu	Rarely used, other compounds are easier to work with. Yields pretty blue color in ammonium perchlorate based compositions; but reacts with ammonium perchlorate and liberates ammonia in presence of moisture. The composition must be kept dry.
Purple	Combination of red and blue compounds	Sr+Cu	
Purple	Rubidium compounds	Rb	rarely used
Silver/White	Aluminium powder	Al	
Silver/White	Magnesium powder	Mg	
Silver/White	Titanium powder	Ti	
Silver/White	Antimony (III) sulfide	Sb_2S_3	
Infrared	Caesium nitrate	$CsNO_3$	two powerful spectral lines at 852.113 nm and 894.347 nm
Infrared	Rubidium nitrate	$RbNO_3$	

The * indicates that the compound will burn orange where x=0,2,3,5.

Radiating species

Despite the wide numbers of metal ion donors, they serve to form only a few atomic and molecular species that are useful as light emitters.

In many cases, chlorine donors have to be added in order to achieve sufficiently deep colors, as the desired emitting molecules have to be generated.

Some color emitters are of atomic nature (e.g. lithium, sodium). Presence of chlorine, and the reaction to monochlorides, may actually impair their color purity or intensity.

At high temperatures, the atoms will ionize. The emission spectra of ions are different than of neutral atoms; the ions may emit in undesired spectral ranges. E.g. Ba^+ emits in blue wavelengths. Ionization can be suppressed by addition of an easier-to-ionize metal with weak visible emission of its own, e.g. potassium; the potassium atoms then act as electron donors, neutralizing the barium ions.

The color blue is notoriously difficult to produce in fireworks, as the copper compounds need to be heated at a specific temperature for the optimal shade of blue to be produced. Thus, a deep, rich blue is usually viewed as the mark of an experienced fireworks maker.

Care should be taken to avoid formation of solid particles in the flame zone, whether metal oxides or carbon; incandescent solid particles emit black body radiation that causes "washing out" of the colors. Addition of aluminium raises the flame temperature but also leads to formation of solid incandescent particles of aluminium oxide and molten aluminium. Magnesium has less such effect and is therefore more suitable for colored flames; it is more volatile than aluminium and more likely to be present as vapors than as particulates. Formation of solid particles of magnesium oxide can further be inhibited by presence of carbon monoxide, either by negative oxygen balance of the composition in presence of organic fuels, or by addition of the colorant in the form of an oxalate, which decomposes to carbon dioxide and carbon monoxide; the carbon monoxide reacts with the magnesium oxide particles to gaseous magnesium and gaseous carbon dioxide.

Colour	Emitter	Wavelengths	Notes
Yellow	Sodium (D-line)	589 nm	very strong, overpowers other colors, avoid contamination
Orange	CaCl (molecular bands)	most intense: 591–599 nm and 603–608 nm, and others	
Red	SrCl (molecular bands)	a: 617–623 nm b: 627–635 nm c: 640–646 nm	The SrCl species tends to be oxidized to less desirable SrO; strontium-containing compositions are therefore usually formulated to be oxygen-deficient.
Red	SrOH(?) (molecular bands)	600–613 nm	
Red	Li (atomic spectral lines)		
Green	BaCl (molecular bands)	a: 511–515 nm b: 524–528 nm d: 530–533 nm	Lines of BaOH and BaO are also present, emitting in yellow and yellowish-green (487, 512, 740, 828, and 867 nm for BaOH, 549, 564, 604 and 649 for BaO). The BaOH lines are much stronger than the BaO lines. In absence of chlorine, the BaCl lines are not present and only

			the BaOH and BaO lines are visible.
			The BaCl species tends to be oxidized to less desirable BaO; barium-containing compositions are therefore usually formulated to be oxygen-deficient. Presence of Ba^+ is undesired, as it emits in a blue region at 455.4 nm. Potassium may be added to suppress barium ionization, as it ionizes easier and acts as an electron donor for the barium ions.
Blue	CuCl (molecular bands)	several intense bands between 403–456 nm, less intense at 460–530 nm	Low dissociation energy of copper compounds causes presence of free copper atoms in the flame, weakly emitting in green (lines between 325–522 nm). In presence of chlorine, CuCl is formed, emitting strongly in blue. At higher temperatures CuCl dissociates and lines of atomic copper are present in the spectrum; CuO and CuOH are also formed, emitting molecular bands at green-yellow (535–555 nm) for CuOH and at orange-red (580–655 nm) for CuOH. Adequate control of temperature is therefore required for blue-burning compositions.
Infrared	Carbon particles	black body radiation	For good broadband infrared output, compositions producing lots of heat and carbon particles are required. The burning temperature should be lower than of visible-illuminating compounds. The intensity of the emitted radiation depends on the burn rate. Temperature can be increased by addition of magnesium. A magnesium/Teflon/Viton composition is common for missile decoy flares.
Infrared	CO_2 (molecular bands)	mostly 4300 nm	Produced by carbon-containing fuels.
Infrared	Cs (atomic spectral lines)	two powerful spectral lines at 852.113 nm and 894.347 nm	Used in infrared illumination compositions. Metal is avoided in the compositions to prevent formation of bright, visible-radiating particles.
Infrared	Rb (atomic spectral lines)	spectral lines in near-infrared	Used in infrared illumination compositions, less commonly than cesium.

Chapter 2

Rocket Propellant

Rocket propellant is mass that is stored in some form of propellant tank, prior to being used as the propulsive mass that is ejected from a rocket engine in the form of a fluid jet to produce thrust. A fuel propellant is often burned with an oxidizer propellant to produce large volumes of very hot gas. These gases expand and push on a nozzle, which accelerates them until they rush out of the back of the rocket at extremely high speed, making thrust. Sometimes the propellant is not burned, but can be externally heated for more performance. For smaller attitude control thrusters, a compressed gas escapes the spacecraft through a propelling nozzle.

Chemical rocket propellants are most commonly used, which undergo exothermic chemical reactions which produce hot gas which is used by a rocket for propulsive purposes.

In ion propulsion, the propellant is made of electrically charged atoms (ions), which are electromagnetically pushed out of the back of the spacecraft. Magnetically accelerated ion drives are not usually considered to be rockets however, but a similar class of thrusters use electrical heating and magnetic nozzles.

Overview

The Space Shuttle Atlantis during ascent.

Rockets create thrust by expelling mass backwards in a high speed jet. Chemical rockets, create thrust by reacting propellants within a combustion chamber into a very hot gas at high pressure, which is then expanded and accelerated by passage through a nozzle at the rear of the rocket. The amount of the resulting forward force, known as thrust, that is produced is the mass flow rate of the propellants multiplied by their exhaust velocity (relative to the rocket), as specified by Newton's third law of motion. Thrust is therefore the equal and opposite reaction that moves the rocket, and not by interaction of the exhaust stream with air around the rocket. Equivalently, one can think of a rocket being accelerated upwards by the pressure of the combusting gases against the combustion chamber and nozzle. This operational principle stands in contrast to the commonly-held assumption that a rocket "pushes" against the air behind or below it. Rockets in fact perform better in outer space (where there is nothing behind or beneath them to push against), because there is a reduction in air pressure on the outside of the engine, and because it is possible to fit a longer nozzle without suffering from flow separation.

The maximum velocity that a rocket can attain in the absence of any external forces is primarily a function of its mass ratio and its *exhaust velocity*. The relationship is described by the *rocket equation*: $V_f = V_e \ln(M_0 / M_f)$. The mass ratio is just a way to express what proportion of the rocket is propellant (fuel/oxidizer combination) prior to engine ignition. Typically, a single-stage rocket might have a mass fraction of 90% propellant, 10% structure, and hence a mass ratio of 10:1 . The impulse delivered by the motor to the rocket vehicle per weight of fuel consumed is often reported as the rocket propellant's *specific impulse*. A propellant with a higher specific impulse is said to be more efficient because more thrust is produced while consuming a given amount of propellant.

Lower stages will usually use high-density (low volume) propellants because of their lighter tankage to propellant weight ratios and because higher performance propellants require higher expansion ratios for maximum performance than can be attained in atmosphere. Thus, the Apollo-Saturn V first stage used kerosene-liquid oxygen rather than the liquid hydrogen-liquid oxygen used on its upper stages Similarly, the Space Shuttle uses high-thrust, high-density solid rocket boosters for its lift-off with the liquid hydrogen-liquid oxygen SSMEs used partly for lift-off but primarily for orbital insertion.

Chemical propellants

There are three main types of propellants: solid, liquid, and hybrid.

Solid propellants

History

The earliest rockets were created hundreds of years ago by the Chinese, and were used primarily for fireworks displays and as weapons. They were fueled with black powder, a type of gunpowder consisting of a mixture of charcoal, sulfur and potassium nitrate (saltpeter). Rocket propellant technology did not advance until the end of the 19th century, by which time smokeless powder had been developed, originally for use in firearms and artillery pieces. Smokeless powders and related compounds have seen use as double-base propellants.

Description

Solid propellants (and almost all rocket propellants) consist of an oxidizer and a fuel. In the case of gunpowder, the fuel is charcoal, the oxidizer is potassium nitrate, and sulfur serves as a catalyst. (Note: sulfur is not a true catalyst in gunpowder as it is consumed to a great extent into a variety of reaction products such as K_2S. The sulfur acts mainly as a sensitizer lowering threshold of ignition.) During the 1950s and 60s researchers in the United States developed what is now the standard high-energy solid rocket fuel, Ammonium Perchlorate Composite Propellant (APCP). This mixture is primarily ammonium perchlorate powder (an oxidizer), combined with fine aluminium powder (a fuel), held together in a base of PBAN or HTPB (rubber-like fuels). The mixture is formed as a liquid, and then cast into the correct shape and cured into a rubbery solid.

Advantages

Solid-fueled rockets are much easier to store and handle than liquid-fueled rockets, which makes them ideal for military applications. In the 1970s and 1980s the U.S. switched entirely to solid-fueled ICBMs: the LGM-30 Minuteman and LG-118A Peacekeeper (MX). In the 1980s and 1990s, the USSR/Russia also deployed solid-fueled ICBMs (RT-23, RT-2PM, and RT-2UTTH), but retains two liquid-fueled ICBMs (R-36 and UR-100N). All solid-fueled ICBMs on both sides have three initial solid stages and a precision maneuverable liquid-fueled bus used to fine tune the trajectory of the reentry vehicle.

Their simplicity also makes solid rockets a good choice whenever large amounts of thrust are needed and cost is an issue. The Space Shuttle and many other orbital launch vehicles use solid-fueled rockets in their first stages (solid rocket boosters) for this reason.

Disadvantages

Relative to liquid fuel rockets, solid rockets have a number of disadvantages. Solid rockets have a lower specific impulse than liquid-fueled rockets. It is also difficult to build a large mass ratio solid rocket because almost the entire rocket is the combustion chamber, and must be built to withstand the high combustion pressures. If a solid rocket is used to go all the way to orbit, the payload fraction is very small. (For example, the Orbital Sciences Pegasus rocket is an air-launched three-stage solid rocket orbital booster. Launch mass is 23,130 kg, low earth orbit payload is 443 kg, for a payload fraction of 1.9%. Compare to a Delta IV Medium, 249,500 kg, payload 8600 kg, payload fraction 3.4% without air-launch assistance.)

A drawback to solid rockets is that they cannot be throttled in real time, although a predesigned thrust schedule can be created by altering the interior propellant geometry.

Solid rockets can often be shut down before they run out of fuel. Essentially, the rocket is vented or an extinguishant injected so as to terminate the combustion process. In some cases termination destroys the rocket, and then this is typically only done by a Range Safety Officer if the rocket goes awry. The third stages of the Minuteman and MX rockets have precision shutdown ports which, when opened, reduce the chamber pressure so abruptly that the interior flame is blown out. This allows a more precise trajectory which improves targeting accuracy.

Finally, casting very large single-grain rocket motors has proved to be a very tricky business. Defects in the grain can cause explosions during the burn, and these explosions can increase the burning propellant surface enough to cause a runaway pressure increase, until the case fails.

Liquid propellants

History

Though early rocket theorists, such as Konstantin Tsiolkovsky, proposed liquid hydrogen and liquid oxygen as propellants, the first liquid-fueled rocket, launched by Robert Goddard on March 16, 1926, used gasoline and liquid oxygen. Liquid hydrogen was first used by the engines designed by Pratt and Whitney for the Lockheed CL-400 Suntan reconnaissance aircraft in the mid-1950s. In the mid-1960s, the Centaur and Saturn upper stages were both using liquid hydrogen and liquid oxygen.

The highest specific impulse chemistry ever test-fired in a rocket engine was lithium and fluorine, with hydrogen added to improve the exhaust thermodynamics (making this a tripropellant). The combination delivered 542 seconds (5.32 kN·s/kg, 5320 m/s) specific impulse in a vacuum. The impracticality of this chemistry highlights why exotic propellants are not actually used: to make all three components liquids, the hydrogen must be kept below -252 °C (just 21 K) and the lithium must be kept above 180 °C (453 K). Lithium and fluorine are both extremely corrosive, liquid lithium ignites on contact with air, fluorine ignites on contact with most fuels, and hydrogen, while not hypergolic, is an explosive hazard. Fluorine and the hydrogen fluoride (HF) in the exhaust are very toxic, which damages the environment, makes work around the launch pad difficult, and makes getting a launch license that much more difficult. The rocket exhaust is also ionized, which would interfere with radio communication with the rocket.

Current Types

The most common liquid propellants in use today:

- LOX and kerosene (RP-1). Used for the lower stages of most Russian and Chinese boosters, the first stages of the Saturn V and Atlas V, and all stages of the developmental Falcon 1 and Falcon 9. Very similar to Robert Goddard's first rocket. This combination is widely regarded as the most practical for boosters that lift off at ground level and therefore must operate at full atmospheric pressure.
- LOX and liquid hydrogen, used in the Space Shuttle orbiter, the Centaur upper stage of the Atlas V, Saturn V upper stages, the newer Delta IV rocket, the H-IIA rocket, and most stages of the European Ariane rockets.

- Nitrogen tetroxide (N_2O_4) and hydrazine (N_2H_4), MMH, or UDMH. Used in military, orbital and deep space rockets, because both liquids are storable for long periods at reasonable temperatures and pressures. N_2O_4/UDMH is the main fuel for the Proton rocket. This combination is hypergolic, making for attractively simple ignition sequences. The major inconvenience is that these propellants are highly toxic, hence they require careful handling.

- Monopropellants such as hydrogen peroxide, hydrazine and nitrous oxide are primarily used for attitude control and spacecraft station-keeping where their long-term storability, simplicity of use and ability to provide the tiny impulses needed, outweighs their lower specific impulse as compared to bipropellants. Hydrogen peroxide is also used to drive the turbopumps on the first stage of the Soyuz launch vehicle.

Historical propellants

These include propellants such as syntin, which is an expensive high energy hydrocarbon fuel which was used on Soyuz U2 until 1995.

Advantages

Liquid fueled rockets have higher specific impulse than solid rockets and are capable of being throttled, shut down, and restarted. Only the combustion chamber of a liquid fueled rocket needs to withstand combustion pressures and temperatures and they can be regeneratively cooled by the liquid propellant. On vehicles employing turbopumps, the propellant tanks are at very much less pressure than the combustion chamber, and thus can be built far more lightly than a solid propellant rocket case, permitting a higher mass ratio. For these reasons, most orbital launch vehicles use liquid propellants.

The primary performance advantage of liquid propellants is due to the oxidizer. Several practical liquid oxidizers (liquid oxygen, nitrogen tetroxide, and hydrogen peroxide) are available which have much better specific impulse than the ammonium perchlorate used in most solid rockets, when paired with comparable fuels. These facts have led to the use of hybrid propellants: a storable oxidizer used with a solid fuel, which retain most virtues of both liquids (high ISP) and solids (simplicity).

While liquid propellants are cheaper than solid propellants, for orbital launchers, the cost savings do not, and historically have not mattered; the cost of propellant is a very small portion of the overall cost of the rocket.

Disadvantages

The main difficulties with liquid propellants are also with the oxidizers. These are generally at least moderately difficult to store and handle due to their high reactivity with common materials, may have extreme toxicity (nitric acids), moderately cryogenic (liquid oxygen), or both (liquid fluorine, FLOX- a fluorine/LOX mix). Several exotic oxidizers have been proposed: liquid ozone (O_3), ClF_3, and ClF_5, all of which are unstable, energetic, and toxic.

Liquid fueled rockets also require potentially troublesome valves and seals and thermally stressed combustion chambers, which increase the cost of the rocket. Many employ specially designed turbopumps which raise the cost enormously due to difficult fluid flow patterns that exist within the casings.

Gas propellants

A gas propellant usually involves some sort of compressed gas. However, due to the low density and high weight of the pressure vessel, gases see little current use, but are sometimes used for vernier engines, particularly with inert propellants.

GOX was used as one of the propellant for the Buran program for the orbital manoeuvring system.

Hybrid propellants

A hybrid rocket usually has a solid fuel and a liquid or gas oxidizer. The fluid oxidizer can make it possible to throttle and restart the motor just like a liquid fueled rocket. Hybrid rockets are also cleaner than solid rockets because practical high-performance solid-phase oxidizers all contain chlorine, versus the more benign liquid oxygen or nitrous oxide used in hybrids. Because just one propellant is a fluid, hybrids are simpler than liquid rockets.

Hybrid motors suffer two major drawbacks. The first, shared with solid rocket motors, is that the casing around the fuel grain must be built to withstand full combustion pressure and often extreme temperatures as well. However, modern composite structures handle this problem well, and when used with nitrous oxide and a solid rubber propellent (HTPB), relatively small percentage of fuel is needed anyway, so the combustion chamber is not especially large.

The primary remaining difficulty with hybrids is with mixing the propellants during the combustion process. In solid propellants, the oxidizer and fuel are mixed in a factory in carefully controlled conditions. Liquid propellants are generally mixed by the injector at the top of the combustion chamber, which directs many small swift-moving streams of fuel and oxidizer into one another. Liquid fueled rocket injector design has been studied at great length and still resists reliable performance prediction. In a hybrid motor, the mixing happens at the melting or evaporating surface of the fuel. The mixing is not a well-controlled process and generally quite a lot of propellant is left unburned, which limits the efficiency and thus the exhaust velocity of the motor. Additionally, as the burn continues, the hole down the center of the grain (the 'port') widens and the mixture ratio tends to become more oxidiser rich.

There has been much less development of hybrid motors than solid and liquid motors. For military use, ease of handling and maintenance have driven the use of solid rockets. For orbital work, liquid fuels are more efficient than hybrids and most development has concentrated there. There has recently been an increase in hybrid motor development for nonmilitary suborbital work:

- The Reaction Research Society, although known primarily for their work with liquid rocket propulsion, has a long history of research and development with hybrid rocket propulsion.

- Several universities have recently experimented with hybrid rockets. Brigham Young University, the University of Utah and Utah State University launched a student-designed rocket called Unity IV in 1995 which burned the solid fuel hydroxy-terminated polybutadiene (HTPB) with an oxidizer of gaseous oxygen, and in 2003 launched a larger version which burned HTPB with nitrous oxide. Stanford University researches nitrous-oxide/paraffin hybrid motors.

- The Rochester Institute of Technology was building a HTPB hybrid rocket to launch small payloads into space and to several near Earth objects. Its first launch was scheduled for Summer 2007.
- Scaled Composites SpaceShipOne, the first private manned spacecraft, is powered by a hybrid rocket burning HTPB with nitrous oxide. The hybrid rocket engine was manufactured by SpaceDev. SpaceDev partially based its motors on experimental data collected from the testing of AMROC's (American Rocket Company) motors at NASA's Stennis Space Center's E1 test stand. Motors ranging from as small as 1000 lbf (4.4 kN) to as large as 250,000 lbf (1.1 MN) thrust were successfully tested. SpaceDev purchased AMROCs assets after the company was shut down for lack of funding.

Inert propellants

Some rocket designs have their propellants obtain their energy from non chemical or even external sources. For example water rockets use the compressed gas, typically air, to force the water out of the rocket.

Solar thermal rockets and Nuclear thermal rockets typically propose to use liquid hydrogen for an I_{sp} (Specific Impulse) of around 600–900 seconds, or in some cases water that is exhausted as steam for an I_{sp} of about 190 seconds.

Additionally for low performance requirements such as attitude jets, inert gases such as nitrogen have been employed.

Mixture ratio

The theoretical exhaust velocity of a given propellant chemistry is a function of the energy released per unit of propellant mass (specific energy). Unburned fuel or oxidizer drags down the specific energy. However, most rockets run fuel-rich.

The usual explanation for fuel-rich mixtures is that fuel-rich mixtures have lower molecular weight exhaust, which by reducing *M* increases the ratio $\frac{\sqrt{T_c}}{M}$ which is approximately equal to the theoretical exhaust velocity. This explanation, though found in some textbooks, is wrong. Fuel-rich mixtures actually have lower theoretical exhaust velocities, because $\sqrt{T_c}$ decreases as fast or faster than *M*.

The nozzle of the rocket converts the thermal energy of the propellants into directed kinetic energy. This conversion happens in a short time, on the order of one millisecond. During the conversion, energy must transfer very quickly from the rotational and vibrational states of the exhaust molecules into translation. Molecules with fewer atoms (like CO and H_2) store less energy in vibration and rotation than molecules with more atoms (like CO_2 and H_2O). These smaller molecules transfer more of their rotational and vibrational energy to translation energy than larger molecules, and the resulting improvement in nozzle efficiency is large enough that real rocket engines improve their actual exhaust velocity by running rich mixtures with somewhat lower theoretical exhaust velocities.

The effect of exhaust molecular weight on nozzle efficiency is most important for nozzles operating near sea level. High expansion rockets operating in a vacuum see a much smaller effect, and so are run less rich. The Saturn-II stage (a LOX/LH_2 rocket) varied its mixture ratio during flight to optimize performance.

LOX/hydrocarbon rockets are run only somewhat rich (O/F mass ratio of 3 rather than stoichiometric of 3.4 to 4), because the energy release per unit mass drops off quickly as the mixture ratio deviates from stoichiometric. LOX/LH_2 rockets are run very rich (O/F mass ratio of 4 rather than stoichiometric 8) because hydrogen is so light that the energy release per unit mass of propellant drops very slowly with extra hydrogen. In fact, LOX/LH_2 rockets are generally limited in how rich they run by the performance penalty of the mass of the extra hydrogen tankage, rather than the mass of the hydrogen itself.

Another reason for running rich is that off-stoichiometric mixtures burn cooler than stoichiometric mixtures, which makes engine cooling easier. And as most engines are made of metal or carbon, hot oxidizer-rich exhaust is extremely corrosive, where fuel-rich exhaust is less so. American engines have all been fuel-rich. Some Soviet engines have been oxidizer-rich.

Additionally, there is a difference between mixture ratios for optimum I_{sp} and optimum thrust. During launch, shortly after takeoff, high thrust is at a premium. This can be achieved at some temporary reduction of I_{sp} by increasing the oxidiser ratio initially, and then transitioning to more fuel-rich mixtures. Since engine size is typically scaled for takeoff thrust this permits reduction of the weight of rocket engine, pipes and pumps and the extra propellant use can be more than compensated by increases of acceleration towards the end of the burn by having a reduced dry mass.

Propellant density

Although liquid hydrogen gives a high I_{sp}, its low density is a significant disadvantage: hydrogen occupies about 7x more volume per kilogram than dense fuels such as kerosene. This not only penalises the tankage, but also the pipes and fuel pumps leading from the tank, which need to be 7x bigger and heavier. (The oxidiser side of the engine and tankage is of course unaffected.) This makes the vehicle's dry mass much higher, so the use of liquid hydrogen is not such a big win as might be expected. Indeed, some dense hydrocarbon/LOX propellant combinations have higher performance when the dry mass penalties are included.

Due to lower I_{sp}, dense propellant launch vehicles have a higher takeoff mass, but this does not mean a proportionately high cost; on the contrary, the vehicle may well end up cheaper. Liquid hydrogen is quite an expensive fuel to produce and store, and causes many practical difficulties with design and manufacture of the vehicle.

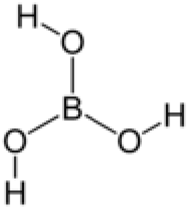
Because of the higher overall weight, a dense-fueled launch vehicle necessarily requires higher takeoff thrust, but it carries this thrust capability all the way to orbit. This, in combination with the better thrust/weight ratios, means that dense-fueled vehicles reach orbit earlier, thereby minimizing losses due to gravity drag. Thus, the effective delta-v requirement for these vehicles are reduced.

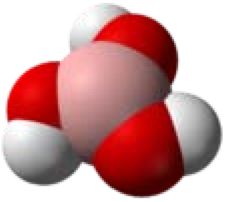
However, liquid hydrogen does give clear advantages when the overall mass needs to be minimised; for example the Saturn V vehicle used it on the upper stages; this reduced weight meant that the dense-fueled first stage could be made significantly smaller, saving quite a lot of money.

Chapter 3

Boric Acid

Boric acid





IUPAC name
Boric acid
Trihydroxidoboron

Other names
Orthoboric acid,
Boracic acid,
Sassolite,
Optibor,
Borofax

Identifiers

CAS number	10043-35-3 ✓
PubChem	7628
ChemSpider	7346 ✓
UNII	R57ZHV85D4 ✓
EC number	233-139-2
KEGG	D01089 ✓

ChEMBL	CHEMBL42403 ✓
Properties	
Molecular formula	H_3BO_3
Molar mass	61.83 g mol^{-1}
Appearance	White crystalline solid
Density	1.435 g/cm^3
Melting point	170.9 °C, 444 K, 340 °F
Boiling point	300 °C, 573 K, 572 °F
Solubility in water	2.52 g/100 mL (0 °C) 4.72 g/100 mL (20 °C) 5.7 g/100 mL (25°C) 19.10 g/100 mL (80 °C) 27.53 g/100 mL (100 °C)
Solubility in other solvents	Soluble in lower alcohols moderately soluble in pyridine very slightly soluble in acetone
Acidity (pK_a)	9.24
Structure	
Molecular shape	Trigonal planar
Dipole moment	Zero
Hazards	
MSDS	External MSDS
EU classification	Harmful (**Xn**) Repr. Cat. 2
R-phrases	R60 R61
S-phrases	S53 S45
Flash point	Non-flammable.
LD_{50}	2660 mg/kg, oral (rat)
Related compounds	
Related compounds	Boron trioxide Borax
Supplementary data page	
Structure and properties	n, ε_r, etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

Boric acid, also called **boracic acid** or **orthoboric acid** or **acidum boricum**, is a weak acid often used as an antiseptic, insecticide, flame retardant, in nuclear power plants to control the fission rate of uranium, and as a precursor of other chemical compounds. It exists in the form of colorless crystals or a white powder and dissolves in water. It has the chemical formula H_3BO_3, sometimes written $B(OH)_3$. When occurring as a mineral, it is called sassolite.

Occurrence

The free acid is found native in certain volcanic districts such as Tuscany, the Lipari Islands and Nevada, issuing mixed with steam from fissures in the ground; it is also found as a constituent of many minerals (borax, boracite, boronatrocaicite and colemanite). The presence of boric acid and its salts has been noted in seawater. It also exists in plants and especially in almost all fruits.

Boric acid was first prepared by Wilhelm Homberg (1652–1715) from borax, by the action of mineral acids, and was given the name *sal sedativum Hombergi* ("sedative salt of Homberg"). However Borates, including boric acid, have been used since the time of the Greeks for cleaning, preserving food, and other activities.

Preparation

Boric acid may be prepared by reacting borax (sodium tetraborate decahydrate) with a mineral acid, such as hydrochloric acid:

$$Na_2B_4O_7{\cdot}10H_2O + 2\ HCl \rightarrow 4\ B(OH)_3\ [\text{or } H_3BO_3] + 2\ NaCl + 5\ H_2O$$

Properties

Boric acid is soluble in boiling water. When heated above 170 °C, it dehydrates, forming *metaboric acid* (HBO_2):

$$H_3BO_3 \rightarrow HBO_2 + H_2O$$

Metaboric acid is a white, cubic crystalline solid and is only slightly soluble in water. Boric acid melts at about 236 °C, and when heated above about 300 °C further dehydrates, forming *tetraboric acid* or *pyroboric acid* ($H_2B_4O_7$):

$$4\ HBO_2 \rightarrow H_2B_4O_7 + H_2O$$

The term *boric acid* may sometimes refer to any of these compounds. Further heating leads to boron trioxide.

$$H_2B_4O_7 \rightarrow 2\ B_2O_3 + H_2O$$

Boric acid does not dissociate in aqueous solution as a Brønsted acid, but is a Lewis acid which interacts with water molecules to form the tetrahydroxyborate ion, as observed by Raman spectroscopy:

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)–4 + H^+\ (K_a = 5.8\text{x}10^{-10}\ \text{mol/l};\ \text{p}K_a = 9.24)$$

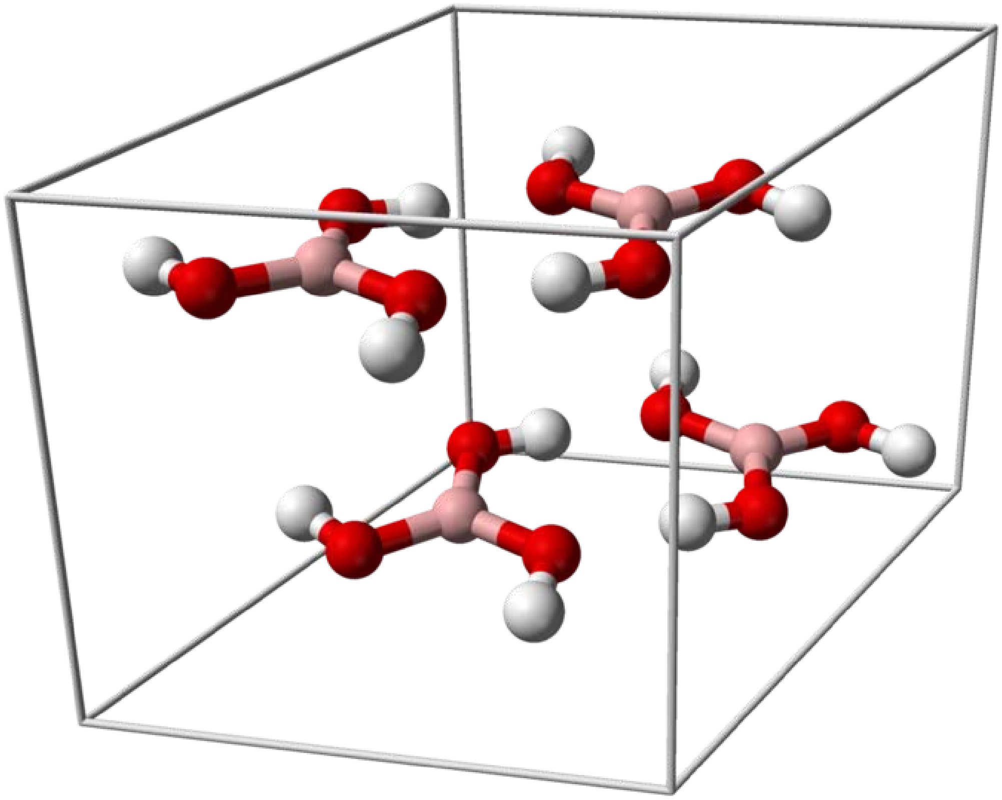
Polyborate anions are formed at pH 7–10 if the boron concentration is higher than about 0.025 mol/L. The best known of these is the *tetraborate* ion, found in the mineral borax:

$$4\ B(OH){-}4 + 2\ H^+ \rightleftharpoons B_4O2{-}7 + 9\ H_2O$$

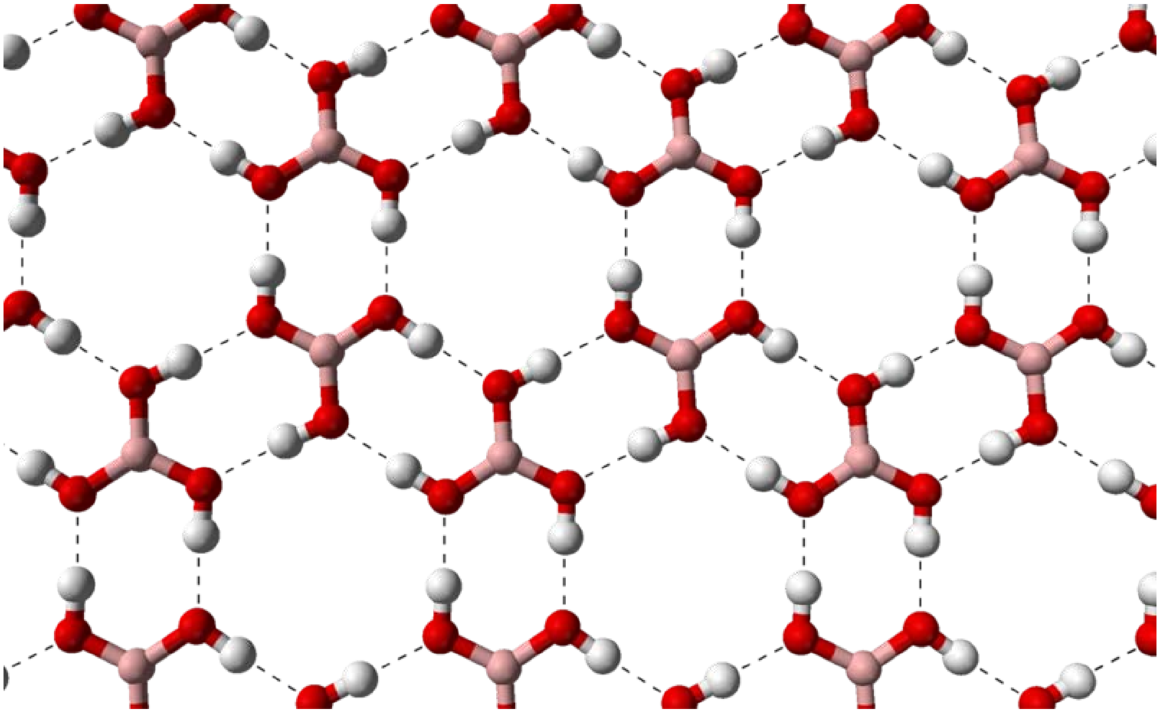
Boric acid makes an important contribution to the absorption of low frequency sound in seawater.

Crystal structure

Crystalline boric acid consists of layers of $B(OH)_3$ molecules held together by hydrogen bonds. The distance between two adjacent layers is 318 pm.



The unit cell of boric acid



Hydrogen bonding (dashed lines)
allows boric acid molecules to form
parallel layers in the solid state

Toxicology

Based on mammalian median lethal dose (LD_{50}) rating of 2,660 mg/kg body mass, boric acid is poisonous if taken internally or inhaled in large quantities. However, it is generally considered to be not much more toxic than table salt. The Thirteenth Edition of the Merck Index indicates that the LD_{50} of boric acid is 5.14 g/kg for oral dosages given to rats, and that 5 to 20 g/kg has produced death in adult humans. The LD_{50} of sodium chloride is reported to be 3.75 g/kg in rats according to the *Merck Index*.

Long term exposure to boric acid may be of more concern, causing kidney damage and eventually kidney failure. Although it does not appear to be carcinogenic, studies in dogs have reported testicular atrophy after exposure to 32 mg/kg bw/day for 90 days. This level is far lower than the LD_{50}.

According to boric acid IUCLID Dataset published by the European Commission, boric acid in high doses shows significant developmental toxicity and teratogenicity in rabbit, rat, and mouse fetuses as well as cardiovascular defects, skeletal variations, mild kidney lesions. As a consequence, in August 2008, in the 30th ATP to EU directive 67/548/EEC, the EC decided to amend its classification as reprotoxic category 2 and to apply the risk phrases R60 (may impair fertility) and R61 (may cause harm to the unborn child).

At a recent European Diagnostics Manufacturing Association (EDMA) Meeting several new additions to the Substance of Very High Concern (SVHC) candidate list in relation to the Registration, Evaluation, Authorisation and restriction of Chemicals Regulations 2007 (REACH) were discussed. The registration and review completed as part of REACH has meant the current classification of Boric Acid CAS 10043-35-3 / 11113-50-1 as of 1 December 2010 will be listed as *H360FD (May damage fertility. May damage the unborn child.)*

Uses

Medicinal

Boric acid solutions used as an eye wash or on abraded skin are known to be especially toxic to infants, especially after repeated use because of its slow elimination rate.

Boric acid can be used as an antiseptic for minor burns or cuts and is sometimes used in dressings or salves or is applied in a very dilute solution as an eye wash in a 1.5% solution (1 tbsp per quart or 15 cm^3 per L) of sterilized water.

As an anti-bacterial compound, boric acid can also be used as an acne treatment. Boric acid can be used to treat yeast and fungal infections such as candidiasis (vaginal yeast infections) by inserting a vaginal suppository containing 600 mg of boric acid daily for 14 days or for yeast infection of the male pubic region (jock-itch or strong genital odor) by applying the powder to the skin all over the pubic region for several days to a week. It is also used as prevention of athlete's foot, by inserting powder in the socks or stockings, and in solution can be used to treat some kinds of otitis externa (ear infection) in both humans and animals. The preservative in urine sample bottles (red cap) in the UK is boric acid.

TBE buffer is widely used for the electrophoresis of nucleic acids and has a higher buffer capacity than a TAE buffer. It can be used for DNA and RNA polyacrylamide and agarose gel electrophoresis.

Insecticidal

Boric acid was first registered in the US as an insecticide in 1948 for control of cockroaches, termites, fire ants, fleas, silverfish, and many other insects. The product is generally considered to be safe to use in household kitchens to control cockroaches and ants. It acts as a stomach poison affecting the insects' metabolism, and the dry powder is abrasive to the insects' exoskeleton.

Boric acid is also made into a paste or gel form as a powerful and effective insecticide much safer to humans than many other insecticides. The paste or gel has attractants in it to attract insects. The boric acid slowly causes dehydration.

Preservation

In combination with its use as an insecticide, boric acid also prevents and destroys existing wet and dry rot in timbers. It can be used in combination with an ethylene glycol carrier to treat external wood against fungal and insect attack. It is possible to buy borate-impregnated rods for insertion into wood via drill holes where dampness and moisture is known to collect and sit. It is available in a gel form and injectable paste form for treating rot affected wood without the need to replace the timber. Concentrates of borate-based treatments can be used to prevent slime, mycelium and algae growth, even in marine environments.

Boric acid is added to salt in the curing of cattle hides, calfskins and sheepskins. This helps to control bacteria development and helps to control insects.

Lubrication

Colloidal suspensions of nano-particles of boric acid dissolved in petroleum or vegetable oil can form a remarkable lubricant on ceramic or metal surfaces with a coefficient of sliding friction that decreases with increasing pressure to a value ranging from 0.10 to 0.02. Self-lubricating H_3BO_3 films result from a spontaneous chemical reaction between water molecules and B_2O_3 coatings in a humid environment. In bulk-scale, an inverse relationship exists between friction coefficient and Hertzian contact pressure induced by applied load.

Boric acid is used to lubricate carrom boards, allowing for faster play.

Industrial

The primary industrial use of boric acid is in the manufacture of monofilament fiberglass usually referred to as textile fiberglass. Textile fiberglass is used to reinforce plastics in applications that range from boats, to industrial piping to computer circuit boards.

Boric acid is used in nuclear power plants as a neutron poison to slow down the rate at which fission is occurring. Fission chain reactions are generally driven by the amount of neutrons present (as products from previous fissions). Natural boron is 20% boron-10 and about 80% boron-11. Boron-10 has a high cross-section for absorption of low energy (thermal) neutrons. By adding more boric acid to the reactor coolant which circulates through the reactor, the probability that a neutron can survive to cause fission is reduced. Therefore, changes in boric acid concentration effectively regulate the rate of fission taking place in the reactor. This method is only used in pressurized water reactors (PWRs). Boron is also dissolved into the spent fuel pools containing used uranium rods. The concentration is high enough to keep neutron multiplication at a minimum.

In the jewelry industry, boric acid is often used in combination with denatured alcohol to reduce surface oxidation and firescale from forming on metals during annealing and soldering operations.

Boric acid is used in the production of the glass in LCD flat panel displays.

In electroplating, boric acid is used as part of some proprietary formulas. One such known formula calls for about a 1 to 10 ratio of H_3BO_3 to $NiSO_4$, a very small portion of sodium lauryl sulfate and a small portion of H_2SO_4.

It is also used in the manufacturing of ramming mass, a fine silica-containing powder used for producing induction furnace linings and ceramics.

Boric Acid is one of the most commonly used substances that can neutralize active hydrofluoric acid (HF). It works by forcing the free F- anions into complex salts. This process removes the virulence of hydrofluoric acid, particularly its ability to attack calcium in human bone (greatly reducing its strength); such an event can occur from just minor skin contact with HF.

Boric acid is added to borax for use as welding flux by blacksmiths and farriers.

Boric acid, in combination with silicone oil, is used to manufacture Silly Putty.

Pyrotechnics

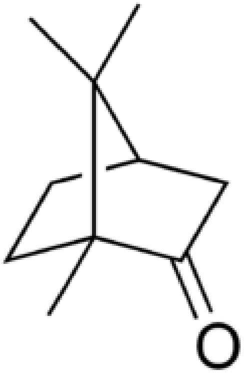
It is used in pyrotechnics to prevent the amide-forming reaction between aluminium and nitrates. A small amount of boric acid is added to the composition to neutralize alkaline amides that can react with the aluminium.

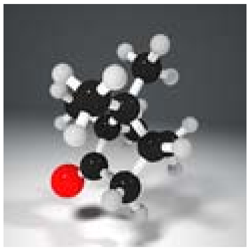
Boric acid can be used as a colorant to make fire green. For example, when dissolved in methanol it is popularly used among fire jugglers and fire spinners to create a deep green flame.

Chapter 4

Camphor

Camphor

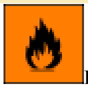
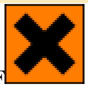




IUPAC name
1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one
Systematic name
1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one
Other names
2-Bornanone

Bornan-2-one
2-Camphanone

Formosa

Identifiers	
CAS number	76-22-2 ✓, 464-49-3 (1*R*)-1-methyl ✓, 464-48-2 (1*S*)-1-methyl ✓
PubChem	2537, 9543187 (1*R*)-1-methyl, 10050 (1*S*)-1-methyl, 6857773 (4*R*)-heptan, 23308299 (4*S*)-heptan
ChemSpider	2441 ✓, 7822160 (1*R*)-1-methyl ✓, 9655 (1*S*)-1-methyl ✓, 5257099 (4*S*)-heptan ✓
UNII	5TJD82A1ET ✓
EC number	200-945-0
UN number	2717
KEGG	D00098 ✓
MeSH	Camphor
ChEBI	CHEBI:36773
ChEMBL	CHEMBL15768 ✓
IUPHAR ligand	2422
RTECS number	EX1225000
Beilstein Reference	1907611
Gmelin Reference	83275
3DMet	B04729
Properties	
Molecular formula	$C_{10}H_{16}O$
Molar mass	152.23 g mol^{-1}
Exact mass	152.120115134 g mol^{-1}
Appearance	White, translucent crystals
Density	0.990 g cm^{-3}
Melting point	175-177 °C, 448-450 K, 347-351 °F
Boiling point	204 °C, 477 K, 399 °F
Solubility in water	1.2 g dm^{-3}
Solubility in acetone	~2500 g dm^{-3}
Solubility in acetic acid	~2000 g dm^{-3}
Solubility in diethyl ether	~2000 g dm^{-3}
Solubility in chloroform	~1000 g dm^{-3}
Solubility in ethanol	~1000 g dm^{-3}
log P	2.089
Vapor pressure	4 mmHg (at 70 °C)
Chiral rotation $[\alpha]_D$	+44.1°
Hazards	
EU classification	 F  Xn

R-phrases	R11, R22, R36/37/38
S-phrases	S16, S26
Flash point	64 °C
Explosive limits	3.5%
Related compounds	
Related Ketones	Fenchone Thujone
Related compounds	Camphene Pinene Borneol Isoborneol Camphorsulfonic acid

Camphor is a waxy, white or transparent solid with a strong, aromatic odor. It is a terpenoid with the chemical formula $C_{10}H_{16}O$. It is found in wood of the **camphor laurel** (*Cinnamomum camphora*), a large evergreen tree found in Asia (particularly in Borneo and Taiwan) and also of *Dryobalanops aromatica*, a giant of the Bornean forests. It also occurs in some other related trees in the laurel family, notably *Ocotea usambarensis*. It can also be synthetically produced from oil of turpentine. It is used for its scent, as an ingredient in cooking (mainly in India), as an embalming fluid, for medicinal purposes, and in religious ceremonies. A major source of camphor in Asia is camphor basil.

Norcamphor is a camphor derivative with the three methyl groups replaced by hydrogen.

History

The word camphor derives from the French word *camphre*, itself from Medieval Latin *camfora*, from Arabic *kafur*, from Sanskrit, *karpoor*. Barus was the port on the western coast of the Indonesian island of Sumatra where foreign traders would call to buy camphor, hence in Malay it became *kapur Barus*. Camphor was known in Arabia in pre-Islamic times, as it is mentioned in the Quran 76:5 as a flavoring for drinks. In the 9th century, the Arab chemist, Al-Kindi (known as *Alkindus* in Europe), provided the earliest recipe for the production of camphor in his *Kitab Kimiya' al-'Itr* (*Book of the Chemistry of Perfume*). By the 13th century, it was used in recipes everywhere in the Muslim world, ranging from main dishes such as tharid, stew, and desserts.

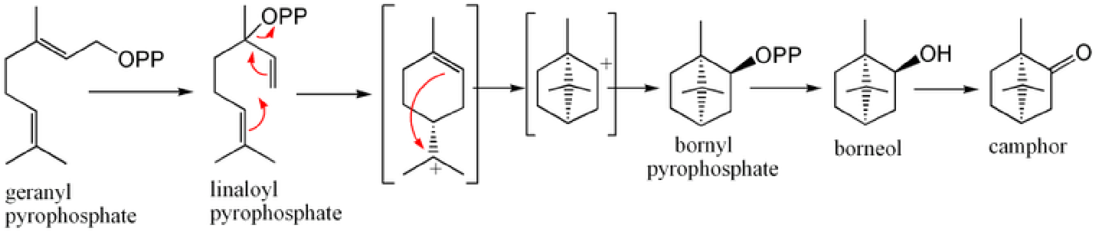
Already in the 19th century, it was known that with nitric acid, camphor could be oxidized into camphoric acid. Haller and Blanc published a semisynthesis of camphor from camphoric acid, which, although demonstrating its structure, would not prove it. The first complete total synthesis for camphoric acid was published by Gustaf Komppa in 1903. Its starting materials were diethyl oxalate and 3,3-dimethylpentanoic acid, which reacted by Claisen condensation to give diketocamphoric acid. Methylation with methyl iodide and a complicated reduction procedure produced camphoric acid. William Perkin published another synthesis a short time later. Previously, some organic compounds (such as urea) had been synthesized in the laboratory as a proof of concept, but camphor was a scarce natural product with a worldwide demand. Komppa realized this and began industrial production of camphor in Tainionkoski, Finland, in 1907.

Production

Camphor can be produced from alpha-pinene, which is abundant in the oils of coniferous trees and can be distilled from turpentine produced as a side product of chemical pulping. With acetic acid as the solvent and with catalysis by a strong acid, alpha-pinene readily rearranges into camphene, which in turn undergoes Wagner-Meerwein rearrangement into the isobornyl cation, which is captured by acetate to give isobornyl acetate. Hydrolysis into isoborneol followed by oxidation gives camphor.

Biosynthesis

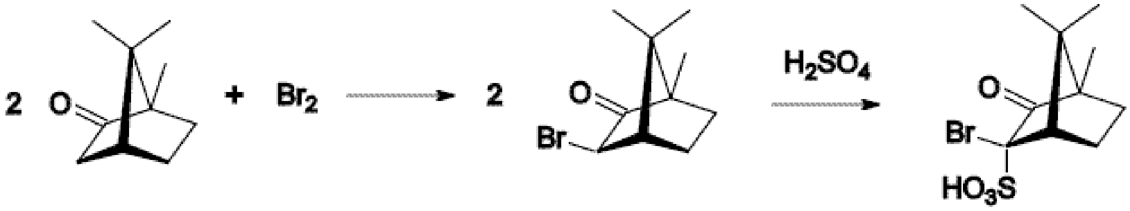
In biosynthesis camphor is produced from geranyl pyrophosphate, via cyclisation of linaloyl pyrophosphate to bornyl pyrophosphate, followed by hydrolysis to borneol and oxidation to camphor.



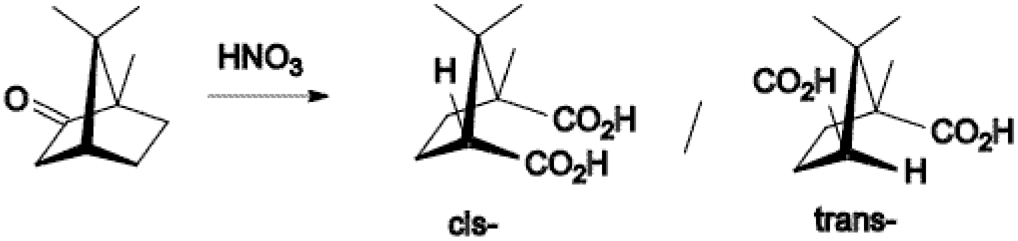
Reactions

Typical camphor reactions are

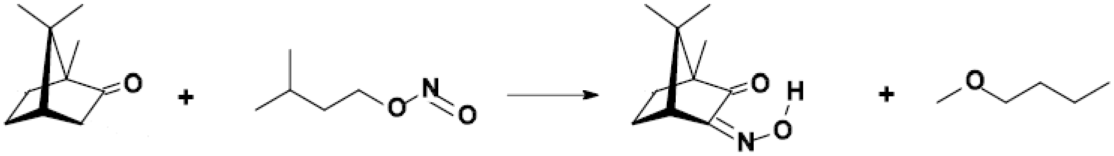
bromination,



oxidation with nitric acid,



conversion to isonitrosocamphor.



Camphor can also be reduced to isoborneol using sodium borohydride.

In 2007, carbon nanotubes were successfully synthesized using camphor in chemical vapor deposition process.

Uses

Modern uses include camphor as a plasticizer for nitrocellulose, as a moth repellent, as an antimicrobial substance, in embalming, and in fireworks. Solid camphor releases fumes that form a rust-preventative coating and is therefore stored in tool chests to protect tools against rust.

Camphor crystals are also used to prevent damage to insect collections by other small insects. Some folk remedies state that camphor will deter snakes and other reptiles due to its strong odor. Similarly, camphor is believed to be toxic to insects and is thus sometimes used as a repellent.

Culinary

In ancient and medieval Europe camphor was used as an ingredient in sweets. It was also used as a flavoring in confections resembling ice cream in China during the Tang dynasty (AD 618–907). It was used in a wide variety of both savory and sweet dishes in medieval Arabic language cookbooks, such as *al–Kitab al–Ṭabikh* compiled by ibn Sayyâr al-Warrâq in the 10th century and An Anonymous Andalusian Cookbook of the 13th Century. And it appears in sweet and savory dishes in a book written in the late 15th century for the sultans of Mandu, the *Ni'matnama*.

Currently, camphor is used as a flavoring, mostly for sweets, in Asia. It is widely used in cooking, mainly for dessert dishes, in India where it is known as *Kachha(raw/crude)*

Karpooram, and is available in Indian grocery stores where it is labeled as "Edible Camphor".

Medicinal

Camphor is readily absorbed through the skin and produces a feeling of cooling similar to that of menthol and acts as slight local anesthetic and antimicrobial substance. There are anti-itch gels and cooling gels with camphor as the active ingredient. Camphor is an active ingredient (along with menthol) in vapor-steam products, such as Vicks VapoRub. Although touted as a cough suppressant, it has no effects on respiratory tract function. A recent publication in Pediatrics suggests that topical application of VapoRub (which contains camphor) may improve symptoms of colds and sleep quality when compared to a control. As a toxic chemical, it should not be orally ingested.

In the 18th century, it was used by Auenbrugger in the treatment of mania.

Hindu religious ceremonies

Camphor is widely used in Hindu religious ceremonies. Hindus worship a holy flame by burning camphor, which forms an important part of many religious ceremonies. Camphor is used in the Mahashivratri celebrations of Shiva, the Hindu god of destruction and (re)creation. As a natural pitch substance, it burns cool without leaving an ash residue, which symbolizes consciousness. Of late, most temples in southern India have stopped lighting camphor in the main Sanctum Sanctorium because of the heavy carbon deposits it produces; however, open areas still burn it.

In Hindu pujas and ceremonies, camphor is burned in a ceremonial spoon for performing aarti. This type of camphor, the processed white crystalline kind, is also sold at Indian grocery stores. However it is not suitable for cooking and is hazardous to health if eaten.

Toxicology

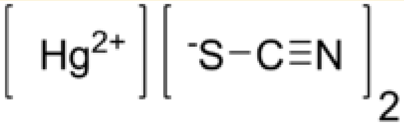
In larger quantities, it is poisonous when ingested and can cause seizures, confusion, irritability, and neuromuscular hyperactivity. In extreme cases, even topical application of camphor may lead to hepatotoxicity. Lethal doses in adults are in the range 50–500 mg/kg (orally). Generally, 2 g causes serious toxicity and 4 g is potentially lethal.

In 1980, the United States Food and Drug Administration set a limit of 11% allowable camphor in consumer products and totally banned products labeled as camphorated oil, camphor oil, camphor liniment, and camphorated liniment (except "white camphor essential oil", which contains no significant amount of camphor). Since alternative treatments exist, medicinal use of camphor is discouraged by the FDA, except for skin-related uses, such as medicated powders, which contain only small amounts of camphor.

Chapter 5

Mercury (II) Thiocyanate

Mercury(II) thiocyanate



Other names
Mercuric thiocyanate
Mercuric sulfocyanate

Identifiers	
CAS number	592-85-8
Properties	
Molecular formula	$Hg(SCN)_2$
Molar mass	316.79 g/mol
Appearance	White monoclinic crystals
Density	3.71 g/cm^3, solid
Melting point	Decomposes at 165 °C
Solubility in water	0.070 g/100 mL
Solubility in other solvents	Soluble in dilute hydrochloric acid

Mercury(II) thiocyanate ($Hg(SCN)_2$) is an inorganic chemical compound, the salt of Hg^{2+} and the thiocyanate anion. It is a stable solid at room temperature that has the appearance of white powder with chunks; it can also be grey in color, depending on purity. Mercury compounds are extremely toxic and protective equipment should be used whenever working with mercury thiocyanate. However, it is commercially available, though expensive. mercury thiocyanate is best known for its former use in pyrotechnics, as it will produce a large, winding “snake” when set on fire. This is known as the Pharaoh’s Serpent. Though some people still use it for this purpose, it is generally avoided because of the production of toxic gases when this reaction occurs.

Synthesis

The first synthesis of mercury thiocyanate was probably completed in 1821 by the chemist Jons Jacob Berzelius with evidence for the first pure sample occurring in 1866 prepared by a chemist named Hermes. Because of its ionic nature, there are several ways to synthesize the compound. Mercury(II) thiocyanate is made by reacting solutions containing mercury(II) and thiocyanate ions. The low solubility product of mercury thiocyanate causes it to precipitate. It is also soluble in several solvents including benzene, hexanes, and methyl isobutyl ketone. Most syntheses are achieved by precipitation. The two early syntheses achieved separately by Berzelius and Friedrich Wohler were completed using the following reactions:

$2\ HSCN + HgO \rightarrow Hg(SCN)_2 + H_2O$ (Berzelius)
$Hg(NO_3)_{2\ (aq)} + 2\ KSCN_{\ (aq)} \rightarrow Hg(SCN)_{2\ (s)} + 2KNO_{3\ (aq)}$ (Wohler)

Pharaoh's Serpent

Mercury thiocyanate was formerly used in pyrotechnics causing an effect known as the Pharaoh's serpent or Pharaoh's snake. When the compound is in the presence of a strong enough heat source, a rapid exothermic reaction is started which produces a large mass of coiling serpent-like solid. An inconspicuous flame which is often blue but can also occur in yellow/orange accompanies the combustion. The resulting solid can range from dark graphite grey to light tan in color with the inside generally much darker than the outside.

This property was discovered soon after the first synthesis of mercury thiocyanate by Wohler in 1821: "winding out from itself at the same time worm-like processes, to many times its former bulk, a very light material the color of graphite…". For some time, a firework product called "Pharaoschlangen" was available to the public in Germany, but was eventually banned when the toxic properties of the product were tragically discovered through the death of several children mistakenly eating the resulting solid.

A similar, though less extreme, effect to the Pharaoh's Serpent can be achieved using a firework known as a black snake. These are generally benign products consisting usually of sodium bicarbonate or a mixture of linseed oil and napthalenes.

Uses and Chemical Properties

Mercury thiocyanate has a few uses in chemical synthesis. It is often involved in the synthesis of related compounds that contain mercury (II) and/or thiocyanates. These compounds include, but are not limited to, potassium tris(thiocyanato)mercurate(II) ($K[Hg(SCN)_3]$) and caesium tris(thiocyanato)mercurate(II) ($Cs[Hg(SCN)_3]$). The $Hg(SCN)_3^-$ ion can also exist independently and is easily reacted to form the compounds above amongst others. These compounds can be examined analytically using infrared spectroscopy, Raman spectroscopy and solid state NMR.

It can also be used in organic synthesis, to replace a halide on an organic compound with a thiocyanate group through a Sn2 mechanism. However, this reaction does not create one pure product as the SCN^- can react on either end with the organohalide. This means that such a reaction would yield two distinct products, one with the sulfur bound to the organic compound and one with the nitrogen bound to the organic compound.

It was discovered that mercury thiocyanate can improve detection limits in the determination of chloride ions in water by UV-visible spectroscopy. This technique was first suggested in 1952 and has been a common method for determination of chloride ions in laboratories worldwide ever since. An automated system was invented in 1964 and then a commercial chloroanalyzer was made available in 1974 by Technicon (Tarrytown, NY, USA). The basic mechanism involves the addition of mercury thiocyanate to a solution with unknown concentration of chloride ions and iron as a reagent. The chloride irons cause the mercury thiocyanate salt to dissociate and the thiocyanate ion to complex with Fe(III), producing $Fe(SCN)^{2+}$, which absorbs visible light at 450 nm. This absorption allows for the measurement of concentration of $Fe(SCN)^{2+}$, produced as a result of the reaction between chloride ion and mercury thiocyanate. From this value the concentration of chloride can then be calculated.

In 1995, a new method for determining the concentration of chloride ions in aqueous solution using mercury thiocyanate was discovered. Mercury thiocyanate without iron (III) is added to a solution with an unknown concentration of chloride ions, forming a complex of the mercury thiocyanate and chloride ion that absorbs light at a wavelength of 254 nm, allowing more accurate measurements of concentration than the aforementioned technique using iron.

Chapter 6

Guar Gum

Guar gum	
	
Identifiers	
CAS number	9000-30-0 ✓
Properties	
Acidity (pK_a)	5-7
Hazards	
MSDS	MSDS

Guar gum, also called **guaran**, is a galactomannan. It is primarily the ground endosperm of guar beans. The guar seeds are dehusked, milled and screened to obtain the guar gum. It is typically produced as a free-flowing, pale, off-white colored, coarse to fine ground powder.

Production

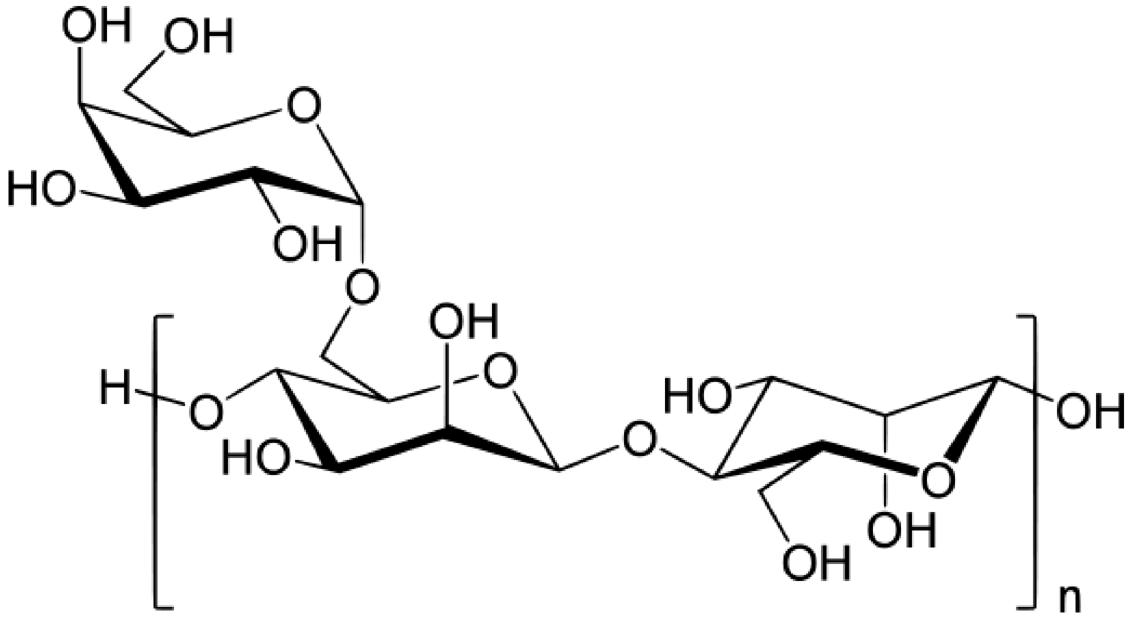
Guar gum is an extract of the guar bean, where it acts as a food and water store. The guar bean is principally grown in India and Pakistan, with smaller crops grown in the U.S., Australia, China, and Africa. The drought-resistant guar bean can be eaten as a green bean, fed to cattle, or used in green manure.

Trade

According to a Reuters report, India accounts for about 80 percent of the global trade in guar products. India exported 11 billion rupees worth of guar products in 2007/08 financial year ending March 2008. Pakistan trails India in the global trade. Industrial guar gum is the most sought after guar product, and accounts for about 45 percent of the total demand. Industrial gum is used as a controlling agent in oil wells to facilitate easy drilling and prevent fluid loss.

In 2007, the Indian industry was hit by a contamination crisis when the European Union suspended imports of Indian guar gum after excessive levels of dioxins were found in one shipment.

Chemical composition



Chemically, guar gum is a polysaccharide composed of the sugars galactose and mannose. The backbone is a linear chain of β 1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose, forming short side-branches.

Solubility and viscosity

Guar gum is more soluble than locust bean gum and is a better emulsifier as it has more galactose branch points. Unlike locust bean gum, it is not self-gelling. However, either borax or calcium can cross-link guar gum, causing it to gel. In water it is nonionic and hydrocolloidal. It is not affected by ionic strength or pH, but will degrade at pH extremes at temperature (e.g. pH 3 at 50°C). It remains stable in solution over pH range 5-7. Strong acids cause hydrolysis and loss of viscosity, and alkalies in strong concentration also tend to reduce viscosity. It is insoluble in most hydrocarbon solvents.

Guar gum shows high low-shear viscosity but is strongly shear-thinning. It is very thixotropic above concentration 1%, but below 0.3% the thixotropy is slight. It has much greater low-shear viscosity than that of locust bean gum, and also generally greater than that of other hydrocolloids. Guar gum shows viscosity synergy with xanthan gum. Guar gum and micellar casein mixtures can be slightly thixotropic if a biphase system forms.

Thickening

Guar gum is economical because it has almost 8 times the water-thickening potency of cornstarch - only a very small quantity is needed for producing sufficient viscosity. Thus it can be used in various multi-phase formulations: as an emulsifier because it helps to prevent oil droplets from coalescing, and/or as a stabilizer because it helps to prevent solid particles from settling.

Ice-crystal growth

Guar gum retards ice crystal growth non-specifically by slowing mass transfer across the solid/liquid interface. It shows good stability during freeze-thaw cycles.

Grading

Manufacturers define different grades and qualities of guar gum by the particle size, the viscosity that is generated with a given concentration, and the rate at which that viscosity develops. Coarse-mesh guar gums, will typically — but not always — develop viscosity more slowly. They may achieve a reasonably high viscosity, but will take longer to achieve. On the other hand, they will disperse better than fine-mesh, all conditions being equal. A finer mesh, like a 200 mesh, requires more effort to dissolve.

Industrial applications

- Textile industry – sizing, finishing and printing
- Paper industry – improved sheet formation, folding and denser surface for printing
- Explosives industry – as waterproofing agent mixed with ammonium nitrate, nitroglycerin etc.

- Pharmaceutical industry – as binder or as disintegrator in tablets; main ingredient in some bulk-forming laxatives
- Cosmetics and toiletries industries – thickener in toothpastes, conditioner in shampoos (usually in a chemically modified version)
- Oil and gas drilling, hydraulic fracturing
- Mining
- Hydroseeding – formation of seed bearing "guar tack"
- Medical institutions, especially nursing homes; used to thicken liquids and foods for patients with dysphagia

Food applications

The largest market for guar gum is in the food industry. In the U.S., differing percentages are set for its allowable concentration in various food applications. In Europe, guar gum has EU food additive code E412.

Applications include:

- Baked goods - increases dough yield, gives greater resiliency, and improves texture and shelf life; in pastry fillings, it prevents "weeping" (syneresis) of the water in the filling, keeping the pastry crust crisp.
- Dairy - thickens milk, yogurt, kefir, and liquid cheese products; helps maintain homogeneity and texture of ice creams and sherbets
- Meat - functions as lubricant and binder.
- improves the stability and appearance of salad dressings, barbecue sauces, relishes, ketchups and others
- Misc. - Dry soups, instant oatmeal, sweet desserts, canned fish in sauce, frozen food items and animal feed.

Nutritional and medicinal effects

Guar gum is a water-soluble fiber that acts as a bulk forming laxative, and as such, it is claimed to be effective in promoting regular bowel movements and relieve constipation and chronic related functional bowel ailments, such as diverticulosis, Crohn's disease, colitis and irritable bowel syndrome, among others. The increased mass in the intestines stimulates the movement of waste and toxins from the system, which is particularly helpful for good colon health, because it speeds the removal of waste and bacteria from the bowel and colon.

Several studies have found significant decreases in human serum cholesterol levels following guar gum ingestion. These decreases are thought to be a function of its high soluble fiber content.

Guar gum has been considered of interest with regards to both weight loss and diabetic diets. It is a thermogenic substance. Moreover, its low digestibility lends its use in recipes as a filler, which can help to provide satiety, or slow the digestion of a meal, thus lowering the glycemic index of that meal. In the late 1980s, guar gum was used and heavily promoted in several weight loss products. The U.S. Food and Drug Administration eventually recalled these due to reports of esophageal blockage from insufficient fluid intake, after one brand alone caused at least 10 users to be hospitalized, and a death. For this reason, guar gum is no longer approved for use in over-the-counter weight loss aids in the United States. Moreover, a meta-analysis that combined the results of 11 randomized controlled trials found guar gum supplements were not effective in reducing body weight.

Two Japanese studies using rats showed guar gum supports increased absorption of calcium occurring in the colon instead of in the small intestine. This means lesser amounts of calcium may be consumed to obtain its recommended minimum daily intake (RDI). This has obvious implications for reduced calorie diets, since calcium-rich dairy products tend to be high in calories.

However, guar gum is also capable of reducing the absorbability of dietary minerals (other than calcium), when foods and/or nutritional supplements containing them are consumed concomitantly with it. However, this is less of a concern with guar gum than with various insoluble dietary fibers.

Some studies have found guar gum to improve dietary glucose tolerance. Research has revealed the water soluble fiber in it may help people with diabetes by slowing the absorption of sugars by the small intestine. Although the rate of absorption is reduced, the amount of sugar absorbed is the same overall. This helps diabetic patients by lowering the amount of insulin needed to keep the blood glucose at a normal level.

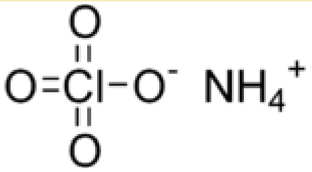
It also functions as an adjuvant for diabetic drugs that are sometimes employed for the treatment of noninsulin dependent diabetes. The effect is to help lower blood glucose levels. Thus, diabetic patients who are taking drugs should consult their doctors before supplementing with guar gum.

Chapter 7

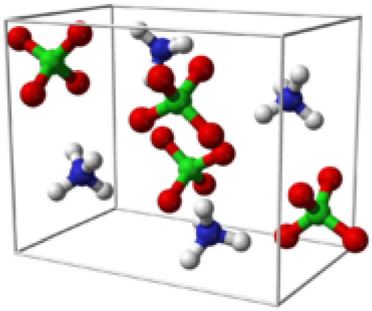
Pyrotechnic Oxidizers

Ammonium Perchlorate

Ammonium perchlorate



$$O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Cl}}{-}O^{-} \quad NH_4^{+}$$



IUPAC name
Ammonium perchlorate

Other names
AP

Identifiers	
CAS number	7790-98-9 ✓
ChemSpider	23041 ✓
EC number	232-235-1
UN number	1442
RTECS number	SC7520000
Properties	
Molecular formula	NH_4ClO_4

Molar mass	117.49 g/mol
Appearance	white granular
Density	1.95 g/cm^3
Melting point	Exothermic decomposition before melting at >200 °C
Solubility in water	11.56 g/100 mL (0 °C) 20.85 g/100 mL (20 °C) 57.01 g/100 mL (100 °C)
Solubility	soluble in methanol partially soluble in acetone insoluble in ether
Structure	
Crystal structure	Orthorhombic (< 513 K) Cubic (> 513 K)
Hazards	
MSDS	External MSDS
EU Index	017-009-00-0
EU classification	Oxidant (**O**)
R-phrases	R9, R44
S-phrases	(S2), S14, S16, S27, S36/37
Related compounds	
Other anions	Ammonium chlorate Ammonium chloride
Other cations	Potassium perchlorate Sodium perchlorate Lithium perchlorate
Related compounds	Perchloric acid

Ammonium perchlorate is an inorganic compound with the formula NH_4ClO_4. It is the salt of perchloric acid and ammonium hydroxide. All perchlorates are potentially powerful oxidizers, but ammonium perchlorate is especially labile.

Production

It is produced by reaction between ammonia and perchloric acid, and is the driver behind the industrial production of perchloric acid. It also can be prepared by treatment of ammonium salts with sodium perchlorate. This process exploits the fact that the solubility of NH_4ClO_4 is about 10% of that for sodium perchlorate.

It crystallises in colorless rhombohedra.

Decomposition

Like most ammonium salts, AP decomposes before melting. Mild heating results in chlorine, nitrogen, oxygen, and water.

$$2\ NH_4ClO_4 \rightarrow Cl_2 + N_2 + 2\ O_2 + 4\ H_2O$$

The combustion of AP is quite complex and is widely studied. Ammonium perchlorate crystals decompose before melting, even though a thin liquid layer has been observed on crystal surfaces during high pressure combustion processes. Strong heating may lead to explosions. Complete reactions leave no residue. Pure crystals cannot sustain a flame below the pressure of 20 bar (2 MPa).

AP is a Class 4 oxidizer (can undergo an explosive reaction) for particle sizes over 15 micrometres and is classified as an explosive for particle sizes less than 15 micrometres.

Other applications

When AP is mixed with a fuel (like a powdered aluminum and/or with an elastomeric binder) it can generate self-sustained combustion at far under atmospheric pressure. It is an important oxidizer with a decades-long history of use in solid rocket propellants--space launch, military, amateur, and hobby high powered rockets--as well as in some fireworks.

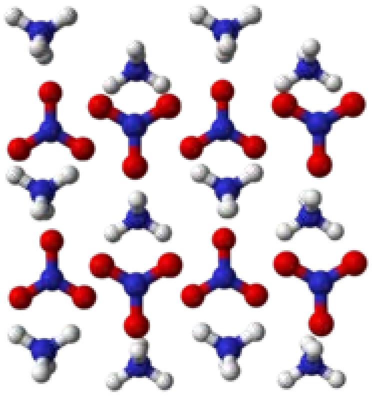
Some "breakable" epoxy adhesives contain suspensions of AP. Upon heating to 300 °C, the AP degrades the organic adhesive, breaking the cemented joint.

Toxicity

Perchlorate itself confers little acute toxicity. For example, sodium perchlorate has an LD_{50} of 2-4 g/kg and is eliminated rapidly after ingestion. However, chronic exposure to perchlorates, even in low concentrations has been shown to cause various thyroid problems, as it is taken up by the thyroid in place of iodine.

Ammonium Nitrate

Ammonium nitrate



IUPAC name
Ammonium nitrate

Identifiers	
CAS number	6484-52-2 ✓
ChemSpider	21511 ✓
UNII	T8YA51M7Y6 ✓
UN number	0222 – *with > 0.2% combustible substances* 1942 – *with <= 0.2% combustible substances* 2067 – *fertilizers* 2426 – *liquid*
RTECS number	BR9050000
Properties	
Molecular formula	$(NH_4)(NO_3)$
Molar mass	80.052 g/mol
Appearance	white solid
Density	1.725 g/cm^3 (20 °C)
Melting point	169.6 °C
Boiling point	*approx.* 210 °C decomp.
Solubility in water	118 g/100 ml (0 °C) 150 g/100 ml (20 °C) 297 g/100 ml (40 °C) 410 g/100 ml (60 °C) 576 g/100 ml (80 °C) 1024 g/100 ml (100 °C)
Structure	
Crystal structure	trigonal

Explosive data	
Shock sensitivity	very low
Friction sensitivity	very low
Explosive velocity	5270 m/s
Hazards	
MSDS	ICSC 0216
EU Index	not listed
Main hazards	Explosive
LD_{50}	2085–5300 mg/kg (oral in rats, mice)
Related compounds	
Other anions	Ammonium nitrite
Other cations	Sodium nitrate Potassium nitrate Hydroxylammonium nitrate
Related compounds	Ammonium perchlorate

The chemical compound **ammonium nitrate**, the nitrate of ammonia with the chemical formula NH_4NO_3, is a white crystalline solid at room temperature and standard pressure. It is commonly used in agriculture as a high-nitrogen fertilizer, and it has also been used as an oxidizing agent in explosives, including improvised explosive devices. It is the main component of ANFO, a very popular explosive.

Ammonium nitrate is used in instant cold packs, as hydrating the salt is an endothermic process.

Production

The processes involved in the production of ammonium nitrate in industry, although chemically simple, are technologically challenging. The acid-base reaction of ammonia with nitric acid gives a solution of ammonium nitrate:

$$HNO_3(aq) + NH_3(g) \rightarrow NH_4NO_3(aq)$$

For industrial production, this is done using anhydrous ammonia gas and concentrated nitric acid. This reaction is violent and very exothermic. After the solution is formed, typically at about 83% concentration, the excess water is evaporated to an ammonium nitrate (AN) content of 95% to 99.9% concentration (AN melt), depending on grade. The AN melt is then made into "prills" or small beads in a spray tower, or into granules by spraying and tumbling in a rotating drum. The prills or granules may be further dried, cooled, and then coated to prevent caking. These prills or granules are the typical AN products in commerce.

The Haber process combines nitrogen and hydrogen to produce ammonia, part of which can be oxidized to nitric acid and combined with the remaining ammonia to produce the nitrate. Another production method is used in the so-called Odda process.

Ammonium nitrate is also manufactured by amateur explosive enthusiasts by metathesis reactions:

$(NH_4)_2SO_4 + 2\ NaNO_3 \rightarrow Na_2SO_4 + 2\ NH_4NO_3$
$Ca(NO_3)_2 + (NH_4)_2SO_4 \rightarrow 2\ NH_4NO_3 + CaSO_4$

Sodium sulfate is removed by lowering the temperature of the mixture. Since sodium sulfate is much less water-soluble than ammonium nitrate, it precipitates, and may be filtered off. For the reaction with calcium nitrate, the calcium sulfate generated is quite insoluble, even at room temperature.

Reactions

Ammonium nitrate reacts with alkali metal hydroxides, releasing ammonia and forming alkali metal nitrate:

$NH_4NO_3 + NaOH \rightarrow NH_3 + H_2O + NaNO_3$

Ammonium nitrate gives ammonium chloride and nitric acid upon reaction with hydrochloric acid:

$NH_4NO_3 + HCl \rightarrow NH_4Cl + HNO_3$

Ammonium nitrate is also formed in the atmosphere from emissions of NO, SO_2 and NH_3 and is a secondary component of PM10.

Crystalline phases

Transformations of the crystal states due to changing conditions (temperature, pressure) affect the physical properties of ammonium nitrate. The following crystalline states have been identified:

System	Temperature (°C)	State	Volume Change (%)
-	>169.6	liquid	-
I	169.6 to 125.2	cubic	+2.1
II	125.2 to 84.2	tetragonal	-1.3
III	84.2 to 32.3	α-rhombic	+3.6
IV	32.3 to −16.8	β-rhombic	−2.9
V	−16.8	tetragonal	-

The type V crystal is a quasi-cubic form which is related to caesium chloride, the nitrogens of the nitrates and the ammoniums are at the sites in a cubic array where Cs and Cl would be in the CsCl lattice.

Disasters

Ammonium nitrate decomposes into gases including oxygen when heated (non-explosive reaction); however, ammonium nitrate can be induced to decompose explosively by detonation. Large stockpiles of the material can be a major fire risk due to their supporting oxidation, and may also detonate, as happened in the Texas City disaster of 1947, which led to major changes in the regulations for storage and handling.

There are two major classes of incidents resulting in explosions:

- In the first case, the explosion happens by the mechanism of shock-to-detonation transition. The initiation happens by an explosive charge going off in the mass, by the detonation of a shell thrown into the mass, or by detonation of an explosive mixture in contact with the mass. The examples are Kriewald, Morgan (present-day Sayreville, New Jersey) Oppau, Tessenderlo and Traskwood.
- In the second case, the explosion results from a fire that spreads into the ammonium nitrate itself (Texas City, Brest, Oakdale), or from a mixture of ammonium nitrate with a combustible material during the fire (Repauno, Cherokee, Nadadores). The fire must be confined at least to a degree for successful transition from a fire to an explosion (a phenomenon known as "deflagration-to-detonation transition", or DDT). Pure, compact AN is stable and very difficult to ignite, and there are numerous cases when even impure AN did not explode in a fire.

Ammonium-nitrate-based explosives were used in the Oklahoma City bombing.

Ammonium nitrate decomposes in temperatures normally well above 200°C. However the presence of impurities (organic and/or inorganic) will often reduce the temperature point when heat is being generated. Once the AN has started to decompose, then a runaway reaction will normally occur as the heat of decomposition is very large. AN evolves so much heat that this runaway reaction is normally impossible to stop. This is a well-known hazard with some types of N-P-K Fertilizers, and it is responsible for the loss of several cargo ships.

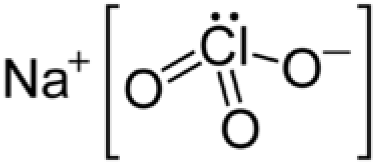
Under normal handling conditions, ammonium nitrate is not harmful. However, inhalation of high concentrations of ammonium nitrate dust can cause respiratory tract irritation. Symptoms may include: coughing, sore throat, shortness of breath, or even suffocation. When swallowed in high concentrations, ammonium nitrate may cause headache, dizziness, abdominal pain, vomiting, bloody diarrhea, weakness, a tingling sensation, heart and circulation irregularities, convulsions, collapse, and suffocation. Ammonium nitrate forms a mild acid when mixed with water. This acid can cause irritation to the eyes, nose, and skin.

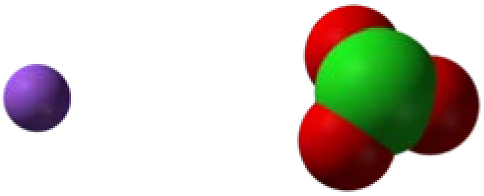
In November 2009, a ban on ammonium sulfate, ammonium nitrate, and calcium ammonium nitrate fertilizers was imposed in the former Malakand Division—comprising the Upper Dir, Lower Dir, Swat, Chitral, and Malakand districts of the North West

Frontier Province (NWFP) of Pakistan—by the NWFP government, following reports that those chemicals were used by militants to make explosives. In January 2010, these substances were also banned in Afghanistan for the same reason.

Sodium Chlorate

Sodium chlorate





IUPAC name
Sodium chlorate

Other names
Sodium chlorate(V)

Identifiers	
CAS number	7775-09-9 ✓
PubChem	24487 ✓
ChemSpider	22895 ✓
UNII	T95DR77GMR ✓
EC number	231-887-4
UN number	1495, 2428
MeSH	Sodium+chlorate
RTECS number	FO0525000
Properties	

Molecular formula	$NaClO_3$
Molar mass	106.44 g/mol
Appearance	white solid
Odor	odorless
Density	2.5 g/cm^3
Melting point	248 °C
Boiling point	~300 °C *decomp.*
Solubility in water	101.0 g/100 ml (20 °C)
Refractive index (n_D)	1.572
Hazards	
MSDS	ICSC 1117
EU Index	017-005-00-9
EU classification	Oxidant (**O**) Harmful (**Xn**) Dangerous for the environment (**N**)
R-phrases	R9, R22, R51/53
S-phrases	(S2), S13, S17, S46, S61
Flash point	none
Related compounds	
Other anions	Sodium chloride Sodium hypochlorite Sodium chlorite Sodium perchlorate Sodium bromate Sodium iodate
Other cations	Ammonium chlorate Potassium chlorate Barium chlorate
Related compounds	Chloric acid

Sodium chlorate is a chemical compound with the chemical formula ($NaClO_3$). When pure, it is a white crystalline powder that is readily soluble in water. It is hygroscopic. It decomposes above 250 °C to release oxygen and leave sodium chloride. As of September 2009, wholesale of sodium chlorate weedkiller was banned in all EU countries, but consumers were allowed to use and store the product until 10 May 2010.

Synthesis

Industrially, sodium chlorate is synthesized from the electrolysis of a hot sodium chloride solution in a mixed electrode tank:

$$NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$$

It can also be synthesized by passing chlorine gas to a hot sodium hydroxide solution. It is then purified by crystallization.

Uses

The main commercial use for sodium chlorate is for making chlorine dioxide, ClO_2. The largest application, approx. 95% of the chlorate, is in bleaching of pulp where chlorine dioxide today is the predominant bleaching agent.

Herbicides

Sodium chlorate is used as a non-selective herbicide. It is considered phytotoxic to all green plant parts. It can also kill through root absorption.

Sodium chlorate may be used to control:

- morning glory,
- Canada thistle,
- johnson grass,
- bamboo,
- ragwort and
- St John's wort.

The herbicide is mainly used on non-crop land for spot treatment and for total vegetation control on roadsides, fenceways, ditches and suchlike.

Sodium chlorate is also used as a defoliant and desiccant for:

- cotton,
- safflower,
- corn,
- flax,
- peppers,
- soybeans,
- grain sorghum,
- southern peas,
- dry beans,
- rice and
- sunflowers.

If used in combination with atrazine, it increases the persistence of the effect. If used in combination with 2,4-D, it improves performance of the material. Sodium chlorate has a soil-sterilant effect. Mixing with other herbicides in aqueous solution is possible to some extent, so long as they are not susceptible to oxidation.

Chemical oxygen generation

Chemical oxygen generator for example in commercial aircraft provide emergency oxygen to passengers to protect them from drops in cabin pressure by catalytic decomposition of sodium chlorate. The catalyst is normally some iron powder. Barium peroxide (BaO_2) is used to absorb the chlorine which is a minor product in the decomposition.

Sodium chlorate is used in some aircraft as a source of supplemental oxygen. Iron powder is mixed with sodium chlorate and ignited by a charge which is activated by pulling on the emergency mask. The reaction produces more oxygen than is required for combustion.

Toxicity in humans

Due to its oxidative nature, sodium chlorate can be very toxic if ingested. The oxidative effect on hemoglobin leads to methaemoglobin formation, which is followed by denaturation of the globin protein and a cross-linking of erythrocyte membrane proteins with resultant damage to the membrane enzymes. This leads to increased permeability of the membrane, and severe hemolysis. The denaturation of hemoglobin overwhelms the capacity of the G6PD metabolic pathway. In addition, this enzyme is directly denatured by chlorate reducing its activity.

Therapy with ascorbic acid and methylene blue are frequently used in the treatment of methemoglobinemia. However, since methylene blue requires the presence of NADPH that requires normal functioning of G6PD system, it is less effective than in other conditions characterized by hemoglobin oxidation.

Acute severe hemolysis results, with multi-organ failure, including DIC and renal failure. In addition there is a direct toxicity to the proximal renal tubule . The treatment will consist of exchange transfusion, peritoneal dialysis or hemodialysis.

Formulations

Sodium chlorate comes in dust, spray and granule formulations. There is a risk of fire and explosion in dry mixtures with other substances, especially organic materials, that is other herbicides, sulfur, phosphorus, powdered metals, strong acids. Particularly when mixed with sugar it has explosive properties. If accidentally mixed with one of these substances it should not be stored in human dwellings.

Marketed formulations contain a fire retardant, but this has little effect if deliberately ignited. Most commercially available chlorate weedkillers contain approximately 53% sodium chlorate with the balance being a fire depressant such as sodium metaborate or ammonium phosphates.

Trade names

The active ingredient sodium chlorate is found in a variety of commercial herbicides. Some trade names for products containing sodium chlorate include Atlacide, Defol, De-Fol-Ate, Drop-Leaf, Fall, Harvest-Aid, Kusatol, Leafex, and Tumbleaf. The compound may be used in combination with other herbicides such as atrazine, 2,4-D, bromacil, diuron, and sodium metaborate.

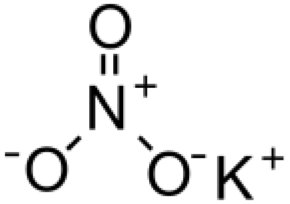
Sodium Chlorate was an extensively used weedkiller within the EU, up until 2009 when it was withdrawn after a decision made under terms of EU Regulations. Its use as a herbicide outside the EU remains unaffected, as does its use in other non-herbicidal applications, such as in the production of chlorine dioxide biocides and for pulp and paper bleaching

Cultural references

- Historian James Watson of Massey University in New Zealand wrote a widely reported article, "The Significance of Mr. Richard Buckley's Exploding Trousers" about accidents with sodium chlorate when used as a herbicide to control ragwort in the 1930s. This later won him an Ig Nobel Prize in 2005, and was the basis for the May 2006 "Exploding Pants" episode of MythBusters.

Potassium Nitrate

Potassium nitrate



IUPAC name
Potassium Nitrate

Other names
Saltpetre
Nitrate of potash
Vesta powder

	Identifiers
CAS number	7757-79-1 ✓
PubChem	24434
ChemSpider	22843 ✓
UNII	RU45X2JN0Z ✓
UN number	1486
KEGG	D02051 ✗
RTECS number	TT3700000
	Properties
Molecular formula	KNO_3
Molar mass	101.103 g/mol
Appearance	white solid
Odor	odorless
Density	2.109 g/cm^3 (16 °C)
Melting point	334 °C
Boiling point	400 °C decomp.
Solubility in water	133 g/L (0 °C) 360 g/L (25 °C) 2470 g/L (100 °C)
Solubility	slightly soluble in ethanol soluble in glycerol, ammonia
	Structure
Crystal structure	Orthorhombic, Aragonite

Hazards	
MSDS	External MSDS
EU Index	Not listed
EU classification	Oxidant (**O**)
R-phrases	R8 R22 R36 R37 R38
S-phrases	S7 S16 S17 S26 S36 S41
Flash point	Non-flammable
LD_{50}	3750 mg/kg
Related compounds	
Other anions	Potassium nitrite
Other cations	Lithium nitrate Sodium nitrate Rubidium nitrate Caesium nitrate
Related compounds	Potassium sulfate Potassium chloride
Supplementary data page	
Structure and properties	n, ε_r, etc.
Thermodynamic data	Phase behaviour Solid, liquid, gas
Spectral data	UV, IR, NMR, MS

Potassium nitrate is a chemical compound with the formula KNO_3. It occurs as a mineral niter and is a natural solid source of nitrogen. Its common names include **saltpetre** (**saltpeter** in American English), from Medieval Latin *sal petræ*: "stone salt" or possibly "Salt of Petra" and **nitrate of potash**. The name *Peru saltpetre* or *Chile saltpetre* (American *Peru saltpeter* or *Chile saltpeter*) refers not to potassium nitrate but to a similar chemical sodium nitrate. Major uses of potassium nitrate are in fertilizers, rocket propellants and fireworks; it is one of the constituents of gunpowder. When used as a food additive in the European Union, the compound is referred to as E252.

History of production

The earliest known complete purification process for potassium nitrate was outlined in 1270 by the Arab chemist and engineer Hasan al-Rammah of Syria in his book *al-Furusiyya wa al-Manasib al-Harbiyya* ('The Book of Military Horsemanship and Ingenious War Devices'), where he first described the use of potassium carbonate (in the form of wood ashes).

Into the 19th century, niter-beds were prepared by mixing manure with either mortar or wood ashes, common earth and organic materials such as straw to give porosity to a compost pile typically 1.5×2×5 meters in size. The heap was usually under a cover from the rain, kept moist with urine, turned often to accelerate the decomposition and leached with water after approximately one year. Dung-heaps were a particularly common source: ammonia from the decomposition of urea and other nitrogenous materials would undergo bacterial oxidation to produce various nitrates, primarily calcium nitrate, which could be converted to potassium nitrate by the addition of potash from wood ashes.

A variation on this process, using only urine, straw and wood ash, is described by LeConte: Stale urine is placed in a container of straw hay and is allowed to sour for many months, after which water is used to wash the resulting chemical salts from the straw. The process is completed by filtering the liquid through wood ashes and air-drying in the sun.

During this period, the major natural sources of potassium nitrate were the deposits crystallizing from cave walls and the accumulations of bat guano in caves. Traditionally guano was the source used in Laos for the manufacture of gunpowder for Bang Fai rockets.

During the 19th century and until around World War I, potassium nitrate was produced on an industrial scale by the Birkeland–Eyde process. Today practically all nitrates are produced from the oxidation of ammonia made by the Haber process.

Production

Potassium nitrate can be made by combining ammonium nitrate and potassium hydroxide.

$$NH_4NO_3\ (aq) + KOH\ (aq) \rightarrow NH_3\ (g) + KNO_3\ (aq) + H_2O\ (l)$$

An alternative way of producing potassium nitrate without a by-product of ammonia is to combine ammonium nitrate and potassium chloride, easily obtained as a sodium-free salt substitute.

$$NH_4NO_3\ (aq) + KCl\ (aq) \rightarrow NH_4Cl\ (aq) + KNO_3\ (aq)$$

Potassium nitrate can also be produced by neutralizing nitric acid with potassium hydroxide. This reaction is highly exothermic.

$$KOH\ (aq) + HNO_3 \rightarrow KNO_3\ (aq) + H_2O\ (l)$$

Properties

Potassium nitrate has an orthorhombic crystal structure at room temperature, which transforms to a trigonal system at 129 °C. Upon heating to temperatures above 560 °C, it decomposes into potassium nitrite, generating oxygen:

$$2\ KNO_3 \rightarrow 2\ KNO_2 + O_2$$

Potassium nitrate is moderately soluble in water, but its solubility increases with temperature. The aqueous solution is almost neutral, exhibiting pH 6.2 at 14 °C for a 10%

solution of commercial powder. It is not very hygroscopic, absorbing about 0.03% water in 80% relative humidity over 50 days. It is insoluble in alcohol and is not poisonous; it can react explosively with reducing agents, but it is not explosive on its own.

Uses

Potassium nitrate is mainly used in fertilizers, as a source of nitrogen and potassium – two of the macro nutrients for plants. When used by itself, it has an NPK rating of 13-0-44. Potassium nitrate is also one of the three components of black powder, along with powdered charcoal (substantially carbon) and sulfur, where it acts as an oxidizer.

In the process of food preservation, potassium nitrate has been a common ingredient of salted meat since the Middle Ages, but its use has been mostly discontinued due to inconsistent results compared to more modern nitrate and nitrite compounds. Even so, saltpetre is still used in some food applications, such as charcuterie and the brine used to make corned beef. Sodium nitrate (and nitrite) have mostly supplanted potassium nitrate's culinary usage, as they are more reliable in preventing bacterial infection than saltpetre. All three give cured salami and corned beef their characteristic pink hue.

Potassium nitrate is an efficient oxidizer, which produces a lilac flame upon burning due to the presence of potassium. It is therefore used in amateur rocket propellants and in several fireworks such as smoke bombs, made with a mixture of sucrose and **potassium nitrate**. It is also added to pre-rolled cigarettes to maintain an even burn of the tobacco.

Potassium nitrate is the main component (usually about 98%) of tree stump remover, as it accelerates the natural decomposition of the stump. It is also commonly used in the heat treatment of metals as a solvent in the post-wash. The oxidizing, water solubility and low cost make it an ideal short-term rust inhibitor.

Potassium nitrate was used to ensure complete combustion of paper cartridges for cap and ball revolvers, as a treatment agent for the paper used to make the cartridges.

Pharmacology

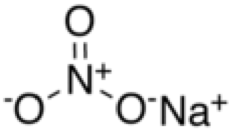
Potassium nitrate can be found in some toothpastes for sensitive teeth. Recently, the use of potassium nitrate in toothpastes for treating sensitive teeth has increased and may be an effective treatment.

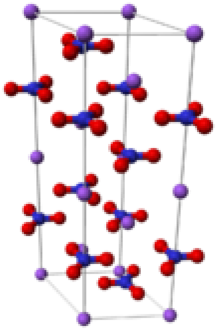
Potassium nitrate successfully combats high blood pressure and was once used as a hypotensive. Other nitrates and nitrites such as glyceryl trinitrate (nitroglycerin), amyl nitrite and isosorbide derivatives are still used to relieve angina.

Potassium nitrate was once thought to induce impotence, and is still falsely rumored to be in institutional food (such as military fare) as an anaphrodisiac; however, there is no scientific evidence for such properties.

Sodium Nitrate

Sodium nitrate





IUPAC name
Sodium nitrate

Other names
Caliche
Chile saltpeter
Nitrate of soda
Nitratine
Peru saltpeter
Soda niter
cubic niter

Identifiers	
CAS number	7631-99-4 ✓
PubChem	24268
ChemSpider	22688 ✓
UNII	8M4L3H2ZVZ ✓
UN number	1498
RTECS number	WC5600000
Properties	
Molecular formula	$NaNO_3$
Molar mass	84.9947 g/mol
Appearance	White powder or colorless crystals with sweet smell
Density	2.257 g/cm^3, solid
Melting point	308 °C
Boiling point	380 °C decomp.
Solubility in water	730 g/L (0°C) 921 g/L (25 °C) 1800 g/L (100 °C)
Solubility	very soluble in ammonia; soluble in alcohol
Refractive index (n_D)	1.587 (trigonal) 1.336 (rhomobohedral)
Structure	
Crystal structure	trigonal and rhombohedral
Thermochemistry	

Std enthalpy of formation $\Delta_f H^\circ_{298}$	−468 kJ/mol
Standard molar entropy S°_{298}	117 J·mol^{-1} K^{-1}
Hazards	
MSDS	ICSC 0185
EU Index	Not listed
Main hazards	Oxidant, irritant
Flash point	Non-flammable
LD_{50}	3236 mg/kg
Related compounds	
Other anions	Sodium nitrite
Other cations	Lithium nitrate Potassium nitrate Rubidium nitrate Caesium nitrate
Related compounds	Sodium sulfate Sodium chloride

Sodium nitrate is the chemical compound with the formula $NaNO_3$. This salt, also known as *Chile saltpeter* or *Peru saltpeter* (due to the large deposits found in each country) to distinguish it from ordinary saltpeter, potassium nitrate, is a white solid which is very soluble in water. The mineral form is also known as *nitratine* or *soda niter*.

Sodium nitrate is used as an ingredient in fertilizers, pyrotechnics, as an ingredient in smoke bombs, as a food preservative, and as a solid rocket propellant, as well as in glass and pottery enamels. The compound has been mined extensively for those purposes.

History

The first shipment of Chile saltpeter to Europe arrived in England in 1820 or 1825, but did not find any buyers and was dumped at sea in order to avoid customs toll. With time, however, the mining of South American saltpeter became a profitable business (in 1859, England alone consumed 47,000 metric tons). Chile fought against the allies Peru and Bolivia in the War of the Pacific 1879-1884 and took over the richest deposits. In 1919, Ralph Walter Graystone Wyckoff determined its crystal structure using X-ray crystallography.

Sources

The largest accumulations of naturally occurring sodium nitrate are found in Chile and Peru, where nitrate salts are bound within mineral deposits called caliche ore. For more than a century, the world supply of the compound was mined almost exclusively from the Atacama desert in northern Chile until, at the turn of the 20th century, German chemists Fritz Haber and Carl Bosch developed a process for producing ammonia from the atmosphere on an industrial scale. With the onset of World War I, Germany began converting ammonia from this process into a synthetic *Chilean saltpeter* which was as practical as the natural compound in production of gunpowder and other munitions. By the 1940s, this conversion process resulted in a dramatic decline in demand for sodium nitrate procured from natural sources.

Chile still has the largest reserves of caliche, with active mines in such locations as Pedro de Valdivia, María Elena and Pampa Blanca, and there it used to be called *white gold*. Sodium nitrate, potassium nitrate, sodium sulfate and iodine are all obtained by the processing of caliche. The former Chilean saltpeter mining communities of Humberstone and Santa Laura were declared Unesco World Heritage sites in 2005.

Sodium nitrate is also synthesized industrially by neutralizing nitric acid with soda ash.

Applications

Sodium nitrate was used extensively as a fertilizer and a raw material for the manufacture of gunpowder in the late 19th century. It can be combined with iron hydroxide to make a resin.

Sodium nitrate should not be confused with the related compound, sodium nitrite.

It can be used in the production of nitric acid by combining it with sulfuric acid and subsequent separation through fractional distillation of the nitric acid, leaving behind a residue of sodium bisulfate. Hobbyist gold refiners use sodium nitrate to make a hybrid aqua regia that dissolves gold and other metals.

Less common applications include its use as a substitute oxidizer used in fireworks as a replacement for potassium nitrate commonly found in black powder and as a component in instant cold packs.

Sodium nitrate is used together with potassium nitrate for heat storage and, more recently, for heat transfer in solar power plants.

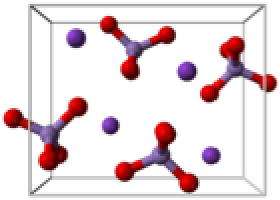
It is also used in the wastewater industry for facultative microorganism respiration. Nitrosomonas, a genus of microorganisms, consumes nitrate in preference to oxygen, enabling it to grow more rapidly in the wastewater to be treated.

Health concerns

Like sodium nitrite, sodium nitrate forms nitrosamines, a human carcinogen, known to cause DNA damage and increased cellular degeneration. Studies have shown a link between increased levels of nitrates and increased deaths from certain diseases including Alzheimer's, diabetes mellitus and Parkinson's, possibly through the damaging effect of nitrosamines on DNA. Nitrosamines, formed in cured meats containing sodium nitrate and nitrite, have been linked to gastric cancer and oesophageal cancer. Sodium nitrate and nitrite are associated with a higher risk of colorectal cancer. World Cancer Research Fund UK, states that one of the reasons that processed meat increases the risk of colon cancer is its content of nitrate. A small amount of the nitrate added to meat as a preservative breaks down into nitrite, in addition to any nitrite that may also be added. The nitrite then reacts with protein-rich foods (such as meat) to produce N-nitroso compounds (NOCs). Some types of NOCs are known to cause cancer. NOCs can be formed either when meat is cured or in the body as meat is digested.

Potassium Permanganate

Potassium permanganate



IUPAC name
Potassium manganate(VII)

Other names
Potassium permanganate
Potassium manganate(VII)
Chameleon mineral
Condy's crystals
Permanganate of potash

Identifiers	
CAS number	7722-64-7 ✓
PubChem	24400
ChemSpider	22810 ✓
EC number	231-760-3
UN number	1490
KEGG	D02053 ✓
RTECS number	SD6475000
Properties	
Molecular formula	$KMnO_4$
Molar mass	158.034 g/mol
Appearance	purplish-bronze-gray needles magenta–rose in solution
Odor	odorless
Density	2.703 g/cm^3
Melting point	240 °C decomp.
Solubility in water	6.38 g/100 ml (20 °C) 25 g/100 mL (65 °C)
Solubility	decomposes in alcohol and organic solvents
Structure	

Crystal structure	Orthorhombic
Thermochemistry	
Std enthalpy of formation $\Delta_f H^\circ_{298}$	−813.4 kJ/mol
Standard molar entropy S°_{298}	171.7 J K^{-1} mol^{-1}
Hazards	
MSDS	External MSDS
EU Index	025-002-00-9
EU classification	Oxidant (**O**) Harmful (**Xn**) Dangerous for the environment (**N**) Non-Flammable
R-phrases	R8, R22, R50/53
S-phrases	(S2), S60, S61
Related compounds	
Other anions	Potassium manganite Potassium manganate
Other cations	Sodium permanganate Ammonium permanganate
Related compounds	Manganese heptoxide

Potassium permanganate is an inorganic chemical compound with the formula $KMnO_4$. It is a salt consisting of K^+ and MnO_4^- ions. Formerly known as **permanganate of potash** or **Condy's crystals**, it is a strong oxidizing agent. It dissolves in water to give intense purple solutions, the evaporation of which gives prismatic purplish-black glistening crystals.

Potassium permanganate decomposes when exposed to light:

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

In 2000, worldwide production was estimated at 30,000 tonnes. In this compound, manganese is in the +7 oxidation state.

Structure and preparation

It forms orthorhombic crystals with constants: $a = 910.5$ pm, $b = 572.0$ pm, $c = 742.5$ pm. The Mn-O bond distances are 162.9 pm.

Potassium permanganate is produced industrially from manganese dioxide, which also occurs as the mineral pyrolusite. The MnO_2 is fused with potassium hydroxide and heated in air or with potassium nitrate (a source of oxygen). This process gives potassium manganate, which upon electrolytic oxidation in alkaline solution gives potassium permanganate.

$$2\ MnO_2 + 4\ KOH + O_2 \rightarrow 2\ K_2MnO_4 + 2\ H_2O$$
$$2\ MnO_4^{2-} + Cl_2 \rightarrow 2\ MnO_4^{-} + 2\ Cl^{-}$$

Permanganates can also be generated by treating a solution of Mn^{2+} ions with strong oxidants such as lead dioxide (PbO_2), or sodium bismuthate ($NaBiO_3$). These reactions use the vivid violet colour of permanganate as a test for the presence of manganese.

Uses

Almost all applications of potassium permanganate exploit its oxidizing properties. As a strong oxidant that does not generate toxic byproducts, $KMnO_4$ has many niche uses.

Potassium permanganate is one of the principal chemicals used in the film and television industries to "age" props and set dressings. Its oxidising effects create "hundred year old" or "ancient" looks on hessian cloth, ropes, timber and glass. It was used on props and sets in films such as "Troy", "300" and "Indiana Jones".

Disinfectant and water treatment

As an oxidant, potassium permanganate can act as an antiseptic. For example, dilute solutions are used to treat canker sores (ulcers), disinfectant for the hands and treatment for mild pompholyx, dermatitis, and fungal infections of the hands or feet. Potassium permanganate is used extensively in the water treatment industry. It is used as a regeneration chemical to remove iron and hydrogen sulfide (rotten egg smell) from well water via a "Manganese Greensand" Filter. "Pot-Perm" is also obtainable at pool supply stores, is used additionally to treat waste water. Historically it was used to disinfect drinking water. It currently finds application in the control of nuisance organisms such as Zebra mussels in fresh water collection and treatment systems.

Biomedical uses

Related to the use of $KMnO_4$ for water treatment, this salt is often employed as a specialized disinfectant for treating human and animal ailments. In histology, it is used to bleach melanin which obscures tissue detail. Potassium permanganate can also be used to differentiate amyloid AA from other types of amyloid pathologically deposited in body tissues. Incubation of fixed tissue with potassium permanganate will prevent amyloid AA from staining with congo red whereas other types of amyloid are unaffected. Permanganate washes were once used to treat gonorrhea and are still used to treat candidiasis.

Organic synthesis

Aside from its use in water treatment, the other major application of $KMnO_4$ is as a reagent for the synthesis of organic compounds. Significant amounts are required for the synthesis of ascorbic acid, chloramphenicol, saccharin, isonicotinic acid, and pyrazinoic acid.

Fruit Preservation

Addition of potassium permanganate substrated to banana shipments adsorbs the ethylene and doubles the fruit ripening period.

Survival kits

In the past potassium permanganate was included in survival kits: as a fire starter, water sterilizer and for creating distress signals on snow.

Chemistry

Analytical

Potassium permanganate can be used to quantitatively determine the total oxidisable organic material in an aqueous sample. The value determined is known as the *permanganate value.* In analytical chemistry, a standardized aqueous solution of $KMnO_4$ is sometimes used as an oxidizing titrant for redox titrations (permanganometry). In a related way, it is used as a reagent to determine the Kappa number of wood pulp. For the standardization of $KMnO_4$ solutions, reduction by oxalic acid is often used.

A solution of $KMnO_4$ in water, in a volumetric flask

Aqueous, acidic solutions of $KMnO_4$ are used to collect gaseous mercury in flue gas during stationary source emissions testing.

Organic

Dilute solutions of $KMnO_4$ convert alkenes into diols (glycols). This behaviour is also used as a qualitative test for the presence of double or triple bonds in a molecule, since the reaction decolourises the permanganate solution; thus it is sometimes referred to as Baeyer's reagent. However, bromine serves better in measuring unsaturation (double or triple bonds) quantitatively, since $KMnO_4$, being a very strong oxidizing agent, can react with impurities in a sample.

Under acidic conditions, the alkene double bond is cleaved to give the appropriate carboxylic acid:

$$CH_3(CH_2)_{17}CH{=}CH_2 + [O] \rightarrow CH_3(CH_2)_{17}COOH$$

Potassium permanganate oxidizes aldehydes to carboxylic acids, such as the conversion of *n*-heptanal to heptanoic acid:

$$C_6H_{13}CHO + [O] \rightarrow C_6H_{13}COOH$$

Even an alkyl group (with a benzylic hydrogen) on an aromatic ring is oxidized, e.g. toluene to benzoic acid.

Glycols are highly reactive toward $KMnO_4$. This vigorous reaction is used in survival kits as a fire starter. For example, a mixture of potassium permanganate and glycerol or pulverized glucose ignites readily. Its sterilizing properties are another reason for inclusion of $KMnO_4$ in a survival kit.

Reaction with acids

Concentrated sulfuric acid reacts with $KMnO_4$ to give Mn_2O_7, which can be explosive. Similarly concentrated hydrochloric acid gives chlorine. The Mn-containing products from redox reactions depend on the pH. Acidic solutions of permanganate are reduced to the faintly pink manganese(II) ion (Mn^{2+}) and water. In neutral solution, permanganate is only reduced by $3e^-$ to give MnO_2, wherein Mn is in a +4 oxidation state. This is the material that stains one's skin when handling $KMnO_4$. $KMnO_4$ spontaneously reduces in an alkaline solution to green K_2MnO_4, wherein manganese is in the +6 oxidation state.

A curious reaction is observed when one adds concentrated sulfuric acid to potassium permanganate. Although no reaction may be apparent, the vapor over the mixture will ignite paper impregnated with alcohol. Potassium permanganate and sulfuric acid react to produce some ozone, which has a high oxidising power and rapidly oxidises the alcohol, causing it to combust. As the reaction also produces explosive Mn_2O_7, this should only be attempted with great care.

Handling

As an oxidizer that generates the dark brown product MnO_2, potassium permanganate rapidly stains virtually any organic material such as skin, paper, and clothing. This staining effect is used to "develop" TLC plates. The redox reaction is used for artistic purposes as an agent to prepare paper for fast bleaching. Lemon juice is enough to quickly remove colour from the paper and applied with a paint brush this can create interesting aesthetics. Even glassware containing solutions of $KMnO_4$ can become brown. MnO_2 can be removed by scrubbing with dilute acids or with Sodium Thiosulfate.

History

In 1659, Johann Rudolf Glauber fused a mixture of the mineral pyrolusite and potassium carbonate to obtain a material that, when dissolved in water, gave a green solution (potassium manganate) which slowly shifted to violet and then finally red. This report represents the first description of the production of potassium permanganate. Just under two hundred years later London chemist Henry Bollmann Condy had an interest in disinfectants, and marketed several products including *ozonised water*. He found that fusing pyrolusite with NaOH and dissolving it in water produced a solution with disinfectant properties. He patented this solution, and marketed it as *Condy's Fluid*. Although effective, the solution was not very stable. This was overcome by using KOH rather than NaOH. This was more stable, and had the advantage of easy conversion to the equally effective potassium permanganate crystals. This crystalline material was known as *Condy's crystals* or *Condy's powder*. Potassium permanganate was comparatively easy to manufacture so Condy was subsequently forced to spend considerable time in litigation in order to stop competitors from marketing products similar to *Condy's Fluid* or *Condy's Crystals*.

Early photographers used it as a component of flash powder. It is now replaced with other oxidizers, due to the instability of permanganate mixtures. Aqueous solutions of $KMnO_4$ have been used together with T-Stoff (i.e. 80% hydrogen peroxide) as propellant for the rocket plane Messerschmitt Me 163. In this application, it was known as Z-Stoff. This combination of propellants is sometimes still used in torpedoes.

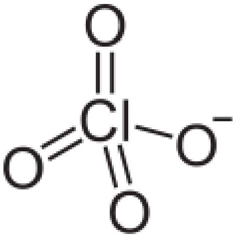
Safety

Solid $KMnO_4$ is a strong oxidizer and thus should be kept separated from oxidizable substances. Reaction with concentrated sulfuric acid produces the highly explosive manganese(VII) oxide (Mn_2O_7). When solid $KMnO_4$ is mixed with pure glycerol or other simple alcohols it will result in a violent combustion reaction.

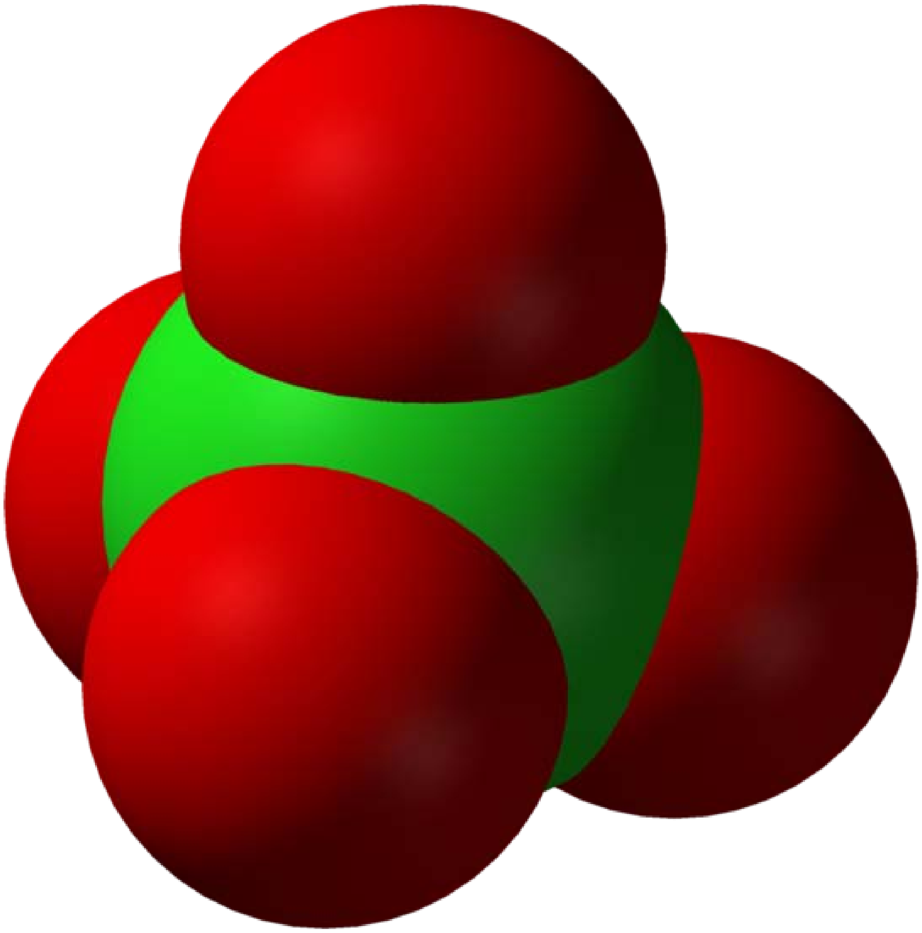
$$3\ C_3H_5(OH)_3 + 14\ KMnO_4 \rightarrow 14\ MnO_2 + 14\ KOH + 9\ CO_2 + 5\ H_2O$$

Potassium permanganate may leave behind a brownish stain which can be removed by using sodium bisulfite.

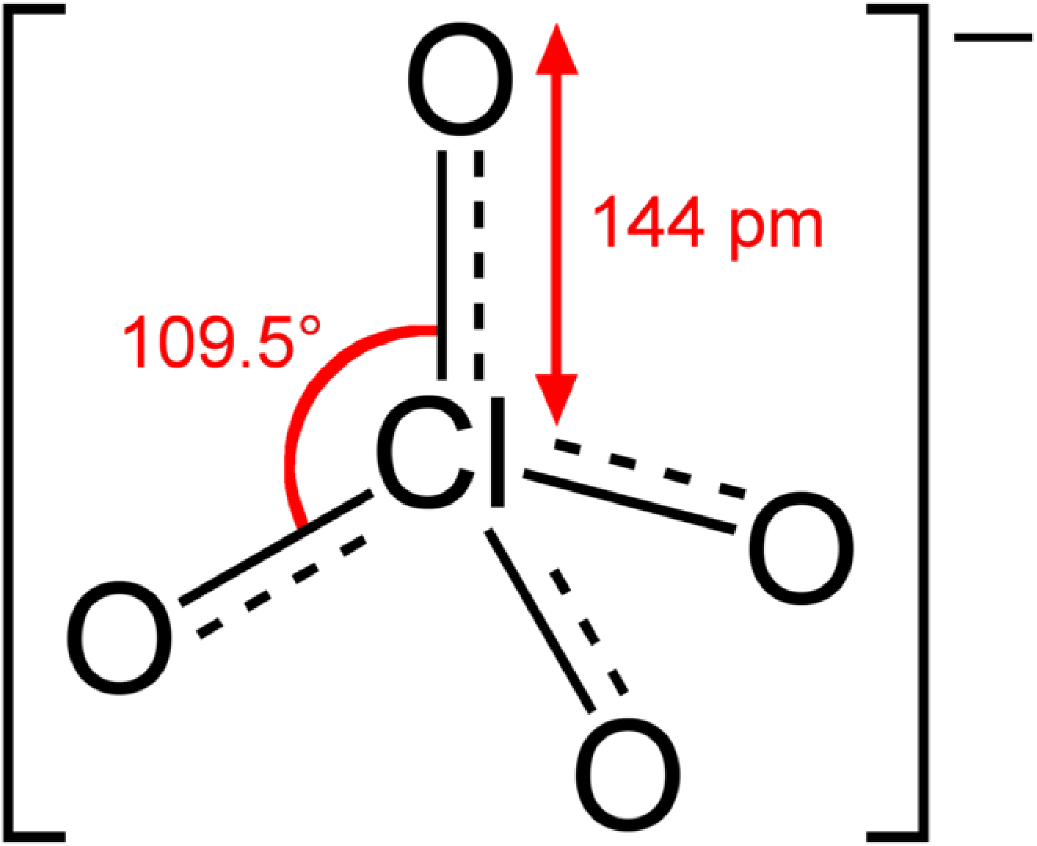
Perchlorate



Perchlorate ion



A space-filling model of the perchlorate ion



The structure and dimensions of the perchlorate ion

Perchlorates are the salts derived from perchloric acid ($HClO_4$). They occur both naturally and through manufacturing. They have been used as a medicine for more than 50 years to treat thyroid gland disorders. They are used extensively within the pyrotechnics industry, and ammonium perchlorate is also a component of solid rocket fuel. Lithium perchlorate, which decomposes exothermically to give oxygen, is used in oxygen "candles" on spacecraft, submarines and in other esoteric situations where a reliable backup or supplementary oxygen supply is needed. Most perchlorate salts are soluble in water.

Chemical definition

The chemical notation for the perchlorate ion is ClO−4. The ion has a molecular mass of 99.45 amu.

A perchlorate (compound) is a compound containing this group, with chlorine in oxidation state +7.

- Ammonium perchlorate, NH_4ClO_4
- Caesium perchlorate, $CsClO_4$
- Lithium perchlorate, $LiClO_4$
- Magnesium perchlorate, $Mg(ClO_4)_2$
- Perchloric acid, $HClO_4$
- Potassium perchlorate, $KClO_4$
- Rubidium perchlorate, $RbClO_4$
- Silver perchlorate, $AgClO_4$
- Sodium perchlorate, $NaClO_4$

Reactivity as an oxidant

The perchlorate ion is the least reactive oxidizer of the generalized chlorates. This is apparently paradoxical, since higher oxidation numbers are expected to be progressively stronger oxidizers, and less stable. A table of reduction potentials of the four chlorates shows that, contrary to expectation, perchlorate is the weakest oxidant among the four in water.

Half-reaction	***E*° (V)**
$H^+ + HOCl + e^- \rightarrow \frac{1}{2}Cl_2(g) + H_2O$	1.63
$3H^+ + HOClO + 3e^- \rightarrow \frac{1}{2}Cl_2(g) + 2H_2O$	1.64
$6H^+ + ClO_3^- + 5e^- \rightarrow \frac{1}{2}Cl_2(g) + 3H_2O$	1.47
$8H^+ + ClO_4^- + 5e^- \rightarrow \frac{1}{2}Cl_2(g) + 4H_2O$	1.42
$\frac{1}{2}Cl_2(g) + e^- \rightarrow Cl^-$	1.36
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.89
$ClO_2^- + 2H_2O + 4e^- \rightarrow Cl^- + 4OH^-$	0.78
$ClO_3^- + 3H_2O + 6e^- \rightarrow Cl^- + 6OH^-$	0.63
$ClO_4^- + 4H_2O + 8e^- \rightarrow Cl^- + 8OH^-$	0.56

Gas phase measurements of heats of reaction (which allow computation of $\Delta H_f°$) of various chlorine oxides do follow the expected trend wherein Cl_2O_7 exhibits the largest endothermic value of $\Delta H_f°$ (238.1 kJ/mol) while Cl_2O exhibits the lowest endothermic value of $\Delta H_f°$ (80.3 kJ/mol).

The central chlorine in the perchlorate anion is a closed shell atom and is well protected by the four oxygens. Hence, perchlorate reacts sluggishly. Most perchlorate compounds, especially salts of electropositive metals such as sodium perchlorate or potassium perchlorate, are slow to react unless heated. This property is useful in many applications, such as flares, where the device should not explode, or even catch fire spontaneously.

Mixtures of perchlorates with organic compounds are more reactive. Although they do not usually catch fire or explode unless heated, there are a number of exceptions. Large amounts of improperly stored ammonium perchlorate led to the PEPCON disaster, in which an explosion destroyed one of the two large scale production plants for ammonium perchlorate in the US.

Other oxyanions

Using Stock nomenclature, if a Roman numeral in brackets follows the word "chlorate", this indicates the oxyanion contains chlorine in the indicated oxidation state, namely

Common name	**Stock name**	**Oxidation state**	**Formula**
Hypochlorite	Chlorate(I)	+1	ClO^-
Chlorite	Chlorate(III)	+3	ClO_2^-
Chlorate	Chlorate(V)	+5	ClO_3^-
Perchlorate	**Chlorate(VII)**	+7	ClO_4^-

Using this convention, "chlorate" means *any* chlorine oxyanion. Commonly, "chlorate" refers only to the oxyanion where chlorine is in the +5 oxidation state.

Use

Oxidizer

The high oxygen content and the high stability of perchlorates make them ideal oxidizers for fireworks and airbags and as key compounds in solid rocket fuel. The solid rocket boosters of the space shuttle contain 350 metric tons of ammonium perchlorate each.

Automotive

Perchlorate is used in airbags, seat belt pre-tensioner, TPMS (tire pressure monitor system) valve sensors, batteries for keyless entry system—mentioned in Hyundai TSB 07-00-001 dated 02-07

Medical applications

Perchlorate has been used as a medication to treat hyperthyroidism since the 1950s. At very high doses (70,000–300,000 ppb) the administration of potassium perchlorate was considered the standard of care in the United States, and remains the approved pharmacologic intervention for many countries. In the early 1960s, potassium perchlorate was implicated in the development of aplastic anemia—a condition where the bone marrow fails to produce new blood cells in sufficient quantity—in thirteen patients, seven of whom died. Subsequent investigations have indicated the connection between administration of potassium perchlorate and development of aplastic anemia to be "equivocable at best", which means that the benefit of treatment, if it is the only known treatment, outweighs the risk, and it appeared a contaminant poisoned the 13.

Production

Natural formation of perchlorates

There are several well-documented mechanisms for natural formation of perchlorate. Involving ozone or hydroxyl radicals as oxidizer for sodium chloride from the sea and are somewhat similar to the formation processes of iodates also present in the atmosphere.

As most perchlorates are readily soluble in water, an accumulation of perchlorates in the environment only occurs in arid areas with little or no rainfall. It is known since the beginning of the 20th century that the Atacama Desert contains not only large amounts of nitrates but also trace amounts of perchlorates. The concentration varies but is in the mg/kg range. The dry southwest of the United States also shows accumulation of perchlorates. With the use of nitrates from the Atacama Desert, so called Chile saltpeter as fertilizer the chlorates were also distributed into the environment. As the Chile saltpeter was mostly substituted by nitrates produced by the Haber Bosch process, which contains no perchlorates this source of perchlorates nearly vanished.

In 2006 a mechanism for the formation of perchlorates was proposed which is particularly apropos to the discovery of perchlorate at the Mars Phoenix lander site. It was shown that soils with high concentrations of natural salts could have some of their chloride converted to perchlorate in the presence of sunlight and/or ultraviolet light. The mechanism was reproduced in the lab using chloride rich soils from Death Valley. In 2010, perchlorate was found at the 1000ppb levels in a vast section of Antarctica, with implications that it is formed naturally and globally on Earth and probably on Mars. Recent isotopic studies have shown that natural perchlorate is produced on Earth by the oxidation of chlorine species through pathways involving tropospheric ozone or its photochemical products.

Industrial production

Perchlorates are either produced by electrolysis of chloride salts or by the neutralization of perchloric acid, which is produced by electrolysis of chlorine, with ammonia or other base.

The electrolysis involves the following reactions:

$$3\ Cl_2 + 6\ OH^- \rightarrow 5\ Cl^- + ClO_3^- + 3\ H_2O$$
$$ClO_3^- + H_2O \rightarrow ClO_4^- + 2\ H^+$$

The industrial scale synthesis for sodium perchlorates starts from sodium chloride. If the electrolysis is not done with the method described at chlorine, but a mixing of the chlorine evolved and the sodium hydroxide is allowed, the reaction mentioned above takes place. The hypochlorite and the chlorate are intermediates in this process.

Perchlorate-free product development

In response to concerns regarding perchlorate, efforts have been undertaken to produce substitutes for products using perchlorate. For example, efforts to create perchlorate-free flares include both spectrally balanced decoy and colored flare compositions which included nitrate or oxide oxidizers. Because nitrate oxidizers are less reactive than perchlorate oxidizers, high-energy fuels have used to compensate for this energy shortfall. Some of these high-energy fuels were produced using mechanical alloying technology.

Environmental presence

Low levels of perchlorate have been detected in both drinking water and groundwater in 26 states in the US according to the Environmental Protection Agency. In 2004, the chemical was also found in cow's milk in California with an average level of 1.3 parts per billion ("ppb" or µg/L), which may have entered the cows through feeding on crops that had exposure to water containing perchlorates. According to the Impact Area Groundwater Study Program, the chemical has been detected as high as 5 µg/L in Massachusetts, well over the state regulation of 2 µg/L.

In some places, perchlorate is detected because of contamination from industrial sites that use or manufacture it. In other places, there is no clear source of perchlorate. In those areas it may be naturally occurring, or could be present because of the use of Chilean fertilizers, which were imported to the U.S. by the hundreds of tons in the early 19th century. One recent area of research has even suggested that perchlorate can be created when lightning strikes a body of water, and perchlorates are created as a byproduct of chlorine generators used in swimming pool chlorination systems. In 2010, perchlorate was found at the 1000ppb levels in a vast section of Antarctica, with implications that it is formed naturally and globally on Earth and probably on Mars most likely by photochemical reactions in the atmosphere].

Fireworks are also a source of perchlorate in lakes.

Regulatory Activity

On February 11, 2011, the U.S. Environmental Protection Agency (EPA) issued a "regulatory determination" that perchlorate meets the Safe Drinking Water Act criteria for regulation as a contaminant. The Agency found that perchlorate may have an adverse effect on the health of persons and is known to occur in public water systems with a frequency and at levels that it presents a public health concern. As a result of EPA's regulatory determination, it begins a process to determine what level of contamination is the appropriate level for regulation. EPA prepared, as part of its regulatory determination, extensive responses to submitted public comments. The "docket ID" for EPA's regulatory action is EPA-HQ-OW-2009-0297 and can be found on regulations.gov.

Prior to issuance of its regulatory determination, EPA issued a recommended Drinking Water Equivalent Level (DWEL) for perchlorate of 24.5 µg/L. In early 2006, EPA issued a “Cleanup Guidance” for this same amount. Both the DWEL and the Cleanup Guidance were based on a thorough review of the existing research by the National Academy of Science (NAS). This followed numerous other studies, including one which suggested human breast milk had an average of 10.5 µg/L of perchlorate. Both the Pentagon and some environmental groups have voiced questions about the NAS report, but no credible science has emerged to challenge the NAS findings. In February 2008, U.S. Food and Drug Administration said that U.S. toddlers on average are being exposed to more than half of the U.S. EPA's safe dose from food alone. In March 2009, a Centers for Disease Control study found 15 brands of infant formula contaminated with perchlorate. Combined with existing perchlorate drinking water contamination, infants could be at risk for exposure to perchlorate above the levels considered safe by E.P.A.

The US Environmental Protection Agency has issued substantial guidance and analysis concerning the impacts of perchlorate on the environment as well as drinking water. California has also issued guidance regarding perchlorate use.

Several states have enacted drinking water standard for perchlorate including Massachusetts in 2006. California's legislature enacted AB 826, the Perchlorate Contamination Prevention Act of 2003, requiring California's Department of Toxic Substance Control (DTSC) to adopt regulations specifying best management practices for perchlorate and perchlorate-containing substances. The Perchlorate Best Management Practices were adopted on December 31, 2005 and became operative on July 1, 2006. California issued drinking water standards in 2007. Several other states, including Arizona, Maryland, Nevada, New Mexico, New York, and Texas have established non-enforceable, advisory levels for perchlorate.

Courts have been called upon to take action with regard to perchlorate. For example, in 2003, a federal district court in California found that Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) applied because perchlorate is ignitable and therefore a “characteristic” hazardous waste.

One example of perchlorate related problems was found at the Olin Flare Facility, Morgan Hill, California - Perchlorate contamination beneath a former flare manufacturing plant in California was first discovered in 2000, several years after the plant had closed. The plant had used potassium perchlorate as one of the ingredients during its 40 years of operation. By late 2003, the state of California and the Santa Clara Valley Water District had confirmed a groundwater plume currently extending over nine miles through residential and agricultural communities.

The Regional Water Quality Control Board and the Santa Clara Valley Water District have engaged in a major outreach effort that has received extensive press and community response. A well testing program is underway for approximately 1,200 residential, municipal, and agricultural wells in the area. Large ion exchange treatment units are operating in three public water supply systems that include seven municipal wells where perchlorate has been detected. The potentially responsible parties, Olin Corporation and Standard Fuse Incorporated, are supplying bottled water to nearly 800 households with private wells. The Regional Water Quality Control Board is overseeing potentially responsible party (PRP) cleanup efforts.

The two production sites of PEPCON and Kerr-McGee in Henderson, Nevada, which were the biggest producers until the explosion of PEPCON in 1988 and the closure of the Kerr McGee plant in 1998, leaked significant amounts of perchlorates into the Las Vegas Wash and from there into Lake Mead and the Colorado River.

The disposal of unused rocket motors and ammunition has led to contamination by perchlorates of several military installations.

Biological functions

Over 40 phylogenetically and metabolically diverse microorganisms capable of perchlorate reduction have been isolated since 1996, including members of the Proteobacteria as well as two recently identified Firmicutes, *Moorella perchloratireducens* and *Sporomusa* sp.

Health effects

Perchlorate adversely affects human health by interfering with iodine uptake into the thyroid gland. In adults, the thyroid gland helps regulate the metabolism by releasing hormones, while in children, the thyroid helps in proper development. Perchlorate is becoming a serious threat to human health and water resources.

The NAS found that perchlorate only affects the thyroid gland. It is not stored in the body, it is not metabolized, and any effects of perchlorate on the thyroid gland are fully reversible once exposure stops. There has been some concern on perchlorate's effects on fetuses, newborns and children, but several peer-reviewed studies on children and newborns also provide reason to believe that low levels of perchlorate do not pose a threat to these populations. On October 1, 2004, the American Thyroid Association (ATA) reported that perchlorate may not be as harmful to newborns, pregnant women and other adults as previously thought.

A study involving healthy adult volunteers determined that at levels above 0.007 milligrams per kilogram per day (mg/(kg·d)), perchlorate can temporarily inhibit the thyroid gland’s ability to absorb iodine from the bloodstream ("iodide uptake inhibition", thus perchlorate is a known goitrogen). The EPA converted this dose into a reference dose of 0.0007 mg/(kg·d) by dividing this level by the standard intraspecies uncertainty factor of 10. The agency then calculated a "drinking water equivalent level" of 24.5 ppb by assuming a person weighs 70 kilograms (154 pounds) and consumes 2 liters (68 ounces) of drinking water per day over a lifetime. Thus, 25 ppb was set as the recommended drinking water standard (the DWEL). For that reason, most media reports call this the "safe" level of exposure. The NAS report also stated additional research would be helpful, but emphasized that the existing database on perchlorate was sufficient to make its reference dose recommendation and ensure it would be protective for everyone.

Recent research, however, has shown inhibition of iodide uptake in the thyroids of women at much lower levels, levels attainable from normally contaminated water and milk.

Discovery of perchlorate on Mars

In the summer of 2008, the Wet Chemistry Laboratory (WCL) on board the 2007 Phoenix Mars Lander performed the first wet chemical analysis of martian soil. The analyses on three samples, two from the surface and one from 5 cm depth, revealed a slightly alkaline soil and low levels of salts typically found on Earth. Most unexpected though was the presence of ~ 0.6 wt % perchlorate (ClO4-), most likely as a Mg(ClO4)2 phase .

The extreme temperatures found on Mars typically lead to either crystallization or evaporation of water, making it difficult to imagine that water could be found in liquid form. The salts formed from perchlorates discovered at the Phoenix landing site act as “anti-freeze” and will substantially lower the freezing point of water. Based on the temperature and pressure conditions on present-day Mars at the Phoenix lander site, conditions would allow a perchlorate salt solution to be present in liquid form for a few hours each day during the summer .

The possibility that the perchlorate was a contaminant brought from Earth has been eliminated by several lines of evidence. The Phoenix retro-rockets used ultra pure hydrazine and launch propellants consisted of ammonium perchlorate. Sensors on board Phoenix found no traces of ammonium, and thus the perchlorate in the quantities present in all three soil samples is indigenous to the martian soil.

Lead Dioxide

Lead dioxide

IUPAC name
Lead(IV) oxide

Other names
Plumbic oxide
Plattnerite

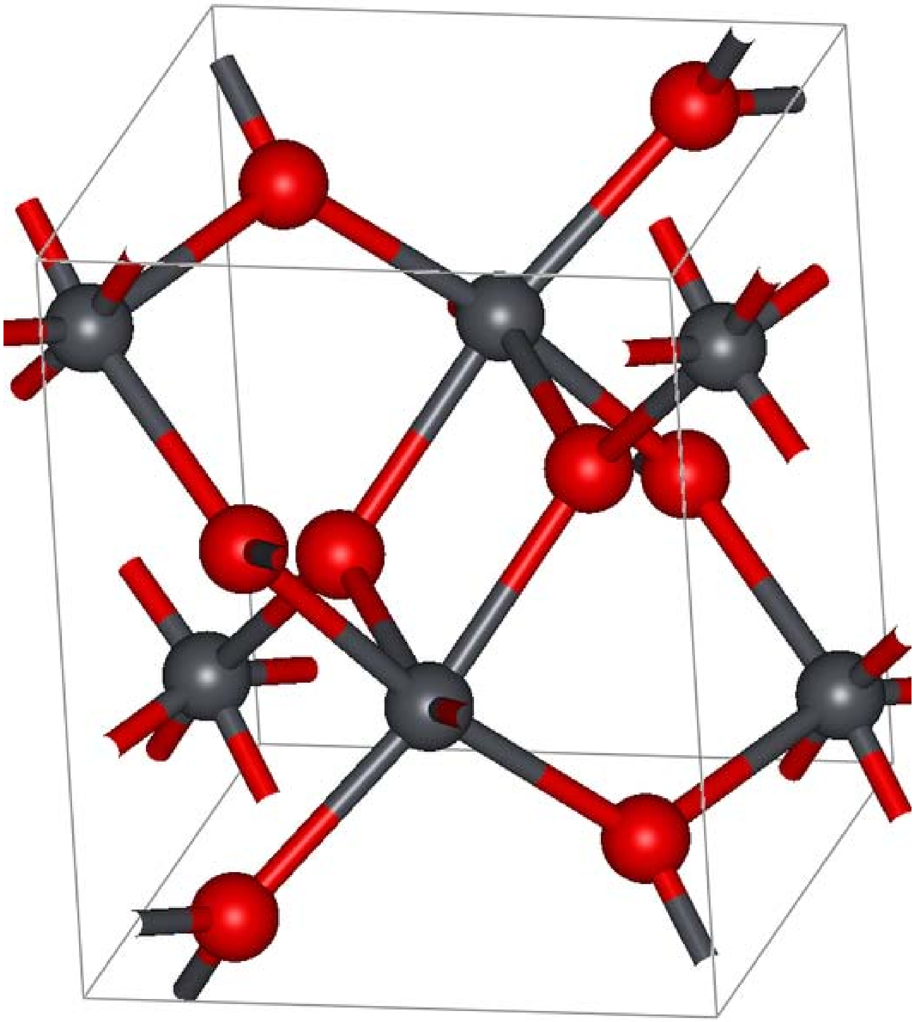
Identifiers	
CAS number	1309-60-0 ✓
UN number	1872
RTECS number	OGO700000
Properties	
Molecular formula	PbO_2
Molar mass	239.2 g/mol
Appearance	black powder
Density	9.38 g/cm^3
Melting point	290 °C decomp.
Solubility in water	insoluble
Hazards	
MSDS	External MSDS
EU Index	082-001-00-6
EU classification	Repr. Cat. 1/3 Harmful (**Xn**) Dangerous for the environment (**N**)
R-phrases	R61, R20/22, R33, R62, R50/53
S-phrases	S53, S45, S60, S61
Flash point	Non-flammable
Related compounds	
Other cations	Carbon dioxide Silicon dioxide Germanium dioxide

	Tin dioxide
Related lead oxides	Lead(II) oxide Lead(II,IV) oxide
Related compounds	Thallium(III) oxide Bismuth(III) oxide

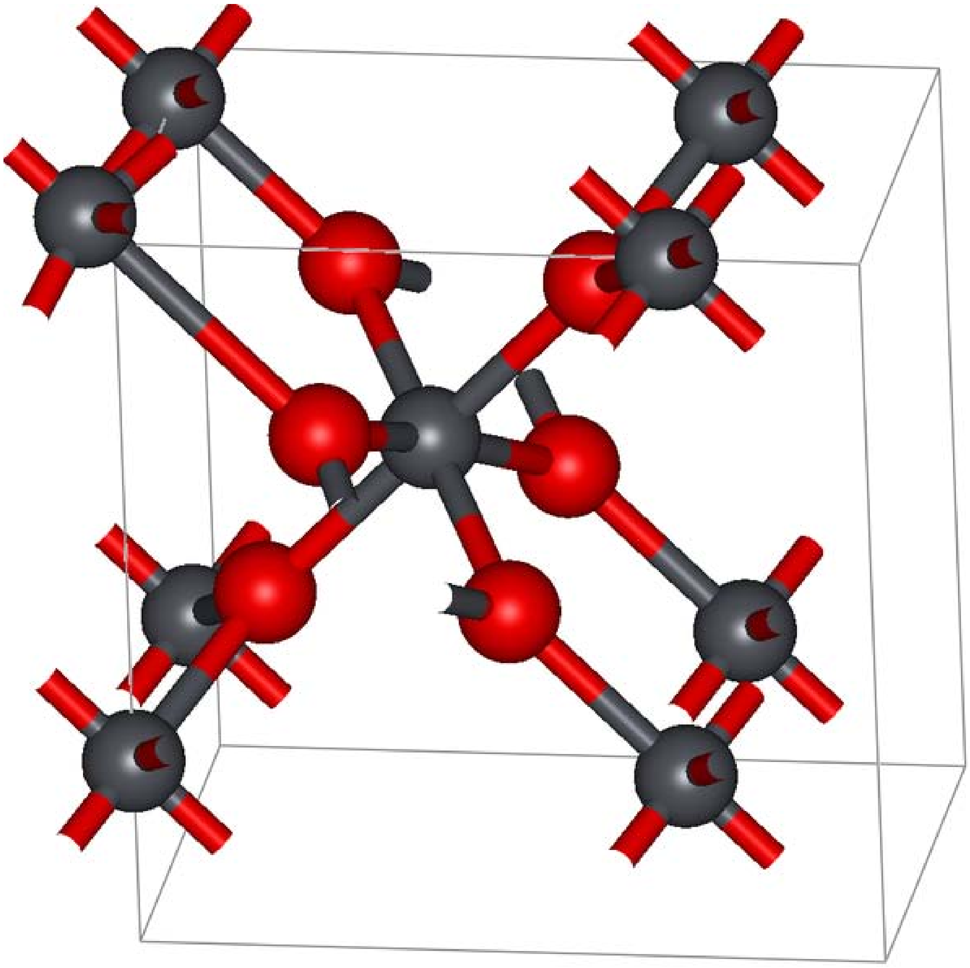
Lead dioxide, PbO_2, also **plumbic oxide** is an oxide of lead in oxidation state +4. It is an odorless dark-brown crystalline powder which is nearly insoluble in water. It exists in two crystalline forms. The alpha phase has orthorhombic symmetry; it has been first synthesized in 1941 and identified in nature as a rare mineral scrutinyite in 1988. On the contrary, the more prevailing, tetragonal beta phase was first identified as the mineral plattnerite around 1845 and later produced synthetically. Lead dioxide is a strong oxidizing agent which is used in the manufacture of matches, pyrotechnics, dyes and other chemicals. It also has several important applications in electrochemistry, in particular as a component of lead acid batteries.

Properties

Physical



Crystal structure of α-PbO_2



Crystal structure of β-PbO_2

Lead dioxide is an odorless dark-brown crystalline powder which is nearly insoluble in water. It has two major polymorphs, alpha and beta, which occur naturally as rare minerals scrutinyite and plattnerite, respectively. Whereas the beta form was known already in 1845, α-PbO_2 was first synthesized in 1941 and identified as a mineral only in 1988. The alpha form has orthorhombic symmetry, space group Pbcn (No. 60), Pearson symbol oP12, lattice constants a = 0.497 nm, b = 0.596 nm, c = 0.544 nm, Z = 4 (four formula units per unit cell). The symmetry of the beta form is tetragonal, space group $P4_2/mnm$ (No. 136), Pearson symbol tP6, lattice constants a = 0.491 nm, c = 0.3385 nm, Z = 2.

Lead dioxide decomposes upon heating in air as follows:

$$PbO_2 \rightarrow Pb_{12}O_{19} \rightarrow Pb_{12}O_{17} \rightarrow Pb_3O_4 \rightarrow PbO$$

The stoichiometry of the end product can be controlled by changing the temperature – for example, in the above reaction, the first step occurs at 290 °C, second at 350 °C, third at 375 °C and fourth at 600 °C. In addition, Pb_2O_3 can be obtained by decomposing PbO_2 at

580–620 °C under oxygen pressure of 1.4 kbar. Therefore, thermal decomposition of lead dioxide is a common industrial way of producing various lead oxides.

Chemical

Lead dioxide is an amphoteric compound with prevalent acidic properties. It dissolves in strong bases to form the hydroxyplumbate ion, $Pb(OH)_6^{2-}$:

$$PbO_2 + 2\ NaOH + 2\ H_2O \rightarrow Na_2[Pb(OH)_6]$$

It also reacts with basic oxides in the melt yielding orthoplumbates $M_4[PbO_4]$.

Because of the instability of its Pb^{4+} cation, lead dioxide reacts with warm acids, converting to the more stable Pb^{2+} state and liberating oxygen:

$$2\ PbO_2 + 2\ H_2SO_4 \rightarrow 2\ PbSO_4 + H_2O + O_2$$
$$2\ PbO_2 + 4\ HNO_3 \rightarrow 2\ Pb(NO_3)_2 + H_2O + O_2$$
$$PbO_2 + 4\ HCl \rightarrow PbCl_2 + 2\ H_2O + Cl_2$$

Lead dioxide is well known for being a good oxidizing agent with example reaction listed below:

$$2\ MnSO_4 + 5\ PbO_2 + 6\ HNO_3 \rightarrow 2\ HMnO_4 + 2\ PbSO_4 + 3\ Pb(NO_3)_2 + 2\ H_2O$$
$$2\ Cr(OH)_3 + 10\ KOH + 3\ PbO_2 \rightarrow 2\ K_2CrO_4 + 3\ K_2PbO_2 + 8\ H_2O$$

Electrochemical

Although the formula of lead dioxide is nominally given as PbO_2, the actual oxygen to lead ratio varies between 1.90 and 1.98 depending on the preparation method. Deficiency of oxygen (or excess of lead) results in the characteristic metallic conductivity of lead dioxide, which can be as low as 10^{-4} Ohm·cm and which is exploited in various electrochemical applications. Like metals, lead dioxide has a characteristic electrode potential, and in electrolytes it can be polarized both anodically and cathodically. Lead dioxide electrodes have a dual action, that is both the lead and oxygen ions take part in the electrochemical reactions.

Production

Lead dioxide is produced commercially by several methods, which include oxidation of Pb_3O_4 in alkaline slurry in a chlorine atmosphere, reaction of lead(II) acetate with calcium chloride, or reacting Pb_3O_4 with dilute nitric acid:

$$Pb_3O_4 + 4\ HNO_3 \rightarrow PbO_2 + 2\ Pb(NO_3)_2 + 2\ H_2O$$

An alternative synthesis method is electrochemical: lead dioxide forms on pure lead, in dilute sulfuric acid, when polarized anodically at electrode potential about +1.5 V at room temperature. This procedure is used for large-scale industrial production of PbO_2 anodes. Lead and copper electrodes are immersed in sulfuric acid flowing at a rate of 5–10 L/min. The electrodeposition is carried out galvanostatically, by applying a current of about 100 A/m^2 for about 30 minutes. The drawback of the lead electrode is its softness, especially compared to the hard and brittle PbO_2 which has a Mohs hardness of 5.5. This mismatch in mechanical properties results in peeling of the coating. Therefore, an alternative method is to use harder substrates, such as titanium, niobium, tantalum or graphite and electrodeposit PbO_2 on them from lead(II) nitrate in static or flowing sulfuric acid. The substrate is usually sand-blasted before the deposition to remove surface oxide and contamination and to increase the surface roughness and adhesion of the coating.

Applications

As a strong oxidizing agent, lead dioxide is widely used in the production of matches, pyrotechnics, dyes and other chemicals. Its another large-scale application is in the curing of sulfide polymers and in high-voltage lightning arresters.

Lead dioxide is used as anode material in electrochemistry. Beta-PbO_2 is more attractive for this purpose than the alpha form because it has relatively low resistivity, good corrosion resistance even in low-pH medium, and a high overvoltage for the evolution of oxygen in sulfuric acid and nitric acid based electrolytes. Lead dioxide can also withstand chlorine evolution in hydrochloric acid. Lead dioxide anodes are inexpensive and were once used instead of conventional platinum and graphite electrodes for regenerating potassium dichromate. They were also applied as oxygen anodes for electroplating copper and zinc in sulfate baths. In organic synthesis, lead dioxide anodes were applied for the production of glyoxylic acid from oxalic acid in a sulfuric acid electrolyte.

The most important use of lead dioxide is as the cathode of lead acid batteries. Its utility arises from the anomalous metallic conductivity of PbO_2. The lead acid battery stores and releases energy by shifting the equilibrium (a comproportionation) between metallic lead, lead dioxide, and lead(II) salts in sulfuric acid.

$$Pb + PbO_2 + 2\ HSO_4^- + 2\ H^+ \rightarrow 2\ PbSO_4 + 2\ H_2O,\ E = +2.05\ V$$

Safety

Being a strong oxidant, lead dioxide is a poison when ingested. The associated symptoms include abdominal pain and spasms, nausea, vomiting and headache. Acute poisoning can lead to muscle weakness, metallic taste, loss of appetite, insomnia, dizziness, with shock, coma and death in extreme cases. The poisoning also results in high lead levels in blood and urine. Contact with skin or eyes results in local irritation and pain.

Lead Tetroxide

Lead tetroxide

IUPAC name
lead(II,IV) oxide

Identifiers	
CAS number	1314-41-6 ✓
ChemSpider	21169908 ✓
Properties	
Molecular formula	Pb_3O_4 $2PbO{\cdot}PbO_2$
Molar mass	685.598 g/mol
Appearance	orange red powder
Density	8.3 g/cm^3
Melting point	500°C
Solubility in water	insoluble
Structure	
Crystal structure	Tetragonal, tP28
Space group	$P4_2$/mbc, No. 135
Hazards	
Main hazards	toxic from lead presence
Flash point	none
Autoignition temperature	none

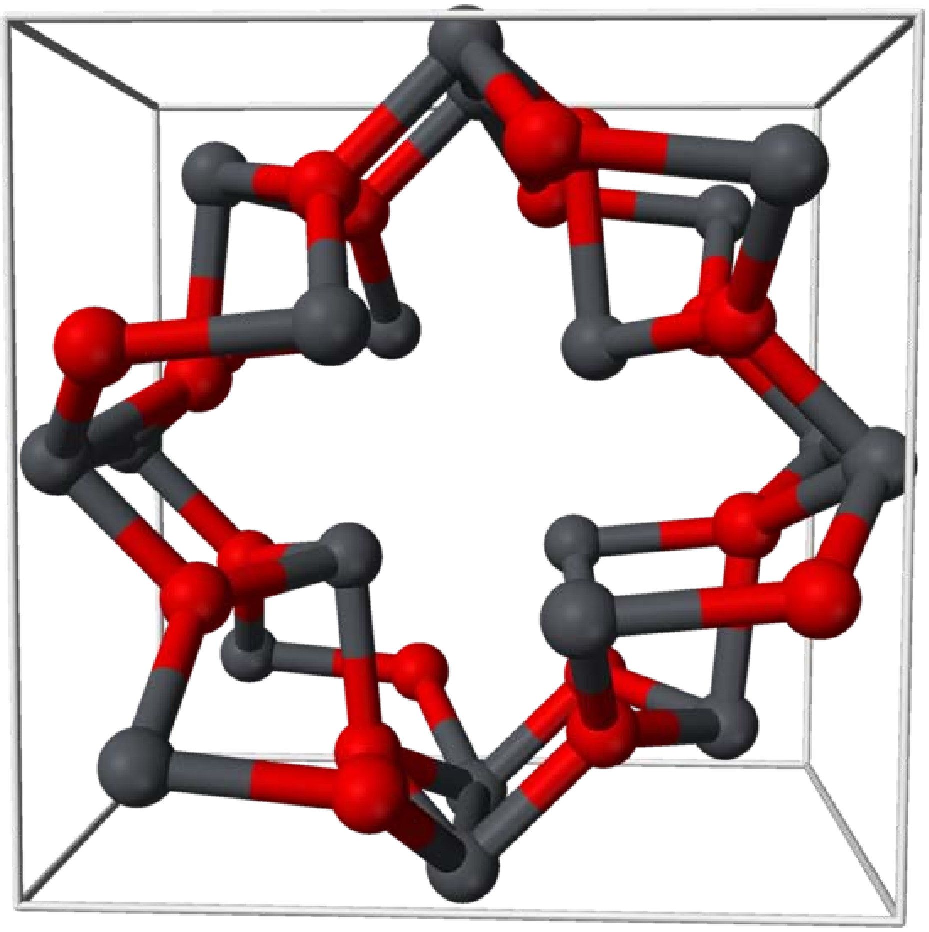
Lead tetroxide, also called **minium**, **red lead** or **triplumbic tetroxide**, is a bright red or orange crystalline or amorphous pigment. Chemically, red lead is lead tetroxide, Pb_3O_4, or $2PbO{\cdot}PbO_2$.

This compound's Latin name *minium* originates from the Minius River in northwest Spain where it was first mined. Natural minium is uncommon, forming only in extreme oxidizing conditions of lead ore bodies. The best specimens known come from Broken Hill, New South Wales, Australia, where they formed as the result of a mine fire.

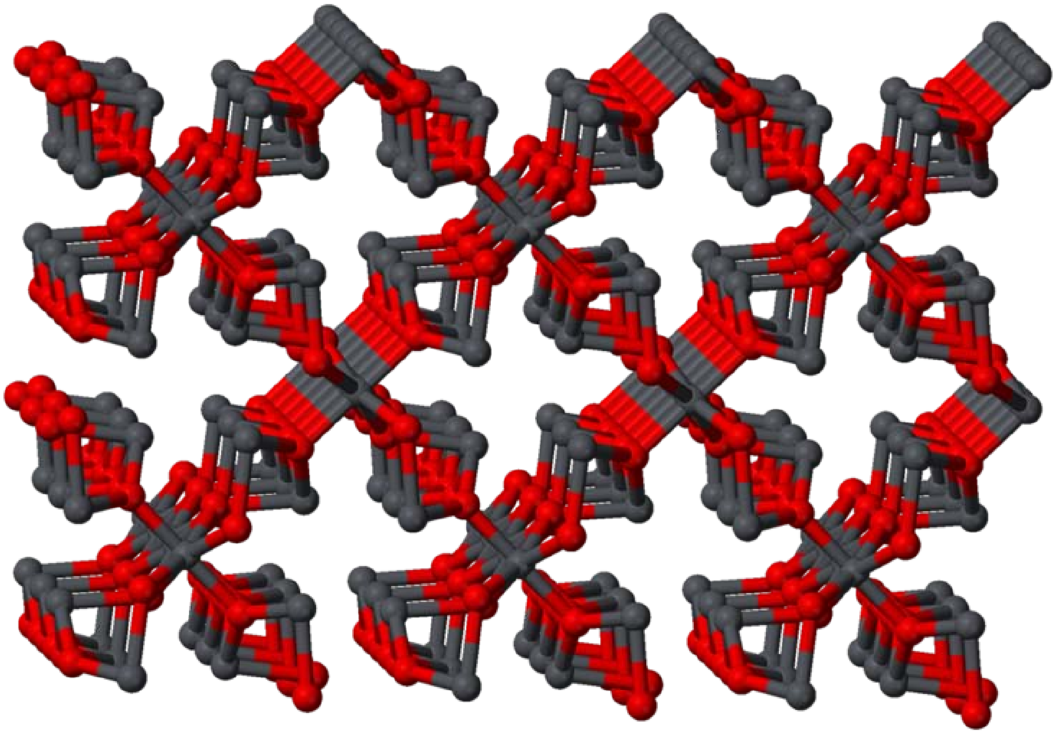
Lead tetroxide is used in the manufacture of batteries, lead glass and rust-proof primer paints.

Structure

Lead tetroxide has a tetragonal crystal structure at room temperature, which transforms to an orthorhombic (Pearson symbol oP28, Space group = Pbam, No 55) form at temperature 170 K. This phase transition only changes the symmetry of the crystal and slightly modifies the interatomic distances and angles.



Unit cell of tetragonal Pb_3O_4



Part of tetragonal red lead's crystal structure

Preparation

Lead tetroxide is prepared by calcination of lead(II) oxide (also called litharge) in air at about 450 to 480 °C:

$$6\ PbO + O_2 \rightarrow 2\ Pb_3O_4$$

The resulting material is contaminated with lead(II) oxide. If a pure compound is desired, PbO can be removed by a potassium hydroxide solution:

$$PbO + KOH + H_2O \rightarrow K[Pb(OH)_3]\ (aq)$$

Another method of preparation relies on annealing of lead carbonate (cerussite) in air:

$$6\ PbCO_3 + O_2 \rightarrow 2\ Pb_3O_4 + 6\ CO_2$$

Yet another method is oxidative annealing of white lead:

$$3\ Pb_2CO_3(OH)_2 + O_2 \rightarrow 2\ Pb_3O_4 + 3\ CO_2 + 3\ H_2O$$

In solution, lead tetroxide can be prepared e.g. by reaction of potassium plumbate with lead acetate, yielding yellow insoluble lead tetroxide monohydrate, $Pb_3O_4·H_2O$, which can be turned into the anhydrous form by gentle heating:

$$K_2PbO_3 + 2\ Pb(OCOCH_3)_2 + H_2O \rightarrow Pb_3O_4 + 2\ KOCOCH_3 + 2\ CH_3COOH$$

Reactions

Red lead is virtually insoluble in water and in alcohol. However, it is soluble in hydrochloric acid present in the stomach, and is therefore toxic when ingested. It also dissolves in glacial acetic acid and a diluted mixture of nitric acid and hydrogen peroxide.

When heated to 500 °C, it decomposes to lead(II) oxide and oxygen. At 580 °C, the reaction is complete.

$$2\ Pb_3O_4 \rightarrow 6\ PbO + O_2$$

Nitric acid dissolves the lead(II) oxide component, leaving behind the insoluble lead(IV) oxide:

$$Pb_3O_4 + 4\ HNO_3 \rightarrow PbO_2 + 2\ Pb(NO_3)_2 + 2\ H_2O$$

With iron oxides and with elemental iron, lead tetroxide forms insoluble iron(II) and iron(III) plumbates, which is the basis of the anti-corrosive properties of lead-based paints applied to iron objects.

Use

Lead tetroxide is most often used as a pigment for primer paints for iron objects. Due to its toxicity, its use is being limited. In the past, it was used in combination with linseed oil as a thick, long-lasting anti-corrosive paint. The combination of minium and linen fibres was also used for plumbing, now replaced with PTFE tape. Currently it is mostly used for manufacture of glass, especially lead glass. It finds limited use in some amateur pyrotechnics as a relatively potent oxidizer.

Red lead was also used for engineer's scraping, before being supplanted by Engineer's blue.

Physiological effects

When inhaled, lead tetroxide irritates lungs. In case of high dose, the victim experiences a metallic taste, chest pain, and abdominal pain. When ingested, it is dissolved in the gastric acid and absorbed, leading to lead poisoning. High concentrations can be absorbed through skin as well, and it is important to follow safety precautions when working with lead-based paint.

Long-term contact with lead tetroxide may lead to accumulation of lead compounds in organisms, with development of symptoms of acute lead poisoning. Chronic poisoning displays as agitation, irritability, vision disorders, hypertension, and also a grayish facial hue.

Lead tetroxide was shown to be carcinogenic for laboratory animals. Its carcinogenicity for humans was not proven.

Minium from a mine fire at Broken Hill, Australia

History

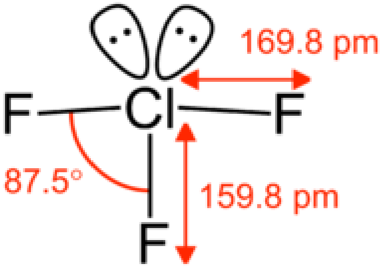
Lead tetroxide was used as a red pigment in ancient Rome, where it was prepared by calcination of white lead. In the ancient and medieval periods it was used as a pigment in the production of illuminated manuscripts, and gave its name to the *minium* or miniature, a style of picture painted with the colour. As a finely divided powder, it was also sprinkled on dielectric surfaces to study Lichtenberg figures. It was first isolated as a pure compound by Arabic chemists and was clearly described by Muhammad ibn Zakarīya Rāzi (Rhazes) in the early 10th century.

Chapter 8

Rocket Oxidizers

Chlorine Trifluoride

Chlorine trifluoride



Identifiers	
CAS number	7790-91-2 ✓
PubChem	24637
ChemSpider	23039 ✓
UN number	1749
RTECS number	FO2800000
Properties	
Molecular formula	ClF_3
Molar mass	92.448 g/mol

Appearance	yellowish gas or liquid
Density	1.77 g/cm^3 (13 °C, liquid) 0.004 g/cm^3 (gas)
Melting point	−76.34 °C
Boiling point	11.75 °C
Solubility in water	hydrolysis
Viscosity	9.182 x 10^{-5} Pa s
Structure	
Molecular shape	T-shaped
Thermochemistry	
Std enthalpy of formation $\Delta_f H^\circ_{298}$	−158.87 kJ/mol
Standard molar entropy S°_{298}	281.59 J K^{-1} mol^{-1}
Hazards	
MSDS	ICSC 0656
EU Index	Not listed
Main hazards	Toxic, corrosive, oxidizer.
Related compounds	
Related compounds	Chlorine pentafluoride Chlorine monofluoride Bromine trifluoride

Chlorine trifluoride is the chemical compound with the formula ClF_3. This colourless, poisonous, corrosive and very reactive gas condenses to a pale-greenish yellow liquid, the form in which it is most often sold (pressurized at room temperature). The compound is primarily of interest as a component in rocket fuels, in industrial cleaning and etching operations in the semiconductor industry, in nuclear reactor fuel processing, and other industrial operations.

Preparation, structure, and properties

It was first reported by Ruff and Krug who prepared it by fluorination of chlorine; this also produced ClF and the mixture was separated by distillation.

$$3 F_2 + Cl_2 \rightarrow 2 ClF_3$$

ClF_3 is approximately T-shaped, with one short bond (1.598 Å) and two long bonds (1.698 Å). This structure agrees with the prediction of VSEPR theory, which predicts lone pairs of electrons as occupying two equatorial positions of a hypothetic trigonal bipyramid. The elongated $Cl\text{-}F_{axial}$ bonds are consistent with hypervalent bonding.

Pure ClF_3 is stable to 180° in glass vessels; above this temperature it decomposes by a free radical mechanism to the elements.

The main use of ClF_3 is to produce uranium hexafluoride, UF_6, as part of nuclear fuel processing and reprocessing, by the reaction:

$U + 3\ ClF_3 \rightarrow UF_6 + 3\ ClF$

Hazards

ClF_3 is a very strong oxidizing and fluorination agent. It is extremely reactive with most inorganic and organic materials, even plastics, and will initiate the combustion of many materials without an ignition source. These reactions are often violent, and in some cases explosive. Reaction with several metals give chlorides and fluorides; phosphorus yields PCl_3 and PF_5; and sulfur yields SCl_2 and SF_4. ClF_3 is also violently reactive with water, in which it hydrolyses to a variety of hazardous chemicals such as hydrofluoric acid. H_2S explodes on being mixed with ClF_3 at room temperature.

The ability to surpass the oxidizing ability of oxygen leads to corrosivity against oxide-containing materials often thought as incombustible. In an industrial accident, a spill of 900 kg of chlorine trifluoride burned itself through 30 cm of concrete and 90 cm of gravel beneath. Any equipment that comes into contact with chlorine trifluoride must be carefully selected and cleaned, because any contamination can ignite on contact. In addition, most general-purpose fire control/suppression hardware (Class A/B/C/K) is either incapable of suppressing this oxidation or can aggravate it; chlorine trifluoride has been reported to burn sand, asbestos, and other highly fire-retardant materials, reacts violently with water-based suppressors, and oxidizes in the absence of atmospheric oxygen, rendering atmosphere-displacement suppressors such as Halon and CO_2 ineffective. It ignites glass on prolonged contact.

Exposure of larger amounts of chlorine trifluoride, as a liquid or as a gas, ignites tissue. The hydrolysis reaction with water is violent and exposure results in a thermal burn. The product of hydrolysis is mainly hydrofluoric acid and hydrochloric acid, usually released as steam or vapor due to the highly exothermic nature of the reaction. Hydrofluoric acid is corrosive to human tissue, absorbs through skin, selectively attacks bone and stimulates pain nerves, and causes a potentially lethal poisoning. Hydrochloric acid is secondary in its danger to living organisms, but is more corrosive to most inorganic materials than hydrofluoric acid.

Military applications

Under the code name **N-stoff** ("substance N"), chlorine trifluoride was investigated for military applications by the Kaiser Wilhelm Institute in Nazi Germany from slightly before the start of World War II. Tests were made against mock-ups of the Maginot Line fortifications, and it was found to be an effective combined incendiary weapon and poison gas. From 1938 construction commenced on a partly bunkered, partly subterranean 31.76 km² munitions factory at Falkenhagen which was intended to produce 50 tonnes of N-stoff per month, plus Sarin. However, by the time it was captured by the advancing Red Army in 1944, the factory had produced only about 30 to 50 tonnes, at a cost of over 100 German Reichsmark per kilogram[a]. N-stoff was never used in war.

Rocket propellant

Chlorine trifluoride has been investigated as a high-performance storable oxidizer in rocket propellant systems. Handling concerns, however, prevented its use. Clark summarized the difficulties:

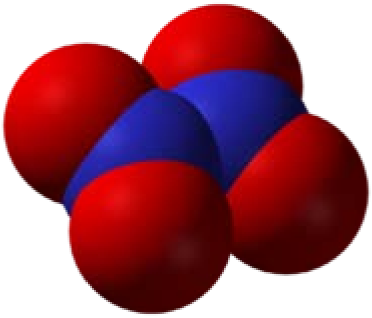
It is, of course, extremely toxic, but that's the least of the problem. It is hypergolic with every known fuel, and so rapidly hypergolic that no ignition delay has ever been measured. It is also hypergolic with such things as cloth, wood, and test engineers, not to mention asbestos, sand, and water — with which it reacts explosively. It can be kept in some of the ordinary structural metals — steel, copper, aluminium, etc. — because of the formation of a thin film of insoluble metal fluoride which protects the bulk of the metal, just as the invisible coat of oxide on aluminium keeps it from burning up in the atmosphere. If, however, this coat is melted or scrubbed off, and has no chance to reform, the operator is confronted with the problem of coping with a metal-fluorine fire. For dealing with this situation, I have always recommended a good pair of running shoes."

Semiconductor industry

In the semiconductor industry chlorine trifluoride is used to clean chemical vapour deposition chambers. It has the advantage that it can be used to remove semiconductor material from the chamber walls without having to dismantle the chamber. Unlike most of the alternative chemicals used in this role it does not need to be activated by the use of plasma since the heat of the chamber is enough to make it decompose and react with the semiconductor material.

Dinitrogen Tetroxide

Dinitrogen tetroxide



IUPAC name
Dinitrogen tetraoxide

Identifiers	
CAS number	10544-72-6 ✓
PubChem	25352
ChemSpider	23681 ✓
EC number	234-126-4
UN number	1067
RTECS number	QW9800000
Properties	
Molecular formula	N_2O_4
Molar mass	92.011 g/mol
Appearance	colourless gas
Density	1.443 g/cm^3 (liquid, 21 °C)
Melting point	−11.2 °C (261.9 K)
Boiling point	21.1 °C (294.3 K)
Solubility in water	reacts
Vapor pressure	96 kPa (20 °C)
Refractive index (n_D)	1.00112
Structure	
Molecular shape	planar, D_{2h}
Dipole moment	zero
Thermochemistry	
Std enthalpy of formation $\Delta_f H^\circ_{298}$	9.16 kJ/mol
Standard molar entropy S°_{298}	150.38 J K^{-1} mol^{-1}
Hazards	
MSDS	External MSDS
EU Index	007-002-00-0
EU classification	Very toxic (**T+**) Corrosive (**C**)
R-phrases	R26, R34
S-phrases	(S1/2), S9, S26, S28, S36/37/39, S45

Flash point	Non-flammable
Related compounds	
Related nitrogen oxides	Nitrous oxide Nitric oxide Dinitrogen trioxide Nitrogen dioxide Dinitrogen pentoxide

Dinitrogen tetroxide (**nitrogen tetroxide** or **nitrogen peroxide**) is the chemical compound N_2O_4. It forms an equilibrium mixture with nitrogen dioxide; some call this mixture dinitrogen tetroxide, while some call it nitrogen dioxide. Dinitrogen tetroxide is a powerful oxidizer, highly toxic and corrosive. N_2O_4 is hypergolic with various forms of hydrazine, i.e., they burn on contact without a separate ignition source, making them popular bipropellant rocket fuels. It is a useful reagent in chemical synthesis.

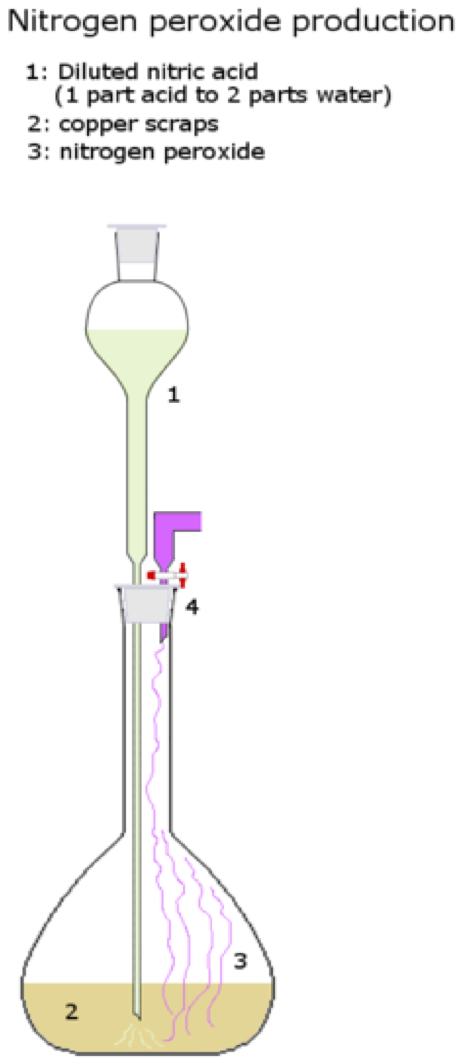
Structure and properties

Dinitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide. The molecule is planar with an N-N bond distance of 1.78 Å and N-O distances of 1.19 Å. Unlike NO_2, N_2O_4 is diamagnetic. It is also colorless but can appear as a brownish yellow liquid due to the presence of NO_2 according to the following equilibrium:

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

Higher temperatures push the equilibrium towards nitrogen dioxide. Inevitably, some dinitrogen tetroxide is a component of smog containing nitrogen dioxide.

Production



Nitrogen peroxide production

Nitrogen dioxide is made by the catalytic oxidation of ammonia: steam is used as a diluent to reduce the combustion temperature. Most of the water is condensed out, and the gases are further cooled; the nitric oxide that was produced is oxidized to nitrogen dioxide, and the remainder of the water is removed as nitric acid. The gas is essentially pure nitrogen tetroxide, which is condensed in a brine-cooled liquefier.

Use as a rocket propellant

Dinitrogen tetroxide is one of the most important rocket propellants ever developed, much like the German developed hydrogen peroxide-based T-Stoff oxidizer used in their World War II rocket propelled combat aircraft designs such as the Messerschmitt Me 163 *Komet*, and by the late 1950s it became the storable oxidizer of choice for rockets in both the USA and USSR. It is a hypergolic propellant often used in combination with a hydrazine-based rocket fuel. One of the earliest uses of this combination was on the Titan rockets used originally as ICBMs and then as launch vehicles for many spacecraft. Used on the U.S. Gemini and Apollo spacecraft, it continues to be used on the Space Shuttle, most geo-stationary satellites, and many deep-space probes. It now seems likely that NASA will continue to use this oxidizer in the next-generation 'crew-vehicles' which will replace the shuttle. It is also the primary oxidizer for Russia's Proton rocket and China's Long March rockets.

When used as a propellant, dinitrogen tetroxide is usually referred to simply as 'Nitrogen Tetroxide' and the abbreviation 'NTO' is extensively used. Additionally, NTO is often used with the addition of a small percentage of nitric oxide, which inhibits stress-corrosion cracking of titanium alloys, and in this form, propellant-grade NTO is referred to as "Mixed Oxides of Nitrogen" or "MON". Most spacecraft now use MON instead of NTO; for example, the Space Shuttle reaction control system uses MON3 (NTO containing 3wt%NO).

On 24 July 1975, NTO poisoning nearly killed the three U.S. astronauts on board the Apollo-Soyuz Test Project during its final descent. This was due to a switch left in the wrong position, which allowed NTO fumes to vent out of the Apollo spacecraft then back in through the cabin air intake from the outside air after the external vents were opened. One crewmember lost consciousness during descent. Upon landing, the crew was hospitalized 14 days for chemical-induced pneumonia and edema.

Power generation using N_2O_4

The tendency of N_2O_4 to reversibly break into NO_2 has led to research into its use in advanced power generation systems as a so-called dissociating gas. "Cool" nitrogen tetroxide is compressed and heated, causing it to dissociate into nitrogen dioxide at half the molecular weight. This hot nitrogen dioxide is expanded through a turbine, cooling it and lowering the pressure, and then cooled further in a heat sink, causing it to recombine into nitrogen tetroxide at the original molecular weight. It is then much easier to compress to start the entire cycle again. Such dissociative gas Brayton cycles have the potential to considerably increase efficiencies of power conversion equipment.

Chemical reactions

Intermediate in the manufacture of nitric acid

Nitric acid is manufactured on a large scale via N_2O_4. This species reacts with water to give both nitrous acid and nitric acid:

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3$$

The coproduct HNO_2 upon heating disproportionates to NO and more nitric acid. When exposed to oxygen, NO is converted back into nitrogen dioxide:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

The resulting NO_2 (and N_2O_4, obviously) can be returned to the cycle to give the mixture of nitrous and nitric acids again.

Synthesis of metal nitrates

N_2O_4 behaves as the salt $[NO^+][NO_3^-]$, the former being a strong oxidant:

$$2\ N_2O_4 + M \rightarrow 2\ NO + M(NO_3)_2$$

where M = Cu, Zn, or Sn.

If metal nitrates are prepared from NTO in completely anhydrous conditions, a range of covalent metal nitrates can be formed with many transition metals. This is because there is a thermodynamic prefence for the nitrate ion to bond covalently with such metals rather than form an ionic structure. Such compounds must be prepared in anydrous conditions since the nitrate ion is a much weaker ligand than water and if water is present the simple hydrated nitrate will form. The anydrous nitrates concerned are themselves covalent and many, e.g. anhydrous copper nitrate, are volatile at room temperature. Anydrous titanium nitrate sublimes in vacuum at only 40 degrees C. Many of the anhydrous transition metal nitrates have striking colours. This branch of chemistry was developed by Clifford Addisson and Noramn Logan at Nottingham University in the UK during the 1960s and 1970s when highly efficient desiccants and dry boxes started to become available.