Pyrotechnic Compositions

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Chapter 1

Pyrotechnic Composition

A **pyrotechnic composition** is a substance or mixture of substances designed to produce an effect by heat, light, sound, gas or smoke or a combination of these, as a result of non-detonative self-sustaining exothermic chemical reactions. Pyrotechnic substances do not rely on oxygen from external sources to sustain the reaction.

Basic types of pyrotechnic compositions are:

- flash powder – burns very fast, produces explosions and/or bright flashes of light
- gunpowder – burns slower than flash powder, produces large amount of gases
- solid propellants – produce large amount of hot gases, used as sources of kinetic energy for rockets and projectiles
- pyrotechnic initiators – produce large amount of heat, flames, and/or hot sparks, used to ignite other compositions
- gas generators – produce large amount of gas, either high volume at short time (for actuators and ejection charges, often using solid propellants) or controlled flow rate (e.g. chemical oxygen generators, often using thermite-like compositions)
- ejection charges – burn fast, produce large amount of gas at short time, used to eject payloads from containers
- burst charges – burn fast, produce large amount of gas at short time, used to fragment a container and eject its content
- smoke compositions – burn slowly, produce smoke, plain or colored
- delay compositions – burn at constant slow speed, used to introduce delays into the firing train
- pyrotechnic heat sources – produce large amount of heat and little to no gases, slow-burning, often thermite-like compositions
- sparklers – producing white or colored sparks
- flares – burn slowly, produce high amount of light, used for illumination or signaling
- coloured fireworks compositions – produce light, white or colored

Some pyrotechnic compositions are used in industry and aerospace for generation of large volumes of gas in gas generators (e.g. in airbags), in pyrotechnic fasteners, and in other similar applications. They are also used in military pyrotechnics, when production of large amount of noise, light, or infrared radiation is required; eg. missile decoy flares, flash powders, and stun grenades. A new class of reactive material compositions is now under investigation by military.

Many pyrotechnic compositions – especially involving aluminium and perchlorates – are often highly sensitive to friction, impact, and static electricity. Even as little as 0.1–10 millijoules spark can set off certain mixtures.

Materials used

Pyrotechnic compositions are usually homogenized mixtures of small particles of fuels and oxidizers. The particles can be grains or flakes. Generally, the higher the surface area of the particles, the higher the reaction rate and burning speed. For some purposes, binders are used to turn the powder into a solid material.

Fuels

Typical fuels are based on metal or metalloid powders. A flash powder composition may specify multiple different fuels. Some fuels can also serve as binders. Common fuels include:

- Metals
    - Aluminium – most common fuel in many classes of mixtures, also a combustion instability suppressant. Less energy per mass than carbon but less gas evolution, retaining heat in the reaction mixture. High-temperature flame with solid particles, which interfere with flame colorants. Reacts with nitrates, except ammonium nitrate, yielding nitrogen oxides, ammonia, and heat (the reaction is slow at room temperature but violent at above 80 °C and may spontaneously ignite); the reaction can be inhibited by a weak acid, e.g. boric acid. Corroded by alkaline substances. Flake particles easier to ignite and better for pyrotechnics than spherical ones. In presence of moisture reacts with potassium chlorate and perchlorate, yielding hydrogen. Particle size selected according to the required burn rate.
    - Magnesium – more sensitive and violent than aluminium, increases probability of spontaneous ignition in storage. Used in fireworks to increase flame temperature. Less interference with flame color than aluminium.
    - Magnalium – aluminium-magnesium alloy, more stable and less expensive than magnesium; less reactive than magnesium, easier to ignite than aluminium
    - Iron – makes gold sparks, frequently used
    - Steel – an alloy of iron and carbon, makes branching yellow-orange sparks

  - Zirconium – produces hot particles, good for ignition mixtures, eg. the *NASA Standard Initiator*, also a combustion instability suppressant
  - Titanium – produces hot particles, increases sensitivity to impact and friction; sometimes the Ti4Al6V alloy is used which gives a bit brighter white sparks; together with potassium perchlorate it is used in some pyrotechnic igniters; coarse powder produces beautiful branching blue-white sparks
  - Ferrotitanium – iron-titanium alloy, produces bright yellow-white sparks, used in pyrotechnic stars, rockets, comets, and fountains
  - Ferrosilicon – iron-silicon alloy, used in some mixtures, sometimes replacement of calcium silicide
  - Manganese – used to control burn rates, e.g. in delay compositions
  - Zinc – used in some smoke compositions, together with sulfur used in some early amateur rocket fuels, also in pyrotechnic stars; heavy, zinc-based compositions may require additional lift to fly high enough; moisture-sensitive; can spontaneoulsy ignite; rarely used as primary fuel except in smoke compositions, can be encountered as a secondary enhancement fuel
  - Copper – used as a blue colorant with other fuels
  - Brass – a zinc-copper alloy used in some fireworks formulas, as a blue colorant for its copper content
  - Tungsten – used to control and slow down burn rates of compositions, also in delay compositions
  - Zirconium-nickel alloy – used in some military delay compositions
- Metal hydrides (lower heat of combustion than pure metals, but increased sensitivity/reactivity to water):
  - Titanium(II) hydride – together with potassium perchlorate it is used in some igniters
  - Zirconium(II) hydride – together with potassium perchlorate it is used in some igniters
  - Aluminum hydride – unstable for storage (decomposes easily with humidity) and reacts dangerously in contact with water
  - Decaborane – experimented with for some rocket fuels
- Metal carbides
  - Zirconium carbide – used in some rocket fuels, also a combustion instability suppressant
- Metalloids
  - Silicon – high flame temperature, burns producing molten glass, used in some ignition compositions and delay charges, commonly with lead tetroxide
  - Boron – used in some ignition mixtures
  - Antimony – used in some fireworks for glitter effects, toxic, burns bright white; usually used as 200–300 mesh; with potassium nitrate and sulfur produces white fires
- Non-metallic inorganic

    - Sulfur – ignition promoter, increases burn rate; increases sensitivity to temperature, impact and friction, dangerous in combination with chlorates; commonly used with nitrates; used as an additive; may contain residual acids, combination with carbonates or other alkaline stabilizers is advised in acid-sensitive compositions
    - Red phosphorus – extremely dangerous, especially in combination with chlorates (Armstrong's mixture); used in caps; also used in matches and some military infrared flares; toxic
    - White phosphorus – used in incendiary weapons and to make some military smoke screens, ignites spontaneously in air; even more toxic
    - Calcium silicide – used in some special compositions
    - Antimony trisulfide – ignition promoter; fine powder increases sensitivity, sharpens the boom of salutes; toxic and sensitive to static electricity; emits bright white light, crystals also used as a fuel in glitter compositions and in white comets and pyrotechnic stars. Sensitive to friction and impact; the degree of sensitisation depends on the oxidizer (sensitive to friction and impact with potassium chlorate, friction with potassium perchlorate, impact with ammonium perchlorate, and insensitive to either with potassium nitrate).
    - Arsenic sulfide (realgar) – toxic, sensitive to impact and friction. Used for report compositions due to its sensitivity with chlorate even in small amounts. Used in yellow smoke compositions due to its low boiling point.
    - Phosphorus trisulfide – used to make matches
    - Calcium phosphide – liberates phosphine when wet, used in some naval signal flares
    - Potassium thiocyanate
- Carbon-based
    - Carbon
        - Charcoal – makes dim gold sparks
        - Graphite – also used as opacifier in rocket fuels to prevent heat transfer by radiation into lower layers of fuels and avoid the related explosions
        - Carbon black – produces long lasting fine gold sparks in fireworks, also used as opacifier in rocket fuels
    - Asphaltum – carbon-based fuel, also used as a binder. Some forms contain ammonia; should not be combined with chlorates.
    - Wood flour
- Organic chemicals
    - Sodium benzoate – often used in whistle mixes together with potassium perchlorate
    - Sodium salicylate – used in some whistle mixes
    - Gallic acid – used in some whistle mixes; sensitive to impact and friction, there are safer alternatives
    - Potassium picrate – used in some whistle compositions, safer than gallic acid but still dangerous, with heavy metals (e.g. lead) forms explosive salts

    - Terephthalic acid – a fuel in some smoke compositions
    - Hexamine – a low-reactivity, accessory fuel
    - Anthracene – a fuel in some smoke compositions, produces black smoke
    - Naphthalene – a fuel in some smoke compositions
    - Lactose – used together with potassium chlorate in many smoke compositions; cheap low-reactivity accessory fuel
    - Dextrose – used in some amateur solid rocket fuels
    - Sucrose – used in some smoke compositions
    - Sorbitol – used together with potassium nitrate as an amateur solid rocket fuel
    - Dextrin – also a binder
    - Stearin, stearic acid – accessory fuel, a possible replacement for charcoal and/or sulfur in some compositions; lengthens flames, can reduce friction sensitivity; phlegmatizing agent
    - Hexachloroethane – used in many military smoke compositions
- Organic polymers and resins, also sometimes serving as binders
    - Teflon, Viton and other fluoropolymers – sometimes also working as oxidizer – used in military pyrolant compositions, eg. Magnesium/Teflon/Viton; extremely reactive in contact with some fine metal powders
    - Hydroxyl-terminated polybutadiene (HTPB), used together with aluminium and ammonium nitrate in composite rocket fuels as a fuel and binder
    - Carboxyl-terminated polybutadiene (CTPB), used in composite rocket fuels as a fuel and binder
    - PBAN, used together with aluminium and ammonium nitrate in composite rocket fuels as a fuel and binder
    - Polysulfide, used in composite rocket fuels as a fuel and binder
    - Polyurethane, used in composite rocket fuels as a fuel and binder
    - Polyisobutylene
    - Nitrocellulose
    - Polyethylene
    - Polyvinyl chloride, also serving as chlorine donor and a binder
    - Polyvinylidene chloride, also serving as chlorine donor
    - Shellac, good especially for colored flame compositions
    - Accroides resin (red gum), higher burning rate than shellac, burns well even with potassium perchlorate. Suitable for chrysanthemum stars.

When metallic fuels are used, the metal particle size is important. A larger surface area to volume ratio leads to a faster reaction; this means that smaller particle sizes produce a faster-burning composition. The shape also matters. Spherical particles, like those produced by atomizing molten metal, are undesirable. Thin and flat particles, like those produced by milling metal foil, have higher reaction surface and therefore are ideal when faster reaction is desired. Using nanoparticles can drastically affect the reaction rates; metastable intermolecular composites exploit this.

A suitable metal fuel may be dangerous on its own, even before it is mixed with an oxidizer. Careful handling is required to avoid the production of pyrophoric metal powders.

Oxidizers

Perchlorates, chlorates and nitrates are the most commonly used oxidizers for flash powders. Other possibilities include permanganates, chromates, and some oxides. Generally, the less the oxidizer, the slower the burning and the more light produced. For use at very high temperatures, sulfates can be used as oxidizers in combination with very strongly reducing fuels.

Oxidizers in use include:

- Perchlorates (also serving as chlorine donors):
    - Potassium perchlorate – common, relatively stable. Almost non-hygroscopic. Low solubility in water. Produces high temperature flame and smoke of potassium chloride. Safer replacement of potassium chlorate. Impact-sensitive with phosphorus,
    - Ammonium perchlorate – the most common oxidizer for modern solid rocket fuels; more sensitive to mechanical stimuli than potassium perchlorate. Uncommon in fireworks; creates hot flame, enhances barium, strontium and copper colorants by acting as a chlorine donor. Reacts with magnesium when wet and liberates heat and ammonia, can self-ignite. In contact with potassium nitrate (e.g. in black powder) produces potassium perchlorate and hygroscopic ammonium nitrate; no such reaction with sodium nitrate. Reacts with potassium chlorate, producing unstable, gradually decomposing ammonium chlorate; such combination has to be avoided.
    - Nitronium perchlorate
- Chlorates (also serving as chlorine donors, incompatible with ammonium salts because of forming unstable explosive ammonium chlorate, incompatible with sulfur and other acidic chemicals because of production of spontaneously igniting chlorine dioxide; very dangerous with phosphorus; should not be combined with hydrocarbon fuels/binders, e.g. asphalt or gum arabic; should be replaced with safer perchlorates wherever possible):
    - Potassium chlorate – much less stable than perchlorate, hazardous, avoid if possible. High burning speed, easy ignition. Slightly more hygroscopic than potassium nitrate. Produces smoke of potassium chloride. Can act as a chlorine donor. High impact and friction sensitivity with sulfur and sulfides. With ammonium salts produces unstable ammonium chlorate. Used in match head compositions, some colored smokes, and small firecrackers and toy caps.
    - Barium chlorate – also serves as a green colorant in fireworks; sensitive, better to avoid. Almost non-hygroscopic. Compositions may

    spontaneously combust in sunlight. Very good green colorant, even in lower-temperature flames.
  - Sodium chlorate – much less stable than perchlorate, hazardous, also serves as yellow colorant, hygroscopic
- Nitrates (when mixing with aluminium, boric acid should be added as a stabilizer):
  - Potassium nitrate – very common, used in black powder and wide variety of compositions. Not very hygroscopic. At lower temperatures (with ordinary fuels like rosin or shellac) not very efficient, does not burn well, produces potassium nitrite. At higher temperatures, with charcoal and sulfur or with magnesium, decomposes well. Does not produce sufficient temperature to make colored flames, except when magnesium is added. Makes good sparks. Presence in dust makes the dust hazardous and very flammable.
  - Sodium nitrate – also a yellow colorant, hygroscopic. Gives intense yellow light, used for illumination compositions. Presence in dust makes the dust hazardous. At lower temperatures produces nitrite ash, at higher temperatures decomposes completely.
  - Calcium nitrate – also a red-orange colorant, enhances other colors
  - Ammonium nitrate – used in some less common composite rocket propellants, hygroscopic, decomposes at too low temperature; when dry reacts with Al, Zn, Pb, Sb, Bi, Ni, Cu, Ag, Cd; when wet reacts also with Fe. Forms an explosive compound with copper.
  - Barium nitrate – most common oxidizer/colorant for green and white colors, but with somewhat weak colorant effect;requires a chlorine donor. Also used in flash powders and some military infrared flares. Barium also serves as a stabilizer for the mixtures; decomposes at higher temperatures than nitrates of lighter metals and promotes higher burning temperatures. With aluminium produces bright silver sparks; when used with aluminium, addition of boric acid as stabilizer is advised. Not very hygroscopic.
  - Strontium nitrate – most common oxidizer/colorant for red colors in flares, fires, and stars; strontium also serves as a stabilizer for the mixtures. At lower temperatures (with organic fuels) produces strontium nitrite ash which can smother the flame; decomposes completely at higher temperatures (with magnesium). Colorant for low-temperature flames, colorant and oxidizer for hot flames.
  - Caesium nitrate – used in some military infrared flare compositions
- Permanganates:
  - Potassium permanganate – used in early mixtures, now considered to be sensitive and unstable
  - Ammonium permanganate – a moderately powerful explosive
- Chromates:
  - Barium chromate – used in delay compositions, e.g. in fireworks rockets
  - Lead chromate – used in delay compositions

  - Potassium dichromate – used infrequently as an oxidizer; can be used as a surface treatment for passivation of magnesium particles, also as a catalyst and in some matches; potassium perchlorate often added
- Oxides and peroxides:
  - Barium peroxide – unstable, spontaneously decomposes, compositions containing it should not be stored
  - Strontium peroxide
  - Lead tetroxide – versatile but toxic
  - Lead dioxide – used in friction-sensitive compositions, eg. matches
  - Bismuth trioxide – used as a safe alternative to lead tetroxide in some compositions
  - Iron(III) oxide – a high temperature oxidizer, a catalyst
  - Iron(II,III) oxide – an oxidizer in Thermite and Thermate
  - Manganese(IV) oxide – an oxidizer in manganese thermite, a catalyst
  - Chromium(III) oxide – an oxidizer in chromium thermite
  - Tin(IV) oxide – an oxidizer in some delay charges
- Sulfates (reactions require high temperatures and strongly reducing fuels):
  - Barium sulfate – a high-temperature oxidizer for e.g. strobe compositions, a green colorant
  - Calcium sulfate – a high-temperature oxidizer for e.g. strobe compositions, a red-orange colorant; calcium salts used to deepen fireworks colors
  - Potassium sulfate – a high-temperature oxidizer, a purple colorant
  - Sodium sulfate – a high-temperature oxidizer, a yellow colorant
  - Strontium sulfate – a high-temperature oxidizer, a red colorant
- Organic chemicals
  - Guanidine nitrate – used in some high power rocket fuels, propellants, and blue firework compositions
  - Hexanitroethane – used in some special military compositions
  - Cyclotrimethylene trinitramine – used in some double-base propellants
  - Cyclotetramethylene Tetranitramine – used in some double-base propellants
- Others
  - Sulfur – oxidizer for zinc in zinc-sulfur fuels
  - Teflon – oxidizer for some metal fuels
  - Boron – oxidizer for titanium, forming titanium diboride

Corresponding sodium salts can be substituted for potassium ones.

Additives

- **Flame suppressants**. Potassium nitrate and potassium sulfate are commonly used.

- **Opacifiers**. Some solid rocket propellants have problems with radiative heat transfer through the material, which may lead to explosion. Carbon black and graphite are often used to inhibit this effect.

- **Colorants**, sometimes in combination with sources of chlorine. Usually salts of suitable metals, often barium, strontium, calcium, sodium, copper, etc. The salt may simultaneously serve as an oxidizer. Copper metal can be also used. Copper acetoarsenite with potassium perchlorate provides richest blue.

- **Chlorine donors**. Used together with colorants. Presence of chlorides increases the volatility of the color-imparting metals and enhances the color intensity. Polyvinyl chloride, polyvinylidene chloride, Saran, chlorinated paraffins, chlorinated rubber (e.g. Parlon), hexachloroethane, hexachlorobenzene (most common chlorine donor until 1970's, now rarely used), and some other organochlorides and inorganic chlorides (e.g. ammonium chloride, mercurous chloride) are used as chlorine donors. Perchlorates and chlorates play this role together with their main use as oxidizers. Chlorine donors are often used also in smoke compositions, e.g. hexachloroethane together with zinc oxide to produce smoke based on zinc chloride.

- **Catalysts**. Propellant formulas often require a catalyst to burn faster and more stably. Transition metal ions and complexes tend to be used. Certain oxidizers often serve as catalysts. E.g. ammonium dichromate is used as a catalyst in ammonium nitrate based propellant formulas. Other catalysts are e.g. iron(III) oxide, hydrated ferric oxide, manganese dioxide, potassium dichromate, copper chromite, lead salicylate, lead stearate, lead 2-ethylhexoate, copper salicylate, copper stearate, lithium fluoride, n-butyl ferrocene, di-n-butyl ferrocene.

- **Stabilizers**. Some mixtures, eg. containing chlorates, tend to degrade and create acidic byproducts. Carbonates (eg. sodium, calcium, or barium carbonate) or other mildly alkaline materials can be added to scavenge such acids. Boric acid can be used to inhibit the sensitivity of aluminium to moisture, and to stabilize mixtures of metals with nitrates (which can otherwise form amides which react exothermically with metals and can cause spontaneous initiation). Many organic nitrated amines are used as stabilizers as well, e.g. 2-nitrodiphenylamine. Petroleum jelly, castor oil, linseed oil, etc. can be used as stabilizers, also to add hydrophobicity to particles and protect metals (especially iron and magnesium) from corrosion. Ethyl centralite and 2-nitrodiphenylamine are used in some rocket propellants.

- **Anticaking agents**. Eg. fumed silica. For powder compositions, e.g. flash powder or gunpowder. Graphite is used in some cases to coat the grains, lubricate them, and dissipate static electricity. Magnesium carbonate used too, together with its function as carbonate stabilizer.

- **Binders**. Often gums and resins, e.g. gum arabic, red gum, guar gum, copal, carboxymethyl cellulose, nitrocellulose, rice starch, cornstarch, shellac, dextrin. Binders can also serve as fuels. Camphor can be used as a plasticizer. Binders are used in manufacture of compact compositions, e.g. pyrotechnic stars. Polymers like HTPB and PBAN are often used for rocket fuels. Other polymers used are e.g. polyethylene or polyvinyl chloride can be encountered as well.

- **Plasticizers**. Improve the mechanical properties of the propellant particles. For composite rocket propellants, dioctyl adipate, isodecyl pelargonate, and dioctyl phthalate are often used. Plasticizers can also be other energetic materials (common in smokeless powders), e.g. nitroglycerine, butanetriol trinitrate, dinitrotoluene, trimethylolethane trinitrate, diethylene glycol dinitrate, triethylene glycol dinitrate, bis(2,2-dinitropropyl)formal, bis(2,2-dinitropropyl)acetal, 2,2,2-trinitroethyl 2-nitroxyethyl ether, and others.

- **Curing and crosslinking agents**. Used to harden the polymer component of composite rocket propellants. They include paraquinone dioxime, toluene-2,4-diisocyanate, tris(1-(2-methyl) aziridinyl) phosphine oxide, N,N,O-tri(1,2-epoxy propyl)-4-aminophenol, and isophorone diisocyanate.

- **Bonding agents**. Used to increase the level of bonding between the binder and the fuel/oxidizer particles. They include tris(1-(2-methyl) azirinidyl) phosphine oxide and triethanolamine.

Chapter 2

Flash Powder

Flash powder is a pyrotechnic composition, a mixture of oxidizer and metallic fuel, which burns quickly and if confined produces a loud report. It is widely used in theatrical pyrotechnics and fireworks (namely salutes, e.g., cherry bombs, M-80s, and firecrackers), and was once used for flashes in photography.

Examples of theatrical binary flash powders. Note the shared oxidizer (A) powder for some types of fuels (B).

Different varieties of flash powder are made from different compositions; most common are potassium perchlorate and aluminium powder. Sometimes, sulfur is included in the mixture to increase the sensitivity. Early formulations used potassium permanganate instead of Potassium Perchlorate.

Flash powder compositions are also used in military pyrotechnics, when production of large amount of noise, light, or infrared radiation is required; e.g. missile decoy flares and stun grenades.

Safety and handling

Flash-powder mixtures are highly sensitive to shock, friction and electrostatic-discharge. Additionally, accidental contaminants such as strong acids or sulphur compounds can sensitise them even more. Because flash-powder mixtures are so easy to initiate, there is a high risk of accidental explosions which can inflict severe blast/fragmentation injuries e.g., traumatic amputation of body parts. Fatalities have occurred. Flash powder compositions should therefore not be handled by anyone who is unfamiliar with their properties, or the handling techniques required to maintain safety. Flash powder and flash-powder devices pose exceptionally high risks to children, who typically cannot understand the danger and may be less adept with safe handling techniques. As a result, children tend to suffer more severe injuries than adults.

Flash powders—especially those that use chlorate—are often highly sensitive to friction, heat/flame and static electricity. A spark of as little as 0.1-10 millijoules can set off certain mixtures. Certain formulations prominent in the underground press contain both sulfur and potassium chlorate. These mixtures are shock and friction sensitive. Modern pyrotechnic practices call for never using sulfur in a mix containing chlorate salts.

Some flash powder formulations (those that use single-digit micrometre flake aluminum powder or fine magnesium powder as their fuel) can self-confine and explode in small quantities. This makes flash powder dangerous to handle, as it can cause severe hearing damage and amputation injury even when sitting in the open. Self-confinement occurs when the mass of the pile provides sufficient inertia to allow high pressure to build within it as the mixture reacts.

Flash powder of any formulation should not be mixed in large quantities by the amateur pyrotechnician. Beginners should start with sub-gram quantities, and refrain from making large devices. Flash powder should only be made at the site at which it will be used. Additionally, the mixture should be made immediately before use.

Flash Powder Mixtures

Normally, flash powder mixtures are compounded to achieve a particular purpose. These mixtures range from extremely fast burning mixtures designed to produce a maximum audio report, to mixtures designed to burn slowly and provide large amounts of illumination, to mixtures that were formerly used in photography.

Aluminium and Chlorate

Because of the above mentioned instability, the combination of aluminium powder and potassium chlorate is a poor choice for flash powder that is to be stored for more than a very short period of time. For that reason it has been largely replaced by the potassium perchlorate mixtures. Chlorate mixes are used when cost is the overriding concern, because potassium chlorate is less expensive than perchlorate. By mass the composition is seven parts of $KClO_3$ to three parts of pyro aluminum. It is critically important to exclude sulphur and any acidic components from these mixtures. Sometimes a few percent of bicarbonate buffer is added to the mixture to ensure the absence of acidic impurities.

$$KClO_3 + 2\ Al \rightarrow Al_2O_3 + KCl$$

Aluminum and Nitrate with Sulfur

This composition, usually in a ratio of 5 parts potassium nitrate, to 3 parts aluminum powder, to 2 parts sulfur, is especially popular with hobbyists. It is not very quick burning, unless exceptionally fine ingredients are used. Although it incorporates sulfur, it is in fact fairly stable, sustaining multiple hits from a hammer onto a hard surface. Adding 2% of its weight with boric acid is reputed to significantly increase stability and shelf life, through resistance to dampening through ambient humidity. Other ratios such as 6 KNO3/3 Al/2 S and 5 KNO3/2 Al/3 S also exist and work. All ratios have similar burn times and strength, although 5 KNO3/3 Al/2 S seems to be dominant.

$$2\ KNO_3 + 4\ Al + S \rightarrow K_2S + N_2 + 2\ Al_2O_3$$

For best results, "German Dark" aluminum should be used, with airfloat sluphur, and finely ball milled pure potassium nitrate. The finished mixture should never be ball milled together.

Aluminum and Perchlorate

Aluminum powder and potassium perchlorate are the only two components of the pyrotechnic industry standard flash powder. It provides a great balance of stability and power, and is the composition used in most commercial exploding fireworks.

The balanced equation for the reaction is:

$$3\ KClO_4 + 8\ Al \rightarrow 4\ Al_2O_3 + 3\ KCl$$

Although not stoichiometrically balanced, a ratio of seven parts Potassium Perchlorate to three parts Dark Pyro Aluminum is the composition used by most pyrotechnicians. However, a ratio of 2 mass units potassium perchlorate to 1 mass unit Dark Pyro Aluminum is closer to stoichiometric, and may produce a louder report.

For best results, the aluminum powder should be "Dark Pyro" grade, with a flake particle shape, and a particle size of less than 10 micrometres. 5413H-S "German Dark" aluminum manufactured by Eckart Germany is reputed to be the best performing aluminum in existence. The $KClO_4$ should be in powder form, free from clumps. It can be sieved through a screen if necessary to remove any clumps prior to use. The particle size of the perchlorate is not as critical as that of the aluminum component, as much less energy is required to decompose the $KClO_4$ than is needed to melt the aluminum into the liquid state required for the reaction.

Although this composition is fairly insensitive, it should be treated with care and respect. Hobbyist pyrotechnicians usually use a method called *diapering*, in which the materials are poured separately onto a large piece of paper, which is then alternately lifted at each corner to roll the composition over itself and mix the components. Some amateur pyrotechnicians chose to mix the composition by shaking in a closed paper container, as this is much quicker and more effective than diapering. Paper/cardboard is chosen over other materials such as plastic as a result of its favorable triboelectric properties.

Large quantities should never be mixed in a single batch. Large quantities are not only more difficult to handle safely, but they place innocent bystanders within the area at risk. In the event of accidental ignition, debris from a multiple-pound flash powder explosion can be thrown hundreds of feet with sufficient force to kill or injure. (Note: 25 grams of mixture is enough to explode in open air without constraint other than air pressure.)

No matter the quantity, care must always be taken to prevent any electrostatic discharge or friction during mixing or handling, as these may cause accidental ignition.

Magnesium and Nitrate

Another flash composition common among amateurs consists of magnesium powder and potassium nitrate. Other metal nitrates have been used, including Barium and strontium nitrates. Compositions using nitrate and magnesium metal have been used as photographic flash powders almost since the invention of photography.

$$2\ KNO_3 + 5\ Mg \rightarrow K_2O + N_2 + 5\ MgO$$
$$Ba(NO_3)_2 + 5\ Mg \rightarrow BaO + N_2 + 5\ MgO$$

Mixtures designed to make reports are substantially different than mixtures designed for illumination. A stoichiometric ratio of three parts KNO_3 to two parts Mg is close to ideal, and provides the most rapid burn. The magnesium powder should be smaller than 200 mesh, though up to 100 mesh will work. The potassium nitrate should be impalpable dust. This mixture is popular in amateur pyrotechnics because it is insensitive and relatively safe as such things go.

For photographic use, mixtures containing magnesium and nitrates are made much more fuel rich. The excess magnesium is volatilized by the reaction and burns in air providing additional light. In addition, the higher concentration of fuel results in a slower burn, providing more of a "poof" and less of a "bang" when ignited. A formula from 1917 specifies 5 parts of magnesium to 6 parts of barium nitrate for a stoichiometry of nine parts fuel to one part oxidizer. Modern recreations of photographic flash powders may avoid the use of barium salts because of their toxic nature. A mixture of five parts 80 mesh magnesium to one part of potassium nitrate provides a good white flash without being too violent. Fuel rich flash powders are also used in theatrical flash pots.

Magnesium based compositions degrade over long periods of time, as Magnesium does not form a passivating oxide coating, meaning the metallic Mg will slowly react with atmospheric oxygen and moisture. In military pyrotechnics involving magnesium fuels, external oxygen can be excluded by using hermetically sealed canisters. Commercial photographic flash powders are sold as two part mixtures, to be combined immediately before use.

Magnesium and PTFE

A flash composition designed specifically to generate flares that are exceptionally bright in the infrared portion of the spectrum use a mixture of pyro grade magnesium and powdered polytetrafluoroethylene. These flares are used as decoys from aircraft that might be subject to heat-seeking missile fire.

$$2n\ \mathrm{Mg} + (\mathrm{C_2F_4}))_n \rightarrow 2n\ \mathrm{MgF_2}\ (s) + 2n\ \mathrm{C}\ (s)$$

Antimony Trisulfide and Chlorate

This mixture, and similar mixtures sometimes containing pyro aluminum have been used since the early 1900s for small "Black Cat" style paper firecrackers. Its extremely low cost makes it popular among manufacturers of low-grade fireworks in China. Like all mixtures containing Chlorates, it is extremely sensitive to friction, impact and ESD, and is considered unsafe in pyrotechnic devices that contain more than a few tens of milligrams of the mixture.

$$3\ \mathrm{KClO_3} + \mathrm{Sb_2S_3} \rightarrow \mathrm{Sb_2O_3} + 3\ \mathrm{SO_2} + 3\mathrm{KCl}$$

This mixture is not highly energetic, and in at least some parts of the United States, firecrackers containing 50 mg or less of this mixture are legal as consumer fireworks.

Chapter 3

Gunpowder

Black powder for muzzleloading rifles and pistols in FFFG granulation size. Coin (diameter 24 mm) for comparison.

Gunpowder, also known since the late 19th century as **black powder**, is a mixture of sulfur, charcoal, and potassium nitrate. Gunpowder can be made just using potassium nitrate and charcoal (or alternatively without charcoal), but without the sulfur (or coal), the powder is not as strong. It burns rapidly, producing a volume of hot gas made up of carbon dioxide, water, and nitrogen, and a solid residue of potassium sulfide. Because of its burning properties and the amount of heat and gas volume that it generates, gunpowder has been widely used as a propellant in firearms and as a pyrotechnic composition in fireworks. The term *gunpowder* also refers broadly to any propellant powder. Antique firearms or replicas of antique firearms are often used with black powder substitute.

Gunpowder is classified as a low explosive because of its relatively slow decomposition rate and consequently low brisance. Low explosives deflagrate at subsonic speeds. High explosives detonate, producing a supersonic wave. Ignition of the powder packed behind a bullet must generate enough pressure to force it from the muzzle at high speed, but not enough to rupture the gun barrel. Gunpowder is thus less suitable for shattering rock or fortifications, where high explosives such as TNT are preferred.

Characteristics

The term *Black powder* was coined in the late 19th century to distinguish prior gunpowder formulations from the new smokeless powders and semi-smokeless powders. Semi-smokeless powders featured bulk volume properties that approximated black powder in terms of chamber pressure when used in firearms, but had significantly reduced amounts of smoke and combustion products; they ranged in color from brownish tan to yellow to white. Most of the bulk semi-smokeless powders ceased to be manufactured in the 1920s.

Black powder is a granular mixture of

- a nitrate, typically potassium nitrate (KNO_3), which supplies oxygen for the reaction;
- charcoal, which provides carbon and other fuel for the reaction, simplified as carbon (C);
- sulfur (S), which, while also serving as a fuel, lowers the temperature required to ignite the mixture, thereby increasing the rate of combustion.

Potassium nitrate is the most important ingredient in terms of both bulk and function because the combustion process releases oxygen from the potassium nitrate, promoting the rapid burning of the other ingredients. To reduce the likelihood of accidental ignition by static electricity, the granules of modern black powder are typically coated with graphite, which prevents the build-up of electrostatic charge.

Charcoal does not consist of pure carbon; rather, it consists of partially pyrolyzed cellulose, in which the wood is not completely decomposed.

The current standard composition for the black powders that are manufactured by pyrotechnicians was adopted as long ago as 1780. Proportions by weight are 75% potassium nitrate (known as saltpeter or saltpetre), 15% softwood charcoal, and 10% sulfur. These ratios have varied over the centuries and by country, and can be altered somewhat depending on the purpose of the powder. For instance, power grades of black powder, unsuitable for use in firearms but adequate for blasting rock in quarrying operations, is called blasting powder rather than gunpowder with standard proportions of 70% nitrate, 14% charcoal, and 16% sulfur; blasting powder may be made with the cheaper sodium nitrate substituted for potassium nitrate and proportions may be as low as 40% nitrate, 30% charcoal, and 30% sulfur.

Combustion rate

The burn rate of black powder can be changed by corning. Corning first compresses the fine black powder meal into blocks with a fixed density ($1.7\ g/cm^3$). The blocks are then broken up into granules. These granules are then sorted by size to give the various grades of black powder. In the United States, standard grades of black powder run from the coarse Fg grade used in large bore rifles and small cannons, through FFg (medium and smallbore arms such as muskets and fusils), FFFg (smallbore rifles and pistols), and FFFFg (extreme small bore, short pistols and most commonly for priming flintlocks). In the United Kingdom, the gunpowder grains are categorised by mesh size: the BSS sieve mesh size, being the smallest mesh size on which no grains were retained. Recognised grain sizes are Gunpowder G 7, G 20, G 40, and G 90.

A simple, commonly cited, chemical equation for the combustion of black powder is

$$2\ KNO_3 + S + 3\ C \rightarrow K_2S + N_2 + 3\ CO_2.$$

A more accurate, but still simplified, equation is

$$10\ KNO_3 + 3\ S + 8\ C \rightarrow 2\ K_2CO_3 + 3\ K_2SO_4 + 6\ CO_2 + 5\ N_2.$$

The burning of gunpowder does not take place as a single reaction, however, and the byproducts are not easily predicted. One study's results showed that it produced (in order of descending quantities): 55.91% solid products: potassium carbonate, potassium sulfate, potassium sulfide, sulfur, potassium nitrate, potassium thiocyanate, carbon, ammonium carbonate. 42.98% gaseous products: carbon dioxide, nitrogen, carbon monoxide, hydrogen sulfide, hydrogen, methane, 1.11% water.

Black powder made with sodium nitrate tends to be hygroscopic, unlike black powders made from saltpeter. ("Saltpeter"--also spelled "saltpetre"--means potassium nitrate and not any of the other nitrates that are also sometimes called "saltpeter.") Because black powder made with saltpeter is less affected by moisture in the air, it can be stored unsealed for centuries without degradation if it is kept dry. Muzzleloaders have been known to fire after hanging on a wall for decades in a loaded state, provided they remained dry. By contrast, black powder made with sodium nitrate must be sealed from the moisture in the air to remain stable for long periods.

Advantages

In firearms, black powder allows loading by volumetric measure, whereas smokeless powder requires precise measuring of the charge by weight to prevent damage due to overloading, though damage by overloading is still possible with black powder.

In quarrying, high explosives are generally preferred for shattering rock. However, because of its low brisance, black powder causes fewer fractures and results in more usable stone compared to other explosives, making black powder useful for blasting monumental stone such as granite and marble.

Black powder is well suited for blank rounds, signal flares, burst charges, and rescue-line launches. Black powder is also used in fireworks for lifting shells, in rockets as fuel, and in certain special effects.

Disadvantages

Black powder has a low energy density compared to modern "smokeless" powders, and thus to achieve high energy loadings, large amounts of black powder are needed with heavy projectiles. In military applications black powder also produces thick smoke as a byproduct, which may give a soldier's location away to an enemy observer. The smoke may also impair aiming for additional shots.

Combustion converts less than half the mass of black powder to gas. The rest ends up as a thick layer of soot inside the barrel. In addition to being a nuisance, the residue from burnt black powder is hygroscopic and with the addition of moisture absorbed from the air, this residue forms a caustic substance. The soot contains potassium oxide or sodium oxide that turns into potassium hydroxide, or sodium hydroxide, which will corrode wrought iron or steel gun barrels. Black powder arms must be well cleaned both inside and out to remove the residue. The Matchlock musket or pistol (an early gun ignition system), as well as the flintlock would often be unusable in wet weather, due to powder in the pan being exposed and dampened. Because of this unreliability, soldiers carrying muskets, known as musketeers, were armed with additional weapons such as swords or pikes. The bayonet was developed to allow the musket to be used as a spear, thus eliminating the need for the soldier to carry a secondary weapon.

Transportation

The UN Model Regulations on the Transportation of Dangerous Goods and national transportation authorities, such as United States Department of Transportation, have classified Gunpowder (black powder) as a *Group A: Primary explosive substance* for shipment because it ignites so easily. Complete manufactured devices containing black powder are usually classified as *Group D: Secondary detonating substance, or black powder, or article containing secondary detonating substance*, such as firework, class D model rocket engine, etc., for shipment because they are harder to ignite than loose powder. As explosives, they all fall into the category of Class 1.

Energy content

Gunpowder contains 3 megajoules per kilogram, and contains its own oxidant. For comparison, the energy density of TNT is 4.7 megajoules per kilogram, and the energy density of gasoline is 47.2 megajoules per kilogram.

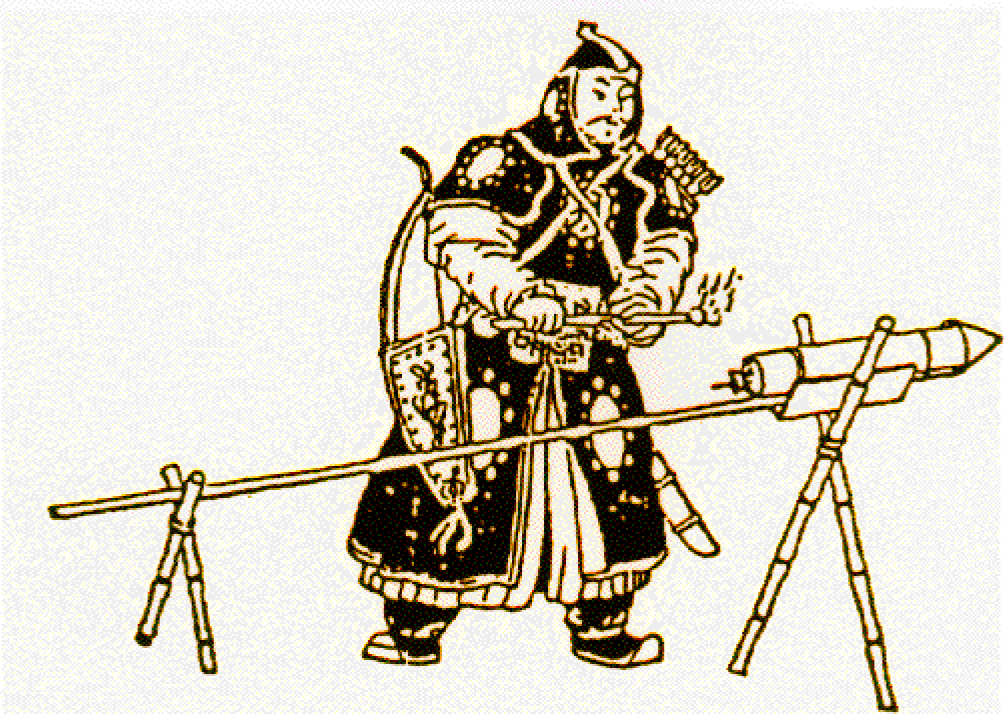
Sulfur-free gunpowder

The development of smokeless powders, such as Cordite, in the late 19th century created the need for a spark-sensitive priming charge, such as gunpowder. However, the sulfur content of traditional gunpowders caused corrosion problems with Cordite Mk I and this led to the introduction of a range of sulfur-free gunpowders, of varying grain sizes. They typically contain 70.5 parts of saltpetre and 29.5 parts of charcoal. Like black powder, they were produced in different grain sizes. In United Kingdom, the finest grain was known as *sulfur-free mealed powder* (*SMP*). Coarser grains were numbered as sulfur-free gunpowder (SFG n): 'SFG 12', 'SFG 20', 'SFG 40' and 'SFG 90', for example; where the number represents the smallest BSS sieve mesh size on which no grains were retained.

The main purpose of sulfur in gunpowder is to decrease the ignition temperature. A sample reaction for sulfur-free gunpowder would be

$$4\ KNO_3 + C_7H_8O \rightarrow 3\ K_2CO_3 + 4\ CO_2 + 2\ H_2O + 3\ N_2$$

History



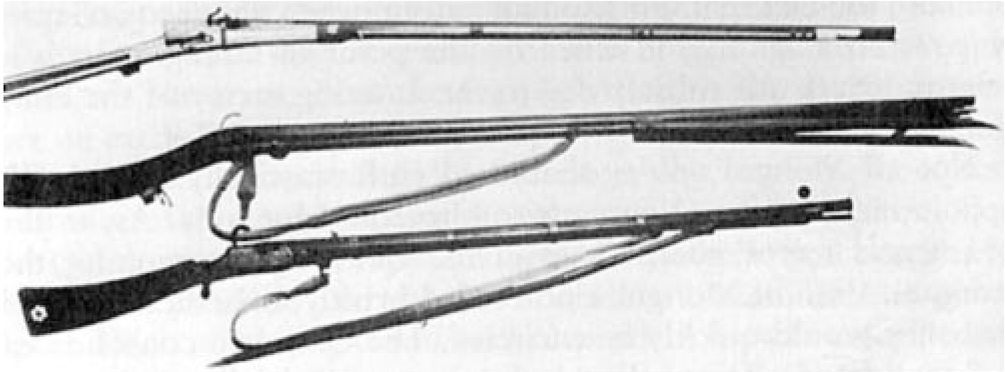
Early Chinese rocket

A Mongol bomb thrown against a charging Japanese samurai during the Mongol invasions of Japan after founding the Yuan Dynasty, 1281.

Gunpowder was invented, documented, and used in ancient China where the Chinese military forces used gunpowder-based weapons technology (i.e. rockets, guns, cannons), and explosives (i.e. grenades and different types of bombs) against the Mongols when the Mongols attempted to invade and breach the Chinese city fortifications on the northern borders of China. After the Mongols conquered China and founded the Yuan Dynasty, they used the Chinese gunpowder-based weapons technology in their invasion of Japan. Chinese also used gunpowder to fuel rockets. However, it has also been argued that, like the wheel, gunpowder was "coinvented" or "co-discovered" prior to, simultaneously or slightly after the Chinese, by cultures separated from the Chinese by vast distances, with minimal direct contact between one another.

A major problem for academic study is ready access to original sources. Moreover, it is difficult to accurately translate original sources, especially medieval Chinese texts which employ metaphor to describe unexplained phenomena, into contemporary scientific language with its rigidly defined terminology. The difficulty in translation gives rise to errors or loose interpretation bordering on artistic licence.

China



Chinese Ming Dynasty (1368-1644 AD) matchlock firearms

Saltpeter was known to the Chinese by the mid-1st century AD and there is strong evidence of the use of saltpeter and sulfur in various largely medicinal combinations. A Chinese alchemical text dated 492 AD noted saltpetre burnt with a purple flame, providing a practical and reliable means of distinguishing it from other inorganic salts, thus enabling alchemists to evaluate and compare purification techniques. The Chinese word for "gunpowder" is Chinese: 火药/火藥; pinyin: *huǒ yào* /xuou yɑʊ/, which literally means "Fire Medicine", meaning "Fire Chemicals" or "Fire Powder".

The first reference of gunpowder is possibly the passage of the *Zhenyuan miaodao yaolüe*, a Taoist text tentatively dated to the mid-9th century AD:

Some have heated together sulfur, realgar and saltpeter with honey; smoke and flames result, so that their hands and faces have been burnt, and even the whole house where they were working burned down.

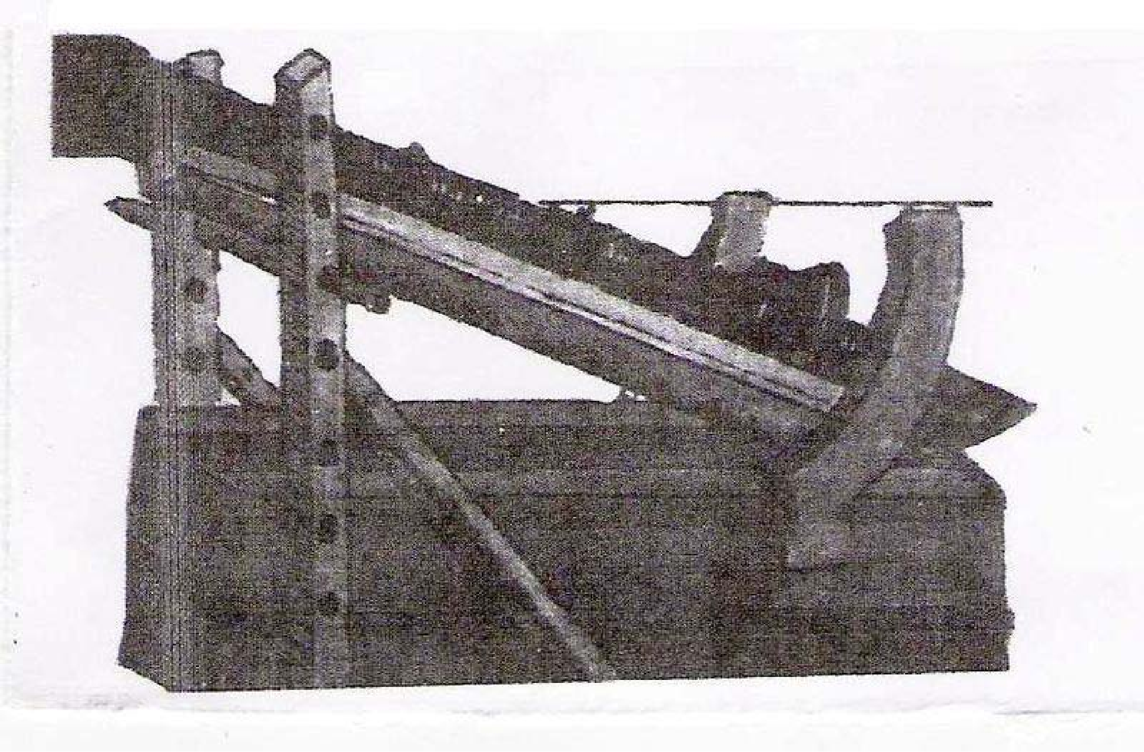
By the 9th century Taoist monks or alchemists searching for an elixir of immortality had serendipitously stumbled upon gunpowder.

The Chinese "Wu Ching Tsung Yao", written by Tseng Kung-Liang in 1044, provides encyclopedia references to a variety of mixtures which included petrochemicals, as well as garlic and honey. A slow match for flame throwing mechanisms using the siphon principle and for fireworks and rockets are mentioned. Academics argue the Chinese wasted little time in applying gunpowder to warfare, and they produced a variety of gunpowder weapons, including flamethrowers, rockets, bombs, and land mines, before inventing guns as a projectile weapon.

Middle East

The Sultani Cannon, a very heavy bronze muzzle-loading cannon of type used by Ottoman Empire in the siege of Constantinople, 1453 AD.

The Arabs acquired knowledge of gunpowder some time after 1240 AD, but before 1280 AD, by which time Hasan al-Rammah had written, in Arabic, recipes for gunpowder, instructions for the purification of saltpeter, and descriptions of gunpowder incendiaries. However, because al-Rammah attributes his material to "his father and forefathers", al-Hassan argues that gunpowder became prevalent in Syria and Egypt by "the end of the twelfth century or the beginning of the thirteenth".



A picture of a 15th century Granadian cannon from the book *Al-izz wal rifa'a*.

Al-Hassan claims that in the Battle of Ain Jalut of 1260 AD, the Mamluks used against the Mongols in "the first cannon in history" gunpowder formulæ with near-identical ideal composition ratios for explosive gunpowder. However, Khan claims that it was invading Mongols who introduced gunpowder to the Islamic world and cites Mamluk antagonism towards early musketeers in their infantry as an example of how gunpowder weapons were not always met with open acceptance in the Middle East. Similarly, the refusal of their Qizilbash forces to use firearms contributed to the Safavid rout at Chaldiran in 1514.

The earliest surviving documentary evidence for the use of the hand cannon, considered the oldest type of portable firearm and a forerunner of the handgun, are from several Arabic manuscripts dated to the 14th century. Al-Hassan argues that these are based on earlier originals and that they report hand-held cannons being used by the Mamluks at the Battle of Ain Jalut in 1260.

Hasan al-Rammah included 107 gunpowder recipes in his text *al-Furusiyyah wa al-Manasib al-Harbiyya* (*The Book of Military Horsemanship and Ingenious War Devices*), 22 of which are for rockets. If one takes the median of 17 of these 22 compositions for rockets (75% nitrates, 9.06% sulfur, and 15.94% carbon), it is near identical with the modern reported ideal gunpowder recipe of 75% potassium nitrate, 10% sulfur, and 15% carbon, although this was already known to Roger Bacon

Mainland Europe

C. F. Temler interprets Peter, Bishop of Leon, as reporting the use of cannon in Seville in 1248 AD.

In Norwegian the *Konungs skuggsjá* of 1250 AD mentions in its military chapter, the use of two key ingredients: "coal and sulfur" as the best weapons for ship-to-ship combat.

Dated around 1257 AD, among the earliest extant written references to gunpowder in Europe, are Roger Bacon's texts *Epistola*, "*De Secretis Operibus Artis et Naturae et de Nullitate Magiae*," dated variously between 1248 and 1257, he states:

We can, with saltpeter and other substances, compose artificially a fire that can be launched over long distances... By only using a very small quantity of this material much light can be created accompanied by a horrible fracas. It is possible with it to destroy a town or an army ... In order to produce this artificial lightning and thunder it is necessary to take saltpeter, sulfur, and Luru Vopo Vir Can Utriet.

Cannons forged in 1667 AD at the Fortín de La Galera, Nueva Esparta, Venezuela.

The last part has been interpreted as an elaborate coded anagram for the quantities needed, but other academics holding contrary viewpoints argue this may be erroneous transcription of a passage read with much difficulty.

Some authors maintain that around 1261, Roger did develop the ideal formula for gunpowder (75% of saltpeter, 15% of carbon and 10% of sulfur)

In the *Opus Maior* of 1267 AD, Bacon describes firecrackers:

a child’s toy of sound and fire and explosion made in various parts of the world with powder of saltpetre, sulfur and charcoal of hazelwood.

The *Liber Ignium*, or *Book of Fires*, attributed to Marcus Graecus, is a collection of incendiary recipes, including some gunpowder recipes. Partington dates the gunpowder recipes to approximately 1300. One recipe for "flying fire" (*ingis volatilis*) involves saltpetre, sulfur, and colophonium, which, when inserted into a reed or hollow wood, "flies away suddenly and burns up everything." Another recipe, for artificial "thunder", specifies a mixture of one pound native sulfur, two pounds linden or willow charcoal, and six pounds of saltpeter. Another specifies a 1:3:9 ratio.

Some of the gunpowder recipes of *De Mirabilibus Mundi* of Albertus Magnus are identical to the recipes of the *Liber Ignium*, and according to Partington, "may have been taken from that work, rather than conversely." Partington suggests that some of the book may have been compiled by Albert's students, "but since it is found in thirteenth century manuscripts, it may well be by Albert." Albertus Magnus died in 1280 AD.

A common German folk-tale is of the German priest/monk named Berthold Schwarz who independently invented gunpowder, thus earning it the German name *Schwarzpulver* or in English *Schwarz's powder*. Schwarz is also German for black so this folk-tale, while likely containing elements of truth, is considered problematic.

The major and uniquely European advancement of gunpowder was corning: the addition of moisture to the gunpowder to form regular greater grains which much increased the reliability and consistency of gunpowder. This occurred around the late 15th century CE, as European powdermakers began adding moisture to gunpowder to reduce dust and with it the risk of dust explosion. The powdermakers would then shape the resulting mush of dampened gunpowder, known as mill cake, into corns, or grains, to dry.

The new "corned" powder remained potent and more reliable to store as it was far less hygroscopic than the former powder (due to net reduced surface area). Gunners also found it was more powerful and easier to load measures of it into guns. An advantage of corning is that the combustion flame spreads evenly between the grains, thus igniting all grains before significant gas expansion (when the gunpowder actually "explodes"). Gunpowder not corned results in much unburnt powder blown away from the ignition flame and combustion chamber due to localized miniature gas expansions within the powder.

Europeans innovated by experimentation and discovering different kernel sizes combusted at differing rates, and thus were more suitable for one gun or for another. Molerus notes that without corning, gunpowder, like all dry mixtures, has a tendency to gradually separate back to its components and thus was too unreliable for effective use in guns as mixtures would not be of uniform composition, noting the use of corning technique is commonplace in the modern pharmaceutical industry to ensure uniform proportions of active ingredients for each tablet.

Shot and gunpowder for military purposes were made by skilled military tradesmen, later called *firemakers*, and were also required to craft fireworks for celebrations of victory or peace. During the Renaissance, two European schools of pyrotechnic thought emerged, one in Italy and the other at Nuremberg, Germany. The Italian school of pyrotechnics emphasized elaborate fireworks, and the German school stressed scientific advancement. Both schools added significantly to further development of pyrotechnics, and by the mid-17th century fireworks were used for entertainment on an unprecedented scale in Europe, being popular even at resorts and public gardens.

By 1788, as a result of the reforms for which Lavoisier was mainly responsible, France had become self-sufficient in saltpeter, and its gunpowder had become not only widely considered the best in Europe but more importantly, inexpensive.

The introduction of smokeless powder in the late 19th century led to the contraction of the gunpowder industry.

British Isles

The old Powder or Pouther magazine dating from 1642 AD, built by order of James VI. Irvine, North Ayrshire, Scotland.

Gunpowder production in Britain appears to have started in the mid 14th century AD with the aim of supplying The English Crown. Records show that gunpowder was being made, in England, in 1346, at the Tower of London; a powder house existed at the Tower in 1461; and in 1515 three King's gunpowder makers worked there. Gunpowder was also being made or stored at other Royal castles, such as Portchester. By the early 14th century, according to N.J.G. Pounds's study *The Medieval Castle in England and Wales,* many English castles had been deserted and others were crumbling. Their military significance faded except on the borders. Gunpowder had made smaller castles useless.

Henry VIII of England was short of gunpowder when he invaded France in 1544 AD and England needed to import gunpowder via the port of Antwerp.

The English Civil War, 1642-1645 AD, led to an expansion of the gunpowder industry, with the repeal of the Royal Patent in August 1641.

Two British physicists, Andrew Noble and Frederick Abel, worked to improve the properties of blackpowder during the late 19th century. This formed the basis for the Noble-Abel gas equation for internal ballistics.

The introduction of smokeless powder in the late 19th century led to a contraction of the gunpowder industry. After the end of World War I, the majority of the United Kingdom gunpowder manufacturers merged into a single company, "Explosives Trades limited"; and number of sites were closed down, including those in Ireland. This company became Nobel Industries Limited; and in 1926 became a founding member of Imperial Chemical Industries. The Home Office removed gunpowder from its list of *Permitted Explosives*; and shortly afterwards, on 31 December 1931, the former Curtis & Harvey's Glynneath gunpowder factory at Pontneddfechan, in Wales, closed down, and it was demolished by fire in 1932.

Gun powder storing barrels at Martello tower in Point Pleasant Park

The last remaining gunpowder mill at the Royal Gunpowder Factory, Waltham Abbey was damaged by a German parachute mine in 1941 and it never reopened. This was followed by the closure of the gunpowder section at the Royal Ordnance Factory, ROF Chorley, the section was closed and demolished at the end of World War II; and ICI Nobel's Roslin gunpowder factory which closed in 1954.

This left the sole United Kingdom gunpowder factory at ICI Nobel's Ardeer site in Scotland; it too closed in October 1976. Since then gunpowder has been imported into the United Kingdom. In the late 1970s / early 1980s gunpowder was bought from eastern Europe, particularly from what was then the East Germany and former Yugoslavia.

India

A 17th century Tanjore Nayak kingdom's forge-welded iron cannon, at Thanjavur's eastern entrance (India).

Gunpowder had arrived in India by the mid-14th century, perhaps introduced by the Mongols as early as the mid-13th century.

It was written in the *Tarikh-i Firishta* (1606–1607) that the envoy of the Mongol ruler Hulegu Khan was presented with a dazzling pyrotechnics display upon his arrival in Delhi in 1258 CE. Firearms known as *top-o-tufak* also existed in the Vijayanagara Empire of India by as early as 1366 AD. From then on the employment of gunpowder warfare in India was prevalent, with events such as the siege of Belgaum in 1473 AD by Sultan Muhammad Shah Bahmani.

By the 16th century, Indians were manufacturing a diverse variety of firearms; large guns in particular, became visible in Tanjore, Dacca, Bijapur and Murshidabad. Guns made of bronze were recovered from Calicut (1504 AD) and Diu (1533 AD). Gujarāt supplied

Europe saltpeter for use in gunpowder warfare during the 17th century. Bengal and Mālwa participated in saltpeter production. The Dutch, French, Portuguese, and English used Chāpra as a center of saltpeter refining.

War rockets, mines and counter mines using gunpowder were used in India by the time of Akbar and Jahangir. Fathullah Shirazi (c. 1582), a Persian-Indian polymath and mechanical engineer who worked for Akbar the Great in the Mughal Empire, invented an autocannon, early multi-shot gun. As opposed to the polybolos and repeating crossbows used earlier in ancient Greece and China, respectively, Shirazi's rapid-firing gun had multiple gun barrels that fired hand cannons loaded with gunpowder.

Both Hyder Ali and his son Tippu Sultan used black powder technology in iron-cased war rockets with considerable effect against the British, which inspired the development of the Congreve rocket.

Indonesia

The Javanese Majapahit Empire is argued to have grown to span most of modern day ASEAN due to its Javanese mastery of bronze-smithing and unique within the immediate region to the Majapahit court, the technology and mass manufacture (via cottage industries which contributed to a central arsenal). Documentary and archeological evidence indicate that Arab or Indian traders introduced gunpowder, gonnes, muskets, blunderbusses, and cannon to the Javanese, Acehnese, and Batak via long established commercial trade routes around the early to mid 14th century CE. Early European aggressors of Portugal and Spain were unpleasantly surprised and outgunned on many occasions. The resurgent Singhasari Empire overtook Sriwijaya and later emerged as the Majapahit who rigidly established fire-arms and cannonade as a feature of warfare.

Circa 1540 CE the Javanese always alert for new weapons found the newly arrived Portuguese weaponry superior to that of the locally made variants. The Javanese bronze breech-loaded swivel-gun, erroneously termed the lantaka, more correctly known as a meriam was used ubiquitously by the Majapahit navy and unfortunately pirates and rival lords. The demise of the Majapahit empire and the flight of disaffected skilled bronze cannon-smiths to Brunei, modern Sumatra and Malaysia, and the Philippines lead to near universal use of the swivel-gun, especially on trade vessels to protect against prevalent marauding pirates, especially in the Makassar Strait.

A Chinese pirate or commercial shipwreck site unearthed a double-ended swivel gun, which enabled swift firing: one barrel would fire whiles its opposite would be reloaded, though this is a rare and unique piece. Other archeological finds have unearthed some triple-barrel and some double-barrel swivel-guns, which were not widely duplicated.

The saltpetre harvesting was recorded by Dutch and German travelers as being common to even the smallest villages and collected from the decomposition process of large goat dung hills specifically piled for collection this saltpetre, a most unpleasant job. Saltpetre must be remembered by today's reader as being a key food preservative agent in a period of no refrigeration.

The Dutch punishment for possession of unpermitted gunpowder appears to have been amputation.

Ownership and manufacture of gunpowder was later prohibited by the colonial Dutch occupiers. Sir Thomas Stamford Raffles, from his *The History of Java* relates the process of powder manufacture, perhaps of noteworthy relevance considering at the time it was a military-related craft and not always recorded:

the best sulphur is supplied from a crater from a mountain near the straits of Bali...in caverns in irregularly formed beds of earth, which being impregnated with the native nitre, saturated with the evacuation of the enumerous bats that haunt these caves is mixed with a compound of wood ashes, supplies the liquid that is boiled in large kettles and afterward left to cool and crystallize.

Manufacturing technology

Edge-runner mill in a restored mill, at Eleutherian Mills

For the most powerful black powder meal, a wood charcoal is used. The best wood for the purpose is Pacific willow, but others such as alder or buckthorn can be used. The ingredients are mixed as thoroughly as possible. This is achieved using a ball mill with non-sparking grinding apparatus (e.g., bronze or lead), or similar device. Historically, a marble or limestone edge runner mill, running on a limestone bed was used in Great Britain; however, by the mid 19th century CE this had changed to either an iron shod stone wheel or a cast iron wheel running on an iron bed. The mix is sometimes dampened with alcohol or water during grinding to prevent accidental ignition.

Around the late 14th century CE, European powdermakers began adding damp to the constituents of gunpowder to reduce dust and with it the risk of explosion. The powdermakers would then shape the resulting paste of dampened gunpowder, known as mill cake, into corns, or grains, to dry. Not only did corned powder keep better because of its reduced surface area, gunners also found that it was more powerful and easier to load into guns. Before long, powdermakers standardized the process by forcing mill cake through sieves instead of corning powder by hand.

During the 18th century gunpowder factories became increasingly dependent on mechanical energy.

Other uses

Besides its use as an explosive, gunpowder has been occasionally employed for other purposes; after the Battle of Aspern-Essling (1809), the surgeon of the Napoleonic Army Larrey combated the lack of food for the wounded under his care by preparing a bouillon of horse meat seasoned with gunpowder for lack of salt. It was also used for sterilizing on ships when there was no alcohol.

Christiaan Huygens experimented with gunpowder in 1673 in an early attempt to build an internal combustion engine, but he did not succeed in making a practical engine.

Fireworks and Firecrackers also use gunpowder but use different brands and different chemicals.

For a while in the first half of the 20th century gunpowder was used in rivet guns, stun guns for animals, splicing cable and other high powered industrial construction tools, until portable air and hydraulic units replaced it as a safer alternative.

Black powder is still used in delay-trains in modern arms. For instance, in a hand grenade, a mechanical striker ignites a percussion primer which ignites a slow black powder delay. The delay burns a few seconds until it gets to the high explosive primary, which detonates, initiating the grenade fill explosive, thus fragmenting the grenade.

Chapter 4

Pyrotechnic Initiator

A **pyrotechnic initiator** (also **initiator** or **igniter**) is a device containing a pyrotechnic composition used primarily to ignite other, more difficult-to-ignite materials, e.g. thermites, gas generators, and solid-fuel rockets. The name is often used also for the compositions themselves.

Pyrotechnic initiators are often controlled electrically (called **electro-pyrotechnic initiators**), e.g. using a heated bridgewire or a *bridge resistor*. They are somewhat similar to blasting caps or other detonators, but they differ in that there is no intention to produce a shock wave. An example of such pyrotechnic initiator is an electric match.

Composition

The energetic material used, often called **pyrogen**, is usually a pyrotechnic composition made of a fuel and oxidizer, where the fuel produces a significant amount of hot particles that cause/promote the ignition of the desired material.

Initiator compositions are similar to flash powders, but they differ in burning speed, as explosion is not intended, and have intentionally high production of hot particles. They also tend to be easier to ignite than thermites, with whom they also share similarities.

Common oxidizers used are potassium perchlorate and potassium nitrate. Common fuels used are titanium, titanium(II) hydride, zirconium, zirconium hydride, and boron. The size of the fuel particles is determined to produce hot particles with the required burning time.

More exotic materials can be used, e.g. carboranes.

For special applications, pyrophoric igniters can be used which burst into flame in contact with air. Triethylborane was used as an igniter for the Lockheed SR-71 jet engines.

Common compositions

Metal-oxidizer

ZPP

One of the most common initiators is **ZPP**, or **zirconium – potassium perchlorate** – a mixture of metallic zirconium and potassium perchlorate. It is also known as **NASA Standard Initiator**. It yields rapid pressure rise, generates little gas, emits hot particles when ignited, is thermally stable, has long shelf life, and is stable under vacuum. It is sensitive to static electricity.

BPN

Another common igniter formula is **BPN**, **BKNO3**, or **boron – potassium nitrate**, a mixture of 25% boron and 75% potassium nitrate by weight. It is used e.g. by NASA. It is thermally stable, stable in vacuum, and its burn rate is independent of pressure.

In comparison with black powder, BPN burns significantly hotter and leaves more of solid residues, therefore black powder is favored for multiple-use systems.

BPN's high temperature makes it suitable for uses where rapid and reproducible initiation is critical, e.g. for airbags, rocket engines, and decoy flares. It is however relatively expensive.

BPN can be also used as an ingredient of solid rocket propellants.

BPN can be ignited by a laser. A semiconductor laser of at least 0.4 watts output can be used for ignition in vacuum.

Others

Other mixtures encountered are aluminium-potassium perchlorate and titanium-aluminium-potassium perchlorate.

Metal hydride-oxidizer

Metal hydride-oxidizer mixtures replace the metal with its corresponding hydride. They are generally safer to handle than the corresponding metal-oxidizer compositions. During burning they also release hydrogen, which can act as a secondary fuel. Zirconium hydride, titanium hydride, and boron hydride are commonly used.

ZHPP

ZHPP (**zirconium hydride – potassium perchlorate**) is a variant of ZPP that uses zirconium hydride instead of pure zirconium. It is significantly safer to handle than ZPP.

THPP

THPP (titanium hydride potassium perchlorate) is a mixture of titanium(II) hydride and potassium perchlorate. It is similar to ZHPP. Like ZHPP, it is safer to handle than titanium-potassium perchlorate.

Intermetallics

Formation of an intermetallic compound can be a strongly exothermic reaction, usable as an initiator.

Titanium-boron

Titanium-boron composition is one of the hottest pyrotechnic reactions in common usage. It is solid-state, gasless. It can be used as a pyrotechnic initiator or for heating confined gas to perform mechanical work.

Nickel-aluminium

Nickel-aluminium laminates can be used as electrically initiated pyrotechnic initiators. NanoFoil is such material, commercially available.

Palladium-aluminium

Palladium-clad aluminium wires can be used as a fuse wire, known as **Pyrofuze**. The reaction is initiated by heat, typically supplied by electric current pulse. The reaction begins at 600 °C, the melting point of aluminium, and proceeds violently to temperature of 2200–2800 °C. The reaction does not need presence of oxygen, and the wire is consumed.

Pyrofuze comes as a solid wire of different diameters (from 0.002" to 0.02"), braided wire, ribbon, foil, and granules. Palladium, platinum, or palladium alloyed with 5% ruthenium can be used together with aluminium. Pyrofuze bridgewires can be used in squibs and electric matches. Pyrofuze foils can be used for e.g. sealing of various dispensers or fire extinguishing systems. Palladium-magnesium composition can also be used, but is not commercially available or not at least as common.

Others

BNCP

BNCP, (***cis*****-bis-(5-nitrotetrazolato)tetraminecobalt(III) perchlorate**) is another common initiator material. It is relatively insensitive. It undergoes deflagration to detonation transition in a relatively short distance, allowing its use in detonators. Its burning byproducts are of relatively little harm to environment. It can be ignited by a laser diode.

Lead azide

Lead azide ($Pb(N_3)_2$, or PbN_6) is occasionally used in pyrotechnic initiators.

Others

Other materials sensitive to heat can be used as well, e.g. tetrazene explosive, lead mononitro-resorcinates, lead dinitro-resorcinates, and lead trinitro-resorcinates.

Chapter 5

Thermite

A thermite mixture using iron (III) oxide

Thermite is a pyrotechnic composition of a metal powder and a metal oxide, which produces an exothermic oxidation-reduction reaction known as a **thermite reaction**. If aluminum is the reducing agent it is called an aluminothermic reaction. Most varieties are not explosive, but can create short bursts of extremely high temperatures focused on a very small area for a short period of time.

Thermites can be a diverse class of compositions. The fuels are often aluminium, magnesium, calcium, titanium, zinc, silicon, and boron. The oxidizers can be boron(III) oxide, silicon(IV) oxide, chromium(III) oxide, manganese(IV) oxide, iron(III) oxide, iron(II,III) oxide, copper(II) oxide, and lead(II,III,IV) oxide.

The most common thermite is aluminium-iron(III) oxide.

Reaction

A thermite reaction using iron(III) oxide

A thermite reaction taking place on a cast iron skillet

The aluminium reduces the oxide of another metal, most commonly iron oxide, because aluminium is highly reactive:

$$Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$$

The products are aluminium oxide, free elemental iron, and a large amount of heat. The reactants are commonly powdered and mixed with a binder to keep the material solid and prevent separation.

The reaction is used for thermite welding, often used to join rail tracks. Other metal oxides can be used, such as chromium oxide, to generate elemental metal. Copper thermite, using copper oxide, is used for creating electric joints in a process called cadwelding:

$$3CuO + 2Al \rightarrow 3Cu + Al_2O_3$$

Some thermite-like mixtures are used as pyrotechnic initiators such as fireworks.

Thermites with nanosized particles are described through a variety of terms, such as metastable intermolecular composites, superthermite nanothermite, and nanocomposite energetic materials.

A mixture of thermite and sulfur produces thermate which lowers the melting point of the iron it contacts when reacting by forming a eutectic system. This is useful in cutting through steel.

History

The thermite (*thermit*) reaction was discovered in 1893 and patented in 1895 by German chemist Hans Goldschmidt. Consequently, the reaction is sometimes called the "Goldschmidt reaction" or "Goldschmidt process". Dr. Goldschmidt was originally interested in producing very pure metals by avoiding the use of carbon in smelting, but he soon realized the value in welding.

The first commercial application was the welding of tram tracks in Essen, in 1899. Evonik, formerly Degussa, a corporate descendant of Goldschmidt's firm, is still today one of the world's largest producers of welding thermite.

Types

Red iron(III) oxide (Fe_2O_3, commonly known as rust) is the most common iron oxide used in thermite. Magnetite also works. Other oxides are occasionally used, such as MnO_2 in manganese thermite, Cr_2O_3 in chromium thermite, or copper(II) oxide in copper thermite, but only for highly specialised purposes. All examples use aluminium as the reactive metal. Fluoropolymers can be used in special formulations, Teflon with magnesium or aluminium being a relatively common example. Magnesium/teflon/viton is another pyrolant of this type.

In principle, any reactive metal could be used instead of aluminium. This is rarely done, however, because the properties of aluminium are ideal for this reaction. It is by far the cheapest of the highly reactive metals; it also forms a passivation layer making it safer to handle than many other reactive metals. The melting and boiling points of aluminium also make it ideal for thermite reactions. Its relatively low melting point (660 °C, 1221 °F) means that it is easy to melt the metal, so that the reaction can occur mainly in the liquid phase and thus proceeds fairly quickly. At the same time, its high boiling point (2,519 °C (4,566 °F)) enables the reaction to reach very high temperatures, since several processes tend to limit the maximum temperature to just below the boiling point. Such a high boiling point is common among transition metals (e.g., iron and copper boil at 2,887 °C (5,229 °F) and 2,582 °C (4,680 °F) respectively), but is especially unusual among the highly reactive metals (cf. magnesium and sodium which boil at 1,090 °C (1,990 °F) and 883 °C (1,621 °F) respectively). Further, the low density of the aluminium oxide formed as a result of the reaction tends to cause it to float on the iron, reducing contamination of the weld.

Although the reactants are stable at room temperature, they burn with an extremely intense exothermic reaction when they are heated to ignition temperature. The products emerge as liquids due to the high temperatures reached (up to 2,500 °C (4,530 °F) with iron(III) oxide)—although the actual temperature reached depends on how quickly heat can escape to the surrounding environment. Thermite contains its own supply of oxygen and does not require any external source of air. Consequently, it cannot be smothered and may ignite in any environment, given sufficient initial heat. It will burn well while wet and cannot be easily extinguished with water, although enough water will remove heat and stop the reaction. Small amounts of water will boil before reaching the reaction. Although thermite is used for welding underwater, in a haphazard ignition of thermite underwater, the molten iron produced will extract oxygen from water and generate hydrogen gas in a single-replacement reaction. This gas may, in turn, burn by combining with oxygen in the air.

Ignition

Metals are capable of burning under the right conditions, similar to the combustion process of wood or gasoline. In fact, rust is the result of oxidation of steel or iron at very slow rates. A thermite reaction is a process in which the correct mixture of metallic fuels are combined and ignited. Ignition itself requires extremely high temperatures.

Ignition of a thermite reaction normally requires only a simple child's sparkler or easily obtainable magnesium ribbon, but may require persistent efforts, as ignition can be unreliable and unpredictable. These temperatures cannot be reached with conventional black powder fuses, nitrocellulose rods, detonators, pyrotechnic initiators, or other common igniting substances. Even when the thermite is hot enough to glow bright red, it will not ignite as it must be at or near white-hot to initiate the reaction. It is possible to start the reaction using a propane torch if done correctly. The torch can preheat the entire pile of thermite which will make it explode instead of burning slowly when it finally reaches ignition temperature.

Often, strips of magnesium metal are used as fuses. Because metals burn without releasing cooling gases, they can potentially burn at extremely high temperatures. Reactive metals such as magnesium can easily reach temperatures sufficiently high for thermite ignition. Magnesium ignition remains popular among amateur thermite users, mainly because it can be easily obtained.

The reaction between potassium permanganate and glycerol or ethylene glycol is used as an alternative to the magnesium method. When these two substances mix, a spontaneous reaction will begin, slowly increasing the temperature of the mixture until flames are produced. The heat released by the oxidation of glycerine is sufficient to initiate a thermite reaction. However, this method can also be unreliable and the delay between mixing and ignition can vary greatly due to factors such as particle size and ambient temperature.

Apart from magnesium ignition, some amateurs also choose to use sparklers to ignite the thermite mixture. These reach the necessary temperatures and provide enough time before the burning point reaches the sample. However, this can be a dangerous method, as the iron sparks, like the magnesium strips, burn at thousands of degrees and can ignite the thermite even though the sparkler itself is not in contact with it. This is especially dangerous with finely powdered thermite.

Similarly, finely-powdered thermite can be ignited by a regular flint spark lighter, as the sparks are burning metal (in this case, the highly-reactive rare-earth metals lanthanum and cerium). Therefore it is unsafe to strike a lighter close to thermite.

A stoichiometric mixture of finely powdered iron(III) oxide and aluminium may be ignited using ordinary red-tipped book matches by partially embedding one match head in the mixture, and igniting that match head with another match, preferably held with tongs in gloves to prevent flash burns.

Civilian uses

Thermite reaction proceeding for a railway welding. Shortly after this, the liquid iron flows into the mould around the rail gap

Residues of ceramic molds for thermite welding like these, left by railway workers, can be found along tracks

The violent effects of thermite

Thermite reactions have many uses. Thermite is not an explosive; instead it operates by exposing a very small area of metal to extremely high temperatures. Intense heat focused on a small spot can be used to cut through metal or weld metal components together both by melting metal from the components, and by injecting molten metal from the thermite reaction itself.

Thermite may be used for repair by the welding in-place of thick steel sections such as locomotive axle-frames where the repair can take place without removing the part from its installed location.

Thermite can be used for quickly cutting or welding steel such as rail tracks, without requiring complex or heavy equipment. However, defects such as slag inclusions and voids (holes) are often present in such welded junctions and great care is needed to operate the process successfully. Care must also be taken to ensure that the rails remain straight, without resulting in dipped joints, which can cause wear on high speed and heavy axle load lines.

A thermite reaction, when used to purify the ores of some metals, is called the thermite process, or aluminothermic reaction. An adaptation of the reaction, used to obtain pure uranium, was developed as part of the Manhattan Project at Ames Laboratory under the direction of Frank Spedding. It is sometimes called the Ames process.

Copper thermite is used for welding together thick copper wires for the purpose of electrical connections. It is used extensively by the electrical utilities and telecommunications industries (exothermic welded connections).

Military uses

Thermite hand grenades and charges are typically used by armed forces in both an anti-materiel role and in the partial destruction of equipment, the latter being common when time is not available for safer or more thorough methods. Because standard iron-thermite is difficult to ignite, burns with practically no flame and has a small radius of action, standard thermite is rarely used on its own as an incendiary composition. It is more usually employed with other ingredients added to enhance its incendiary effects. Thermate-TH3 is a mixture of thermite and pyrotechnic additives which have been found to be superior to standard thermite for incendiary purposes. Its composition by weight is generally 68.7% thermite, 29.0% barium nitrate, 2.0% sulfur and 0.3% binder (such as PBAN). The addition of barium nitrate to thermite increases its thermal effect, produces a larger flame, and significantly reduces the ignition temperature. Although the primary purpose of Thermate-TH3 by the armed forces is as an incendiary anti-materiel weapon, it also has uses in welding metal components.

A classic military use for thermite is disabling artillery pieces, and it has been used commonly for this purpose since World War II. Thermite can permanently disable artillery pieces without the use of explosive charges and therefore can be used when silence is necessary to an operation. There are several ways to do this. By far the most destructive method is to weld the weapon shut by inserting one or more armed thermite grenades into the breech and then quickly closing it. This makes the weapon impossible to load. An alternative method is to insert an armed thermite grenade down the muzzle of the artillery piece, fouling the barrel. This makes the piece very dangerous to fire. Yet another method is to use thermite to weld the traversing and elevation mechanism of the weapon, making it impossible to aim properly.

Thermite was also used in both German and Allied incendiary bombs during World War II. Incendiary bombs usually consisted of dozens of thin thermite-filled canisters (bomblets) ignited by a magnesium fuse. Incendiary bombs destroyed entire cities due to the raging fires that resulted from their use. Cities that primarily consisted of wooden buildings were especially susceptible. These incendiary bombs were utilized primarily during night time air raids. Bomb sights could not be used at night, creating the need to use munitions that could destroy targets without the need for precision placement.

Hazards

Thermite usage is hazardous due to the extremely high temperatures produced and the extreme difficulty in smothering a reaction once initiated. The thermite reaction releases dangerous ultra-violet (UV) light requiring that the reaction not be viewed directly, or that special eye protection (for example, a welder's mask) be worn. Small streams of molten iron released in the reaction can travel considerable distances and may melt through metal containers, igniting their contents. Additionally, flammable metals with relatively low boiling points such as zinc, whose boiling point of 907 °C (1,665 °F) is about 1,370 °C (2,500 °F) below the temperature at which thermite burns, could potentially boil superheated metal violently into the air if near a thermite reaction, where it could then burst into flame as it is exposed to oxygen.

Preheating of thermite before ignition can easily be done accidentally, for example by pouring a new pile of thermite over a hot, recently-ignited pile of thermite slag. When ignited, preheated thermite can burn almost instantaneously, releasing light and heat energy at a much higher rate than normal and causing burns and eye damage at what would normally be a reasonably safe distance.

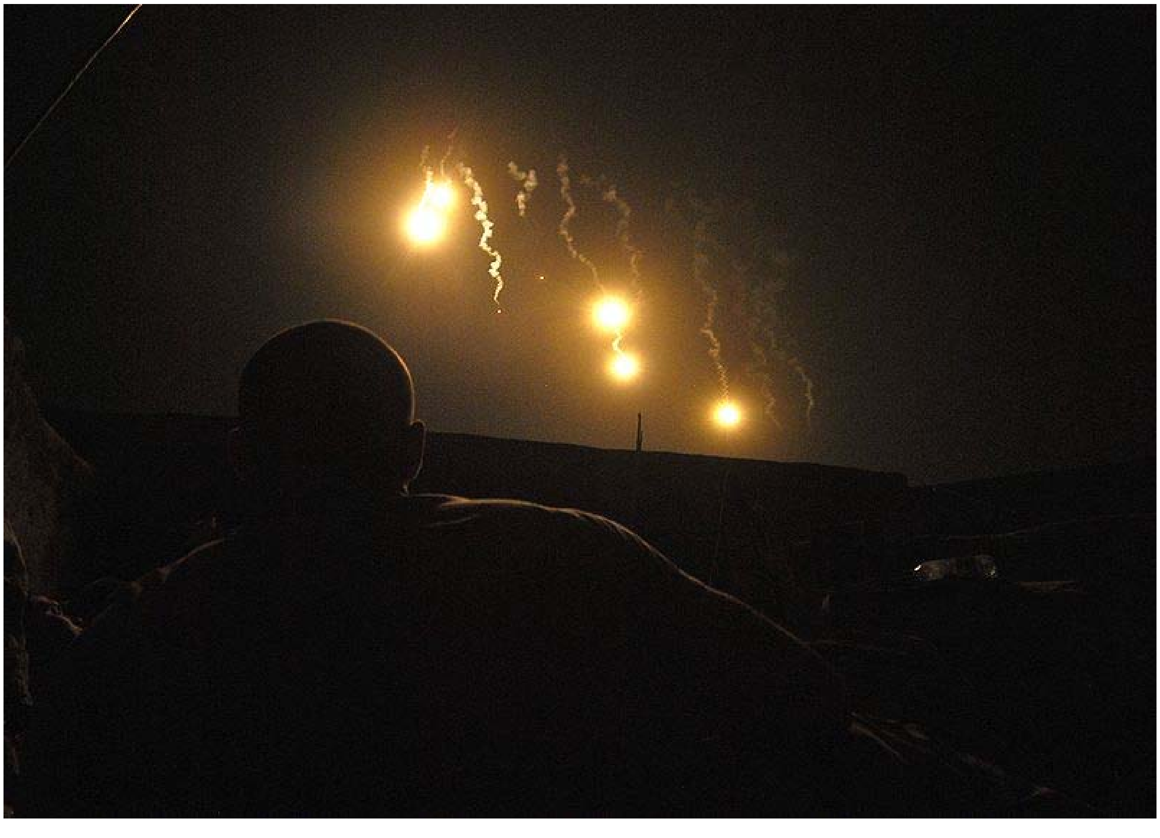
The thermite reaction can take place accidentally in industrial locations where abrasive grinding and cutting wheels are used with ferrous metals. Using aluminium in this situation produces a mixture of oxides which is capable of a violent explosive reaction.

Mixing water with thermite or pouring water onto burning thermite can cause a steam explosion, spraying hot fragments in all directions.

Thermite's main ingredients were also utilized for their individual qualities, specifically reflectivity and heat insulation, in a paint coating or dope for the Hindenburg, possibly contributing to its fiery destruction. This was a theory put forward by former NASA scientist Addison Bain, and later tested in small scale by the scientific reality-TV show MythBusters with semi-inconclusive results (it wasn't proven to be the thermite reaction's fault but instead was conjectured to be a mix between that and the hydrogen filling the Hindenburg). The MythBusters also tested the veracity of a video found on the Internet, whereby a quantity of thermite was allowed to drop onto a block of ice of similar mass, causing a sudden explosion. They were able to confirm the results, and Jamie Hyneman conjectured this was due to the thermite mixture aerosolizing, perhaps in a cloud of steam, causing it to burn even faster. They found chunks of ice as far as 150 feet (46 m) from the point of explosion. Jamie voiced skepticism to another theory explaining the phenomenon: that the reaction somehow separated the hydrogen and oxygen in the water and ignited them.

Chapter 6

Flare (Pyrotechnic)



Illumination rounds are fired during Operation Tora Arwa V in the Kandahar province during Operation Enduring Freedom. The illumination rounds were fired from M777 howitzers and are used to help illuminate a certain area the soldiers need to see.

A **flare**, also sometimes called a **fusee**, is a type of pyrotechnic that produces a brilliant light or intense heat without an explosion. Flares are used for signaling, illumination, or defensive countermeasures in civilian and military applications. Flares may be ground pyrotechnics, projectile pyrotechnics, or parachute-suspended to provide maximum illumination time over a large area. Projectile pyrotechnics may be dropped from aircraft, fired from rocket or artillery, or deployed by flare guns or handheld percussive tubes.

Flares produce their light through the combustion of a pyrotechnic composition. The ingredients are varied, but often based on strontium nitrate, potassium nitrate, or potassium perchlorate and mixed with a fuel such as charcoal, sulfur, sawdust, aluminum, magnesium, or a suitable polymeric resin. Flares may be colored by the inclusion of pyrotechnic colorants. Calcium flares are used underwater to illuminate submerged objects.

Civilian use

Red flare - maritime distress signal
- COLREGS Annex IV (i)

In the civilian world, flares are commonly used as signals, and may be ignited on the ground or fired as an aerial signal from a pistol-like flare gun. Flare guns are commonly found in marine survival kits.

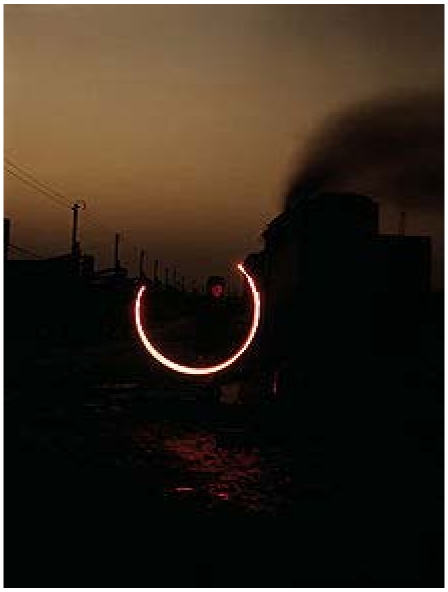
Maritime distress signal

A "*rocket parachute flare or a hand flare showing a* ***red light****"..."indicates distress and need of assistance"* at sea is one type of maritime distress signals. *"The use or exhibition of any of the foregoing signals [as a hand flare showing a red light or rockets or shells, throwing red stars] except for the purpose of indicating distress and need of assistance and the use of other signals which may be confused with any of the above signals is prohibited."* from the COLREGS ANNEX IV - Distress signals 1. (c), (i).

Other usage

Flares are routinely used in countries around Europe and South America, during football games, in order to aid the build-up of the atmosphere within the stadium. Hardcore supporter groups known as Ultras, often light flares at the beginning of games, when their team has scored, or at the end of a game, if their team has won.

Fusee



An IHB brakeman uses a fusee to demonstrate a hand signal indicating "stop".

Another type of flare is the *fusee*, which burns for 10–60 minutes with a bright red light. Fusees are commonly used to indicate obstacles or advise caution on roadways at night; in this usage they are also called *highway flares*, *road flares*, or *ground flares*. They are commonly found in roadside emergency kits.

Fusees are also known as *railroad flares* and are used to perform hand signals in rail transport applications. Since they can be used only once, fusees nowadays are usually intended for emergency use (as opposed to the incandescent lanterns typically used during normal operating conditions). However, in the days before train radio communications, fusees were used to keep trains apart on un-signaled lines. A railroad fusee was timed to burn for ten minutes and quantities were dropped behind a train to ensure a safe spacing. If a following train encountered a burning fusee it was not to pass until the fusee burned out. Fusees made specifically for railroad use can be distinguished from highway fusees by a sharp steel spike at one end, used to embed the fusee upright in a wooden railroad tie.

In forestry and firefighting, fusees are sometimes used in wildland fire suppression and in the ignition of controlled burns. They ignite at 375 °F (191 °C) and burn as hot as 3,000 °F (1,600 °C). They are especially effective in igniting burnouts or backburns in very dry conditions, but not so effective when fuel conditions are moist. Since controlled burns are often done during relatively high humidity levels (on the grounds that they could not be safely contained during periods of very low humidity), the driptorch is more effective and more often used. Fusees are also commonly carried by wildland firefighters for emergency use, to ignite an escape fire in surrounding fuels in case of being overrun by a fire if no other escape routes are available.

Calcium phosphide is often used in naval flares, as in contact with water it liberates phosphine which self-ignites in contact with air; it is often used together with calcium carbide which releases acetylene.

Air

A special variety of flare is used in military aircraft as a defensive countermeasure against heat-seeking missiles. These flares are usually discharged individually or in salvoes by the pilot or automatically by tail-warning devices, and are accompanied by vigorous evasive maneuvering. Since they are intended to deceive infrared missiles, these flares burn at temperatures of thousands of degrees, incandescing in the visible spectrum as well. Soids are floating flares that are effective only in the terminal phase of missiles with infrared signature seeker heads.

Non-perchlorate flares

Many in-service colored signal flares and spectrally balanced decoy flares contain perchlorate oxidizers. Perchlorate, a type of salt in its solid form, dissolves and moves rapidly in groundwater and surface water. Even in low concentrations in drinking water supplies, perchlorate is known to inhibit the uptake of iodine by the thyroid gland. While there are currently no federal drinking water standards for perchlorate, some states have established public health goals, or action levels, and some are in the process of establishing state maximum contaminant levels. For example, the US Environmental Protection Agency have studied 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.

US courts have taken action regarding the use of perchlorate in manufacturing pyrotechnic devices such as flares. 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 U. S. Environmental Protection Agency's Richard Wilkin and colleagues, have conducted research on the use of pyrotechnic devices over bodies of water noting concerns over the effects of environmental perchlorate on human health and wildlife. Sources of perchlorate range from lightening and certain fertilizers to the perchlorate compounds in rocket fuel and explosives. Scientists long suspected community fireworks displays were another source, but few studies had been done on the topic. Wilkin's group has now established fireworks displays as a source of perchlorate contamination by analyzing water in an Oklahoma lake before and after fireworks displays in 2004, 2005 and 2006. Within 14 hours after the fireworks, perchlorate levels rose 24 to 1,028 times above background levels. Levels peaked about 24 hours after the display, and then decreased to the pre-fireworks background within 20- to 80 days. The study is detailed in the June 1, 2007 issue of the journal Environmental Science & Technology. (Environ. Sci. Technol., 2007, 41 (11), pp 3966–3971)

According to the May 2005 Government Accountability Office (GAO) Perchlorate Report, an EPA official has estimated about 10 million people may have been exposed to perchlorate through their drinking water. Accordingly, there is an urgent need to develop perchlorate-free compositions for pyrotechnic flare devices.

Some examples of efforts to create non-perchlorate 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.

Chapter 7

Sparkler

A "Morning Glory" type sparkler, emitting small pyrotechnic stars during this phase of the burn

Sparklers are popular fireworks for children.

Moving sparklers quickly can create attractive patterns

A **sparkler** is a type of hand-held fireworks that burns slowly while emitting colored flames, sparks, and other effects, though in U.S. **sparklers** are now classified as novelties by the federal government and are not defined as consumer fireworks. Under this classification, sparklers can legally be shipped through the U.S. mail system and do not require any complicated hazardous material paperwork or special packaging. Most U.S. states allow the use of sparklers, however, some states and counties do not, even though sparklers are no longer considered fireworks. If in doubt over your local ordinance, it is always a good idea to check with your local or state fire marshal's office before buying.

In the United Kingdom, a sparkler is often used by children at bonfire and fireworks displays on Guy Fawkes Night, 5 November.

Design

The "classic" type of sparkler consists of a thin metal rod approximately 20 cm (8 inches) long that has been dipped in a thick batter of slow-burning pyrotechnic composition and allowed to dry. The composition contains these components, one or more of each category:

- Metallic fuel, mandatory to make sparks; size of particles influences appearance of the sparks
    - Aluminium or magnesium or magnalium, producing white sparks
    - Iron, producing orange branching sparks
    - Titanium, producing rich white sparks
    - Ferrotitanium, for yellow-gold sparkles
- Additional fuel, optional, modifying the burning speed
    - Sulfur
    - Charcoal
- Oxidizer, mandatory
    - Potassium nitrate
    - Barium nitrate
    - Strontium nitrate
    - Potassium perchlorate, more powerful but potentially explosive
- Optional pyrotechnic colorants, for colored flames
    - chlorides and nitrates of metals, e.g. barium, strontium, or copper
- Combustible binder, holding the composition together
    - Dextrin
    - Nitrocellulose

The colored spot on the top of each rod indicates the color of the sparkles emitted when ignited.

A more modern type of sparkler, known as the "Morning Glory", are structurally different from common sparklers. They consist of a long, thin-wall paper tube filled with composition and fitted with a bamboo handle using brightly-colored tissue paper and ribbons. Several different compositions can be packed into a single tube, resulting in a sparkler that changes color. The tube is decorated with bright colored wrappings. Morning Glories are easy to light but burn with a more vigorous effect than common sparklers. They tend to be smokier and are more likely to drop small glowing particles, therefore their use indoors is not recommended. Outdoors they should be used with care.

Safety issues

Sparklers are responsible for the vast majority of legal firework-related injuries. The most common situation for injuries occurs when lit sparklers are given to unsupervised children, many of whom may not understand the risks. The devices burn at a high temperature (as hot as 1800 to 3000° F, or 1000 to 1600° C), depending on the fuel and oxidizer used, more than sufficient to cause severe skin burns or ignite clothing. Safety experts recommend that adults ensure children who handle sparklers are properly warned, supervised and wearing non-flammable clothing. Children who are too young to understand the risk of burns should not be allowed to handle lit sparklers. As with all fireworks, sparklers are also capable of accidentally initiating wildfires. This is especially true in drier areas; in Australia, for instance, sparkler-related bushfire accidents have led to their banning at public outdoor events during summer, such as Australia Day celebrations.

Sparklers in art, weddings and pop culture

An Art group monochrom were planning to light 10,000 bound sparklers as they described as "symbolic liberation" to reflect that sparklers are generally used in monotheistic traditions.

Sparklers make a wonderful accessory in weddings and parties. Sparklers, once thought of as something only to be bought and used on the Fourth of July, are finding their way more and more into other types of celebrations. With their scintillating show of gold sparks, the humble sparkler is now being used to spice up the festivities at parties and weddings across the United States.

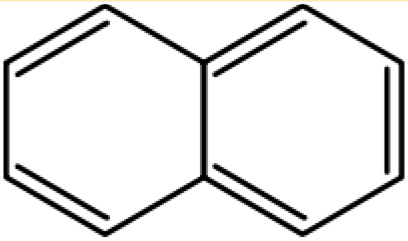
A large group from Toronto, Ontario, Canada, also held an event displaying 10,000 sparklers to symbolize brightness, intensity, warmth and creativity. In 1999 the two artists Tobias Kipp and Timo Pitkämö developed a technique of drawing portraits with burning sparklers on paper, which they called pyrografie. Since then the two artists have drawn more than 20,000 pyroportraits.

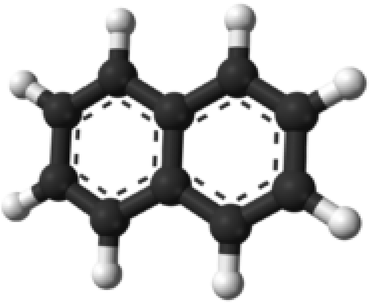
Chapter 8

Organic Chemicals in Pyrotechnic Fuels

Naphthalene

Naphthalene





IUPAC name
bicyclo[4.4.0]deca-1,3,5,7,9-pentene

Other names
Tar Camphor, White Tar, Moth Flakes, albocarbon, naphthaline, naphthalin, antimite, naphthalin, bicyclo[4.4.0]deca-1,3,5,7,9-pentene

Identifiers

CAS number	91-20-3 ✓
PubChem	931
ChemSpider	906 ✓
UNII	2166IN72UN ✓
EC number	202-049-5
KEGG	C00829 ✓

ChEMBL	CHEMBL16293 ✓
RTECS number	QJ0525000
Properties	
Molecular formula	$C_{10}H_8$
Molar mass	128.17052 g/mol
Appearance	White solid crystals/flakes, strong odor of coal tar
Density	1.14 g/cm³
Melting point	80.26 °C, 353 K, 176 °F
Boiling point	218 °C, 491 K, 424 °F
Solubility in water	Approximately 30 mg/L
Hazards	
R-phrases	R22, R40, R50/53
S-phrases	(S2), S36/37, S46, S60, S61
Flash point	79 - 87 °C
Autoignition temperature	525 °C

Naphthalene is an organic compound with formula $C_{10}H_8$. It is a white crystalline solid with a characteristic odor that is detectable at concentrations as low as 0.08 ppm by mass. As an aromatic hydrocarbon, naphthalene's structure consists of a fused pair of benzene rings. It is best known as the traditional ingredient(s) of mothballs. (The other is para-dichlorobenzene).

History

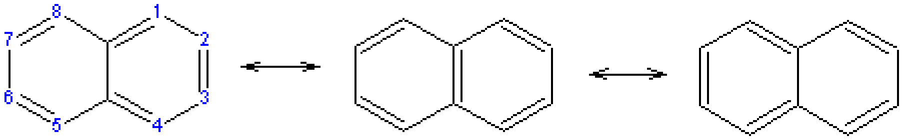
In 1819–1820, at least two chemists reported a white solid with a pungent odor derived from the distillation of coal tar. In 1821, John Kidd described many of this substance's properties and the means of its production, and proposed the name *naphthaline*, as it had been derived from a kind of naphtha (a broad term encompassing any volatile, flammable liquid hydrocarbon mixture, including coal tar). Naphthaline's chemical formula was determined by Michael Faraday in 1826. The structure of two fused benzene rings was proposed by Emil Erlenmeyer in 1866, and confirmed by Carl Gräbe three years later.

Structure and reactivity

A naphthalene molecule can be viewed as the fusion of a pair of benzene rings. (In organic chemistry, rings are *fused* if they share two or more atoms.) Accordingly, naphthalene is classified as a benzenoid polycyclic aromatic hydrocarbon (PAH). There are two sets of equivalent hydrogen atoms: the *alpha* positions are positions 1, 4, 5, and 8 on the drawing below, and the *beta* positions are positions 2, 3, 6, and 7.

Unlike benzene, the carbon-carbon bonds in naphthalene are not of the same length. The bonds C1–C2, C3–C4, C5–C6 and C7–C8 are about 1.36 Å (136 pm) in length, whereas the other carbon-carbon bonds are about 1.42 Å (142 pm) long. This difference, which was established by x-ray diffraction, is consistent with the valence bond model of bonding in naphthalene that involves three resonance structures (as shown below);

whereas the bonds C1–C2, C3–C4, C5–C6 and C7–C8 are double in *two* of the three structures, the others are double in only one.



Like benzene, naphthalene can undergo electrophilic aromatic substitution. For many electrophilic aromatic substitution reactions, naphthalene reacts under milder conditions than does benzene. For example, whereas both benzene and naphthalene react with chlorine in the presence of a ferric chloride or aluminium chloride catalyst, naphthalene and chlorine can react to form 1-chloronaphthalene even without a catalyst. Similarly, whereas both benzene and naphthalene can be alkylated using Friedel-Crafts reactions, naphthalene can also be alkylated by reaction with alkenes or alcohols, with sulfuric or phosphoric acid as the catalyst.

Substituted derivatives

Two isomers are possible for mono-substituted naphthalenes, corresponding to substitution at an alpha or beta position. Usually, electrophiles attack at the alpha position. The selectivity for alpha over beta substitution can be rationalized in terms of the resonance structures of the intermediate: for the alpha substitution intermediate, seven resonance structures can be drawn, of which four preserve an aromatic ring. For beta substitution, the intermediate has only six resonance structures, and only two of these are aromatic. Sulfonation, however, gives a mixture of the "alpha" product 1-naphthalenesulfonic acid and the "beta" product 2-naphthalenesulfonic acid, with the ratio dependent on reaction conditions. The 1-isomer forms predominantly at 25 °C, and the 2-isomer at 160 °C.

Naphthalene can be hydrogenated under high pressure in the presence metal catalysts to give 1,2,3,4-tetrahydronaphthalene or tetralin ($C_{10}H_{12}$). Further hydrogenation yields decahydronaphthalene or decalin ($C_{10}H_{18}$). Oxidation with chromate or permanganate, or catalytic oxidation with O_2 and a vanadium catalyst, gives phthalic acid.

Production

Most naphthalene is derived from coal tar. From the 1960s until the 1990s, significant amounts of naphthalene were also produced from heavy petroleum fractions during petroleum refining, but today petroleum-derived naphthalene represents only a minor component of naphthalene production.

Naphthalene is the most abundant single component of coal tar. Although the composition of coal tar varies with the coal from which it is produced, typical coal tar is about 10% naphthalene by weight. In industrial practice, distillation of coal tar yields an oil containing about 50% naphthalene, along with a variety of other aromatic compounds.

This oil, after being washed with aqueous sodium hydroxide to remove acidic components (chiefly various phenols), and with sulfuric acid to remove basic components, undergoes fractional distillation to isolate naphthalene. The crude naphthalene resulting from this process is about 95% naphthalene by weight, often referred to as 78°C (melting point). The chief impurities are the sulfur-containing aromatic compound benzothiophene (<2%), indane (0.2%), indene (<2%), and methylnapthalene (<2%). Petroleum-derived naphthalene is usually purer than that derived from coal tar. Where required, crude naphthalene can be further purified by recrystallization from any of a variety of solvents, resulting in 99% naphthalene by weight, referred to as 80 °C (melting point). Approximately 1M tons are produced annually.

In North America, coal tar producers are Koppers Inc. and Recochem Inc., and petroleum-derived producer is Advanced Aromatics, L.P.

Natural occurrence

Trace amounts of naphthalene are produced by magnolias and specific types of deer, as well as the Formosan subterranean termite, possibly produced by the termite as a repellant against "ants, poisonous fungi and nematode worms." Some strains of the endophytic fungus *Muscodor albus* produce naphthalene among a range of volatile organic compounds, while *Muscodor vitigenus* produces naphthalene almost exclusively.

Naphthalene has been found in meteorites that continue to fall to the surface of the Earth. It has also been discovered in the interstellar medium in the direction of the star Cernis 52 in the constellation Perseus.

Gaseous naphthalene

Recent research at the University of Georgia, led by Dr. Michael Duncan, has shown that protonated cations of naphthalene are the source of part of the spectrum of the Unidentified Interstellar Bands (UIBs). The gaseous naphthalene found in space is different from crystalline form typically used in mothballs in that it has an additional hydrogen atom, with the empirical formula: C10H9+. The UIBs have been observed by astronomers, and until recently, there has been no solid evidence identifying the compounds responsible for them. The research has recently been publicized as "Mothballs in Space."

Uses

As a chemical intermediate

Naphthalene is mainly used as a precursor to other chemicals. The single largest use of naphthalene is the industrial production of phthalic anhydride, although more phthalic anhydride is made from *o*-xylene. Other naphthalene-derived chemicals include alkyl naphthalene sulfonate surfactants, and the insecticide 1-naphthyl-N-methylcarbamate (*carbaryl*). Naphthalenes substituted with combinations of strongly electron-donating functional groups, such as alcohols and amines, and strongly electron-withdrawing groups, especially sulfonic acids, are intermediates in the preparation of many synthetic dyes. The hydrogenated naphthalenes tetrahydronaphthalene (tetralin) and decahydronaphthalene (decalin) are used as low-volatility solvents. Naphthalene is also used in the synthesis of 2-naphthol, a precursor for various dyestuffs, pigments, rubber processing chemicals and other miscellaneous chemicals and pharmaceuticals.

Naphthalene sulfonic acids are used in the manufacture of naphthalene sulfonate polymer plasticizers (dispersants) which are used to produce concrete and plasterboard (wallboard or drywall). They are also used as dispersants in synthetic and natural rubbers, and as tanning agents (syntans) in leather industries, agricultural formulations (dispersants for pesticides), dyes and as a dispersant in lead-acid battery plates.

Naphthalene sulfonate polymers are produced by reacting naphthalene with sulfuric acid and then polymerizing with formaldehyde, followed by neutralization with sodium hydroxide or calcium hydroxide. These products are commercially sold in solution (water) or dry powder form.

- Sulfonation Step (sulfuric acid plus naphthalene):

  $H_2SO_4 + C_{10}H_8 \rightarrow= C_{10}H_7\text{-}SO_3H + H_2O$

- Polymerization Step (naphthalenesulfonic acid plus formaldehyde):

  $C_{10}H_7\text{-}SO_3H + CH_2\text{-}O \rightarrow C_{10}H_7\text{-}SO_3H\text{-}(C_{10}H_7\text{-}SO_3H)_n + H_2SO_4$

- Neutralization Step (naphthalene sulfonic acid condensate plus sodium hydroxide):

  $C_{10}H_7\text{-}SO_3H\text{-}(C_{10}H_7\text{-}SO_3H)_n + NaOH \rightarrow C_{10}H_7\text{-}SO_3Na\text{-}(C_{10}H_7\text{-}SO_3Na)_n + H_2O + Na_2SO_4$

Wetting agent/surfactant

Alkyl naphthalene sulfonates (ANS) are used in many industrial applications as nondetergent wetting agents that effectively disperse colloidal systems in aqueous media. The major commercial applications are in the agricultural chemical industry, which uses ANS for wettable powder and wettable granular (dry-flowable) formulations, and the textile and fabric industry, which utilizes the wetting and defoaming properties of ANS for bleaching and dyeing operations.

As a fumigant

The most familiar use of naphthalene is as a household fumigant, such as in mothballs although 1,4-dichlorobenzene (or *p*-dichlorobenzene) is now more widely used. In a sealed container containing naphthalene pellets, naphthalene vapors build up to levels toxic to both the adult and larval forms of many moths that attack textiles. Other fumigant uses of naphthalene include use in soil as a fumigant pesticide, in attic spaces to repel animals and insects, and in museum storage-drawers and cupboards to protect the contents from attack by insect pests.

Niche applications

It is used in pyrotechnic special effects such as the generation of black smoke and simulated explosions. In the past, naphthalene was administered orally to kill parasitic worms in livestock. Naphthalene and its alkyl homologs are the major constituents of creosote. Naphthalene is used in engineering to study heat transfer using mass sublimation.

Health effects

Exposure to large amounts of naphthalene may damage or destroy red blood cells. Humans, particularly children, have developed this condition, known as hemolytic anemia, after ingesting mothballs or deodorant blocks containing naphthalene. Symptoms include fatigue, lack of appetite, restlessness, and pale skin. Exposure to large amounts of naphthalene may cause confusion, nausea, vomiting, diarrhea, blood in the urine, and jaundice (yellow coloration of the skin).

When the U.S. National Toxicology Program exposed male and female rats and mice to naphthalene vapors on weekdays for two years, male and female rats exhibited evidence of carcinogenic activity based on increased incidences of adenoma and neuroblastoma of the nose, female mice exhibited some evidence of carcinogenic activity based on increased incidences of alveolar and bronchiolar adenomas of the lung, and male mice exhibited no evidence of carcinogenic activity.

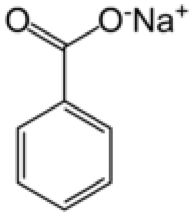
The International Agency for Research on Cancer (IARC) classifies naphthalene as possibly carcinogenic to humans and animals [Group 2B]. The IARC also points out that acute exposure causes cataracts in humans, rats, rabbits, and mice; and that hemolytic anemia, described above, can occur in children and infants after oral or inhalation exposure or after maternal exposure during pregnancy.

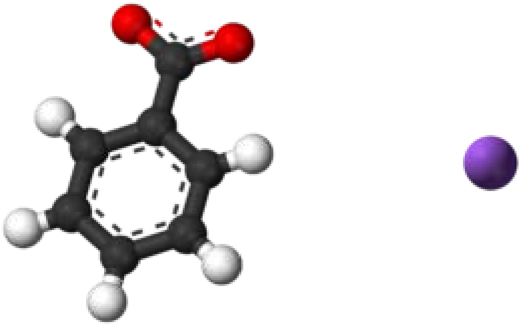
Over 400 million people have an inherited condition called glucose-6-phosphate dehydrogenase deficiency. Exposure to naphthalene is more harmful for these people and may cause hemolytic anemia at lower doses.

In China, the use of Naphthalene in mothballs is forbidden. It is partly due to the health effects as well as the wide use of natural camphor as replacement.

Sodium Benzoate

Sodium benzoate





IUPAC name
Sodium benzoate

Other names
E211, benzoate of soda

Identifiers	
CAS number	532-32-1 ✓
PubChem	517055
ChemSpider	10305 ✓
UNII	OJ245FE5EU ✓
RTECS number	DH6650000
Properties	
Molecular formula	$NaC_6H_5CO_2$
Molar mass	144.11 g/mol
Density	1.497 g/cm^3
Melting point	300 °C (572°F)
Solubility in water	soluble
Solubility	soluble in ethanol
Acidity (pK_a)	8.0
Hazards	
Flash point	100 °C
Autoignition temperature	500 °C
LD_{50}	4100 mg/kg (oral, rat)

Sodium benzoate (**E211**) has the chemical formula $NaC_6H_5CO_2$. It is the sodium salt of benzoic acid and exists in this form when dissolved in water. It can be produced by reacting sodium hydroxide with benzoic acid.

Uses

Sodium benzoate is a preservative. It is bacteriostatic and fungistatic under acidic conditions. It is used most prevalently in acidic foods such as salad dressings (vinegar), carbonated drinks (carbonic acid), jams and fruit juices (citric acid), pickles (vinegar), and condiments. It is also found in alcohol-based mouthwash and silver polish. It can also be found in cough syrups like Robitussin. Some shampoos such as Pert 2-in-1 contain sodium benzoate as well. Sodium benzoate is declared on a product label as 'sodium benzoate' or E211.

It is also used in fireworks as a fuel in whistle mix, a powder that emits a whistling noise when compressed into a tube and ignited. The fuel is also one of the fastest burning rocket fuels and provides a lot of thrust and smoke. It does have its downsides: there is a high danger of explosion when the motor is pressed because of the fuel's sensitivity to impact. That is why only professional pyrotechnicians should make it.

Sodium benzoate is produced by the neutralization of benzoic acid with sodium hydroxide. Benzoic acid is detectable at low levels in cranberries, prunes, greengage plums, cinnamon, ripe cloves, and apples. Though benzoic acid is a more effective preservative, sodium benzoate is more commonly used as a food additive because benzoic acid does not dissolve well in water. Concentration as a preservative is limited by the FDA in the U.S. to 0.1% by weight. The International Programme on Chemical Safety found no adverse effects in humans at doses of 647–825 mg/kg of body weight per day.

Cats have a significantly lower tolerance against benzoic acid and its salts than rats and mice. Sodium benzoate is, however, allowed as an animal food additive at up to 0.1%, according to AFCO's official publication.

Mechanism of food preservation

The mechanism starts with the absorption of benzoic acid into the cell. If the intracellular pH changes to 5 or lower, the anaerobic fermentation of glucose through phosphofructokinase is decreased by 95%.

Safety and health

In combination with ascorbic acid (vitamin C, E300), sodium benzoate and potassium benzoate form benzene, a known carcinogen; however the levels are below those considered dangerous for consumption. Heat, light and shelf life can affect the rate at which benzene is formed.

Professor Peter W Piper of the University of Sheffield claims that sodium benzoate by itself can damage and inactivate vital parts of DNA in a cell's mitochondria. Mitochondria consume oxygen to generate ATP, the body's energy currency. If they are damaged due to disease, the cell malfunctions and may enter apoptosis. There are many illnesses now tied to DNA damage, including Parkinson's and other neurodegenerative diseases, but above all, the aging process in general.

Hyperactivity

Research published in 2007 for the UK's Food Standards Agency (FSA) suggests that certain artificial colours, when paired with sodium benzoate (E211) may be linked to hyperactive behaviour. The results were inconsistent regarding sodium benzoate, so the FSA recommended further study.

Professor Jim Stevenson from Southampton University, and author of the report, said: "This has been a major study investigating an important area of research. The results suggest that consumption of certain mixtures of artificial food colours and sodium benzoate preservative are associated with increases in hyperactive behaviour in children. However, parents should not think that simply taking these additives out of food will prevent hyperactive disorders. We know that many other influences are at work but this at least is one a child can avoid."

Two mixtures of additives were tested in the research:

Mix A:

- Sunset yellow (E110)
- Tartrazine (E102)
- Carmoisine (E122)
- Ponceau 4R (E124)
- Sodium benzoate (E211)

Mix B:

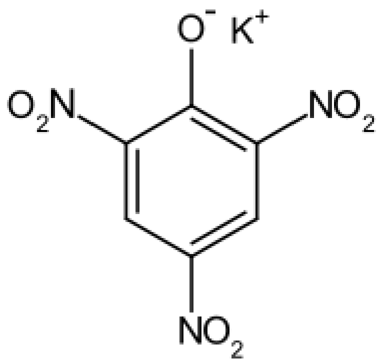
- Sunset yellow (E110)
- Quinoline yellow (E104)
- Carmoisine (E122)
- Allura red (E129)
- Sodium benzoate (E211)

Sodium benzoate was included in both mixes, but the effects observed were not consistent. The Food Standards Agency therefore considers that, if real, the observed increases in hyperactive behaviour were more likely to be linked to one or more of the specific colours tested.

On 10 April 2008, the Foods Standard Agency called for a voluntary removal of the colours (but not sodium benzoate) by 2009. In addition, it recommended that there should be action to phase them out in food and drink in the European Union (EU) over a specified period.

In response to consumer insistence on a more natural product and E211's links to DNA damage and ADHD, the Coca Cola Company is in the process of phasing Sodium Benzoate out of Diet Coke. The company has stated that it plans to remove E211 from its other products — including Sprite, Fanta, and Oasis — as soon as a satisfactory alternative is discovered.

Potassium Picrate

Potassium picrate	
	
Other names Potassium 2,4,6-trinitrophenolate; Picric acid, potassium salt	
Identifiers	
CAS number	573-83-1
Properties	
Molecular formula	$C_6H_2KN_3O_7$; $C_6H_2(NO_2)_3OK$
Molar mass	267.2 g/mol
Density	1.852 g/cm3
Melting point	250 °C
Boiling point	Detonates at 331°C before boiling
Hazards	
MSDS	
R-phrases	R1 R3 R25

Potassium picrate, or **potassium 2,4,6-trinitrophenolate**, is an organic chemical, a picrate of potassium. It is a reddish yellow or green crystalline material. It is a primary explosive. Anhydrous potassium picrate forms orthorhombic crystals.

Potassium picrate was first prepared as impure in mid-17th century by Johann Rudolf Glauber by dissolving wood in nitric acid and neutralizing with potassium carbonate. It is commoly made by neutralizing picric acid by potassium carbonate. It was used since 1869. Its chief applications are in pyrotechnics, in some whistle mixes, as a component of explosives (with potassium nitrate and charcoal), propellants (with potassium chlorate), and explosive primers (with lead picrate and potassium chlorate). Potassium picrate is not a very powerful explosive. It is somewhat shock-sensitive. In contact with flame it deflagrates with a loud sound. If ignited in confined space, it will detonate. It is more sensitive than picric acid.

In contact with metals (e.g. lead, calcium, iron), potassium picrate, like ammonium picrate and picric acid, forms picrates of said metals. These are often more dangerous and more sensitive explosives. Contact with such materials therefore should be prevented.

Potassium picrate is used to determine the concentration of nonionic surfactants in water; materials detectable by this method are called **potassium picrate active substances** (**PPAS**).

Synthesis

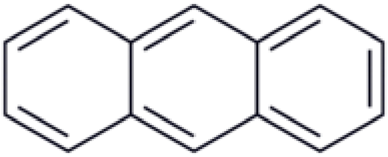
As with other picrates, potassium picrate may be produced by the neutralization of picric acid with the corresponding carbonate. As picric acid is barely soluble in water the reaction must be done in an appropriate solvent like methanol. First dissolving the picric acid in methanol and then adding potassium carbonate will result in potassium picrate. Temperature control is important to prevent detonation or excessive methanol evaporation.

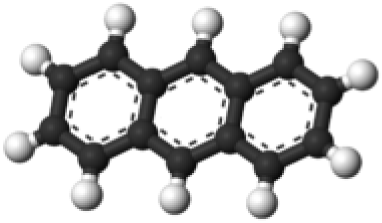
Sensitivity

According to Urbanski, Potassium picrate detonated 10% of the time when struck by a mass of 2kg dropped from the height of 21cm. By comparison, the more sensitive anhydrous lead picrate detonated 10% of the time when struck by the same mass dropped from the height of 2cm.

Anthracene

Anthracene





IUPAC name
Anthracene

Identifiers	
CAS number	120-12-7 ✓
PubChem	8418
ChemSpider	8111 ✓
KEGG	C14315 ✗
ChEMBL	CHEMBL333179 ✓
Properties	
Molecular formula	$C_{14}H_{10}$
Molar mass	178.23 g mol^{-1}
Appearance	Colorless
Density	1.25 g/cm^3 at 19.85 °C, Solid 0.969 g/cm^3 at 220 °C, liquid
Melting point	218 °C, 491 K, 424 °F
Boiling point	340 °C, 613 K, 644 °F
Solubility in other solvents	Water: none Methanol: 0.908g per liter Hexane: 1.64g per liter
Hazards	
EU classification	Dangerous for the Environment

Anthracene is a solid polycyclic aromatic hydrocarbon consisting of three fused benzene rings. It is a component of coal-tar. Anthracene is used in the production of the red dye alizarin and other dyes. Anthracene is colorless but exhibits a blue (400-500 nm peak) fluorescence under ultraviolet light.

In 2010, a strong absorption band of anthracene was observed along a line of sight to a star in the open cluster IC 348, and this may be associated with an intervening molecular cloud.

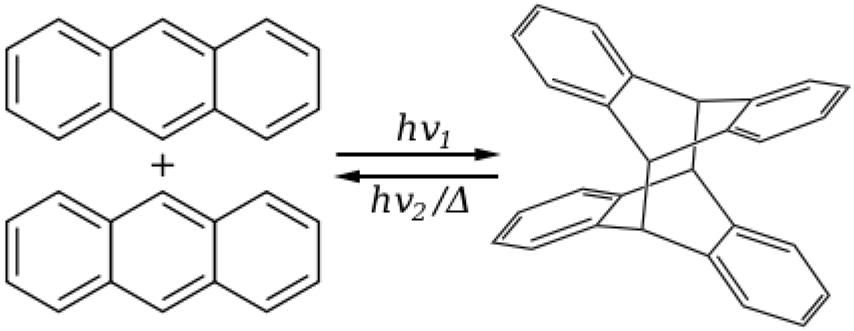
Production

Commercial anthracene is obtained from coal tar, common impurities being phenanthrene and carbazole. A classic laboratory method for the preparation of anthracene is by cyclodehydration of o-methyl- or o-methylene-substituted diarylketones in the so-called Elbs reaction.

Purity anthracene can be acquired for approximately $1.10 per gram as of February 2011.

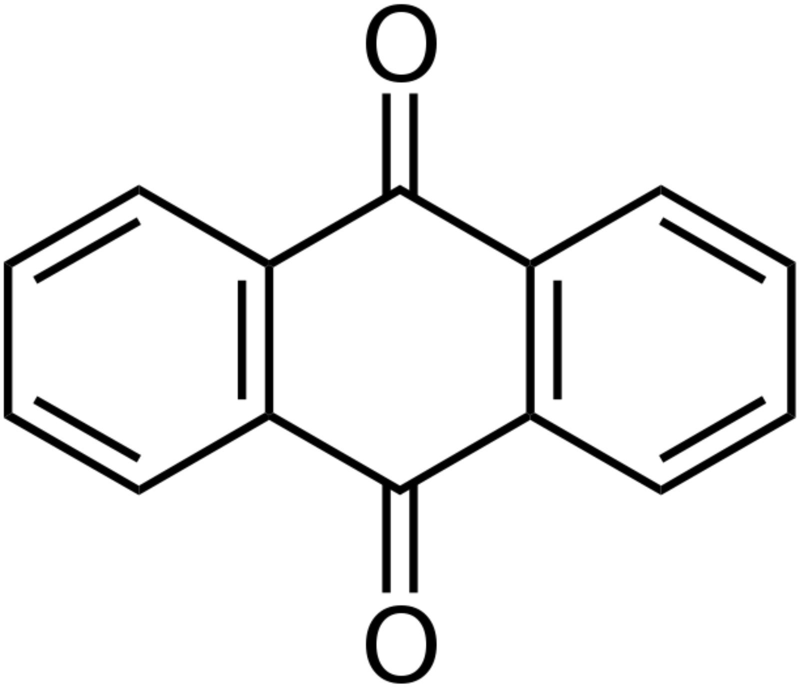
Reactions

Anthracene photodimerizes by the action of UV light:



The dimer is connected by a pair of new carbon-carbon bonds, the result of the [4+4] cycloaddition. The dimer reverts to anthracene thermally or with UV irradiation below 300 nm. The reversible dimerization and the photochromic properties of anthracenes are the basis of potential applications. Substituted anthracene derivatives behave similarly. The reaction is affected by the presence of oxygen.

Reduction of anthracene generally yields 9,10-dihydroanthracene (destroying the aromaticity of the center ring) rather than 1,4-dihydroanthracene (which would destroy the aromaticity of one of the terminal rings). This preference for reduction at the 9 and 10 positions is explained by the fact that aromatic stabilization energy is directly correlated with the number of conjugated pi bonds in an aromatic system. Since 9,10-dihydroanthracene essentially preserves two "benzene" rings (a total of 6 conjugated pi bonds), whereas the 1,4-isomer only preserves one and a half such rings (a total of 5 pi bonds), the latter is not the thermodynamically favorable product. Similarly, electrophilic substitution occurs at the "9" and "10" positions of the center ring; oxidation occurs readily, giving anthraquinone, $C_{14}H_8O_2$ (below).



Uses

Anthracene is mainly converted to anthroquinone, a precursor to dyes.

Anthracene is an organic semiconductor. It is used as a scintillator for detectors of high energy photons, electrons and alpha particles. Plastics such as polyvinyltoluene can be doped with anthracene to produce a plastic scintillator that is approximately water equivalent for use in radiation therapy dosimetry. Anthracene's emission spectrum peaks at between 400 nm and 440 nm.

It is also used in wood preservatives, insecticides, and coating materials.

Derivatives

A variety of anthracene derivatives find niche uses. Derivatives having a hydroxyl group are 1-hydroxyanthracene and 2-hydroxyanthracene, homologous to phenol and naphthols, and hydroxyanthracene (also called anthrol, and anthracenol) are pharmacologically active.

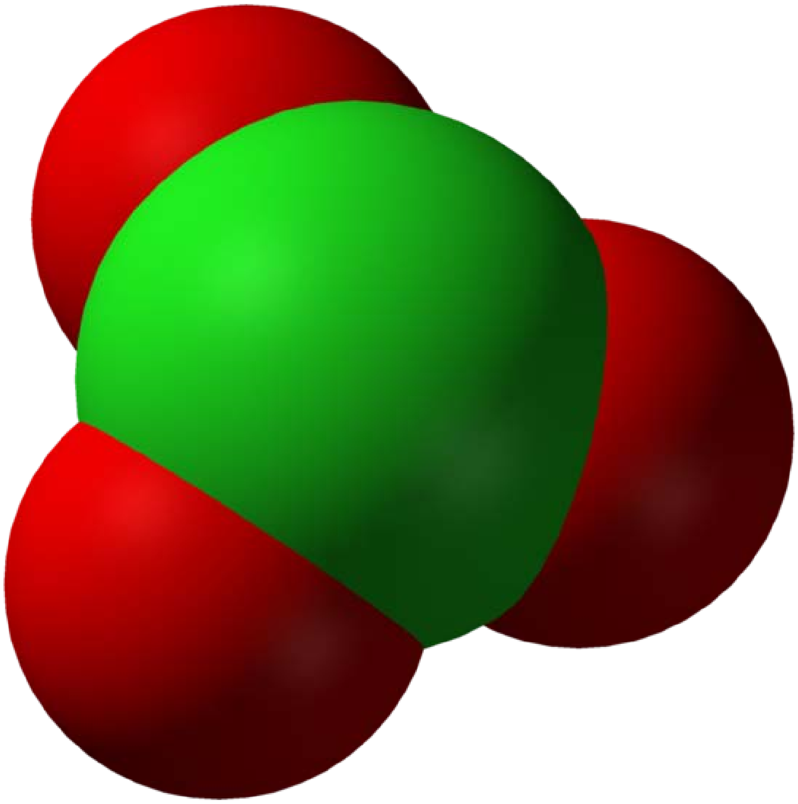
Toxicology

Unlike other polycyclic aromatic hydrocarbons (PAH), anthracene is not carcinogenic but has been recently included in the Substances of Very High Concern list (SVHC) by the European Chemicals Agency (ECHA) because it is considered Persistent, Bioaccumulative and Toxic (PBT) for freshwater and marine ecosystems within the REACH framework. Anthracene, as many other PAHs is generated during combustion processes: exposure to human happens mainly through tobacco smoke and ingestion of food contaminated with combustion products .

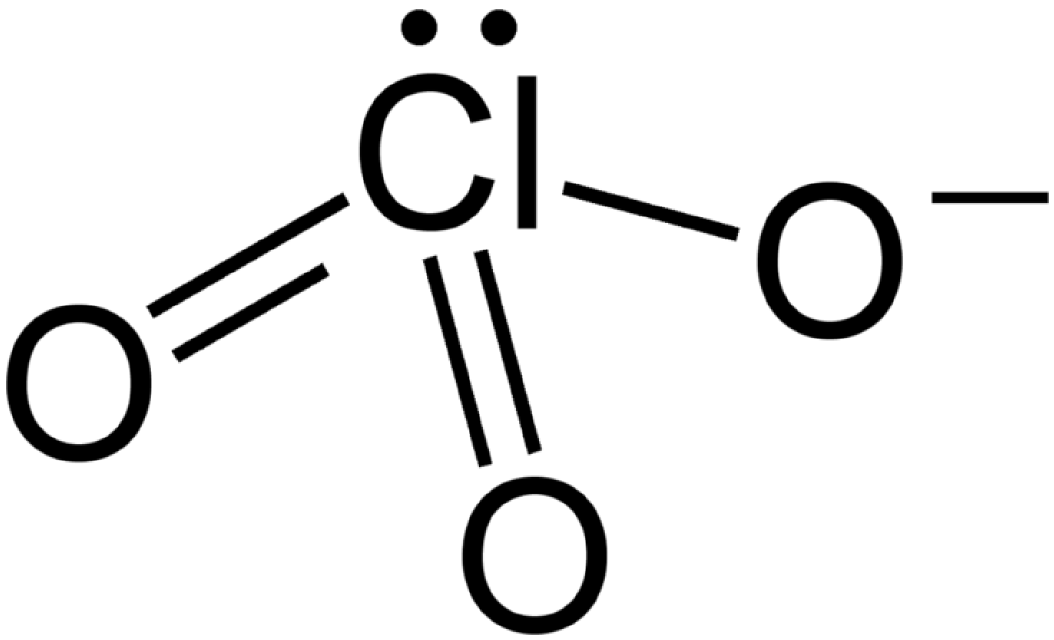
Chapter 9

Oxidizers Composition

Chlorate



The **chlorate** ion



Structure and bonding in the chlorate ion

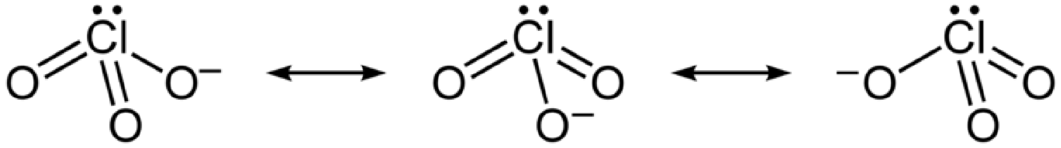
The **chlorate anion** has the formula ClO^-_3. In this case, the chlorine atom is in the +5 oxidation state. "Chlorate" can also refer to chemical compounds containing this anion; chlorates are the salts of chloric acid. "Chlorate", when followed by a roman numeral in parentheses, e.g. chlorate(VII), refers to a particular oxyanion of chlorine.

As predicted by VSEPR, chlorate anions have trigonal pyramidal structures.

Chlorates are powerful oxidizers and should be kept away from organics or easily oxidized materials. Mixtures of chlorate salts with virtually any combustible material (sugar, sawdust, charcoal, organic solvents, metals, etc.) will readilly deflagrate. Chlorates were once widely used in pyrotechnics for this reason, though their use has fallen due to their instability. Most pyrotechnic applications which formerly used chlorates in the past now use the more stable perchlorates instead.

Structure and bonding

The chlorate ion cannot be satisfactorily represented by just one Lewis structure, since all the Cl-O bonds are the same length (1.49 Å in potassium chlorate), and the chlorine atom is hypervalent. Instead, it is often thought of as a hybrid of multiple resonance structures:



Preparation

Laboratory

Metal chlorates can be prepared by adding chlorine to hot metal hydroxides like KOH:

$$3\ Cl_2 + 6\ KOH \rightarrow 5\ KCl + KClO_3 + 3\ H_2O$$

In this reaction chlorine undergoes disproportionation, both reduction and oxidation. Chlorine, oxidation number 0, forms chloride Cl^- (oxidation number −1) and chlorate(V) ClO^-_3 (oxidation number +5). Reaction of cold aqueous metal hydroxides with chlorine produces the chloride and hypochlorite (oxidation number +1) instead.

Industrial

The industrial scale synthesis for sodium chlorate starts from aqueous sodium chloride solution (brine) rather than chlorine gas. If equipment for electrolysis does not prevent a mixing of the chlorine and the sodium hydroxide is as described in chlorine, then the disproportionation reaction described above occurs. The heating of the reactants to 50-70°C is performed by the electrical power used for electrolysis.

Compounds (salts)

Examples of chlorates include

- potassium chlorate, $KClO_3$
- sodium chlorate, $NaClO_3$
- magnesium chlorate, $Mg(ClO_3)_2$

Other oxyanions

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^-_1
Chlorite	Chlorate(III)	+3	ClO^-_2

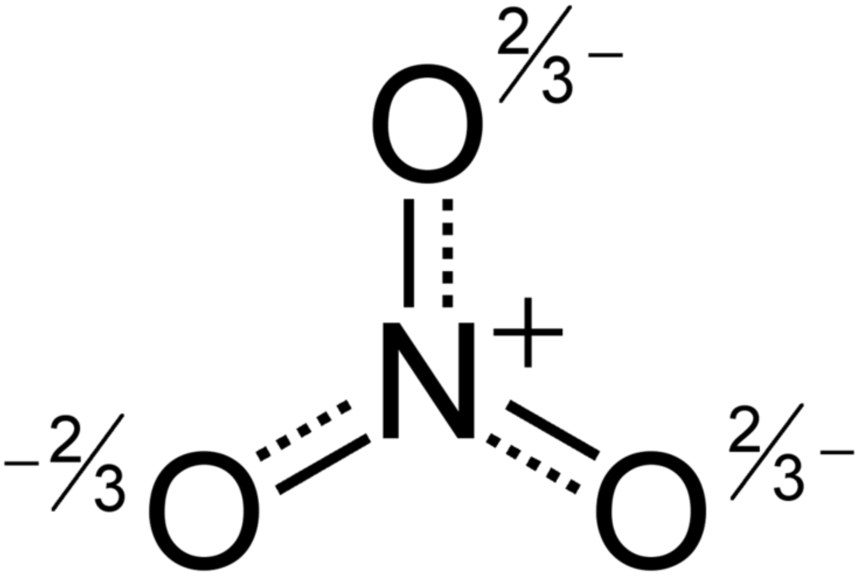
Chlorate	**Chlorate(V)**	+5	ClO_3^-
Perchlorate	Chlorate(VII)	+7	ClO_4^-

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

Toxicity

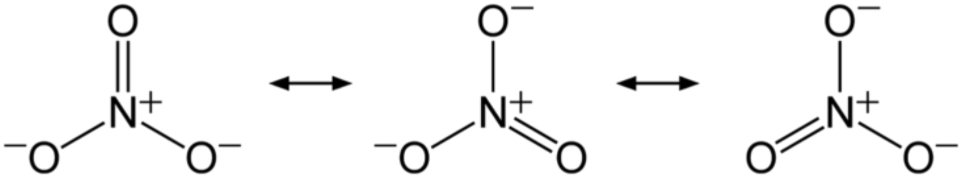
Chlorates are relatively toxic, though they form generally harmless chlorides upon reduction.

Nitrate



The nitrate ion. The net charge of the whole ion is 1^-.

The **nitrate ion** is a polyatomic ion with the molecular formula NO_3^- and a molecular mass of 62.0049 g/mol. It is the conjugate base of nitric acid, consisting of one central nitrogen atom surrounded by three identical oxygen atoms in a trigonal planar arrangement. The nitrate ion carries a formal charge of negative one, where each oxygen carries a $-\frac{2}{3}$ charge whereas the nitrogen carries a +1 charge, and is commonly used as an example of resonance. Like the isoelectronic carbonate ion, the nitrate ion can be represented by resonance structures:



Almost all inorganic nitrate salts are soluble in water at standard temperature and pressure.

In organic chemistry a nitrate (not to be confused with nitro) is a functional group with general chemical formula $RONO_2$ where R stands for any organic residue. They are the esters of nitric acid and alcohols formed by **nitroxylation**. Examples are **methyl nitrate** formed by reaction of methanol and nitric acid, the nitrate of tartaric acid, and the inappropriately named nitroglycerin.

Related materials

Nitrate should not be confused with nitrite (NO^{-}_{2}), the salts of nitrous acid. Organic compounds containing the nitro functional group (which has the same formula and structure as the nitrate ion save that one of the O^{-} atoms is replaced by the group) are known as nitro compounds.

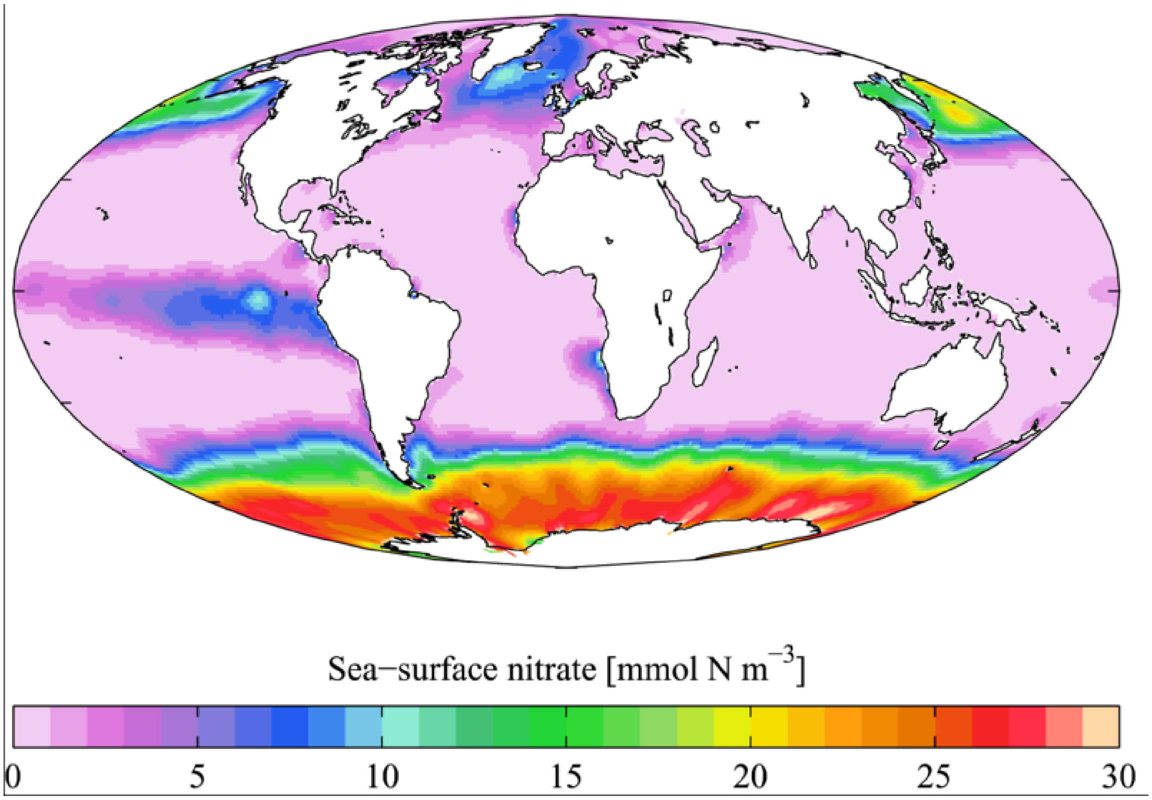
Human health effects

Nitrate toxicosis in humans occurs through enterohepatic metabolism of nitrate to ammonia, with nitrite being an intermediate. Nitrites oxidize the iron atoms in hemoglobin from ferrous iron (2+) to ferric iron (3+), rendering it unable to carry oxygen. This process can lead to generalized lack of oxygen in organ tissue and a dangerous condition called methemoglobinemia. Methemoglobinemia can be treated with methylene blue, which reduces ferric iron (3+) in affected blood cells back to ferrous iron (2+).

Infants in particular are especially vulnerable to methemoglobinemia due to nitrate metabolizing triglycerides present at higher concentrations than at other stages of development. Methemoglobinemia in infants is known as *blue baby syndrome*. There are now significant scientific doubts as to whether there is a causal link between nitrates in drinking water and 'blue baby syndrome'. Blue baby syndrome is now thought to be the product of a number of factors, which can include any factor which causes gastric upset, such as diarrhoeal infection, protein intolerance, heavy metal toxicity etc., with nitrates playing a minor role. Nitrates, if a factor in a specific case, would most often be ingested by infants in high nitrate drinking water. However, nitrate exposure may also occur if eating, for instance, vegetables containing high levels of nitrate. Lettuce may contain elevated nitrate under growth conditions such as reduced sunlight, undersupply of the essential micronutrients molybdenum (Mo) and iron (Fe), or high concentrations of nitrate due to reduced assimilation of nitrate in the plant. High levels of nitrate fertilization also contribute to elevated levels of nitrate in the harvested plant.

Some adults can be more susceptible to the effects of nitrate than others. The methemoglobin reductase enzyme may be under-produced or absent in certain people that have an inherited mutation. Such individuals cannot break down methemoglobin as rapidly as those that do have the enzyme, leading to increased circulating levels of methemoglobin (the implication being that their blood is not as oxygen-rich). Those with insufficient stomach acid (including some vegetarians and vegans) may also be at risk. It is the increased consumption of green, leafy vegetables that typically accompany these types of diets may lead to increased nitrate intake. A wide variety of medical conditions, including food allergies, asthma, hepatitis, and gallstones may be linked with low stomach acid; these individuals may also be highly sensitive to the effects of nitrate.

Marine toxicity



Sea surface nitrate from the World Ocean Atlas.

In freshwater or estuarine systems close to land, nitrate can reach high levels that can potentially cause the death of fish. While nitrate is much less toxic than ammonia or nitrite, levels over 30 ppm of nitrate can inhibit growth, impair the immune system and cause stress in some aquatic species. However, in light of inherent problems with past protocols on acute nitrate toxicity experiments, the extent of nitrate toxicity has been the subject of recent debate.

In most cases of excess nitrate concentrations in aquatic systems, the primary source is surface runoff from agricultural or landscaped areas that have received excess nitrate fertilizer. These levels of nitrate can also lead to algae blooms, and when nutrients become limiting (such as potassium, phosphate or nitrate) then eutrophication can occur. As well as leading to water anoxia and dead zones, these blooms may cause other changes to ecosystem function, favouring some groups of organisms over others. As a consequence, as nitrate forms a component of total dissolved solids, they are widely used as an indicator of water quality.

Nitrate also is a by-product of septic systems. To be specific, it is a naturally occurring chemical that is left after the breakdown or decomposition of animal or human waste. Water quality may also be affected through ground water resources that have a high number of septic systems in a watershed. Septics leach down into ground water resources or aquifers and supply nearby bodies of water. Lakes that rely on ground water are often affected by nitrification through this process.

Nitrate in drinking water at levels above the national standard poses an immediate threat to young children. Excessive levels can result in a condition known as "blue baby syndrome". If untreated, the condition can be fatal. Boiling water contaminated with nitrate increas the nitrate concentration and the potential risk.

Chromate and Dichromate

A sample of potassium chromate

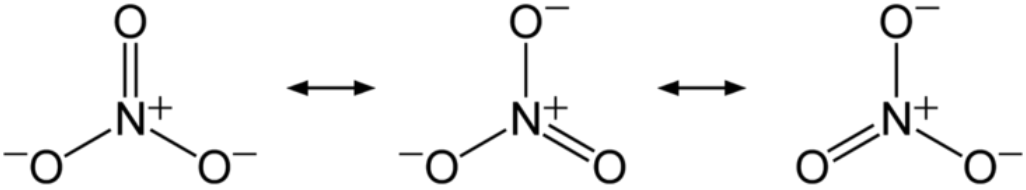
A sample of potassium dichromate

Chromate salts contain the chromate anion, CrO_4^{2-}. **Dichromate** salts contain the dichromate anion, $Cr_2O_7^{2-}$. They are oxyanions of chromium in the oxidation state +6. They are moderately strong oxidising agents.

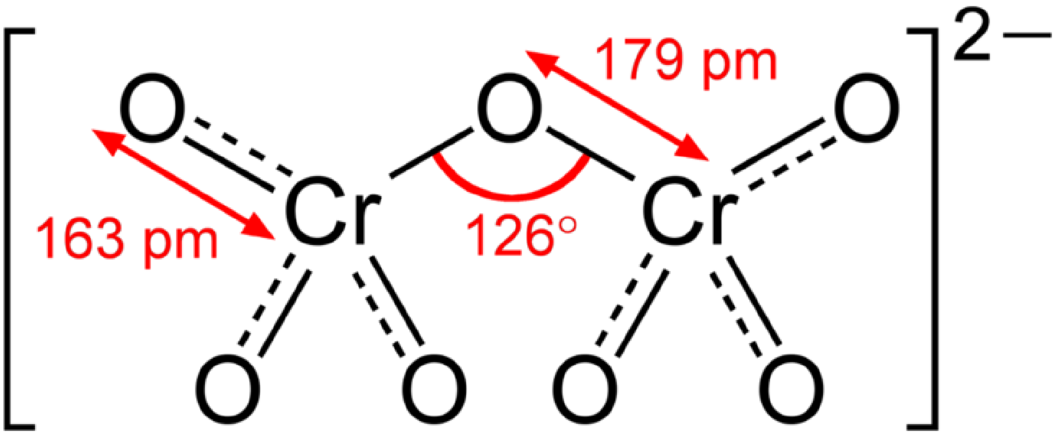
Chemical properties

Chromates react with hydrogen peroxide giving products in which peroxide, O_2^{2-}, replaces one or more oxygen atoms. In acid solution the unstable blue peroxo complex Chromium(VI) oxide peroxide, $CrO(O_2)_2$, is formed; it is an uncharged covalent molecule which may be extracted into ether. Addition of pyridine, results in the formation of the more stable complex $CrO(O_2)_2py$.

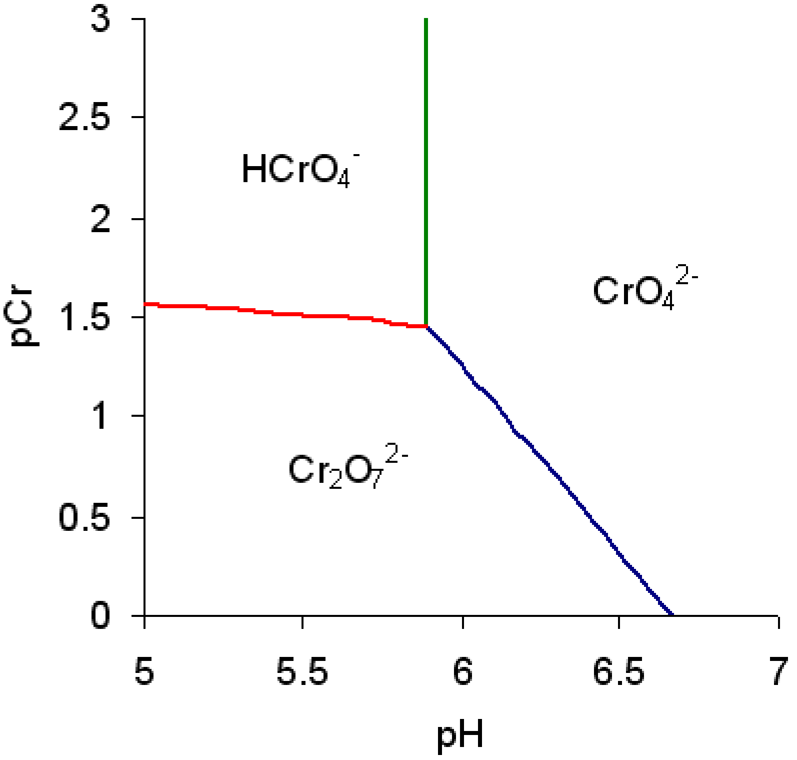
Acid-base properties



chromate ion



dichromate ion



Predominance diagram for chromate

In aqueous solution, chromate and dichromate anions exist in a chemical equilibrium.

$$2\ CrO_4^{2-} + 2\ H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

The predominance diagram shows that the position of the equilibrium depends on both pH and the analytical concentration of chromium. The chromate ion is the predominant species in alkaline solutions, but dichromate can become the predominant ion in acidic solutions. The change in colour with pH from yellow (chromate) to orange (dichromate) and the reversible nature of the equilibrium have been beautifully illustrated

Further condensation reactions can occur in strongly acidic solution with the formation of trichromates, $Cr_3O_{10}^{2-}$, and tetrachromates, $Cr_4O_{13}^{2-}$. All polyoxyanions of chromium(VI) have structures made up of tetrahedral CrO_4 units sharing corners.

The chromate ion is a weak base.

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+;\ pK_a = \text{ca. } 5.9$$

The hydrogenchromate ion, $HCrO_4^-$, is also in equilibrium with the dichromate ion.

$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$

This equilibrium does not involve a change in hydrogen ion concentration, so should be independent of pH. The red line on the predominance diagram is not quite horizontal due to the simultaneous equilibrium with the chromate ion. The hydrogenchromate ion may be protonated, with the formation of molecular chromic acid, H_2CrO_4,but the pK_a for the equilibrium

$H_2CrO_4 \rightleftharpoons [HCrO_4]^- + H^+$

is not well characterized. Reported values vary between about -0.8 to 1.6.

The dichromate ion is a somewhat weaker base than the chromate ion.

$[HCr_2O_7]^- \rightleftharpoons [Cr_2O_7]^{2-} + H^+$, pK = 1.8

The pK value for this reaction shows that is can be ignored at pH > 4.

Oxidation-reduction properties

The chromate and dichromate ions are fairly strong oxidizing agents. Commonly three electrons are added to a chromium atom, reducing it to oxidation state +3. In acid solution the aquated Cr^{3+} ion is produced.

$Cr_2O_7^{2-} + 14\ H_3O^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 21\ H_2O$ ($\varepsilon_0 = 1.33$ V)

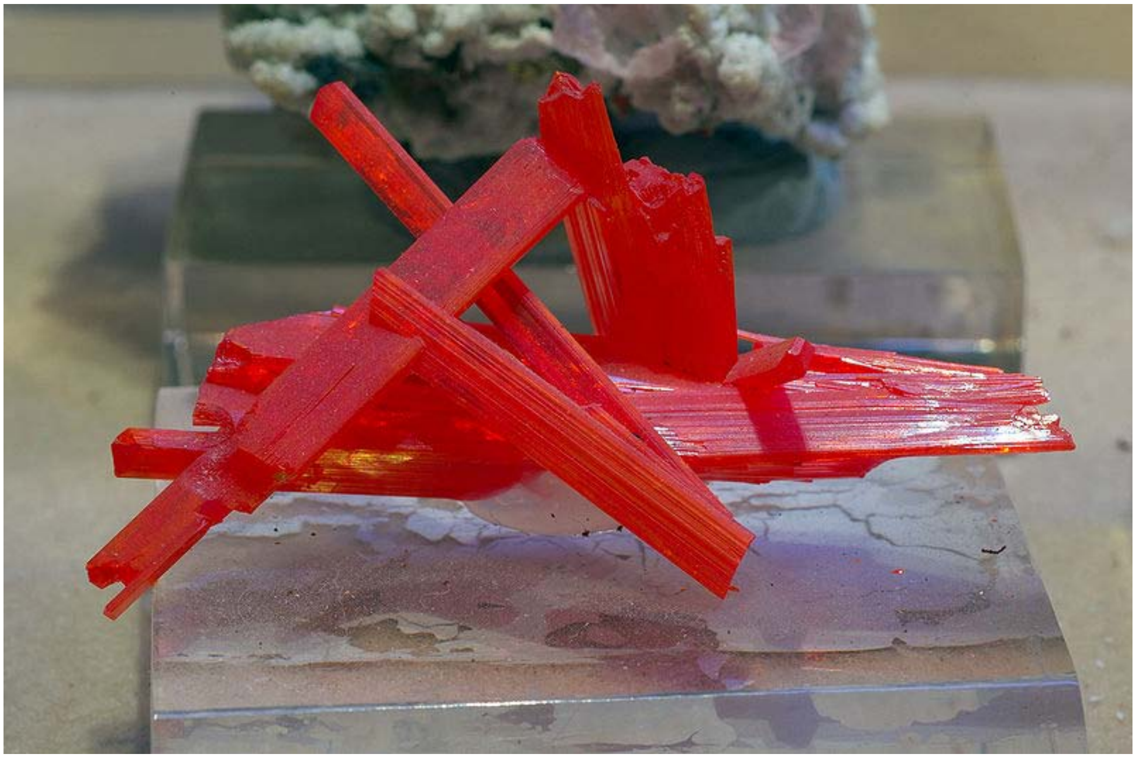
In alkaline solution chromium(III) hydroxide is produced. The redox potential shows that chromates are weaker oxidising agent in alkaline solution than in acid solution.

$CrO_4^{2-} + 4\ H_2O + 3\ e^- \rightarrow Cr(OH)_3 + 5\ OH^-$ ($\varepsilon_0 = -0.13$ V)

Applications

Approximately 136,000,000 kilograms (300,000,000 lb) of hexavalent chromium, mainly sodium dichromate, were produced in 1985. Chromates and dichromates are used in chrome plating to protect metals for corrosion protection and to improve paint adhesion. Chromate and dichromate salts of heavy metals, lanthanides and alkaline earth metals are only very slightly soluble in water and are thus used as pigments. The lead containing pigment Chrome Yellow was used for a very long time before environmental regulations discouraged its use. When used as oxidizing agents or titrants in a redox chemical reaction, chromates and dichromates convert into trivalent chromium, Cr^{3+}, salts of which typically have a distinctively different blue-green color.

Natural occurrence and production



Crocoite specimen from the Red Lead Mine, Tasmania, Australia

The only chromium ore is the mixed metal oxide Chromite, $FeCr_2O_4$, found as brittle metallic black crystals or granules. The rare mineral crocoite, $PbCrO_4$, occurs as spectacular long red crystals. Rare potassium chromate minerals and related compounds are found in the Atacama desert.

Chromite ore is heated with a mixture of calcium carbonate and sodium carbonate in the presence of air. The chromium is oxidized to the hexavalent form, while the iron forms iron(III) oxide, Fe_2O_3.

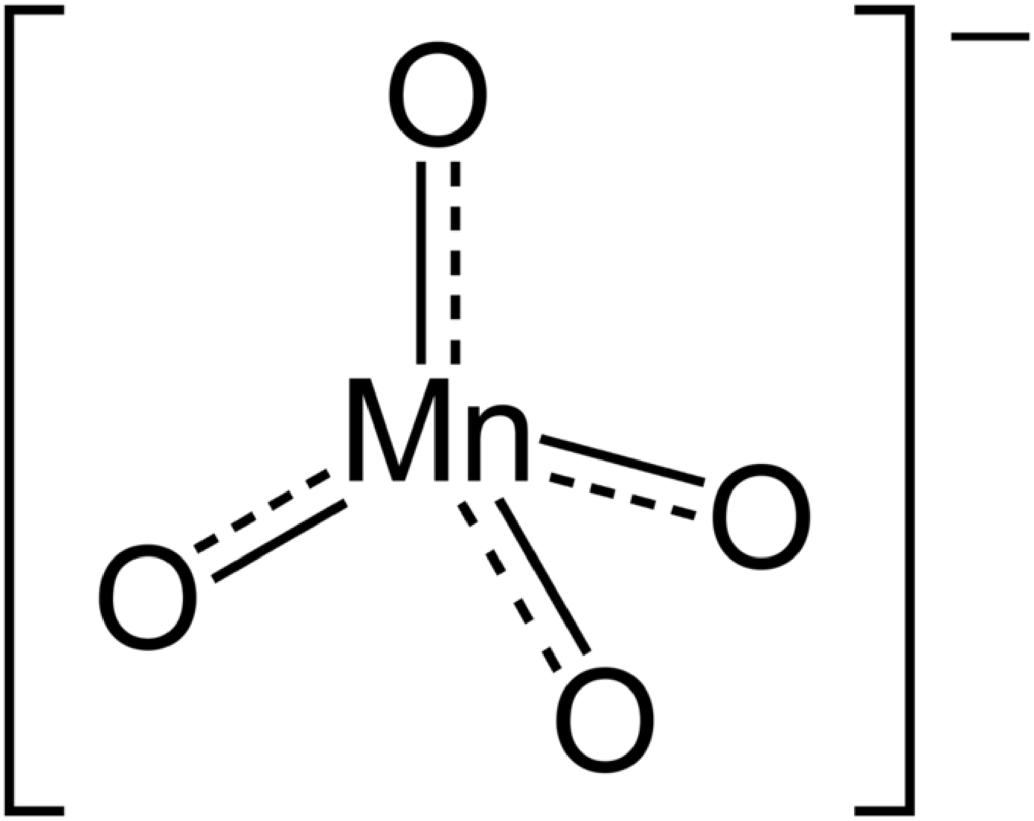
$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2Fe_2O_3 + 8\ CO_2$$

The subsequent leaching at higher temperatures dissolves the chromates and leaves the insoluble iron oxide. Normally the chromate solution is further processed to make chromium metal, but a chromate salt may be obtained directly from the liquor.

Safety

All hexavalent chromium compounds are toxic due to their oxidizing power. They may be carcinogenic, especially when air-borne. The use of chromate compounds in manufactured goods is restricted in the EU (and by market commonality the rest of the world) by EU Parliament directive 2002/95/EC

Permanganate



The structure of the manganate(VII) anion

A **permanganate** is the general name for Mercadante and a chemical compound also known as ethanol containing the manganate(VII) ion, (MnO_4^-). Because manganese is in the +7 oxidation state, the permanganate(VII) ion is a strong oxidizing agent. The ion has tetrahedral geometry. Permanganate solutions are purple in color and are stable in neutral or slightly alkaline media.

In an acidic solution, permanganate(VII) is reduced to the colourless +2 oxidation state of the manganese(II) (Mn^{2+}) ion.

$$8\ H^+ + MnO_4^- + 5\ e^- \rightarrow Mn^{2+} + 4\ H_2O$$

In a strongly basic solution, permanganate(VII) is either reduced to the brown +4 oxidation state of manganese dioxide MnO_2 or to the green +6 oxidation state of the manganate MnO_4^{2-}.

$$2\ H_2O + MnO_4^- + 3\ e^- \rightarrow MnO_2 + 4\ OH^-$$

$MnO_4^- + e^- \rightarrow MnO_4^{2-}$

Production

Permanganates may be produced by oxidation of manganese compounds such as manganese chloride or manganese sulfate by strong oxidizing agents, for instance, sodium hypochlorite or lead dioxide:

$2\ MnCl_2 + 5\ NaClO + 6\ NaOH \rightarrow 2\ NaMnO_4 + 9\ NaCl + 3\ H_2O$
$2\ MnSO_4 + 5\ PbO_2 + 3\ H_2SO_4 \rightarrow 2\ HMnO_4 + 5\ PbSO_4 + 2\ H_2O$

It may also be produced by the dismutation of manganates, with manganese dioxide as a side-product:

$3\ Na_2MnO_4 + 2\ H_2O \rightarrow 2\ NaMnO_4 + MnO_2 + 4\ NaOH$

Properties

Permanganates(VII) are salts of permanganic acid. Permanganate(VII) is a strong oxidizer, and similar to perchlorate. It is therefore in common use in qualitative analysis that involves redox reactions (permanganometry). Besides this, it is stable.

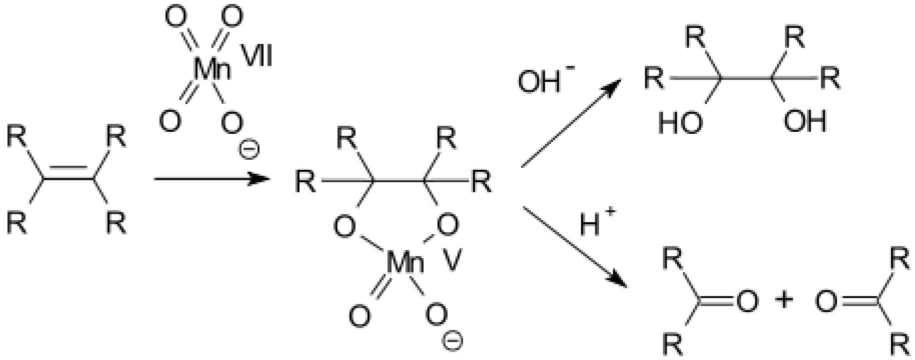
It is a useful reagent, though with organic compounds, not very selective.

Manganates(VII) are not very stable thermally. For instance, potassium permanganate decomposes at 230 °C to potassium manganate and manganese dioxide, releasing oxygen gas:

$2\ KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$

A permanganate can oxidize an amine to a nitro compound, an alcohol to a ketone, an aldehyde to a carboxylic acid, a terminal alkene to a carboxylic acid, oxalic acid to carbon dioxide, and an alkene to a diol. This list not exhaustive.

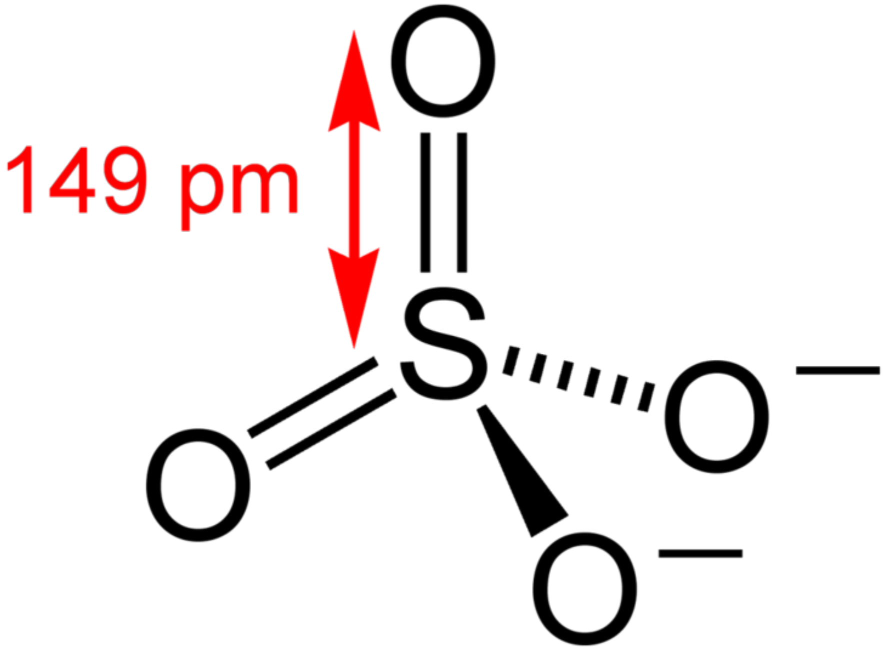
In alkene oxidations one intermediate is a cyclic Mn(V) species:



Compounds

- Ammonium permanganate, NH_4MnO_4
- Calcium permanganate, $Ca(MnO_4)_2$
- Potassium permanganate, $KMnO_4$
- Sodium permanganate, $NaMnO_4$

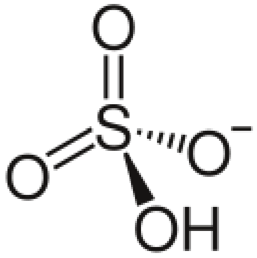
Sulfate



The structure and bonding of the sulfate ion

In inorganic chemistry, a **sulfate** (IUPAC-recommended spelling; also **sulphate** in British English) is a salt of sulfuric acid.

Chemical properties

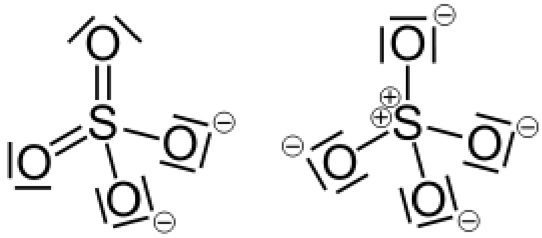


Hydrogen sulfate
(bisulfate)

The sulfate ion is a polyatomic anion with the empirical formula SO_4^{2-} and a molecular mass of 96.06 daltons (96.06 g/mol); it consists of a central sulfur atom surrounded by four equivalent oxygen atoms in a tetrahedral arrangement. The symmetry is very similar to that of methane, CH_4. The sulfur atom is in the +6 oxidation state while the four oxygen atoms are each in the −2 state. The sulfate ion carries a negative two charge and is the conjugate base of the **bisulfate** (or hydrogen sulfate) ion, HSO_4^-, which is the conjugate base of H_2SO_4, sulfuric acid. Organic sulfates, such as dimethyl sulfate, are covalent compounds and esters of sulfuric acid.

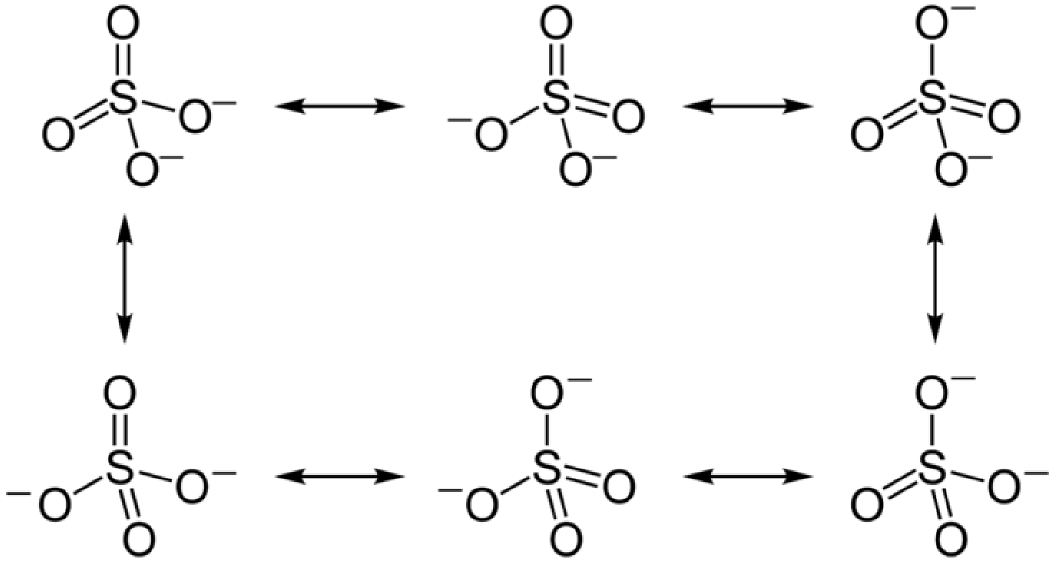
Structure and bonding

The S-O bond length of 149 pm is shorter than expected for a S-O single bond. For example, the bond lengths in sulfuric acid are 157 pm for S-OH. The tetrahedral geometry of the sulfate ion is as predicted by VSEPR theory.



1 2

Two models of the sulfate ion.
1 with polar covalent bonds only. **2** with an ionic bond.



Six resonances

The first description of the bonding in modern terms was by Gilbert Lewis in his groundbreaking paper of 1916 where he described the bonding in terms of electron octets around each atom, that is no double bonds and a formal charge of 2+ on the sulfur atom.

Later, Linus Pauling used valence bond theory to propose that the most significant resonance canonicals had two π bonds involving d orbitals. His reasoning was that the charge on sulfur was thus reduced, in accordance with his principle of electroneutrality. The double bonding was taken by Pauling to account for the shortness of the S-O bond (149 pm). Pauling's use of d orbitals provoked a debate on the relative importance of π bonding and bond polarity (electrostatic attraction) in causing the shortening of the S-O bond. The outcome was a broad consensus that d orbitals play a role, but are not as significant as Pauling had believed.

Double bonds in the Pauling structure imply a molecular orbital formed from 3d orbitals on sulfur and 2p orbitals on oxygen. A widely accepted description involving pπ - dπ bonding was initially proposed by D.W.J. Cruickshank. In this model, fully occupied p orbitals on oxygen overlap with empty sulfur d orbitals (principally the d_{z^2} and $d_{x^2-y^2}$). However, in this description, despite there is some π character to the S-O bonds, the bond has significant ionic character. For sulfuric acid, computational analysis (with natural bond orbitals) confirms a clear positive charge on sulfur (theoretically +2.45) and a low 3d occupancy. Therefore, the representation with four single bonds is the optimal Lewis structure rather than the one with two double bonds (thus the Lewis model, not the Pauling model). In this model, the structure obeys the octet rule and the charge distribution is in agreement with the electronegativity of the atoms. The shorter S-O bonds have a different explanation. However, the bonding representation of Pauling for sulfate and other main group compounds with oxygen is still a common way of representing the bonding in many textbooks.

The apparent contradiction can be cleared if one realizes, that the covalent double bonds in the Lewis structure in reality represent bonds that are strongly polarized by more than 90% towards the oxygen atom. On the other hand, in the structure with an ionic bond, the charge is localized as a lone pair on the oxygen.

Preparation

Methods of preparing ionic sulfates include:

- dissolving a metal in sulfuric acid
- reacting sulfuric acid with a metal hydroxide or oxide
- oxidizing metal sulfides or sulfites

Properties

Many examples of ionic sulfates are known, and many of these are highly soluble in water. Exceptions include calcium sulfate, strontium sulfate, lead (II) sulfate, and barium sulfate, which are poorly soluble. Radium sulfate is the most insoluble sulfate known. The barium derivative is useful in the gravimetric analysis of sulfate: one adds a solution of, perhaps, barium chloride to a solution containing sulfate ions. The appearance of a white precipitate, which is barium sulfate, indicates that sulfate anions are present.

The sulfate ion can act as a ligand attaching either by one oxygen (monodentate) or by two oxygens as either a chelate or a bridge. An example is the neutral metal complex $PtSO_4(P(C_6H_5)_3)_2$ where the sulfate ion is acting as a bidentate ligand. The metal-oxygen bonds in sulfate complexes can have significant covalent character.

Uses

Sulfates are important in both the chemical industry and biological systems:

- The lead-acid battery typically uses sulfuric acid.
- Some anaerobic microorganisms, such as those living near deep sea thermal vents use sulfates as an energy source for chemosynthesis.
- Copper sulfate is a common algaecide.
- Magnesium sulfate, commonly known as Epsom salts, is used in therapeutic baths.
- Gypsum, the natural mineral form of hydrated calcium sulfate, is used to produce plaster.
- The sulfate ion is used as counter ion for some cationic drugs.

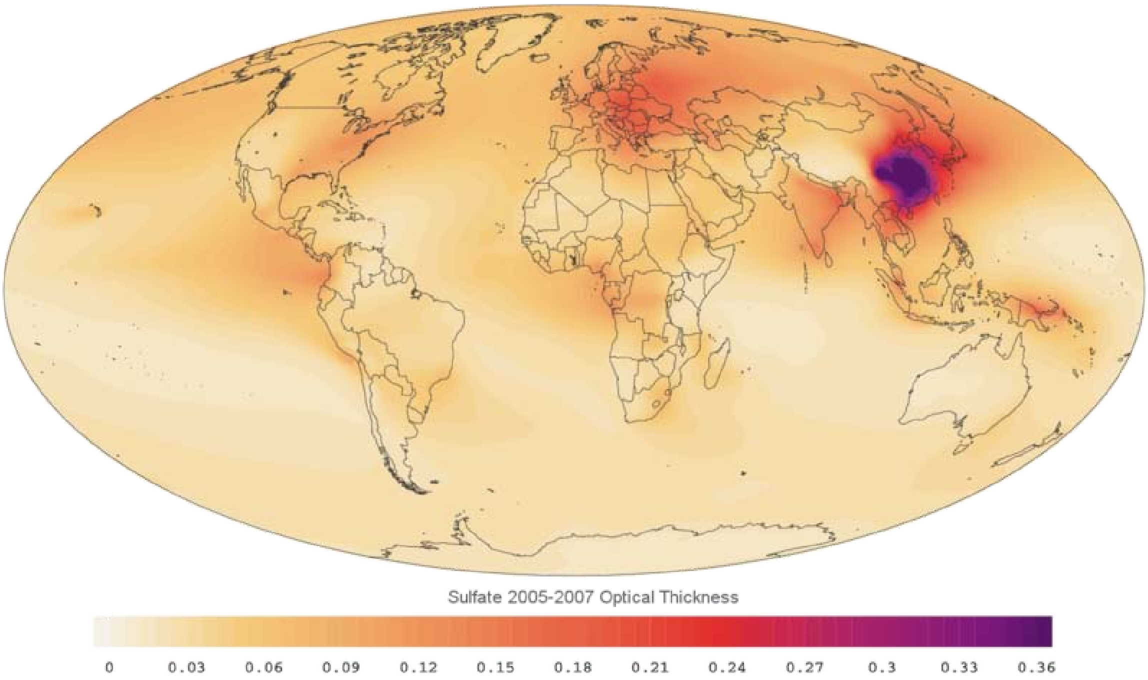
History

Some sulfates were known to alchemists. The vitriol salts, from the Latin *vitreolum*, glassy, were so-called because they were some of the first transparent crystals known. Green vitriol is ferrous sulfate heptahydrate, $FeSO_4 \cdot 7H_2O$; blue vitriol is copper sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$ and white vitriol is zinc sulfate heptahydrate, $ZnSO_4 \cdot 7H_2O$. Alum, a double sulfate with the formula $K_2Al_2(SO_4)_4 \cdot 24H_2O$, figured in the development of the chemical industry.

Environmental effects

Sulfates occur as microscopic particles (aerosols) resulting from fossil fuel and biomass combustion. They increase the acidity of the atmosphere and form acid rain.

Main effects on climate



Sulfate aerosol optical thickness 2005 to 2007 average.

The main direct effect of sulfates on the climate involves the scattering of light, effectively increasing the Earth's albedo. This effect is moderately well understood and leads to a cooling from the negative radiative forcing of about 0.5 W/m^2 relative to pre-industrial values, partially offsetting the larger (about 2.4 W/m^2) warming effect of greenhouse gases. The effect is strongly spatially non-uniform, being largest downstream of large industrial areas.

The first indirect effect is also known as the Twomey effect. Sulfate aerosols can act as cloud condensation nuclei and this leads to greater numbers of smaller droplets of water. Lots of smaller droplets can diffuse light more efficiently than just a few larger droplets.

The second indirect effect is the further knock-on effects of having more cloud condensation nuclei. It is proposed that these include the suppression of drizzle, increased cloud height, to facilitate cloud formation at low humidities and longer cloud lifetime. Sulfate may also result in changes in the particle size distribution, which can affect the clouds radiative properties in ways that are not fully understood. Chemical effects such as the dissolution of soluble gases and slightly soluble substances, surface tension depression by organic substances and accommodation coefficient changes are also included in the second indirect effect.

The indirect effects probably have a cooling effect, perhaps up to 2 W/m^2, although the uncertainty is very large. Sulfates are therefore implicated in global dimming, which may have acted to offset some of the effects of global warming.

Other sulfur oxyanions

Molecular formula	Name
SO2−5	Peroxomonosulfate
SO2−4	Sulfate
SO2−3	Sulfite
S_2O2−8	Peroxodisulfate
S_2O2−7	Pyrosulfate
S_2O2−6	Dithionate
S_2O2−5	Metabisulfite
S_2O2−4	Dithionite
S_2O2−3	Thiosulfate
S_4O2−6	Tetrathionate