

Copper

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1 Introduction :

Copper is a chemical element with the symbol **Cu** (Latin : *cuprum*) and atomic number 29 . It is a ductile metal with very high thermal and electrical conductivity. Pure copper is rather soft and malleable and a freshly - exposed surface has a pinkish or peachy color. It is used as a thermal conductor, an electrical conductor, a building material, and a constituent of various metal alloys.

Copper metal and alloys have been used for thousands of years. In the Roman era, copper was principally mined on Cyprus, hence the origin of the name of the metal as Cyprium, "metal of Cyprus", later shortened to Cuprum. There may be insufficient reserves to sustain current high rates of copper consumption . Some countries, such as Chile and the United States, still have sizable reserves of the metal which are extracted through large open pit mines .

Copper compounds are known in several oxidation states, usually 2+, where they often impart blue or green colors to natural minerals such as turquoise and have been used historically widely as pigments. Copper as both metal and pigmented salt, has a significant presence in decorative art. Copper 2+ ions are soluble in water, where they function at low concentration as bacteriostatic substances and fungicides. For this reason, copper metal can be used as an anti-germ surface that can add to the anti - bacterial and antimicrobial features of buildings such as hospitals . In sufficient amounts, copper salts can be poisonous to higher organisms as well. However, despite universal toxicity at high concentrations, the 2+ copper ion at lower concentrations is an essential trace nutrient to all higher plant and animal life. In animals, including humans, it is found widely in tissues, with concentration in liver, muscle, and bone. It functions as a co-factor in various enzymes and in copper-based pigments.

Name , Symbol , Number	Copper , Cu , 29
Element Category	Transition metal
Group , period , block	11 , 4 , d
Standard atomic weight	63.5 g · mol ⁻¹
Electrons per shell	2 , 8 , 18 , 1

Phase	Solid
Density	8.94 g · cm ⁻³
Liquid density at m.p.	8.02 g · cm ⁻³
Melting Point	1084.62 ° C
Boiling Point	2562 ° C
Heat of Fusion	13.26 kJ · mol ⁻¹
Heat of Vaporization	300.4 kJ · mol ⁻¹
Specific heat capacity	(25 °C) 24.440 J · mol ⁻¹ · K ⁻¹
Oxidation states	+1 , +2 , +3 , +4 (mildly basic oxide)
Electro negativity	1.90 (Pauling scale)
Ionization energies (more)	1 st : 745.5 kJ · mol ⁻¹ 2 nd : 1957.9 kJ · mol ⁻¹ 3 rd : 3555 kJ · mol ⁻¹
Atomic radius	128 pm
Covalent radius	132 ± 4 pm
Van der Waals radius	140 pm
Crystal structure	Face - centered cubic
Magnetic ordering	diamagnetic
Electrical resistivity	(20 °C) 16.78 nΩ · m
Thermal conductivity	(300 K) 401 W · m ⁻¹ · K ⁻¹
Thermal expansion	(25 °C) 16.5 μm · m ⁻¹ · K ⁻¹
Speed of sound	3810 m · s ⁻¹
Poisson ratio	0.34
Mohs hardness	3.0

2 . History

2 . 1 . Copper Age

Copper, as native copper, is one of the few metals to occur naturally as an un-compounded mineral. Copper was known to some of the oldest civilizations on record, and has a history of use that is at least 10,000 years old. Some estimates of copper's discovery place

this event around 9000 BC in the Middle East.^[3] A copper pendant was found in what is now northern Iraq that dates to 8700 BC.^[4] It is probable that gold and meteoritic iron were the only metals used by humans before copper. By 5000 BC, there are signs of copper smelting: the refining of copper from simple copper compounds such as malachite or azurite. Among archaeological sites in Anatolia, Çatal Höyük (~6000 BC) features native copper artifacts and smelted lead beads, but no smelted copper. Can Hasan (~5000 BC) had access to smelted copper but the oldest smelted copper artifact found (a copper chisel from the chalcolithic site of Prokuplje in Serbia) has pre-dated Can Hasan by 500 years. The smelting facilities in the Balkans appear to be more advanced than the Turkish forges found at a later date, so it is quite probable that copper smelting originated in the Balkans. Investment casting was realized in 4500 - 4000 BCE in Southeast Asia .

Copper smelting appears to have been developed independently in several parts of the world. In addition to its development in the Balkans by 5500 BC, it was developed in China before 2800 BC, in the Andes around 2000 BC, in Central America around 600 AD, and in West Africa around 900 AD . Copper is found extensively in the Indus Valley Civilization by the 3rd millennium BC . In Europe, Ötzi the Iceman, a well - preserved male dated to 3300 - 3200 BC, was found with an axe with a copper head 99.7% pure. High levels of arsenic in his hair suggest he was involved in copper smelting. Over the course of centuries, experience with copper has assisted the development of other metals; for example, knowledge of copper smelting led to the discovery of iron smelting.

In the Americas production in the Old Copper Complex, located in present day Michigan and Wisconsin, was dated back to between 6000 to 3000 BC .

2 . 2 . Bronze Age

Alloying of copper with zinc or tin to make brass or bronze was practiced soon after the discovery of copper itself. There exist copper and bronze artifacts from Sumerian cities that date to 3000 BC,^[8] and

Egyptian artifacts of copper and copper-tin alloys nearly as old. In one pyramid, a copper plumbing system was found that is 5000 years old . The Egyptians found that adding a small amount of tin made the metal easier to cast, so copper - tin (bronze) alloys were found in Egypt almost as soon as copper was found . Very important sources of copper in the Levant were located in Timna valley (Negev Desert) .

By 2000 BC, Europe was using bronze . The use of bronze became so widespread in Europe approximately from 2500 BC to 600 BC that it has been named the Bronze Age. The transitional period in certain regions between the preceding Neolithic period and the Bronze Age is termed the Chalcolithic (" copper - stone") , with some high - purity copper tools being used alongside stone tools. Brass (copper - zinc alloy) was known to the Greeks, but only became a significant supplement to bronze during the Roman empire.

During the Bronze Age, one copper mine at Great Orme in North Wales, extended for a depth of 70 meters . At Alderley Edge in Cheshire, carbon dates have established mining at around 2280 to 1890 BC (at 95 % probability) .

2 . 3 . Antiquity and Middle Ages

In alchemy the symbol for copper, perhaps a stylized mirror, was also the symbol for the goddess and planet Venus . In Greek the metal was known by the name *chalkos* (χαλκός) . Copper was a very important resource for the Romans, Greeks and other ancient peoples. In Roman times, it became known as *aes Cyprium* (*aes* being the generic Latin term for copper alloys such as bronze and other metals, and *Cyprium* because so much of it was mined in Cyprus) . From this, the phrase was simplified to *cuprum*, hence the English *copper*. Copper was associated with the goddess Aphrodite/Venus in mythology and alchemy, owing to its lustrous beauty, its ancient use in producing mirrors, and its association with Cyprus, which was sacred to the goddess. In astrology, alchemy the seven heavenly bodies known to the ancients were associated with seven metals also known in antiquity, and Venus was assigned to copper.

Britain's first use of brass occurred around the 3rd - 2nd century B.C. In North America, copper mining began with marginal workings by Native Americans. Native copper is known to have been extracted from sites on Isle Royale with primitive stone tools between 800 and 1600 .

Copper metallurgy was flourishing in South America, particularly in Peru around the beginning of the first millennium AD. Copper technology proceeded at a much slower rate on other continents. Africa's major location for copper reserves is Zambia. Copper burial ornamentals dated from the 15th century have been uncovered, but the metal's commercial production did not start until the early 1900s. Australian copper artifacts exist, but they appear only after the arrival of the Europeans; the aboriginal culture apparently did not develop their own metallurgical abilities.

Crucial in the metallurgical and technological worlds, copper has also played an important cultural role, particularly in currency. Romans in the 6th through 3rd centuries B.C. used copper lumps as money. At first, just the copper itself was valued, but gradually the shape and look of the copper became more important. Julius Caesar had his own coins, made from a copper-zinc alloy, while Octavianus Augustus Caesar's) coins were made from Cu - Pb - Sn alloys.

The gates of the Temple of Jerusalem used Corinthian bronze made by depletion gilding. Corinthian bronze was most prevalent in Alexandria, where alchemy is thought to have begun . In ancient India (before 1000 B.C.) , copper was used in the holistic medical science Ayurveda for surgical instruments and other medical equipment. Ancient Egyptians (~2400 B.C.) used copper for sterilizing wounds and drinking water, and as time passed, (~ 1500 B.C.) for headaches, burns, and itching. Hippocrates (~ 400 B.C.) used copper to treat leg ulcers associated with varicose veins. Ancient Aztecs fought sore throats by gargling with copper mixtures.

Copper is also the part of many rich stories and legends, such as that of Iraq's Baghdad Battery. Copper cylinders soldered to lead, which date back to 248 B.C. to 226 A.D, resemble a galvanic cell,

leading people to believe this may have been the first battery. This claim has so far not been substantiated.

The Bible also refers to the importance of copper: " Men know how to mine silver and refine gold , to dig iron from the earth and melt copper from stone" (Job. 28 : 1- 2).

2 . 4 . Modern period

Throughout history, copper's use in art has extended far beyond currency. Vannoccio Biringuccio, Giorgio Vasari and Benvenuto Cellini are three Renaissance sculptors from the mid 1500s, notable for their work with bronze. From about 1560 to about 1775, thin sheets of copper were commonly used as a canvas for paintings. Silver plated copper was used in the pre-photograph known as the daguerreotype. The Statue of Liberty, dedicated on October 28, 1886 , was constructed of copper thought to have come from French - owned mines in Norway.

Plating was a technology that began started in the mid 1600s in some areas. One common use for copper plating, widespread in the 1700s, was the sheathing of ships' hulls. Copper sheathing could be used to protect wooden hulled ships from algae, and from the shipworm "toredo", a saltwater clam. The ships of Christopher Columbus were among the earliest to have this protection .

In 1801 Paul Revere established America's first copper rolling mill in Canton, Massachusetts. In the early 1800s, it was discovered that copper wire could be used as a conductor, but it wasn't until 1990 that copper, in oxide form, was discovered for use as a superconducting material. The German scientist Gottfried Osann invented powder metallurgy of copper in 1830 while determining the metal's atomic weight. Around then it was also discovered that the amount and type of alloying element (e.g. tin) would affect the tones of bells, allowing for a variety of rich sounds, leading to bell casting, another common use for copper and its alloys.

The Norddeutsche Affinerie in Hamburg was the first modern electroplating plant starting its production in 1876.^[17]

Flash smelting, was developed by Outokumpu in Finland and first applied at the Harjavalta plant in 1949. The process makes smelting more energy efficient and is today used for 50% of the world's primary copper production .

Copper has been pivotal in the economic and sociological worlds, notably disputes involving copper mines. The 1906 Cananea Strike in Mexico dealt with issues of work organization. The Teniente copper mine (1904 – 1951) raised political issues about capitalism and class structure. Japan's largest copper mine, the Ashio mine, was the site of a riot in 1907. The Arizona miners' strike of 1938 dealt with American labor issues including the " right to strike " .

3 . Characteristics

3 .1 .Color

Copper has a reddish, orangish, or brownish color because a thin layer of tarnish (including oxides) gradually forms on its surface when gases (especially oxygen) in the air react with it. But pure copper, when fresh, is actually a pinkish or peachy metal. Copper, caesium and gold are the only three elemental metals with a natural color other than gray or silver.^[19] The usual gray color of metals depends on their "electron sea" that is capable of absorbing and re-emitting photons over a wide range of frequencies. Copper has its characteristic color because of its unique band structure. By Madelung's rule the 4s subshell should be filled before electrons are placed in the 3d subshell but copper is an exception to the rule with only one electron in the 4s subshell instead of two. The energy of a photon of blue or violet light is sufficient for a *d* band electron to absorb it and transition to the half-full *s* band. Thus the light reflected by copper is missing some blue/violet components and appears red. This phenomenon is shared with gold which has a corresponding 5s/4d structure . In its liquefied state, a pure copper surface without ambient light appears somewhat greenish, a characteristic shared with gold. When liquid copper is in bright ambient light, it retains some of its pinkish luster. When copper is burnt in oxygen it gives off a black oxide.

3.2. Group 11 of the periodic table

Copper occupies the same family of the periodic table as silver and gold, since they each have one s - orbital electron on top of a filled electron shell which forms metallic bonds. This similarity in electron structure makes them similar in many characteristics. All have very high thermal and electrical conductivity, and all are malleable metals. Among pure metals at room temperature, copper has the second highest electrical and thermal conductivity, after silver

3.3. Occurrence

Copper can be found as native copper in mineral form (for example, in Michigan's Keewenaw Peninsula) . It is a polycrystal , with the largest single crystals measuring $4.4 \times 3.2 \times 3.2 \text{ cm}^3$. Minerals such as the sulfides : chalcopyrite (Cu Fe S_2) , bornite ($\text{Cu}_5 \text{Fe S}_4$) , covellite (Cu S) , chalcocite ($\text{Cu}_2 \text{S}$) are sources of copper, as are the carbonates: azurite ($\text{Cu}_3 (\text{CO}_3)_2 (\text{OH})_2$) and malachite ($\text{Cu}_2 \text{CO}_3 (\text{OH})_2$) and the oxide: cuprite (Cu_2O) .

3.4. Mechanical properties

Copper is easily worked, being both ductile and malleable . The ease with which it can be drawn into wire makes it useful for electrical work in addition to its excellent electrical properties. Copper can be machined, although it is usually necessary to use an alloy for intricate parts, such as threaded components, to get really good machinability characteristics. Good thermal conduction makes it useful for heatsinks and in heat exchangers. Copper has good corrosion resistance, but not as good as gold. It has excellent brazing and soldering properties and can also be welded, although best results are obtained with gas metal arc welding .

Copper is normally supplied, as with nearly all metals for industrial and commercial use, in a fine grained polycrystalline form. Polycrystalline metals have greater strength than monocrystalline forms, and the difference is greater for smaller grain (crystal) sizes. The reason is due to the inability of stress dislocations in the crystal structure to cross the grain boundaries.

3 . 5 . Electrical properties

At $59.6 \times 10^6 \text{ S / m}$ copper has the second highest electrical conductivity of any element, just after silver. This high value is due to virtually all the valence electrons (one per atom) taking part in conduction. The resulting free electrons in the copper amount to a huge charge density of $13.6 \times 10^9 \text{ C / m}^3$. This high charge density is responsible for the rather slow drift velocity of currents in copper cable (drift velocity may be calculated as the ratio of current density to charge density) . For instance, at a current density of $5 \times 10^6 \text{ A/m}^2$ (typically, the maximum current density present in household wiring and grid distribution) the drift velocity is just a little over $\frac{1}{3} \text{ mm / s}$.

3 . 6 . Corrosion

3 . 6 . 1 . Pure water and air / oxygen

The Pourbaix diagram for copper in pure water, or acidic or alkali conditions. It can be seen that copper in neutral water is more noble than hydrogen.

Copper is a metal that does not react with water (H_2O), but the oxygen of the air will react slowly at room temperature to form a layer of brown-black copper oxide on copper metal.

It is important to note that in contrast to the oxidation of iron by wet air that the layer formed by the reaction of air with copper has a protective effect against further corrosion. On old copper roofs a green layer of copper carbonate, called verdigris, can often be seen. A notable example of this is on the Statue of Liberty.

3 . 6 . 2 . In contact with other metals (Galvanic corrosion) :

Copper should not be in direct mechanical contact with metals of different electropotential (for example, a copper pipe joined to an iron pipe) , especially in the presence of moisture, as the completion of an electrical circuit (for instance through the common ground) will cause the juncture to act as an electrochemical cell (like a single cell of a battery) . The weak electrical currents themselves are harmless

but the electrochemical reaction will cause the conversion of the iron to other compounds, eventually destroying the functionality of the union. This problem is usually solved in plumbing by separating copper pipe from iron pipe with some non - conducting segment (usually plastic or rubber) .

3 . 6 . 3 . Sulfide media

Copper metal reacts with hydrogen sulfide - and sulfide - containing solutions, forming a series of different copper sulfides on its surface.

The Pourbaix diagram is very complex due to the existence of many different sulfides. In sulfide-containing solutions copper is less noble than hydrogen and will corrode. This can be observed in everyday life when copper metal surfaces tarnish after exposure to air containing sulfur compounds.

3 . 6 . 4 . Ammonia media

Copper is slowly dissolved in oxygen-containing ammonia solutions because the ammonia forms water - soluble copper complexes. The formation of these complexes causes the corrosion to become more thermodynamically favored than the corrosion of copper in an identical solution that does not contain the ammonia.

3 . 6 . 5 . Chloride media

Copper reacts with a combination of oxygen and hydrochloric acid to form a series of copper chlorides. Copper (II) chloride (green / blue) when boiled with copper metal undergoes a symproportionation reaction to form white copper (I) chloride.

3 . 7 . Germicidal effect

Copper is germicidal, via the oligodynamic effect . For example, brass doorknobs disinfect themselves of many bacteria within a period of eight hours . Antimicrobial properties of copper are effective against MRSA , Escherichia coli and other pathogens . In colder temperature, longer time is required to kill bacteria.

Copper has the intrinsic ability to kill a variety of potentially harmful pathogens. On February 29, 2008, the United States EPA registered 275 alloys, containing greater than 65% nominal copper content, as antimicrobial materials. Registered alloys include pure copper, an assortment of brasses and bronzes, and additional alloys. EPA-sanctioned tests using Good Laboratory Practices were conducted in order to obtain several antimicrobial claims valid against: methicillin-resistant *Staphylococcus aureus* (MRSA), *Enterobacter aerogenes*, *Escherichia coli* O157: H7 and *Pseudomonas aeruginosa*. The EPA registration allows the manufacturers of these copper alloys to legally make public health claims as to the health effects of these materials. Several of the aforementioned bacteria are responsible for a large portion of the nearly two million hospital-acquired infections contracted each year in the United States^[33]. Frequently touched surfaces in hospitals and public facilities harbor bacteria and increase the risk for contracting infections. Covering touch surfaces with copper alloys can help reduce microbial contamination associated with hospital-acquired-infections on these surfaces.

3.8. Isotopes of Copper ;

Copper has 29 distinct isotopes ranging in atomic mass from 52 to 80. Two of these, ^{63}Cu and ^{65}Cu , are stable and occur naturally, with ^{63}Cu comprising approximately 69% of naturally occurring copper.

The other 27 isotopes are radioactive and do not occur naturally. The most stable of these is ^{67}Cu with a half-life of 61.83 hours. The least stable is ^{54}Cu with a half-life of approximately 75 ns. Unstable copper isotopes with atomic masses below 63 tend to undergo β^+ decay, while isotopes with atomic masses above 65 tend to undergo β^- decay. ^{64}Cu decays by both β^+ and β^- .

^{68}Cu , ^{69}Cu , ^{71}Cu , ^{72}Cu , and ^{76}Cu each have one metastable isomer. ^{70}Cu has two isomers, making a total of 7 distinct isomers. The most stable of these is $^{68\text{m}}\text{Cu}$ with a half-life of 3.75 minutes. The least stable is $^{69\text{m}}\text{Cu}$ with a half-life of 360 ns

4 . Production

Most copper ore is mined or extracted as copper sulfides from large open pit mines in porphyry copper deposits that contain 0.4 to 1.0 percent copper. Examples include: Chuquicamata in Chile and El Chino Mine in New Mexico. The average abundance of copper found within crustal rocks is approximately 68 ppm by mass, and 22 ppm by atoms. In 2005, Chile was the top mine producer of copper with at least one-third world share followed by the USA , Indonesia and Peru, reports the British Geological Survey .

The Intergovernmental Council of Copper Exporting Countries (CIPEC) , defunct since 1992 , once tried to play a similar role for copper as OPEC does for oil, but never achieved the same influence, not least because the second-largest producer, the United States, was never a member. Formed in 1967, its principal members were Chile, Peru, Zaire, and Zambia.

5 . Applications

Copper is malleable and ductile and is a good conductor of both heat and electricity.

The purity of copper is expressed as 4N for 99.99 % pure or 7N for 99.99999 % pure. The numeral gives the number of nines after the decimal point when expressed as a decimal (e.g. 4N means 0.9999 , or 99.99 %). Copper is often too soft for its applications, so it is incorporated in numerous alloys. For example, brass is a copper - zinc alloy, and bronze is a copper-tin alloy .

It is used extensively, in products such as :

5 . 1 . Piping

- including water supply.
- used extensively in refrigeration and air conditioning equipment because of its ease of fabrication and soldering, as well as high conductivity to heat.

5 . 2 . Electrical applications

- Copper wire.
- Oxygen - free copper.
- Electromagnets.
- Printed circuit boards.
- Lead free solder , alloyed with tin.
- Electrical machines, especially electromagnetic motors, generators and transformers.
 - Electrical relays, electrical busbars and electrical switches.
 - Vacuum tubes, cathode ray tubes, and the magnetrons in microwave ovens.
 - Wave guides for microwave radiation.
 - Integrated circuits, increasingly replacing aluminium because of its superior electrical conductivity.
 - As a material in the manufacture of computer heat sinks, as a result of its superior heat dissipation capacity to aluminium.

5 . 3 . Architecture / Industry

- Copper has been used as water - proof roofing material since ancient times, giving many old buildings their greenish roofs and domes. Initially copper oxide forms, replaced by cuprous and cupric sulfide, and finally by copper carbonate. The final carbonate patina (termed verdigris) is highly resistant to corrosion .
 - Statuary : The Statue of Liberty, for example, contains 81.3 tonnes of copper.
 - Alloyed with nickel, e.g. cupronickel and Monel, used as corrosive resistant materials in shipbuilding.
 - Copper compounds in liquid form are used as a wood preservative, particularly in treating original portion of structures during restoration of damage due to dry rot.
 - Copper wires may be placed over non-conductive roofing materials to discourage the growth of moss. (Zinc may also be used for this purpose) .

- Copper is used to prevent a building being directly struck by lightning. High above the roof, copper spikes (lightning rods) are connected to a very thick copper cable which leads to a large metal plate underneath the ground. The voltage is dispersed throughout the ground harmlessly, instead of destroying the main structure .

5 . 4 . Household products

- Copper plumbing fittings and compression tubes.
- Doorknobs and other fixtures in houses.
- Roofing, guttering, and rainspouts on buildings.
- In cookware, such as frying pans.
- Some older flatware: (knives, forks, spoons) contains some copper if made from Electroplated Nickel silver (EPNS).
 - Sterling silver, if it is to be used in dinnerware, must contain a few percent copper.
 - Copper water heating cylinders
 - Copper Range Hoods
 - Copper Bath Tubs
 - Copper Counters
 - Copper Sinks
 - Copper slug tape

5 . 5 Coinage

- As a component of coins, often as cupronickel alloy, or some form of brass or bronze.
- Coins in the following countries all contain copper: European Union (Euro) , United States,^[43] United Kingdom (sterling) , Australia and New Zealand .

5 . 6 . Biomedical applications

- As a biostatic surface in hospitals, and to line parts of ships to protect against barnacles and mussels, originally used pure, but superseded by Muntz metal. Bacteria will not grow on a copper surface because it is biostatic. Copper doorknobs are used by hospitals to reduce the transfer of disease, and

Legionnaires' disease is suppressed by copper tubing in air-conditioning systems.

- Copper(II) sulfate is used as a fungicide and as algae control in domestic lakes and ponds. It is used in gardening powders and sprays to kill mildew.

- Copper - 62 - PTSM, a complex containing radioactive copper - 62, is used as a positron emission tomography radiotracer for heart blood flow measurements.

- Copper - 64 can be used as a positron emission tomography radiotracer for medical imaging. When complexed with a chelate it can be used to treat cancer through radiation therapy.

5.7. Chemical applications

- Compounds, such as Fehling's solution, have applications in chemistry.

- As a component in ceramic glazes, and to color glass.

5.8. Other

- Musical instruments, especially brass instruments and timpani.

- Class D Fire Extinguisher, used in powder form to extinguish lithium fires by covering the burning metal and performing similar to a heat sink.

- Textile fibers to create antimicrobial protective fabrics.

- Weaponry:

- Small arms ammunition commonly uses copper as a jacketing material around the bullet core.

- Copper is also commonly used as a case material, in the form of brass.

- Copper is used as a liner in shaped-charge armor-piercing warheads.

- Copper is frequently used in electroplating, usually as a base for other metals such as Nickel.

6 . Alloys

Numerous copper alloys exist, many with important historical and contemporary uses. Speculum metal and **bronze** are alloys of copper and tin . **Brass** is an alloy of copper and zinc. **Monel metal**, also called cupronickel , is an alloy of copper and nickel. While the metal "bronze" usually refers to copper-tin alloys, it also is a generic term for any alloy of copper, such as aluminium bronze, silicon bronze, and manganese bronze. Copper is one of the most important constituents of carat silver and gold alloys and carat solders used in the jewelry industry, modifying the color, hardness and melting point of the resulting alloys .

7 . Compounds

Common oxidation states of copper include the less stable copper (I) state , Cu^+ ; and the more stable copper (II) state , Cu^{2+} which forms blue or blue-green salts and solutions. Under unusual conditions , a 3+ state and even an extremely rare 4+ state can be obtained . Using old nomenclature for the naming of salts, copper (I) is called *cuprous* , and copper (II) is *cupric* . In oxidation copper is mildly basic.

Copper (II) carbonate is green from which arises the unique appearance of copper - clad roofs or domes on some buildings. Copper (II) sulfate forms a blue crystalline pentahydrate which is perhaps the most familiar copper compound in the laboratory. It is used as a fungicide, known as Bordeaux mixture.

There are two stable copper oxides, copper (II) oxide (CuO) and copper (I) oxide (Cu_2O) . Copper oxides are used to make yttrium barium copper oxide ($\text{Y Ba}_2 \text{Cu}_3 \text{O}_{7-\delta}$) or Y B C O which forms the basis of many unconventional superconductors.

- **Copper (I) compounds** : copper (I) chloride , copper (I) bromide , copper (I) iodide , copper (I) oxide .
- **Copper (II) compounds** : copper (II) acetate , copper (II) carbonate , copper (II) chloride , copper (II)

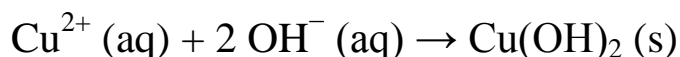
hydroxide , copper (II) nitrate , copper (II) oxide , copper (II) sulfate, copper (II) sulfide , copper (II) tetrafluoro borate, copper (II) triflate.

- **Copper (III) compounds**, rare : potassium hexa fluoro cuprate ($K_3 Cu F_6$)

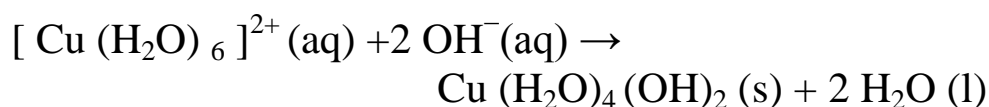
- **Copper (IV) compounds** , extremely rare: caesium hexa fluoro cuprate ($Cs_2 Cu F_6$) .

7 . 1 . Tests for copper (II) ion

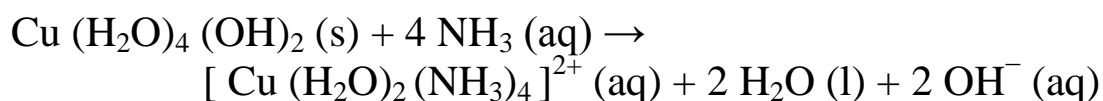
Adding an aqueous solution of sodium hydroxide will form a blue precipitate of copper (II) hydroxide . The ionic equation is:



The full equation shows that the reaction is due to hydroxide ions deprotonating the hexa aqua copper (II) complex :



Adding ammonium hydroxide (aqueous ammonia) causes the same precipitate to form. Upon adding excess ammonia, the precipitate dissolves , forming a deep blue ammonia complex , tetra ammine copper (II):



A more delicate test than ammonia is potassium ferrocyanide, which gives a brown precipitate with copper salts.

8 . Biological role

Rich sources of Copper include oysters , beef or lamb liver, Brazil nuts , black strap molasses , coco , and black pepper . Good sources include lobster , nuts and sunflower seeds , green olives , avocados and wheat bran .

Copper is essential in all plants and animals. The human body normally contains copper at a level of about 1.4 to 2.1 mg for each kg of body weight . Copper is distributed widely in the body and occurs in liver, muscle and bone. Copper is transported in the bloodstream on a plasma protein called ceruloplasmin. When copper is first absorbed in the gut it is transported to the liver bound to albumin. Copper metabolism and excretion is controlled delivery of copper to the liver by ceruloplasmin, where it is excreted in bile.

Copper is found in a variety of enzymes, including the copper centers of cytochrome c oxidase and the enzyme superoxide dismutase (containing copper and zinc) . In addition to its enzymatic roles, copper is used for biological electron transport. The blue copper proteins that participate in electron transport include azurin and plastocyanin. The name "blue copper" comes from their intense blue color arising from a ligand – to - metal charge transfer (LMCT) absorption band around 600 nm.

Most molluscs and some arthropods such as the horseshoe crab use the copper - containing pigment hemocyanin rather than iron-containing hemoglobin for oxygen transport , so their blood is blue when oxygenated rather than red .

It is believed that zinc and copper compete for absorption in the digestive tract so that a diet that is excessive in one of these minerals may result in a deficiency in the other. The RDA for copper in normal healthy adults is 0.9 mg / day. On the other hand, professional research on the subject recommends 3.0 mg/day.^[51] Because of its role in facilitating iron uptake, copper deficiency can often produce anemia-like symptoms. In humans, the symptoms of Wilson's disease are caused by an accumulation of copper in body tissues.

Reference ranges for blood tests, comparing blood content of copper (shown in light blue in middle) with other constituents.

Chronic copper depletion leads to abnormalities in metabolism of fats, high triglycerides, non-alcoholic steatohepatitis (NASH), fatty liver disease and poor melanin and dopamine synthesis causing

depression and sunburn. Food rich in copper should be eaten away from any milk or egg proteins as they block absorption .

8 . 1 . Copper Toxicity

Toxicity can occur from eating acidic food that has been cooked with copper cookware. Cirrhosis of the liver in children (Indian Childhood Cirrhosis) has been linked to boiling milk in copper cookware. The Merck Manual states that recent studies suggest that a genetic defect is associated with this cirrhosis.^[52] Since copper is actively excreted by the normal body, chronic copper toxicosis in humans without a genetic defect in copper handling has not been demonstrated . However, large amounts (gram quantities) of copper salts taken in suicide attempts have produced acute copper toxicity in normal humans. Equivalent amounts of copper salts (30 mg / kg) are toxic in animals^[53]

8 . 2 . Miscellaneous hazards

The metal, when powdered, is a fire hazard. At concentrations higher than 1 mg / L, copper can stain clothes and items washed in water.

9 . Recycling

Copper is 100 % recyclable without any loss of quality whether in a raw state or contained in a manufactured product. Copper is the third most recycled metal after iron and aluminum. It is estimated that 80 % of the copper ever mined is still in use today . Common grades of copper for recycling are:

- Bare bright - very clean and pure copper wire usually 12 AWG or larger that has insulation and any tarnish removed
- #1 copper - pipe with a new appearance and free of any foreign material
- #2 copper - pipe with corrosion or foreign material and small gauge wire with no insulation

Insulated wire is also commonly recycled .

copper alloys

Contents

- 1 Introduction
- 2 Compositions
- 3 Brasses
- 4 Bronzes
- 5 Precious metal alloys

1 – Introduction :

Copper alloys are metal **alloys** that have **copper** as their principal component. They have high resistance against **corrosion**. The best known traditional types are **bronze**, where **tin** is a significant addition, and **brass**, using **zinc** instead. Both these are imprecise terms, and today the term *copper alloy* tends to be substituted, especially by museums.

2 - Compositions

The similarity in external appearance of the various alloys, along with the different combinations of elements used when making each alloy, can lead to confusion when categorizing the different compositions. There are as many as 400 different copper and copper-alloy compositions loosely grouped into the categories: copper, high copper alloy, brasses, bronzes, copper **nickels**, copper–nickel–zinc (nickel silver), **leaded** copper, and special alloys. The following table lists the principal alloying element for four of the more common types used in modern industry, along with the name for each type. Historical types, such as those that characterize the **Bronze Age**, are vaguer as the mixtures were generally .

Family	Principal alloying element
Copper alloys , brass	Zinc (Zn)
Phosphor bronze	Tin (Sn)
Aluminium bronzes	Aluminium (Al)
Silicon bronzes	Silicon (Si)
Copper nickel, nickel silvers	Nickel (Ni)

The following table outlines the chemical composition of various grades of copper alloys :

Family	Cu %	Sn %	Pb %	Zn %	Ni %	Fe %	Al %	Other %
Red brass	93	1.5	1.5	4				
	90			10				
	85	5	5	5				
	83	4	6	7				
	81	3	7	9				
Semi-red brass	78	3	7	12				
	76	3	6	15				
	67	0.5		21		3	5	Mn 4
Manganese bronze	64			26		3	4	Mn 3
	63			25		3	6	Mn 3
	58	0.5		39.5		1	1	Mn 0.25
Tin bronze	88	8		4				
	88	10	0.3 max	2				
	89	11	0.5 max	0.5 max				
Leaded tin bronze	88	6	1.5	4.5				
	87	8	1 max	4				
	87	10	1	2				

	88	10	2	0.7 max				
	83	7	7	3				
	84	8	8	0.7 max				
High - leaded tin bronze	85	5	9	1	0.5 max			
	80	10	10		0.7 max			
	78	7	15		0.75 max			
	70	5	25		0.7 max			
Aluminium bronze	88					3	9	
	89					1	10	
	85					4	11	
	85					4	11	Ni 2
	81			4		4	11	
	91						7	Si 2
	75			2		3	8	Mn 12
	81			5		4	9	Mn 1
Silicon bronze	89							Si 4
	83			14				Si 3
	82			14				Si 4
	90			5.5				Si 4.5
	80			14				Si 4
	65			34				Si 1

3 - Brasses

A brass is an alloy of copper with zinc. Brasses are usually yellow in color. The zinc content can vary between few % to about 40%; as long as it is kept under 15 %, it does not markedly decrease corrosion resistance of copper.

Brasses can be sensitive to [selective leaching](#) corrosion under certain conditions, when zinc is leached from the alloy (*dezincification*), leaving behind a spongy copper structure.

4 - Bronzes

A bronze is an alloy of copper and other metals, most often tin, but also aluminium and silicon.

- Aluminium bronzes are alloys of copper and aluminium. The content of aluminium ranges mostly between 5 - 11 %. Iron, nickel, manganese and silicon are sometimes added. They have higher strength and corrosion resistance than other bronzes, especially in marine environment, and have low reactivity to sulfur compounds. Aluminium forms a thin [passivation layer](#) on the surface of the metal.
- [Bell metal](#)
- [Phosphor bronze](#)
- Nickel bronzes, e.g. nickel silver and cupronickel

5 - Precious metal alloys

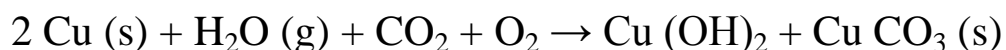
Copper is often alloyed with [precious metals](#) like [silver](#) and [gold](#), to create, for example, [Corinthian bronze](#), [hepatizon](#), [tumbaga](#) and [shakudo](#).

Copper (II) Carbonate

1 . Introduction :

Copper (II) carbonate (often called **copper carbonate** or **cupric carbonate**) is a blue - green compound (chemical formula Cu CO_3) forming part of the verdigris patina one sees on weathered brass, bronze, and copper. The colour can vary from bright blue to green, because there may be a mixture of both copper carbonate and basic copper carbonate in various stages of hydration. It was formerly much used as a pigment, and is still in use for artist's colours. It has also been used in some types of make-up, like lipstick, although it can also be toxic to humans. It also has been used for many years as an effective algaecide in farm ponds and in aquaculture operations. Copper carbonate was the first compound to be broken down into several separate elements (copper, carbon, and oxygen). It was broken down in 1794 by the French chemist Joseph Louis Proust (1754 – 1826) .When burnt, it turns into a black powder. It can be used to bronze plate a metallic surface by adding sulfuric acid and heat it then passing a charge through it with the meal in the liquid.

Copper in moist air slowly acquires a dull green coating because its top layer has oxidised with the air. Some architects use this material on rooftops for the interesting colour. The green material is a 1:1 mole mixture of Cu (OH)_2 and CuCO_3 :



Copper carbonate decomposes at high temperatures, giving off carbon dioxide and leaving copper (II) oxide :



Basic copper (II) carbonate occurs naturally as malachite ($\text{Cu CO}_3 \cdot \text{Cu (OH)}_2$) and azurite ($\text{Cu}_3 \text{ (CO}_3)_2 \text{ (OH)}_2$) .

Other Names	copper	carbonate
-------------	--------	-----------

	cupric carbonate basic copper carbonate
Molecular Formula	Cu CO_3
Molar Mass	123.5 g / mol
Density	3.9 g / cm^3
Melting Point	200° C
Boiling Point	None Applicable (will decompose when heated)
Solubility in Water & other solvents	insoluble in water , found effective in melting ice

Copper (I) chloride

Contents

- 1 Introduction
- 2 Chemical properties
- 3 Uses
 - 3.1 In organic synthesis
 - 3.2 In polymer chemistry

1 Introduction :

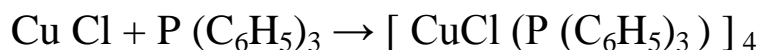
Copper(I) chloride, commonly called cuprous chloride , is the lower chloride of copper, with the formula Cu Cl . It can be prepared by dissolving copper in hydrochloric acid . This colorless solid is a versatile precursor to other copper compounds , including some of commercial significance. It occurs naturally as the rare mineral nantokite. Unlike other first-row transition metal halides, it forms stable complexes with carbon monoxide. It crystallizes in a diamondoid motif, reflecting the tendency of copper (I) to form tetrahedral complexes.

Other Names	Cuprous chloride
Molecular Formula	Cu Cl
Molar Mass	99 g / mol
Appearance	white powder , slightly green from oxidized impurities
Density	4.145 g / cm^3
Melting point	426 °C
Boiling point	1490 °C (decomp)
Solubility in water	0.0062 g / 100 mL (20 °C)
Solubility product , K_{sp}	1.72×10^{-7}
Solubility	Insoluble in ethanol acetone ; Soluble in concentrated HCl , NH_4OH
Refractive index (n_{D})	1.930

EU classification	Harmful (Xn) Dangerous for the environment (N)
Flash point	Non - flammable
LD ₅₀	140 mg/kg

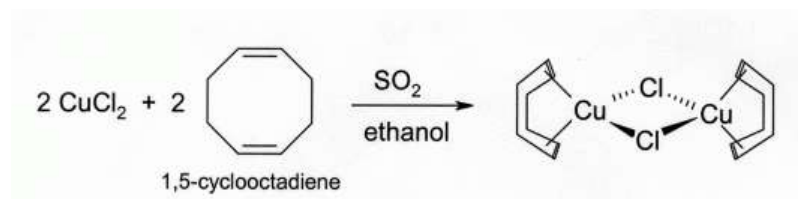
2 . Chemical properties :

CuCl is more affordable and less toxic than other soft Lewis acids. In addition, copper can exist in multiple redox states, including I, II, and III. This combination of properties define some of the useful features of copper (I) chloride. It is a soft Lewis acid, classified as soft according to the Hard - Soft Acid - Base concept. Thus, it tends to form stable complexes with soft Lewis bases such as triphenyl phosphine :



Although CuCl is insoluble in water, it dissolves in aqueous solutions containing suitable donor molecules. It forms complexes with halide ions, for example forming $\text{H}_3\text{O}^+ \text{CuCl}_2^-$ with concentrated hydrochloric acid. It also dissolves in solutions containing CN^- , $\text{S}_2\text{O}_3^{2-}$, and NH_3 to give complexes.

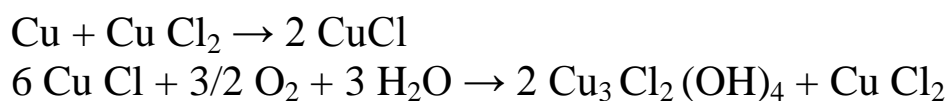
Solutions of Cu Cl in HCl or NH_3 absorb carbon monoxide to form colourless complexes such as the chloride-bridged dimer $[\text{CuCl}(\text{CO})]_2$. The same hydrochloric acid solutions also react with acetylene gas to form $[\text{CuCl}(\text{C}_2\text{H}_2)]$. Ammoniacal solutions of CuCl react with acetylenes to form the explosive copper (I) acetylide. Complexes of CuCl with alkenes can be prepared by reduction of Cu Cl_2 by sulfur dioxide in the presence of the alkene in alcohol solution . Complexes with dienes such as 1,5- cyclo octadiene are particularly stable :



Although only poorly soluble in water, its aqueous solution are unstable with respect to disproportionation into Cu and CuCl₂. In part for this reason samples assume a green coloration.

3. Uses

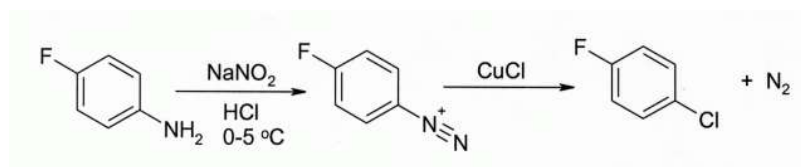
The main use of copper (I) chloride is as a precursor to the fungicide copper oxychloride. For this purpose aqueous copper (I) chloride is generated by comproportionation and then air-oxidized:



Copper (I) chloride catalyzes a variety of organic reactions, as discussed above. Its affinity for carbon monoxide in the presence of aluminium chloride is exploited in the CO PureSM process.

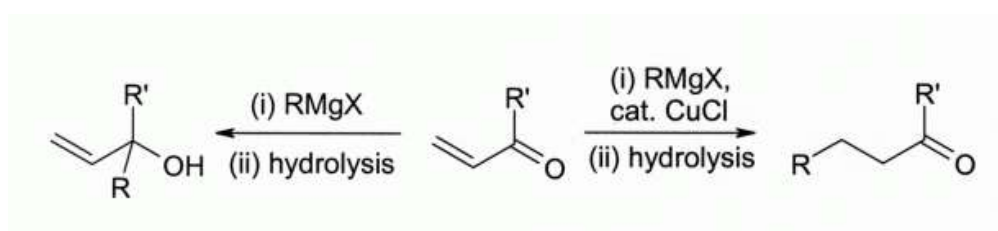
3.1. In organic synthesis

In the Sandmeyer reaction. Treatment of an arenediazonium salt with CuCl leads to an aryl chloride, for example:

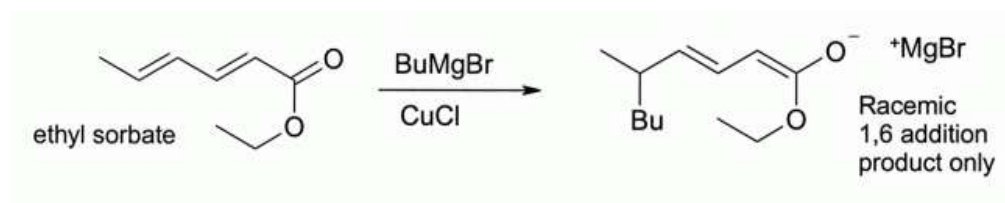


The reaction has wide scope and usually gives good yields.

Early investigators observed that copper (I) halides catalyse 1, 4 - addition of Grignard reagents to alpha,beta - unsaturated ketones led to the development of organocuprate reagents that are widely used today in organic synthesis:



This finding led to the development of organocopper chemistry. For example, Cu Cl reacts with methyl lithium ($\text{CH}_3 \text{Li}$) to form " Gilman reagents " such as $(\text{CH}_3)_2 \text{CuLi}$, which find extensive use in organic synthesis. Grignard reagents react similarly. Although other copper (I) compounds such as copper (I) iodide are now more often used for these types of reactions, copper (I) chloride is still recommended in some case:



Here , Bu indicates an n - butyl group. Without CuCl, the Grignard reagent alone gives a mixture of 1 , 2 - and 1 , 4 -addition products (i.e., the butyl adds at the C closer to the $\text{C} = \text{O}$) .

3 .2 . In polymer chemistry

Copper (I) chloride is also an intermediate formed from copper (II) chloride in the Wacker process. Cu Cl is used as a catalyst in Atom Transfer Radical Polymerization (ATRP) .

Copper (II) chloride

Contents

- 1 Introduction
- 2 Structure
- 3 Properties
- 4 Preparation
- 5 Uses
- 6 Natural occurrence

1 . Introduction :

Copper (II) chloride is the chemical compound with the formula Cu Cl_2 . This is a yellow - brown solid which slowly absorbs moisture to form a blue - green dihydrate.

Other Names	Cupric chloride
Molecular Formula	Cu Cl_2
Molar Mass	134. 5 g / mol (anhydrous) 170.5 g / mol (dihydrate)
Appearance	Yellow- brown solid (anhydrous) Blue - green solid (dihydrate)
Density	3.386 g / cm^3 (anhydrous) 2.51 g / cm^3 (dihydrate)
Melting Point	498 °C (anhydrous) 100 °C (dehydration of dihydrate)
Boiling Point	993 °C (anhydrous , decomp)
Solubility in Water	70.6 g / 100 mL (0 °C) 75.7 g / 100 mL (25 °C)
Crystal structure	distorted CdI_2 structure
Coordination geometry	Octahedral
Flash Point	Non - flammable

2 . Structure

Anhydrous Cu Cl₂ adopts a distorted cadmium iodide structure. Most copper (II) compounds exhibit distortions from idealized octahedral geometry due to the Jahn - Teller effect, which in this case describes the localisation of one d - electron into a molecular orbital that is strongly antibonding with respect to a pair of ligands. In CuCl₂ (H₂O)₂ the copper can be described as a highly distorted octahedral complex, the Cu (II) center being surrounded by two water ligands and four chloride ligands, which bridge asymmetrically to other Cu centers .

3 . Properties

Copper (II) chloride dissociates in aqueous solution to give the blue color of [Cu (H₂O)₆]²⁺ and yellow or red color of the halide complexes of the formula [Cu Cl_{2+x}]^{x-} . Concentrated solutions of Cu Cl₂ appear green because of the combination of these various chromophores. The color of the dilute solution depends on temperature, being green around 100 °C and blue at room temperature . When copper (II) chloride is heated in a flame, it emits a green - blue colour .

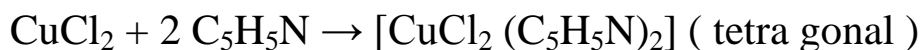
It is a weak Lewis acid, and a mild oxidizing agent. It has a crystal structure consisting of polymeric chains of flat CuCl₄ units with opposite edges shared. It decomposes to CuCl and Cl₂ at 1000 °C



In its reaction with HCl (or other chloride sources) to form the complex ions CuCl₃⁻ and Cu Cl₄²⁻ .

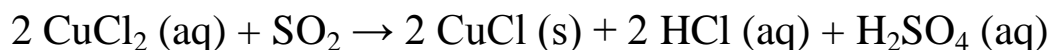
Some of these complexes can be crystallized from aqueous solution, and they adopt a wide variety structural types .

Copper (II) chloride also forms a rich variety of other coordination complexes with ligands such as pyridine or triphenyl phosphine oxide :

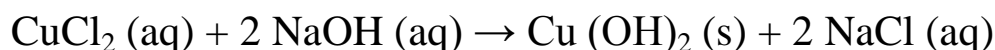




However " soft " ligands such as phosphines (e.g., triphenyl phosphine) , iodide, and cyanide as well as some tertiary amines cause reduction to give copper (I) complexes. To convert copper (II) chloride to copper (I) derivatives it is generally more convenient to reduce an aqueous solution with the reducing agent sulfur dioxide :



Cu Cl_2 can simply react as a source of Cu^{2+} in precipitation reactions for making insoluble copper (II) salts, for example copper (II) hydroxide, which can then decompose above 30°C to give copper (II) oxide:

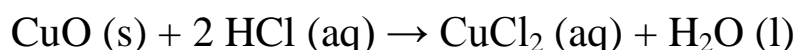


Followed by



4 . Preparation

Copper (II) chloride is prepared by the action of hydrochloric acid on copper (II) oxide, copper (II) hydroxide or copper(II) carbonate, for example :



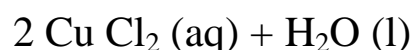
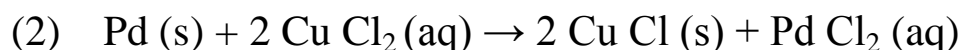
Anhydrous CuCl_2 may be prepared directly by union of the elements, copper and chlorine.

CuCl_2 may be purified by crystallisation from hot dilute hydrochloric acid, by cooling in a CaCl_2 - ice bath .

Electrolysis of aqueous sodium chloride with copper electrodes produces (among other things) CuCl_2 as a blue-green foam that can be skimmed off the top, collected, and dried to the hydrate .

5 . Uses

A major industrial application for copper (II) chloride is as a co - catalyst (along with palladium (II) chloride) in the Wacker process. In this process ethylene is converted to acetaldehyde using water and air. In the process Pd Cl₂ is reduced to Pd , and the CuCl₂ serves to re - oxidise this back to Pd Cl₂. Air can then oxidise the resultant Cu Cl back to Cu Cl₂, completing the cycle.



Copper (II) chloride has a variety of applications in organic synthesis . It can effect chlorination of aromatic hydrocarbons- this is often performed in the presence of aluminium oxide . It is able to chlorinate the alpha position of carbonyl compounds :

This reaction is performed in a polar solvent such as DMF, often in the presence of lithium chloride, which speeds up the reaction rate.

Cu Cl₂ , in the presence of oxygen, can also oxidise phenols. The major product can be directed to give either a quinone or a coupled product from oxidative dimerisation. The latter process provides a high - yield synthesis of 1 , 1- binaphthol (also called BINOL) and its derivatives, these can even be made as a single enantiomer in high enantiomeric excess :

Such compounds are valuable intermediates in the synthesis of BINAP and its derivatives, popular as chiral ligands for asymmetric hydrogenation catalysts .

Cu Cl_2 also catalyses the free radical addition of sulfonyl chlorides to alkenes; the alpha - chlorosulfone may then undergo elimination with base to give a vinyl sulfone product.

Copper (II) chloride is also used in pyro technics as a blue/green coloring agent .

6 . Natural occurrence

Copper (II) chloride occurs naturally as the very rare mineral tolbachite and the dihydrate eriochalcite. Both are known from fumaroles. More common are mixed oxyhydroxide-chlorides like atacamite $\text{Cu}_2 (\text{OH})_3 \text{Cl}$, arising among Cu ore beds oxidation zones in arid climate (also known from some altered slags) .

Copper (II) fluoride



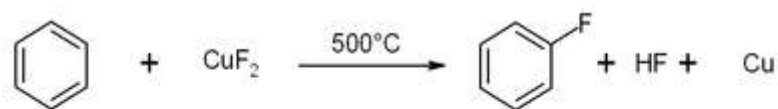
1 – Introduction :

Copper (II) fluoride is an **inorganic compound** with the chemical formula CuF_2 . It is a white or green, crystalline, hygroscopic solid. It has a **rutile** - type **crystal structure** similar to other fluorides of chemical formulae MF_2 .

IUPAC name :	Copper difluoride
Other names :	Cupric fluoride ; Copper Fluoride
Molecular Formula	Cu F_2
Molar mass	101.5 g / mol (anhydrous) 137.5 g / mol (dihydrate)
Appearance	White crystalline powder When hydrated: Blue
Density	4.23 g/cm ³ (anhydrous) 2.934 g/cm ³ (dihydrate) ^[1]
Melting point	836 °C (anhydrous) 130 °C (dihydrate, decomposes)
Boiling point	1676 °C (anhydrous)
Solubility in other solvents	Hygroscopic

2 – Uses :

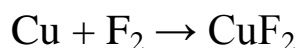
It has been shown that **aromatic hydrocarbons** react with copper (II) fluoride, in an **oxygen** - containing atmosphere at temperatures above 450 °C, to form fluorinated aromatic hydrocarbons. This reaction is simpler than the **Sandmeyer reaction**, but is only applicable for compounds which are stable enough to survive the high temperature.^[2]



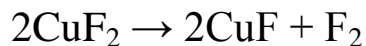
Half mole of oxygen is used with 2 HF and Cu to make a mole of water and copper (II) fluoride.

3 - Chemistry :

Copper fluoride can be synthesised from [copper](#) and [fluorine](#) at temperatures of 400 °C.



It loses fluorine in molten stage at temperatures above 950 °C.



The complex anions of CuF_3^- , CuF_4^{2-} and CuF_6^{4-} are formed if CuF_2 is exposed to substances containing [fluoride](#) ions F^- .

Copper (I) bromide



1 – Introduction :

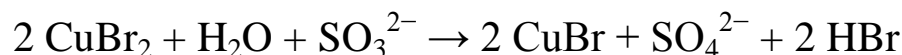
Copper (I) bromide is the **chemical compound** with the **formula** CuBr. This **diamagnetic** solid adopts a polymeric structure akin to that for **zinc sulfide**. The compound is widely used in the **synthesis** of organic compounds.

Other names :	Cuprous bromide
Molecular formula	Cu Br
Molar mass	143.5 g / mol
Appearance	green powder
Density	4.71 g/cm ³ , solid
Melting point	492 °C
Boiling point	1345 °C
Solubility in water	slightly soluble
Refractive index (n_D)	2.09
Hazards	
EU Index	Not listed
Flash point	Non-flammable

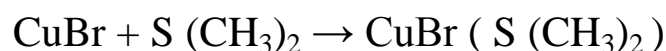
2 - Preparation , basic properties , structure :

The pure solid is colourless, although samples are often colored due to the presence of copper (II) impurities. The copper (I) ion also oxidizes easily in air. It is commonly prepared by the reduction of cupric salts with **sulfite** in the presence of bromide. For example, the

reduction of **copper (II) bromide** with sulfite yields copper (I) bromide and **hydrogen bromide**:



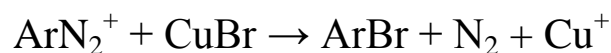
CuBr is insoluble in most solvents due to its polymeric structure, which features four-coordinated, tetrahedral Cu centers interconnected by bromide ligands (ZnS structure). Upon treatment with **Lewis bases**, CuBr converts to molecular **adducts**. For example with **dimethyl sulfide**, the colorless complex is formed:^[3]



In this **coordination complex**, the copper is two-coordinate, with a linear geometry. Other soft ligands afford related complexes. For example **triphenylphosphine** gives $\text{CuBr}(\text{P}(\text{C}_6\text{H}_5)_3)$, although this species has a more complex structure.

3 - Applications in organic chemistry

In the **Sandmeyer reaction**, Cu Br is employed to convert diazonium salts into the corresponding **aryl** bromides :



The aforementioned complex $\text{CuBr}(\text{S}(\text{CH}_3)_2)$ is widely used to generate **organocopper** reagents . Related CuBr complexes are **catalysts** for **Atom Transfer Radical Polymerization** and Cu - catalyzed Cross - Dehydrogenative Couplings (C D C) .

Copper (I) Iodide



1 – Introduction :

Copper (I) iodide is the **inorganic compound** with the formula CuI . It is also known as **cuprous iodide**. It is useful in a variety of applications ranging from **organic synthesis** to **cloud seeding**.

Copper(I) iodide is white, but samples are often tan or even, when found in nature as rare mineral marshite, reddish brown, but such color is due to impurities. It is common for samples of iodide-containing compounds to become discolored because of the easy aerobic oxidation of the iodide anion to iodine.

IUPAC Name :	Copper (I) iodide
Other names :	Cuprous iodide
Molecular Formula	Cu I
Molar Mass	190.5 g / mol
Appearance	White powder when impure : tan or brownish
Density	5.67 g/cm ³
Melting point	606 °C
Boiling point	1290 °C (decomposes)
Solubility in water	insoluble
Solubility product , K_{sp}	1×10^{-12}
Solubility	soluble in 3.5 M KI soln.

Refractive index (n_D)	2.346
Flash point	Non-flammable
Infobox references	

2 - Structure

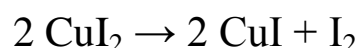
Copper (I) iodide , like most "binary" (containing only two elements) metal halides, is an inorganic polymer. It has a rich [phase diagram](#), meaning that it exists in several crystalline forms. It adopts a [zinc blende structure](#) below 390 °C (γ - CuI) , a [wurtzite](#) structure between 390 and 440 °C (β -CuI), and a [rock salt](#) structure above 440 °C (α -CuI). The ions are tetrahedrally coordinated when in the [zinc blende](#) or the [wurtzite](#) structure, with a Cu-I distance of 2.338 Å. [Copper\(I\) bromide](#) and [copper\(I\) chloride](#) also transform from the zinc blende structure to the wurtzite structure at 405 and 435 °C, respectively. Therefore, the longer the copper - halide bond length, the lower the temperature needs to be to change the structure from the zinc blende structure to the wurtzite structure. The interatomic distances in copper(I) bromide and copper(I) chloride are 2.173 and 2.051 Å respectively.

3 – Preparation :

Copper (I) iodide can be prepared by heating iodine and copper in concentrated [hydriodic acid](#), HI. In the laboratory however, copper(I) iodide is prepared by simply mixing an aqueous solution of sodium or potassium iodide and a soluble copper (II) salt such [copper sulfate](#).



The CuI_2 immediately decomposes to iodine and insoluble copper(I) iodide, releasing I_2 .



This reaction has been employed as a means of assaying copper (II) samples , since the evolved I_2 can be analyzed by redox titration. The reaction in itself may look rather odd, as using the rule of thumb

for a proceeding [redox reaction](#), $E^{\circ}_{\text{oxidator}} - E^{\circ}_{\text{reductor}} > 0$, this reaction fails. The quantity is below zero, so the reaction should not proceed. But the equilibrium constant for the reaction is 1.38×10^{-13} . By using fairly moderate concentrations of 0.1 Mol.L^{-1} for both iodide and Cu^{2+} , the concentration of Cu^{+} is calculated as 3×10^{-7} . As a consequence, the product of the concentrations is far in excess of the solubility product, so copper (I)iodide precipitates. The process of precipitation lowers the copper (I) concentration, allowing the redox reaction to proceed.

CuI is poorly soluble in water (0.00042 g/L at $25 \text{ }^{\circ}\text{C}$), but it dissolves in the presence of NaI or KI to give the linear anion $[\text{CuI}_2]^{-}$. Dilution of such solutions with water reprecipitates CuI . This dissolution-precipitation process is employed to purify CuI , affording colorless samples.

4 - Uses

CuI has several uses :

- CuI is used as a reagent in [organic synthesis](#). In combination with 1,2 - or 1,3 diamine ligands, CuI catalyzes the conversion of aryl, heteroaryl, and vinyl bromides into the corresponding iodides. NaI is the typical iodide source and dioxane is a typical solvent. Aryl halides are used to form carbon-carbon and carbon-heteroatom bonds in process such as the [Heck](#) , [Stille](#) , [Suzuki](#) and [Ullman](#) type coupling reactions. Aryl iodides, however, are more reactive than the corresponding aryl bromides or aryl chlorides. 2-Bromo-1-octen-3-ol and 1-nonyne are coupled when combined with [dichloro bis\(triphenyl phosphine \) palladium\(II\)](#), CuI , and [diethylamine](#) to form 7- methylene -8- hexadecyn-6- ol.

- CuI is used in [cloud seeding](#), altering the amount or type of precipitation of a cloud, or their structure by dispersing substances into the atmosphere which increase water's ability to form droplets or crystals. CuI provides a sphere for moisture in the cloud to condense around, causing precipitation to increase and cloud density to decrease.

- The structural properties of CuI allow CuI to stabilize heat in [nylon](#) in commercial and residential carpet industries, automotive engine accessories, and other markets where durability and weight are a factor .
- CuI is used as a source of dietary iodine in table salt and animal feed .
- CuI is used in the detection of [mercury](#). Upon contact with mercury vapors, the originally white compound changes color to form copper tetraiodomercurate, which has a brown color.

Copper chromite

1 – Introduction :

Copper chromite is a complex inorganic composition $\text{Cu}_2\text{Cr}_2\text{O}_5$, but often containing barium oxide that is used to catalyse certain reactions in [organic synthesis](#). It was first described in 1908. A variety of composition are recognized including $\text{Cr}_2\text{CuO}_4 \cdot \text{CuO} \cdot \text{BaCrO}_4$ and $\text{Cr}_2\text{Cu}_2\text{O}_5$. The latter is sometimes intentionally poisoned with [quinoline](#), when the catalyst is used for [decarboxylation](#) reactions. The catalyst was developed in North America by [Homer Burton Adkins](#) and [Wilbur Arthur Lazier](#) partly based on interrogation of [German](#) chemists after [World War II](#) in relation to the [Fischer-Tropsch process](#). For this reason it is referred to as the **Lazier catalyst**. The catalyst $\text{Cr}_2\text{CuO}_4 \cdot \text{CuO} \cdot \text{BaCrO}_4$ is prepared by addition of a solution containing both [barium nitrate](#) and [copper \(II\) nitrate](#) to a solution of ammonium [chromate](#). This resulting precipitate is [calcined](#) at 350 - 400 °C.

2 - Illustrative reactions

- [Hydrogenolysis](#) of [ester](#) compounds to the corresponding [alcohols](#). For example, sebacion, derived from the [acyloin condensation](#) of [dimethyl sebacate](#), is hydrogenated to 1,2-cyclodecanediol by this catalyst.^[5] [Phenanthrene](#) is also reduced, at the 9,10 position.
 - [Hydrogenolysis](#) of [2-furfuryl alcohol](#) to [1,5-pentanediol](#) at 250 - 300 °C under 3300 - 6000 psi of H_2 .
 - [Decarboxylation](#) of α -phenylcinnamic acid to [cis-stilbene](#).

Reactions involving hydrogen are conducted at relatively high gas pressure (135 [atm](#)) and high temperatures (150-300 °C) in a so-called hydrogenation bomb. More active catalysts requiring less vigorous conditions are known but are typically derived from more expensive metals, such as [platinum](#).

Copper Chromated Arsenate

Chromated copper arsenate (CCA) is a [wood preservative](#) used for [timber treatment](#) since the mid-1930s. It is a mix of [chromium](#), [copper](#) and [arsenic](#) (as [Copper \(II\) arsenate](#)) formulated as oxides or salts. It preserves the wood from decay fungi, wood attacking insects, including termites, and marine borers. It also improves the weather-resistance of treated timber and may assist paint adherence in the long term.

CCA is known by many trade names, including the worldwide brands "Tanalith" "SupaTimber" and "Celcure". The [chromium](#) acts as a chemical fixing agent and has little or no preserving properties; it helps the other chemicals to fix in the timber, binding them through chemical complexes to the wood's [cellulose](#) and [lignin](#). The copper acts primarily to protect the wood against decay fungi and bacteria, while the arsenic is the main insecticidal component of CCA.

CCA is widely used around the world as a heavy duty preservative, often as an alternative to [creosote](#), and [pentachlorophenol](#). Other water-borne preservatives like CCA include alkaline copper quaternary compounds ([ACQ](#)), copper azole (CuAz), ammoniacal copper zinc arsenate (ACZA), copper citrate, and copper HDO (CuHDO)

Recognized for the greenish tint it imparts to timber, CCA is a preservative that has been extremely common for many decades. Over time small amounts of the CCA chemicals, mainly the arsenic, may leach out of the treated timber. This is particularly the case in acidic environments. The chemicals may leach from the wood into surrounding [soil](#), resulting in concentrations higher than naturally occurring background levels. A study found that 12–13 percent of the CCA leached from treated wood buried in [compost](#) during a 12-month period.^[1] On the other hand there have been many other studies in less aggressive soil types that show leaching to be as low as 0.5 ppm (red pine poles in service,) or up to 14 ppm (treated pine in garden beds). [Soil contamination](#) due to the presence of CCA-treated wood after 45 years is minimal.

Should any chemicals leach from the wood they are likely to bind to soil particles, especially in soils with [clay](#) or soils that are more [alkaline](#) than neutral.

A number of countries have reviewed CCA during recent years and have looked at limiting the public exposure to CCA-treated timber by restricting its application in residential situations. These reviews have resulted from increasing public pressures and perceptions that arsenic-containing timber poses a health hazard. In response to these pressures the preservation industry in the USA and Canada volunteered not to use CCA for the treatment of residential timber, and on 1 January 2004 the [United States Environmental Protection Agency](#) (EPA) began restricting the use of CCA for such purposes. Exceptions were allowed, including the treatment of shakes and [shingles](#), permanent wood [foundations](#), and certain commercial applications. It should be emphasised however that the regulatory agencies advised that CCA - treated timber products already in use pose no significant threat to health. Indeed CCA will continue to be used in North America in a wide variety of commercial and industrial applications such as poles, piling, retaining structures and many others.

Following the USA and Canada actions in restricting CCA, similar actions have been taken in other parts of the world, including the EU and Australia. In New Zealand the [Environmental Risk Management Authority](#), reviewing the same data that prompted the actions elsewhere, concluded that there was no reason to restrict CCA use for any applications .

CCA timber is still in widespread use in many countries and remains an economical option for conferring durability to perishable timbers such as plantation grown pine.

Although widespread restrictions (see above) followed the publication of studies which showed low-level leaching from in-situ timbers (such as children's [playground](#) equipment) into surrounding [soil](#), a more serious risk is presented if CCA-treated timber is burnt in confined spaces such as a domestic fire or barbecue. Scrap CCA

construction timber continues to be widely burnt through ignorance, in both commercial, and domestic fires.

Notwithstanding this, disposal by burning i.e. in approved incinerators, is an acceptable option. It is particularly attractive if there is some energy captured in the process. In addition, CCA treated timber wastes can also be effectively incinerated using high temperatures, i.e. 800°-1100°C.

Disposal of large quantities of CCA-treated wastes or spent timber at the end of its lifecycle has been traditionally through controlled landfill sites. Such sites are lined to make them impervious in order to prevent losses to the water table and they are covered to prevent rainfall washing out any contained potential toxicants. These controlled sites handle a range of waste materials potentially more noxious than that posed by CCA-treated timber, e.g. paint-stuffs, car batteries, etc. Today, landfill sites are becoming scarcer and disposal of waste materials is becoming economically unattractive. The wood preservation and timber industries are therefore researching better ways of dealing with waste treated timber, including CCA-treated material.

Copper (I) cyanide

1 – Introduction :

Copper (I) cyanide is an **inorganic compound** with the formula CuCN. This off - white solid occurs in two **polymorphs**; impure samples can be green due to the presence of Cu (II) impurities. The compound is useful as a **catalyst**, in electroplating copper, and as a **reagent** in the preparation of **nitriles**.

IUPAC Name :	Copper (I) cyanide
Other Names :	Cuprous cyanide, copper cyanide, cupricin
Molecular Formula	Cu CN
Molar Mass	89.5 g / mol
Appearance	Off - white / pale yellow powder
Density	2.92 g / cm ³
Melting point	474 °C,
Solubility in water	negligible
Solubility	insoluble in ethanol , cold dilute acids ; soluble in NH ₄ OH, KCN
Hazards	
EU classification	Very toxic (T+) Dangerous for the environment (N)
Flash point	Non-flammable

2 - Structure :

Copper cyanide is a **coordination polymer**. It exists in two polymorphs both of which contain $-\text{[Cu-CN]}-$ chains made from linear copper(I) centres linked by **cyanide bridges**. In the high - temperature polymorph , HT- Cu CN , which is isostructural with **AgCN**, the linear chains pack on a hexagonal lattice and adjacent chains are off set by $+ / - 1 / 3 c$, Figure 1. In the low - temperature polymorph , LT- Cu CN , the chains deviate from linearity and pack into rippled layers

which pack in an AB fashion with chains in adjacent layers rotated by 49 °, Figure 2

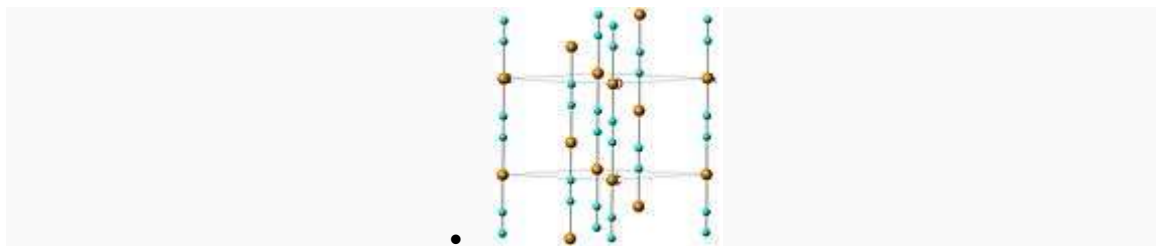


Figure 1: The structure of HT- Cu CN showing the chains running along the c axis. Key: copper = orange and cyan = head-to-tail disordered cyanide groups.

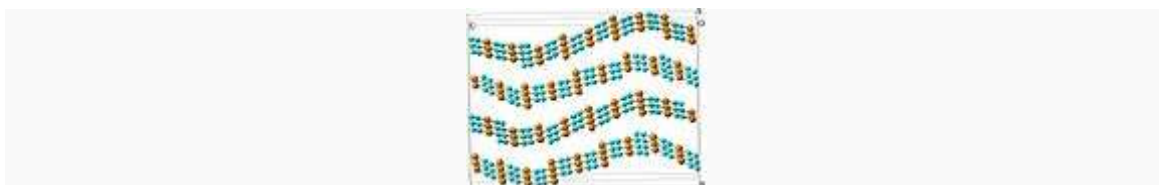


Figure 2: The structure of LT-CuCN showing sheets of chains staking in an ABAB fashion. Key copper = orange and cyan = head-to-tail disordered cyanide groups.

LT- Cu CN can be converted to HT- Cu CN by heating to 563 K in an inert atmosphere. In both polymorphs the copper to carbon and copper to nitrogen bond lengths are $\sim 1.85 \text{ \AA}$ and bridging cyanide groups show head - to - tail disorder.

3 – Preparation :

Cuprous cyanide is commercially available and is supplied as the low - temperature polymorph. It can be prepared by the reduction of [copper \(II\) sulfate](#) with sodium bisulphite at 60 °C, followed by the addition of [sodium cyanide](#) to precipitate pure LT-CuCN as a pale yellow powder.



On addition of sodium bisulphite the copper sulphate solution turns from blue to green, at which point the sodium cyanide is added. The reaction is performed under mildly acidic conditions. Copper

cyanide has historically been prepared by treating [copper\(II\) sulfate](#) with [sodium cyanide](#), in this redox reaction, copper (I) cyanide forms together with [cyanogen](#) :



Because this synthetic route produces [cyanogen](#), uses two equivalents of sodium cyanide per equivalent of Cu CN made and the resulting copper cyanide is impure it is not the industrial production method. The similarity of this reaction to that between copper sulphate and sodium iodide to form copper (I) iodide is one example of cyanide ions acting as a pseudo halide. It also explains why copper (II) cyanide, $\text{Cu}(\text{CN})_2$, has not been synthesised.

4 - Reactions :

Copper cyanide is insoluble in water but rapidly dissolves in solutions containing CN^- to form $[\text{Cu}(\text{CN})_3]^{2-}$ and $[\text{Cu}(\text{CN})_4]^{3-}$, these ions are trigonal planar and tetra hedral respectively. This is in contrast to both silver and gold cyanides which form $[\text{M}(\text{CN})_2]^-$ ions in solution . The coordination polymer $\text{KCu}(\text{CN})_2$ contains $[\text{Cu}(\text{CN})_2]^-$ units which link together forming helical anionic chains.

Copper cyanide is also soluble in 0.88 aqueous ammonia, pyridine and N - methylpyrrolidone.

5 - Applications

Cuprous cyanide is used for electro plating copper. The compound is useful reagent in [organic synthesis](#), for example in the regioselective and stereoselective allylation and conjugate addition of N-Boc-2-lithiopyrrolidine and N-Boc-2-lithiopiperidine , or the copper cyanide catalyzed palladium coupling of α - lithio amines and aryl iodides.

Copper (II) hydroxide

Contents

- 1 Introduction
- 2 History
- 3 Chemical Properties
 - 3.1 Synthesis
 - 3.2 Reactions
 - 3.3 Use as an organic reagent
- 4 Natural occurrence
- 5 Uses
- 6 Precautions

Copper (II) hydroxide (chemical formula $\text{Cu}(\text{OH})_2$) is the hydroxide of the metal copper. Copper hydroxide is a pale blue, gelatinous solid. Some forms of copper (II) hydroxide are sold as "stabilized" copper hydroxide, quite likely a mixture of copper(II) carbonate and hydroxide. These are often greener in color.

Other Names	Cupric hydroxide
Molecular Formula	$\text{Cu}(\text{OH})_2$
Molar Mass	97.5 g / mol
Appearance	Blue or blue - green solid
Density	3.368 g / cm^3 , solid
Melting Point	80 °C (decomp into CuO)
Solubility in Water	Negligible
Solubility product, K_{sp}	2.20×10^{-20}
Solubility	Insoluble in ethanol ; Soluble in NH_4OH , KCN
Main hazards	Skin , Eye , & Respiratory Irritant
Flash point	Non - flammable
LD_{50}	1000 mg / kg (oral , rat)

2 . History

Copper (II) hydroxide has been known since copper smelting began around 5000 BCE although the alchemists were probably the first to manufacture it . This was easily done by mixing solutions of lye and blue vitriol, both chemicals which were known in antiquity.

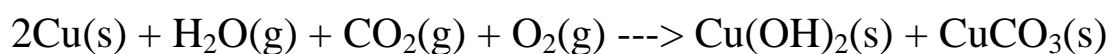
It was produced on an industrial scale during the 17th and 18th centuries for use in pigments such as blue verditer and Bremen green . These pigments were used in ceramics and painting.

3 . Chemical Properties

3 . 1 . Synthesis

Copper (II) hydroxide can be produced by adding a small amount of sodium hydroxide to a dilute solution of copper (II) sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) . The precipitate produced in this manner, however, often contains an appreciable amount of sodium hydroxide impurity and a purer product can be attained if ammonium chloride is added to the solution beforehand. Alternatively, copper hydroxide is readily made by electrolysis of water (containing a little electrolyte such as sodium bicarbonate) . A copper anode is used, often made from scrap copper.

" Copper in moist air slowly acquires a dull green coating . The green material is a 1:1 mole mixture of $\text{Cu}(\text{OH})_2$ and CuCO_3 " .



This is the patina that forms on bronze and other copper alloy statues such as the Statue of Liberty.

3 . 2 . Reactions

Moist samples of copper (II) hydroxide slowly turn black due to the formation of copper (II) oxide . When it is dry , how ever , copper (II) hydroxide does not decompose unless it is heated to 185°C .

Copper (II) hydroxide reacts with a solution of ammonia to form a deep blue solution consisting of the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion, but the hydroxide is reformed when the solution is diluted with water. Copper (II) hydroxide in ammonia solution, known as Schweizer's reagent, possesses the interesting ability to dissolve cellulose. This property led to it being used in the production of rayon, a cellulosic fiber.

Since copper (II) hydroxide is mildly amphoteric, it dissolves slightly in concentrated alkali, forming $[\text{Cu}(\text{OH})_4]^{2-}$.

3.3. Use as an organic reagent

Copper (II) hydroxide has a rather specialized role in organic synthesis. Often, when it is utilized for this purpose, it is prepared in situ by mixing a soluble copper (II) salt and potassium hydroxide.

It is sometimes used in the synthesis of aryl amines. For example, copper (II) hydroxide catalyzes the reaction of ethylenediamine with 1-bromoanthraquinone or 1-amino-4-bromoanthraquinone to form 1-((2-aminoethyl)amino)anthraquinone or 1-amino-4-((2-aminoethyl)amino)anthraquinone, respectively.

Copper (II) hydroxide also converts acid hydrazides to carboxylic acids at room temperature. This is especially useful in synthesizing carboxylic acids with other fragile functional groups. The published yields are generally excellent as is the case with the production of benzoic acid and octanoic acid.

4. Natural occurrence

Copper (II) hydroxide is found in several different copper minerals, most notably azurite, malachite, antlerite, and brochantite. Azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) and malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$) are carbonates while antlerite ($\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$) and brochantite ($\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$) are sulfates. Copper (II) hydroxide is rarely found as an uncombined mineral because it slowly reacts

with carbon dioxide from the atmosphere to form a basic copper (II) carbonate. The mineral of the formula $\text{Cu}(\text{OH})_2$ is called spertiniite.

5 . Uses

Copper (II) hydroxide has been used as an alternative to the **Bordeaux** mixture, a fungicide and nematocide . Nowadays , it is disfavored because of environmental contamination problems. Copper (II) hydroxide is also occasionally used as ceramic colorant.

Copper (II) hydroxide has been combined with latex paint, making a product designed to control root growth in potted plants. Secondary and lateral roots thrive and expand, resulting in a dense and healthy root system. It is sold under the name Spin Out, which was first introduced by Griffin L.L.C.

6 . Precautions

Copper (II) hydroxide is a skin, eye and respiratory irritant. Always wear safety glasses when handling copper hydroxide. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

Copper (II) nitrate

1 . Introduction :

Copper (II) nitrate is the chemical compound with the formula $\text{Cu}(\text{NO}_3)_2$. Commonly referred to simply as copper nitrate, the anhydrous form is a blue, crystalline solid. Hydrated forms of copper nitrate, also blue, are commonly used in school laboratories to demonstrate chemical voltaic cell reactions. The Roman numeral sign is to specify that the copper has an oxidation state of +2 .

Other Names	Cupric nitrate
Molecular Formula	$\text{Cu}(\text{NO}_3)_2$
Molar Mass	187.5 g / mol (anhydrous) 241.5 g / mol (tri hydrate) 295. 5 g / mol (hexa hydrate)
Appearance	Blue crystals , hygroscopic
Density	3.05 g / cm ³ (anhydrous) 2.32 g / cm ³ (tri hydrate) 2.07 g / cm ³ (hexa hydrate)
Melting Point	256 °C (anhydrous , decomp) 114 °C (tri hydrate) 26 °C (hexa hydrate , decomposes)
Boiling Point	170 °C (tri hydrate , decomposes)
Solubility in Water	137.8 g / 100 mL (0 °C) (tri hydrate)
Solubility	Hydrates very soluble in ethanol, water
Crystal structure	Orthorhombic (anhydrous) Rhombohedral (hydrates)
Main hazards	Toxic , Irritant

2 . Synthesis and reactions

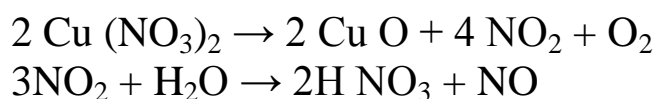
$\text{Cu}(\text{NO}_3)_2$ forms when copper metal is treated with N_2O_4 :



Hydrated copper nitrate can be prepared by hydrolysis of the anhydrous material or by treating copper metal with an aqueous solution of silver nitrate or dilute nitric acid :



Copper nitrate can be used to generate nitric acid by heating it until decomposition and passing the fumes directly into water. This method is similar to the last step in the Ostwald process. The equations are as follows :













3 . Use in organic synthesis

Copper nitrate, in combination with acetic anhydride, is an effective reagent for nitration of aromatic compounds, under what are known as " Menke conditions " , in honor of the Dutch chemist who discovered that metal nitrates are effective reagents for nitration . Hydrated copper nitrate absorbed onto clay affords a reagent called " Claycop ". The resulting blue-colored clay is used as a slurry, for example for the oxidation of thiols to disulfides . Claycop is also used to convert dithioacetals to carbonyls . A related reagent based on Montmorillonite has proven useful for the nitration of aromatic compounds .

Copper Ores

Following is a list of **minerals** which serve as **copper ores** in the **copper mining** process :

	
<i>Chalcocite</i> Cu_2S	<i>Chalcopyrite</i> Cu Fe S_2
	
<i>Tetrahedrite</i> $\text{Cu}_3\text{SbS}_3 + x(\text{Fe,Zn})_6\text{Sb}_2\text{S}_9$	<i>Covellite</i> Cu S
	
<i>Malachite</i> $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	<i>Bornite</i> $2\text{Cu}_2\text{S} \cdot \text{CuS} \cdot \text{FeS}$
	
<i>Cuprite</i> Cu_2O	<i>Azurite</i> $2\text{Cu CO}_3 \cdot \text{Cu}(\text{OH})_2$
	
<i>Tennantite</i> $\text{Cu}_{12}\text{As}_4\text{S}_{13}$	<i>Chrysocolla</i> $\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$

Diopase



Diopase from Altyn Tübe, Kazakhstan, the type locality

1 – Introduction :

Diopase is an intense **emerald**-green to bluish - green **copper cyclosilicate mineral**. It is transparent to **translucent**. Its **luster** is vitreous to sub - **adamantine**. Its formula is $\text{Cu Si O}_3 \cdot \text{H}_2\text{O}$ (also reported as $\text{Cu Si O}_2 (\text{OH})_2$). It has a hardness of 5, the same as tooth enamel. Its **specific gravity** is 3.28 – 3.35 , and it has two perfect and one very good **cleavage** directions. Additionally, diopase is very fragile and specimens must be handled with great care. It is a **trigonal** mineral, forming 6 - sided **crystals** that are terminated by rhombohedra.

Category	Silicate mineral
Chemical Formula	$\text{Cu SiO}_3 \cdot \text{H}_2\text{O}$
Crystal Symmetry	Trigonal 3 Rhombohedral
Unit cell	$a = 14.566 \text{ \AA}$, $c = 7.778 \text{ \AA}$; $Z = 18$
Color	Dark blue green, emerald green
Crystal habit	Six sided prisms terminated by rhombohedrons to massive
Crystal system	Trigonal
Cleavage	Perfect in three directions
Fracture	Conchoidal

Tenacity	Brittle
Mohs scale hardness	5
Luster	Vitreous
Streak	Green
Diaphaneity	Transparent to translucent
Specific gravity	3.28 – 3.35
Optical properties	Uniaxial (+)
Refractive index	$n_{\omega} = 1.652 - 1.658$ $n_{\epsilon} = 1.704 - 1.710$
Birefringence	$\delta = 0.052$

2 – History :



Late in the 18th century, copper miners at the Altyn-Tyube (Altyn-Tube) mine, [Karagandy Province, Kazakhstan](#) thought they found the [emerald](#) deposit of their dreams. They found fantastic cavities in [quartz](#) veins in a [limestone](#), filled with thousands of lustrous emerald-green transparent crystals. The crystals were dispatched to [Moscow, Russia](#) for analysis. However the mineral's inferior hardness of 5 compared with emerald's greater hardness of 8 easily distinguished it. Later Fr. [René Just Haüy](#) (the famed French [mineralogist](#)) in 1797 determined that the enigmatic Altyn-Tyube mineral was new to science and named it diopase ([Greek](#), *dia*, "through" and *optima*, "vision"), alluding to the mineral's two cleavage directions that are visible inside unbroken crystals.

3 – Occurrence :

Diopase is an uncommon mineral found mostly in [desert](#) regions where it forms as a secondary mineral in the [oxidized](#) zone of copper [sulfide](#) mineral deposits. However, the process of its formation is not simple, the [oxidation](#) of copper sulfides should be insufficient to crystallize diopase as [silica](#) is normally minutely soluble in water except at highly [alkaline pH](#). The oxidation of sulfides will generate highly [acidic](#) fluids rich in [sulfuric acid](#) that should suppress silica

solubility. However, in dry climates and with enough time, especially in areas of a mineral deposit where acids are buffered by carbonate, minute quantities of silica may react with dissolved copper forming diopside and chrysocolla.

The Altyn Tube mine in Kazakhstan still provides handsome specimens; a brownish quartzite host distinguishes its specimens from other localities. The finest specimens of all were found at the Tsumeb Mine in Tsumeb, Namibia. Tsumeb diopside is wonderfully lustrous and transparent, with its crystal often perched on an attractive snow-white carbonate matrix. Diopside is also found in the deserts of the southwestern USA. A notable occurrence is the old Mammoth-Saint Anthony Mine near Mammoth, Arizona where small crystals that make fine micromount specimens are found. In addition, many small, pale-green colored crystals of diopside have come from the Christmas Mine near Hayden, Arizona. Another classic locality for fine specimens is Ren eville, Congo - Brazzaville. Finally, an interesting occurrence is the Malpaso Quarry in Argentina. Here tiny bluish-green diopside is found on and in quartz. It appears at this occurrence, diopside is primary and has crystallized with quartz, native copper, and malachite.

	
<p><i>Diopside crystals from Democratic Republic of the Congo, displaying the diopside crystal habit of six sided prisms terminated by rhombohedrons</i></p>	<p><i>Diopside from the Tsumeb Mine, Tsumeb, Namibia</i></p>

4 – Use :

Dioptase is popular with [mineral collectors](#) and it is occasionally cut into small emerald-like [gems](#). Dioptase and [chrysocolla](#) are the only relatively common copper silicate minerals. A dioptase gemstone should never be exposed to [ultrasonic cleaning](#) or the fragile gem will shatter.

Malachite



Malachite from the Congo

1 – Introduction :

Malachite is a copper [carbonate mineral](#) , with the [formula](#) $\text{Cu}_2\text{CO}_3(\text{OH})_2$. This green - colored mineral crystallizes in the [monoclinic](#) crystal system, and most often forms [botryoidal](#), fibrous, or [stalagmitic](#) masses. Individual crystals are rare but do occur as slender to [acicular](#) prisms. [Pseudomorphs](#) after more tabular or blocky [azurite](#) crystals also occur.

Category	Carbonate mineral
Chemical formula	$\text{Cu}_2\text{CO}_3(\text{OH})_2$
Molar mass	221 g / mol
Color	Bright green, dark green, blackish green, commonly banded in masses ; green to yellowish green in transmitted light
Crystal habit	Massive, botryoidal, stalactitic, crystals are acicular to tabular prismatic
Crystal system	Monoclinic
Fracture	Subconchoidal to uneven
Mohs scale hardness	3.5 – 4.0
Luster	Adamantine to vitreous; silky if fibrous; dull to earthy if massive
Streak	light green

Diaphaneity	Translucent to opaque
Specific gravity	3.6–4
Optical properties	Biaxial (–)
Refractive index	$n_{\alpha} = 1.655$ $n_{\beta} = 1.875$ $n_{\gamma} = 1.909$
Birefringence	$\delta = 0.254$

2 - Etymology and history :

The stone's name derives (via **Latin**: *molochītis*, **Middle French**: *melochite*, and **Middle English** *melochites*) from **Greek** *Μολοχίτης λίθος molochitis lithos*, "mallow-green stone", from *μολόχη molōchē*, variant of *μαλάχη malāchē*, "mallow". The mineral was given this name due to its resemblance to the leaves of the **Mallow plant**.^[5] Malachite was used as a mineral pigment in green paints from antiquity until about 1800. The pigment is moderately lightfast, very sensitive to **acids** and varying in color. The natural form was being replaced by its synthetic form, **verditer** amongst other synthetic greens. It is also used for decorative purposes, such as in the Malachite Room in the **Hermitage**, which features a large malachite vase. "The **Tazza**", one of the largest pieces of malachite in North America and a gift from **Tsar Nicholas II**, stands as the focal point in the center of the room of **Linda Hall Library**.

3 - Occurrence and historical uses :

Malachite often results from weathering of **copper ores** and is often found together with **azurite** ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), **goethite**, and **calcite**. Except for its vibrant green color, the properties of malachite are similar to those of azurite and aggregates of the two minerals occur frequently. Malachite is more common than **azurite** and is typically associated with copper deposits around **limestones**, the source of the carbonate.

Large quantities of malachite have been mined in the **Urals, Russia**. It is found worldwide including in the **Democratic Republic of Congo; Gabon; Zambia; Tsumeb, Namibia; Mexico; Broken Hill,**

New South Wales; Lyon, France; and in the Southwestern United States notably in Arizona.

In Israel, malachite is extensively mined at Timna valley, often called King Solomon's Mines, although research has revealed an interruption in mining activity at the site during the 10th century BC, the time of the biblical Solomon. Archeological evidence indicates that the mineral has been mined and smelted at the site for over 3,000 years. Most of Timna's current production is also smelted, but the finest pieces are worked into silver jewelry.

4 - Malachite gallery :



Slice through a double stalactite, from Kolwezi, Democratic Republic of Congo



A polished slab of malachite, from the Democratic Republic of Congo



Malachite and azurite, from Morenci, Arizona USA



Malachite stalactites (to 9 cm height), from Kasompi Mine, Katanga Province, Democratic Republic of Congo.



Botryoidal malachite from Bisbee, Arizona USA



Neoclassical vase in malachite in the Hermitage Museum, St Petersburg

Copper (I) oxide

1 . Introduction :

Copper (I) oxide or **cuprous oxide** (Cu_2O) is an oxide of copper. It is insoluble in water and organic solvents. Copper (I) oxide dissolves in concentrated ammonia solution to form the colorless complex $[\text{Cu}(\text{NH}_3)_2]^+$, which easily oxidizes in air to the blue $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. It dissolves in hydrochloric acid to form H Cu Cl_2 (a complex of CuCl), while dilute sulfuric acid and nitric acid produce copper (II) sulfate and copper (II) nitrate, respectively.

Copper (I) oxide is found as the mineral cuprite in some red-colored rocks. When it is exposed to oxygen, copper will naturally oxidize to copper (I) oxide, but this takes extensive time. Artificial formation is usually accomplished at high temperature or at high oxygen pressure. With further heating, copper (I) oxide will form copper (II) oxide.

Formation of copper (I) oxide is the basis of the Fehling's test and Benedict's test for reducing sugars which reduce an alkaline solution of a copper (II) salt and give a precipitate of Cu_2O .

Cuprous oxide forms on silver - plated copper parts exposed to moisture when the silver layer is porous or damaged; this kind of corrosion is known as red plague .

Other Names	Cuprous oxide Dicopper oxide Cuprite Red copper oxide
Molecular Formula	Cu_2O
Molar Mass	143. g / mol
Appearance	Brownish - red solid
Density	6.0 g / cm^3
Melting point	$1235 \text{ }^\circ\text{C}$

Boiling point	1800 °C
Solubility in Water	Insoluble
Solubility in Acid	Soluble
Crystal structure	Cubic
EU classification	Harmful (Xn) Dangerous for the environment (N)

2 . General applications

Cuprous oxide is commonly used as a pigment, a fungicide, and an antifouling agent for marine paints.

2 .1 . Applications as semi conductor

Copper (I) oxide was the first substance known to behave as a semiconductor. Rectifier diodes based on this material were used industrially as early as 1924, long before silicon became the standard.

Copper (I) oxide shows four well-understood series of excitons with resonance widths in the range of neV. The associated polaritons are also well understood; their group velocity turns out to be very low, almost down to the speed of sound. That means light moves almost as slow as sound in this medium. This results in high polariton densities, and effects like Bose-Einstein condensation, the dynamical Stark effect, and phonoritons have been demonstrated.

Another extraordinary feature of the ground state excitons is that all primary scattering mechanisms are known quantitatively. Cu_2O was the first substance where an entirely parameter - free model of absorption linewidth broadening by temperature could be established, allowing the corresponding absorption coefficient to be deduced. It can be shown using Cu_2O that the Kramers – Kronig relations do not apply to polaritons.

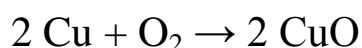
Copper (II) oxide

Copper (II) oxide or **cupric oxide** (CuO) is the higher oxide of copper. As a mineral, it is known as tenorite.

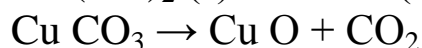
Other Names	Cupric oxide
Molecular Formula	Cu O
Molar Mass	79.5 g / mol
Appearance	black powder
Density	6.31 g / cm ³
Melting Point	1201 ° C
Boiling Point	2000 ° C
Solubility in Water	Insoluble
Solubility in NH ₄ OH	Soluble
Crystal Structure	Monoclinic , mS8

2 . Chemistry

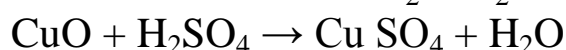
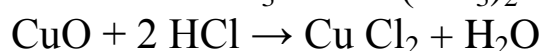
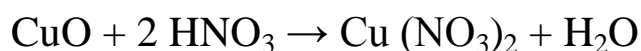
It is a black solid with an ionic structure which melts above 1200 °C with some loss of oxygen. It can be formed by heating copper in air:



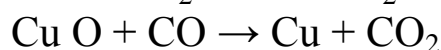
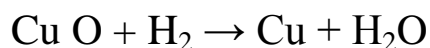
Here, it is formed along with copper(I) oxide as a side product; thus, it is better prepared by heating copper(II) nitrate, copper(II) hydroxide or copper (II) carbonate:



Copper (II) oxide is a basic oxide, so it dissolves in mineral acids such as hydrochloric acid, sulfuric acid or nitric acid to give the corresponding copper (II) salts:



It can also be reduced to copper metal using hydrogen or carbon monoxide :



3 . Crystal structure

Copper (II) oxide belongs to the monoclinic crystal system, with a crystallographic point group of $2/m$ or C_{2h} . The space group of its unit cell is $C2/c$, and its lattice parameters are $a = 4.6837(5)$, $b = 3.4226(5)$, $c = 5.1288(6)$, $\alpha = 90^\circ$, $\beta = 99.54(1)^\circ$, $\gamma = 90^\circ$ The copper atom is coordinated by 4 oxygen atoms in an approximately square planar configuration .

4 . Health effects

Copper (II) oxide is an irritant. It also can cause damage to the endocrine and central nervous system. Contact to the eyes can cause irritation and damage to the corneas, and potentially can cause conjunctivitis. Contact to the skin can cause irritation and discoloration. Ingesting cupric oxide can lead to central nervous system depression, liver and kidney damage, gastro-intestinal damage, circulatory system failure or damage to the vascular system. Inhalation can lead to damage to the lungs and septum. Inhalation of fumes of cupric oxide can lead to a disease called metal fume fever, which has symptoms similar to influenza. Prolonged exposure to cupric oxide can lead to dermatitis, and can cause a toxic build-up of copper in people with Wilson's disease. Handling copper (II) oxide should be done in well ventilated area, and care should be taken to avoid contact with the skin or eyes. After handling, one should wash thoroughly.

5 . Uses

Cupric oxide is used as a pigment in ceramics to produce blue, red, and green (and sometimes gray, pink, or black) glazes. It is also used to produce cuprammonium hydroxide solutions, used to make rayon. It is also occasionally used as a dietary supplement in animals, against copper deficiency . Copper (II) oxide has application as a p - type semiconductor, because it has a narrow band gap of 1.2 eV. It is an abrasive used to polish optical equipment. Cupric oxide can be used to produce dry cell batteries. It has also been used in wet cell batteries as the cathode, with lithium as an anode, and dioxalane mixed with lithium perchlorate as the electrolyte. Copper (II) oxide can be used to produce other copper salts. It is also used when welding with copper alloys .

Another use for cupric oxide is as a substitute for iron oxide in thermite. This can turn the thermite from an incendiary to a low explosive.

Copper (I) phosphide

Copper phosphide, Cu_3P , also **copper (I) phosphide, cuprous phosphide , cuprophosphorus** and **phosphor copper**, is a compound of copper and phosphorus, a phosphide of copper. It has the appearance of yellowish - grey very brittle mass of crystalline structure. It does not react with water

Copper phosphide has a role in copper alloys, namely in phosphor bronze. It is a very good deoxidizer of copper.

Copper phosphide can be produced in a reverberatory furnace or in a crucible, eg. by a reaction of red phosphorus with a copper-rich material. It can also be prepared photochemically, by irradiating cupric hypophosphite with ultraviolet radiation .

When subjected to ultraviolet light, copper phosphide shows fluorescence .

A blue - black film of copper phosphide forms on white phosphorus when subjected to a solution of copper salt; wounds containing particles of phosphorus therefore have to be washed with 1% solution of copper sulfate. The particles then can be easily removed, which is helped by their fluorescence. Formation of protective layer of copper phosphide is also used in cases of phosphorus ingestion, when gastric lavage with copper sulfate is employed as part of the cure .

Other Names	Copper phosphide , Cuprous phosphide
Molecular Formula	Cu_3P
Molar Mass	221.5 g / mol
Appearance	Yellowish grey crystals
Melting Point	900 °C
Crystal structure	Hexagonal

Copper (II) Sulfate

Contents

- 1 Introduction
- 2 Preparation
- 3 Chemical properties
- 4 Uses
 - 4.1 As a herbicide , fungicide & pesticide
 - 4.2 Analytical reagent
 - 4.3 Organic synthesis
 - 4.4 Chemistry education

1 . Introduction :

Copper (II) sulfate is the chemical compound with the formula CuSO_4 . This salt exists as a series of compounds that differ in their degree of hydration. The anhydrous form is a pale green or gray-white powder, whereas the pentahydrate, the most commonly encountered salt, is bright blue. The anhydrous form occurs as a rare mineral known as chalcocyanite. The hydrated copper sulfate occurs in nature as chalcantite (pentahydrate), and two more rare ones: bonattite (trihydrate) and boothite (heptahydrate). Archaic names for copper (II) sulfate are " blue vitriol " and " blue stone".

Other Names	Cupric sulfate , Blue vitriol , Bluestone . Chalcantite
Molecular Formula	Cu SO_4
Molar Mass	159.5 g /mol (anhydrous) 249.5 g /mol (penta hydrate)
Appearance	Blue crystalline solid (penta hydrate) Gray - white powder (anhydrous)
Density	3.603 g / cm^3 (anhydrous) 2.284 g / cm^3 (penta hydrate)

Melting Point	110 °C (– 4H ₂ O) 150 °C (423 K) (–5H ₂ O) < 650 °C <i>decomp.</i>
Solubility in Water	31.6 g / 100 ml (0 °C)
Solubility	<i>anhydrous</i> insoluble in ethanol <i>Penta hydrate</i> soluble in methanol and ethanol
Refractive index (n_D)	1.514 (penta hydrate)
Crystal structure	Triclinic
Coordination geometry	Octahedral
EU classification	Harmful (Xn) Irritant (Xi) Dangerous for the environment (N)
LD ₅₀	300 mg / kg

2 . Preparation

Preparation of copper (II) sulfate by electrolyzing sulfuric acid , using copper electrodes

Since it is available commercially, copper sulfate is usually purchased and not prepared in the laboratory. It can be made by the action of sulfuric acid on a variety of copper (II) compounds, for example copper (II) oxide; this oxide can be generated with the addition of hydrogen peroxide to the acid. It may also be prepared by electrolyzing sulfuric acid, using copper electrodes.

3 . Chemical properties

Copper (II) sulfate pentahydrate decomposes before melting, losing four water molecules at 110 °C and all five at 150 °C. At 650 °C, copper (II) sulfate decomposes into copper(II) oxide (Cu O) and sulfur trioxide (SO₃). Its blue color is due to water of hydration. When

heated in an open flame the crystals are dehydrated and turn grayish-white .

4 . Uses

4 . 1 . As a herbicide , fungicide and pesticide

Copper sulfate pentahydrate is a fungicide. Mixed with lime it is called Bordeaux mixture and used to control fungus on grapes, melons, and other berries . Another application is Cheshunt compound, a mixture of copper sulfate and ammonium carbonate used in horticulture to prevent damping off in seedlings. Its use as a herbicide is not agricultural, but instead for control of invasive exotic aquatic plants and the roots of other invasive plants near various pipes that contain water. A dilute solution of copper sulfate is used to treat aquarium fish for various parasitic infections , and is also used to remove snails from aquariums. However, as the copper ions are also highly toxic to the fish, care must be taken with the dosage. Most species of algae can be controlled with very low concentrations of copper sulfate. Copper sulfate inhibits growth of bacteria such as *E. coli* .

4 . 2 . Analytical reagent

Several chemical tests utilize copper sulfate. It is used in Fehling's solution and Benedict's solution to test for reducing sugars, which reduce the soluble blue copper (II) sulfate to insoluble red copper (I) oxide. Copper (II) sulfate is also used in the Biuret reagent to test for proteins.

Copper sulfate is also used to test blood for anemia. The blood is tested by dropping it into a solution of copper sulfate of known specific gravity — blood which contains sufficient hemoglobin sinks rapidly due to its density, whereas blood which does not, floats or sinks slowly .

In a flame test, its copper ions emit a deep blue - green light, much more blue than the flame test for barium.

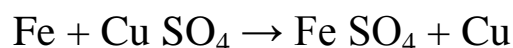
4.3. Organic synthesis

Copper sulfate is employed in organic synthesis. The anhydrous salt catalyses the transacetalization in organic synthesis . The hydrated salt reacts with potassium permanganate to give an oxidant for the conversion of primary alcohols .

4.4. Chemistry education

Copper sulfate is a commonly included chemical in children's chemistry sets and is often used to grow crystals in schools and in copper plating experiments. Due to its toxicity, it is not recommended for small children. Copper sulfate is often used to demonstrate an exothermic reaction, in which steel wool or magnesium ribbon is placed in an aqueous solution of CuSO_4 . It is used in school chemistry courses to demonstrate the principle of mineral hydration. The pentahydrate form, which is blue, is heated, turning the copper sulfate into the anhydrous form which is white, while the water that was present in the pentahydrate form evaporates. When water is then added to the anhydrous compound, it turns back into the pentahydrate form, regaining its blue color, and is known as blue copperas .

In an illustration of a " single metal replacement reaction" , iron is submerged in a solution of copper sulfate. Upon standing, iron dissolves, producing iron (II) sulfate, and copper precipitates.



The copper can also be electroplated to the iron .

Copper sulfate was also used in the past as an emetic.^[10] It is now considered too toxic for this use . It is still listed as an antidote in the World Health Organization's ATC code V03 .

Copper Sulfides

1 . Introduction :

Copper Sulfides describe a family of chemical compounds and minerals with the formula Cu_xS_y . Both minerals and synthetic materials comprise these compounds. Some copper sulfides are economically important ores.

Prominent copper sulfide minerals include Cu_2S (chalcocite) and CuS (covellite). In the mining industry, the minerals bornite or chalcopyrite, which consist of mixed copper-iron sulfides, are often referred to as "copper sulfides ". In chemistry, a " binary copper sulfide " is any binary chemical compound of the elements copper and sulfur. Whatever their source, copper sulfides vary widely in composition with $0.5 \leq \text{Cu/S} \leq 2$, including numerous of non-stoichiometric compounds.

2 . Known copper sulfides

The binary compounds of copper and sulfur are listed below. There are probably more yet to be discovered, for example investigations of " blaubleibender covellite " (blue remaining covellite) formed by natural leaching of covellite,(CuS) indicate that there are other metastable Cu - S phases still to be fully characterised .

- Cu S_2 , villamaninite
- Cu S , covellite
- $\text{Cu}_9 \text{S}_8$ ($\text{Cu}_{1.12}\text{S}$) yarrowite
- $\text{Cu}_{39} \text{S}_{28}$ ($\text{Cu}_{1.39}\text{S}$) spionkopite
- $\text{Cu}_8 \text{S}_5$ ($\text{Cu}_{1.6}\text{S}$) geerite
- $\text{Cu}_7 \text{S}_4$ ($\text{Cu}_{1.75}\text{S}$) anilite
- $\text{Cu}_9 \text{S}_5$ ($\text{Cu}_{1.8}\text{S}$) digenite
- $\text{Cu}_{31} \text{S}_{16}$ $\text{Cu}_{1.96}\text{S}$ djurleite
- $\text{Cu}_2 \text{S}$ chalcocite

3 . Classes of copper sulfides

Copper sulfides can be classified into three groups :

Mono Sulfides , $1.6 \leq \text{Cu} / \text{S} \leq 2$: their crystal structures consist of isolated sulfide anions that are closely related to either hcp or fcc lattices, without any direct S - S bonds. The copper ions are distributed in a complicated manner over interstitial sites with both trigonal as well as distorted tetrahedral coordination and are rather mobile. Therefore, this group of copper sulfides shows ionic conductivity at slightly elevated temperatures. In addition, the majority of its members are semiconductors.

Mixed Mono Sulfide and Disulfide compounds of copper contain both monosulfide (S^{2-}) as well as disulfide (S_2)ⁿ⁻ anions. Their crystal structures usually consist of alternating hexagonal layers of monosulfide and disulfide anions with Cu cations in trigonal and tetrahedral interstices. Cu_3S , for example, can be written as $\text{Cu}_3(\text{S}_2)\text{S}$. Several nonstoichiometric compounds with Cu:S ratios between 1.0 and 1.4 also contain both monosulfide as well as disulfide ions. Depending on their composition, these copper sulfides are either semiconductors or metallic conductors.

At very high pressures , a **copper disulfide** , Cu S_2 , can be synthesized. Its crystal structure is analogous to that of pyrite, with all sulfur atoms occurring as S-S units. Copper disulfide is a metallic conductor due to the incomplete occupancy of the sulfur p band.

4 . Oxidation states of copper and sulfur

The bonding in copper sulfides cannot be correctly described in terms of a simple oxidation state formalism because the Cu-S bonds are somewhat covalent rather than ionic in character, and have a high degree of delocalization resulting in complicated electronic band structures. Although many textbooks (e.g. ^[5]) give the mixed valence formula $(\text{Cu}^+)_2(\text{Cu}^{2+})(\text{S}^{2-})(\text{S}_2)^{2-}$ for CuS , X - ray photo electron spectroscopic data give strong evidence that, in terms of the simple oxidation state formalism, *all* the known copper sulfides should be considered as purely monovalent copper compounds, and more appropriate formulae would be $(\text{Cu}^+)_3(\text{S}^{2-})(\text{S}_2)^-$ for CuS , and $(\text{Cu}^+)(\text{S}_2)^-$ for Cu S_2 , respectively . Further evidence that the assignment of the so-called "valence hole" should be to the S_2 units in these two

formulae is the length of the S - S bonds, which are significantly shorter in CuS (0.207 nm) and CuS₂ (0.203 nm) than in the "classical" disulfide Fe²⁺(S₂)²⁻ (0.218 nm). This bond length difference has been ascribed to the higher bond order in (S - S)⁻ compared to (S - S)²⁻ due to electrons being removed from a π* antibonding orbital . NMR studies on CuS show that there are two distinct species of copper atom, one with a more metallic nature than the other . and this apparent discrepancy with the X - ray photo - electron spectrum data simply highlights the problem of assigning oxidation states in a mixed - valence compound.

Copper (I) sulfide

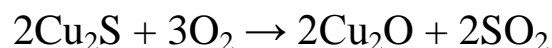
1 – Introduction :

Copper (I) sulfide is a copper sulfide, a chemical compound of copper and sulfur. It has the chemical compound Cu_2S . It is found in nature as the mineral chalcocite. It has a narrow range of stoichiometry ranging from $\text{Cu}_{1.997}\text{S}$ to $\text{Cu}_{2.000}\text{S}$.

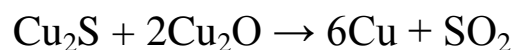
Other Names	Cuprous sulfide Chalcocite Copper glance
Molecular Formula	Cu_2S
Molar Mass	159 g / mol
Density	5.6 g /cm ³
Melting Point	1130 °C
Solubility in Water	Insoluble
Solubility	Slightly soluble in HCl Soluble in NH_4OH Dissolves in KCN Decomposes in HNO_3 , H_2SO_4

2 - Preparation and Reactions

Cu_2S can be prepared by heating copper strongly in sulfur vapour or H_2S . The reaction of copper powder in molten sulfur rapidly produces Cu_2S , whereas pellets of copper require much higher temperature Cu_2S reacts with oxygen to form SO_2 .^[5]



In the production of copper two thirds of the molten copper sulfide is oxidised as above, and the Cu_2O reacts with unoxidised Cu_2S to give Cu metal :



3 - Structure

There are two forms of Cu_2S a low temperature monoclinic form ("low-chalcocite") which has a complex structure with 96 copper atoms in the unit cell^[6] and a hexagonal form stable above 104°C . In this structure there are 24 crystallographically distinct Cu atoms and the structure has been described as approximating to a hexagonal close packed array of sulfur atoms with Cu atoms in planar 3 coordination. This structure was initially assigned an orthorhombic cell due to the twinning of the sample crystal.

There is also a crystallographically-distinct phase (the mineral djurleite) with stoichiometry $\text{Cu}_{1.96}\text{S}$ which is non-stoichiometric (range $\text{Cu}_{1.934}\text{S}$ - $\text{Cu}_{1.965}\text{S}$) and has a monoclinic structure with 248 copper and 128 sulfur atoms in the unit cell^[6]. Cu_2S and $\text{Cu}_{1.96}\text{S}$ are similar in appearance and hard to distinguish one from another.

Copper mono sulfide

1 – Introduction :

Copper monosulfide is a chemical compound of copper and sulfur. It occurs in nature as the dark indigo blue mineral covellite. It is a moderate conductor of electricity. ^[3] A black colloidal precipitate of CuS is formed when hydrogen sulfide, H₂S, is bubbled through solutions of Cu (II) salts . It is one of a number of binary compounds of copper and sulfur (see copper sulfide for an overview of this subject), and has attracted interest because of its potential uses in catalysis and photovoltaics.

Other names	covellite Copper (II) sulfide
Molecular Formula	Cu S
Molar Mass	95.5 g / mol
Density	4.6 g / cm ³
Melting Point	above 500°C (decomposes)
Solubility in Water	insoluble
Solubility	Soluble in HNO ₃ , NH ₄ OH , KCN , HCl , H ₂ SO ₄
Refractive index (nD)	1.45

2 - CuS structure and bonding

Copper mono sulfide crystallizes in the hexagonal crystal system, and this is the form of the mineral covellite. There is also an amorphous high pressure form which on the basis of the Raman spectrum has been described as having a distorted covellite structure. An amorphous room temperature semiconducting form produced by the reaction of a Cu (II) ethylenediamine complex with thiourea has been reported, which transforms to the crystalline covellite form at 30 °C. ^[8]

The crystal structure of covellite has been reported several times , and whilst these studies are in general agreement on assigning the space group $P6_3/mmc$ there are small discrepancies in bond lengths and angles between them. The structure was described as "extraordinary" by Wells and is quite different from copper (II) oxide, but similar to Cu Se (klockmannite) . The covellite unit cell contains 6 formula units (12 atoms) in which :

- 4 Cu atoms have tetrahedral coordination
- 2 Cu atoms have trigonal planar coordination
- 2 pairs of S atoms are only 207.1 pm apart indicating the existence of an S-S bond (a disulfide unit).
 - the 2 remaining S atoms form trigonal planar triangles around the copper atoms, and are surrounded by five Cu atoms in a pentagonal bipyramid .
 - The S atoms at each end of a disulfide unit are tetrahedrally coordinated to 3 tetrahedrally coordinated Cu atoms and the other S atom in the disulfide unit .

The formulation of copper monosulfide as $Cu^{II}S$ (i.e. containing no sulfur - sulfur bond) is clearly incompatible with the crystal structure, and also at variance with the observed diamagnetism ^[13] as a Cu (II) compound would have a d^9 configuration and be expected to be paramagnetic .

Studies using XPS indicate that **all** of the copper atoms have an oxidation state of +1. This contradicts a formulation based on the crystal structure and obeying the octet rule that is found in many textbooks (e.g.) describing CuS as containing both Cu^I and Cu^{II} i.e. $(Cu^+)_2Cu^{2+}(S_2)^{2-}S^{2-}$. An alternative formulation as $(Cu^+)_3(S^{2-})(S_2)^-$ was proposed and supported by calculations . The formulation should not be interpreted as containing radical anion, but rather that there is a delocalized valence "hole". Electron paramagnetic resonance studies on the precipitation of Cu (II) salts indicates that the reduction of Cu (II) to Cu (I) occurs in solution.

Benedict's reagent

1 – Introduction :

Benedict's reagent (also called **Benedict's solution** or **Benedict's test**) is a chemical **reagent** named after an American chemist, **Stanley Rossiter Benedict**.

Benedict's reagent is used as a test for the presence of **reducing sugars**. This includes all **mono saccharides** and the **di saccharides**, **lactose** and **maltose**. Even more generally, Benedict's test will detect the presence of **aldehydes** (except aromatic ones), and **alpha-hydroxy-ketones**, including those that occur in certain ketoses. Thus, although the ketose **fructose** is not strictly a reducing sugar, it is an alpha-hydroxy-ketone, and gives a positive test because it is converted to the aldoses **glucose** and **mannose** by the base in the reagent.^[2]

One litre of Benedict's reagent can be prepared from 100 g of anhydrous **sodium carbonate**, 173 g of **sodium citrate** and 17.3 g of **copper (II) sulfate pentahydrate** . It is often used in place of **Fehling's solution** .

Benedict's reagent contains blue copper (II) ions (Cu^{2+}) which are reduced to copper (I) ions (Cu^+). These are **precipitated** as red **copper (I) oxide** which is insoluble in water.

2 - Chemical test :

To test for the presence of **mono saccharides** and reducing di saccharide sugars in food, the food sample is dissolved in water, and a small amount of Benedict's reagent is added. During a **water bath**, which is usually 4 – moiety, after **isomerization**.

Sucrose (table **sugar**) contains two sugars (fructose and glucose) joined by their **glycosidic bond** in such a way as to prevent the glucose **isomerizing** to aldehyde , or the fructose to alpha – hydroxy - ketone form . Sucrose is thus a non - reducing sugar which does not react with Benedict's reagent. Sucrose indirectly produces a positive result with Benedict's reagent if heated with dilute

hydrochloric acid prior to the test, although after this treatment it is no longer sucrose. The acidic conditions and heat break the **glycosidic bond** in sucrose through **hydrolysis**. The products of sucrose decomposition are glucose and fructose, both of which can be detected by Benedict's reagent, as described above.

Starches do not react or react very poorly with Benedict's reagent, due to the relatively small number of reducing sugar moieties, which occur only at the ends of **carbohydrate** chains. **Inositol** (myo – inositol) is another carbohydrate which produces a negative test.

Benedict's reagent can be used to test for the presence of **glucose** in **urine**. Glucose found to be present in urine is an indication of **diabetes mellitus**. Once a reducing sugar is detected in urine, further tests have to be undergone in order to ascertain which sugar is present. Only glucose is indicative of diabetes.

Experiment	Observation	Inference
Substance in water + 3 ml Benedict's solution, then boil for few minutes and allow to cool.	Red ppt or green ppt or yellow ppt obtained	Reducing sugar e.g. Glucose is present
Substance in water + 3ml Benedict's solution, then boil for few minutes and allow to cool.	Solution remains clear	Reducing sugar is not present

3 - Quantitative reagent

Benedict's quantitative reagent is used to determine how much reducing sugar is present. This solution forms as white precipitate rather than a red one and so can be used in a **titration**. The titration should be repeated with 1 % glucose solution instead of the sample for **calibration**

Egyptian blue

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- 2 Definition
- 3 History and background
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- 7 Connections with other vitreous material and with metals
- 8 Occurrences outside of Egypt

1 – Introduction :

7 Occurrences outside of Egypt **Egyptian blue** is chemically known as **calcium copper silicate** ($\text{CaCuSi}_4\text{O}_{10}$ or $\text{CaO}\cdot\text{CuO}\cdot 4\text{SiO}_2$) It is a pigment used by Egyptians for thousands of years. It is considered to be the first synthetic pigment. The pigment was known to the Romans by the name **caeruleum** . Vitruvius describes in his work *de architectura* how it was produced by grinding sand, copper and natron and heating the mixture, shaped into small balls, in a furnace. Lime is necessary for the production as well, but probably lime - rich sand was used. After the Roman era Egyptian Blue was not used anymore.

The ancient Egyptian word *wedjet* signifies blue, and the same word is used for the human eye, as in the *Eye of Ra*.

2 - Definition

Egyptian blue is a synthetic blue pigment made up of a mixture of silica, lime, copper, and alkali. It is a calcium - copper tetra silicate $\text{CaCuSi}_4\text{O}_{10}$, and is of the exact same composition as the naturally occurring mineral cuprorivaite. It occurs in Egypt during the 3rd millennium BC and is the first synthetic pigment to have been produced there, continuing in use until the end of the Greco - Roman period (332 BC – 395 AD) . The term for it in the Egyptian language is *hsbd*, meaning both Egyptian blue and semi - precious lapis lazuli

along with its imitations. It was used in antiquity¹ as a blue pigment to color a variety of different mediums such as stone, wood, plaster, papyrus, and canvas², and in the production of numerous types of objects, including cylinder seals, beads, scarabs, inlays, pots and statuettes. It is also sometimes referred to in Egyptological literature as blue frit. Some have argued that this is an erroneous term that should be reserved for use to describe the initial phase of glass or glaze production while others argue that Egyptian blue is a frit in both the fine and coarse form since it is a product of solid state reaction. Its characteristic blue color, resulting from one of its main components - copper - ranges from a light to a dark hue, depending on differential processing and composition. Apart from Egypt, it has also been found in the Near East, the Eastern Mediterranean and at the limits of the Roman Empire. Although undoubtedly an Egyptian invention, it is unclear as to whether its existence elsewhere was a result of parallel inventions or whether its technology had spread to these areas.

3 - History and background

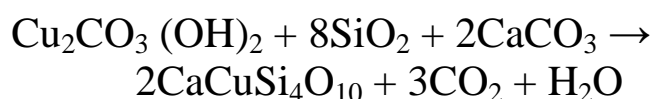
The ancient Egyptians held the color blue in very high regard and were eager to present it on many media and in a variety of forms. They also desired to imitate the semi - precious stones turquoise and lapis lazuli, which were valued for their rarity and stark blue color. Use of naturally occurring minerals, such as azurite, to acquire this blue, was impractical as these minerals were rare and difficult to work. Therefore to appropriate the large quantities of blue color that the Egyptians sought, it was necessary for them to manufacture the pigment themselves.

The Egyptians developed a wide range of pigment variety including what is now known as Egyptian blue, which was the first of its color at the time of its development. This accomplishment was due to the advancement of Egypt as a settled agricultural society. This stable and established civilization encouraged the growth of a non - labor workforce, including clerics and the Egyptian theocracy. Egyptian pharaohs were patrons of the arts and consequently were devoted to the advancement of pigment technology.

The earliest evidence for the use of Egyptian blue is in the 4th Dynasty, limestone sculptures from that period in addition to being shaped into a variety of cylinder seals and beads. In the Middle Kingdom it continued to be used as a pigment in the decoration of tombs, wall paintings, furnishings and statues and by the New Kingdom began to be more widely utilized in the production of numerous objects. Its use continued throughout the Late period, and Greco - Roman period , only dying out in the 4th century AD, when the secret to its manufacture was lost . There is no written information in ancient Egyptian texts about the manufacture of Egyptian blue in antiquity and was only first mentioned in Roman literature by Vitruvius during the first century BC. He refers to it as coeruleum and erroneously states that it was invented in Alexandria, and was made by mixing sand, copper filings, and natron, failing to mention lime — a major component of Egyptian blue. Theophrastus gives it the Greek term cyanos, which probably originally referred to lapis lazuli. Finally, it was only at the beginning of the 19th c. that there was a renewed interest in learning more about its manufacture when it was investigated by Sir Humphry Davy in 1815 and others such as W. T. Russell and Foque.

4 - Composition and manufacture :

Several experiments have been carried out by scientists and archaeologists interested in analyzing the composition of Egyptian blue and the techniques used to manufacture it . It is now generally regarded as a multi - phase material that was produced by heating together quartz sand, a copper compound, calcium carbonate, and a small amount of an alkali (plant ash or natron) at temperatures ranging between 800 – 1000 °C (depending on the amount of alkali used) for several hours . The result is cuprorivaite or Egyptian blue, carbon dioxide and water vapour :



In its final state, Egyptian blue consists of rectangular blue crystals together with unreacted quartz and some glass. From the

analysis of a number of samples from Egypt and elsewhere , it was determined that the weight percentage of the materials used to obtain Egyptian blue in antiquity usually ranged within the following amounts :

- 60 – 70 % silica (SiO_2)
- 7 – 15 % calcium oxide (CaO)
- 10 – 20 % copper oxide (CuO)

To obtain the theoretical cuprorivaite, where there are only blue crystals, with no excess of unreacted quartz or formation of glass, the following percentages would need to be used :

- 64 % silica
- 15 % calcium oxide
- 21 % copper oxide

How ever none of the analyzed samples from antiquity were made of this definitive composition as all had excesses of silica, together with an excess of either CuO or CaO . It is unclear as to whether the past craftsman, working on Egyptian blue, was aware of these excesses in the final product and had intentionally utilized specified percentages to achieve them as such, or whether it had been beyond their control. In contrast though, it has been suggested that the variation in the amount of alkali added to the Egyptian blue mixture was undoubtedly an intentional act on the part of the past craftsman since a variation in the alkali levels has been shown to directly influence specific characteristics related to the texture and hardness of the Egyptian blue product. This is because an increase in the alkali content results in Egyptian blue containing more unreacted quartz embedded in a glass matrix, which in turn results in a harder texture (Tite, Bimson & Cowell 1987). Lowering the alkali content (less than 1 %), on the other hand, does not allow glass to form and the resultant Egyptian blue is softer, with a hardness at the lower end of Mohs' scale, 1 – 2 Mohs (Tite, Bimson & Cowell 1984). Desiring a variation in the hardness and softness of Egyptian blue could be associated with the use of the product for a variety of purposes in which different textures were required.

In addition to the way the level of the different compositions influenced texture, the way Egyptian blue was processed also had an effect on its texture, in terms of coarseness and fineness. Following a number of experiments, it was concluded that for fine-textured Egyptian blue, two stages were necessary in order to obtain uniformly interspersed crystals. First the ingredients are heated, and the result is a coarse-textured product. This is then ground up to a fine powder and water is added. The paste is then reshaped and fired again at temperatures ranging between 850 – 950 °C for one hour. It is possible that these two stages were needed to produce a paste that was fine enough for the production of small objects. Coarse-textured Egyptian blue, on the other hand, would not have gone through the second stage. Since it is usually found in the form of slabs (in the dynastic periods) and balls (in the Greco-Roman period) it is suggested that these could have either been awaiting to be processed through a second stage, where they would be ground and finely-textured, or they would have been ground for use as a blue pigment.

The shade of blue reached was also related to the coarseness and fineness of Egyptian blue as it was determined by the degree of aggregation of the Egyptian blue crystals. Coarse Egyptian blue, was relatively thick in form, due to the large clusters of crystals which adhere to the unreacted quartz. This clustering results in a dark blue color that is the appearance of coarse Egyptian blue. Alternatively, fine-textured Egyptian blue consists of smaller clusters that are uniformly interspersed between the unreacted quartz grains and tends to be light blue in color. Diluted light blue on the other hand is used to describe the color of fine-textured Egyptian blue that has a large amount of glass formed in its composition, which masks the blue color, and gives it a diluted appearance. It depends on the level of alkali added to the mixture and therefore the more the alkali, and thus more glass formed, the more the diluted appearance. This type of Egyptian blue is especially evident during the 18th dynasty and later and is probably associated with the surge in glass technology at this time.

If certain conditions were not met, the Egyptian blue would not be satisfactorily produced. For example, if the temperatures were

above 1050 °C, it would become unstable (Jakcsh, Seipel, Weiner, El Goresy 1983). If too much lime was added, wollastonite (CaSiO_3) forms and gives the pigment a green color. Too much of the copper ingredients results in excesses of copper oxides like cuprite and tenorite (Jakcsh, Seipel, Weiner, El Goresy 1983).

5 - Sources

The main component of Egyptian blue was the silica and it has been suggested that quartz sand found adjacent to the sites where Egyptian blue was being manufactured, was the source for this , although there is no concrete evidence to support this hypothesis. The only evidence cited is by Jakcsh...et al. (1983) who found crystals of titanomagnetite in samples collected from the tomb of Sabni (6th dynasty), which is a mineral found in desert sand. Its presence in Egyptian blue indicates that quartz sand, rather than flint or chert were used as the silica source. It would be interesting to compare this evidence with the evidence for the source of silica used for glass making at Qantir (New Kingdom Ramesside site), which is quartz pebbles and not sand .

It is believed that calcium oxide was not added on its own in the manufacture of Egyptian blue, but introduced as an impurity in the quartz sand and alkali . It is not clear from this then as to whether the craftsmen involved in the manufacture realized the importance of adding lime to the Egyptian blue mixture?

The source of copper could have either been a copper ore (such as malachite), filings from copper ingots or bronze scrap and other alloys. Prior to the New Kingdom there is scarce evidence as to which copper source was being used, but it is believed to have been copper ores. During the New Kingdom, there is evidence for the use of copper alloys, such as bronze, due to the presence of varying amounts of tin, arsenic, or lead found in the Egyptian blue material . Some have argued that the presence of tin oxide could have come from copper ores that itself contained tin oxide and not from the use of bronze. However, no copper ores have been found with these amounts of tin oxide . It is unclear as yet, why there would have been a switch

from the use of copper ores in earlier periods, to the use of bronze scrap during the Late Bronze Age. It is possible that reserves had run out.

The total alkali content in analyzed samples of Egyptian blue is greater than 1 %, suggesting that the alkali was introduced deliberately into the mixture and not as an impurity from other components . Sources of alkali could either have been natron from areas such as Wadi Natroun and El – Kab , or plant ash. By measuring the amounts of potash and magnesia in the samples of Egyptian blue, it is generally possible to identify which source of alkali had been used, since the plantash contains higher amounts of potash and magnesia than the natron. However, due to the low concentration of alkali in Egyptian blue, which is a mere 4% or less, compared to glass, for example, which is at 10 – 20 %, identifying the source is not always easy. It has been suggested, nonetheless, that the alkali source was natron . although the reasons for this assumption are unclear. On the other hand, analysis by Jaksch...et al. (1983) of various samples of Egyptian blue identified variable amounts of phosphorus (up to 2 wt %), suggesting that the alkali source used was in actuality plantash and not natron. Since the glass industry during the Late Bronze Age used plantash as its source of alkali , there might have possibly been a link in terms of the alkali used for Egyptian blue before and after the introduction of the glass industry.

6 - Archaeological evidence

Amarna: In the excavations at Amarna, Lisht and Malkata at the beginning of the 20thc, Petrie uncovered two types of vessels that he suggested were used in antiquity to make Egyptian blue: bowl - shaped pans and cylindrical vessels / saggars. In recent excavations at Amarna by Barry Kemp (1989), very small numbers of these “fritting” pans were uncovered, although various remaining pieces of Egyptian blue ‘cake’ were found, which allowed the identification of five different categories of Egyptian blue forms and the vessels associated with them: large round flat cakes, large flat rectangular cakes, bowl-shaped cakes, small sack-shaped pieces and spherical shapes. No tin was found present in the samples analyzed, which the

authors suggest (Weatherhead & Buckley 1989) is an indication that there was possible use of scrap copper instead of bronze.

Qantir : In the 1930s Mahmud Hamza excavated a number of objects related to the production of Egyptian blue at Qantir, such as Egyptian blue cakes and fragments in various stages of production providing evidence that Egyptian blue was actually produced at the site of Qantir. Recent excavations at the same site, uncovered a large copper - based industry, with several associated crafts, namely bronze-casting, red - glass making, faience production and Egyptian blue . Ceramic crucibles with adhering remains of Egyptian blue were found in the excavations, suggesting again that it had been manufactured on site. It is also possible that these Egyptian blue ‘cakes’ were later exported to other areas around the country to be worked as there was a scarcity of finished Egyptian blue products on site. For example, Egyptian blue cakes were found at Zawiyet Umm el-Rakham, a Ramesside fort near the Libyan coast, indicating that cakes were in fact traded, and worked at and reshaped away from their primary production site (Rehren, Pusch & Herold 2001).

7 - Connections with other vitreous material and with metals :

Egyptian blue is closely related to the other vitreous materials produced by the ancient Egyptians, namely glass and faience, and it is possible that the Egyptians themselves did not employ separate terms to distinguish the three products from one another (Chase 1971). Although it is easier to distinguish between faience and Egyptian blue, due to the distinct core of faience objects and their separate glaze layers, it is sometimes difficult to differentiate glass from Egyptian blue due to the very fine texture that Egyptian blue could occasionally have. This is especially true during the New Kingdom as Egyptian blue became more refined and glassy and continued as such into the Greco-Roman period (Nicholson & Peltenburg 2000). Since Egyptian blue, like faience, is a much older technology than glass, which only begins during the reign of Thutmose III (1479–1425 BC), there are no doubt changes in the manufacture of Egyptian blue that were associated with the introduction of the glass industry.

Analysis of the source of copper used in the manufacture of Egyptian blue indicates a relationship with the contemporaneous metal industry. Whereas in the earlier periods, it is most probable that copper ores were used, during the reign of Tutmosis III, the copper ore is replaced by the use of bronze filings . This has been established by the detection of a specific amount of tin oxide in Egyptian blue which could only have resulted from the use of tin bronze scraps as the source of copper, which coincides with the time that bronze became widely available in ancient Egypt.

8 - Occurrences outside of Egypt

Egyptian blue was found in Western Asia during the middle of 3rd millennium BC in the form of small artifacts and inlays, but not as a pigment . It was found in the Mediterranean area at the end of the Middle Bronze age, and traces of tin were found in its composition suggesting the use of bronze scrap instead of copper ore as the source of copper . During the Roman period there was extensive use of Egyptian blue, as a pot containing the unused pigment, found in 1814 in Pompeii, illustrates. It was also found as unused pigment in the tombs of a number of painters. Etruscans also used it in their wall paintings. The related Chinese Blue is generally believed to have Egyptian roots.

Fehling's solution

1 - Introduction :

Fehling's solution is a solution used to differentiate between water soluble aldehyde and ketone functional groups, although ketose mono saccharides (such as fructose) will also test positive, due to conversion to aldoses by the base in the reagent . For this reason, Fehling's reagent is some times referred to as a general test for mono saccharides.

Fehling's is used to test for aldoses and ketoses, although formic acid (methanoic acid) also gives a positive Fehling's test result, as it does with Tollens' test, Benedict's test, and many more aldehyde tests.

To carry out the test the substance to be tested is heated together with Fehling's solution; a red precipitate indicates the presence of an aldehyde. Ketones (except alpha-hydroxy-ketones) do not react. An example for its use is to screen for glucose in urine, thus detecting diabetes. It was developed by German chemist Hermann von Fehling in 1849. ^[2]

Fehling's solution is always made just prior to the test. It is comprised of equal parts of the following solutions:

- 69.28 grams copper (II) sulfate penta hydrate dissolved in 1 litre of distilled water (Fehling's solution A)
- 346 grams Rochelle salt (potassium sodium tartrate tetrahydrate) and 120 grams sodium hydroxide in 1 litre of distilled water (Fehling's Solution B)

2 - Fehling test

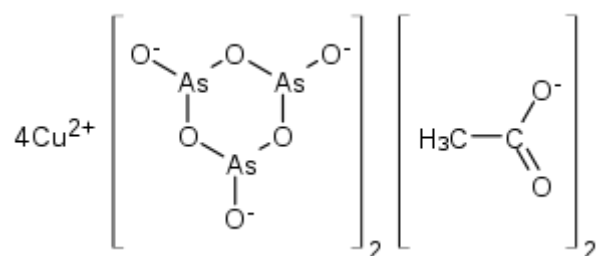
An aldehyde is first added to the Fehling solution and the mixture is heated. Aldehyde oxidizes to acid and red precipitates of cuprous oxide are formed. The cupric ion is complexed with the tartrate ion. Contact with an aldehyde group reduces it to a cuprous ion, which then precipitates as red Cu_2O (copper (I) oxide) . Ketones (except alpha hydroxy ketones such as are present in ketoses and

other metabolites) and aromatic aldehydes do not respond to the Fehling test.

Fehling's solution in the present day is often replaced by Benedict's solution.

Note: Fehling's solution can only be used to test for aliphatic aldehydes, whereas tollen's reagent can be used to test for both aliphatic and aromatic aldehydes .

Paris Green



1 – Introduction :

Paris Green is an inorganic compound more precisely known as copper (II) aceto arsenite . It is a highly toxic emerald - green crystalline powder that has been used as a **rodenticide** and **insecticide** , and also as a pigment, despite its toxicity. It is also used as a blue colorant for fireworks . The color of Paris Green is said to range from a pale, but vivid , blue green when very finely ground, to a deeper true green when coarsely ground.

2 – Preparation :

Paris Green may be prepared by combining copper (II) acetate and arsenic trioxide.

3 - Uses

3 - 1 - Insecticide

Paris Green was once used to kill rats in **Parisian** sewers, hence the common name. It was also used in America and elsewhere as an **insecticide** for produce, such as **apples**, around 1900, where it was blended with **lead arsenate**. This quite toxic mixture is said to have burned the trees and the grass around the trees. Paris green was heavily sprayed by airplane in Italy, Sardinia, and Corsica during 1944 and in Italy in 1945 to control malaria.

3 - 2 – Pigment :

Paris Green was once a popular pigment used in artists' paints.



Paris Green pigment



Paris Green pigment

3 - 3 – Related pigments :

Similar natural compounds are the minerals :

Chalcophyllite $\text{Cu}_{18}\text{Al}_2(\text{AsO}_4)_3(\text{SO}_4)_3(\text{OH})_{27} \cdot 36(\text{H}_2\text{O})$

, **Conichalcite** $a\text{Cu}(\text{AsO}_4)(\text{OH})$,

Cornubite $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4 \cdot (\text{H}_2\text{O})$,

Cornwallite $\text{Cu}_5(\text{AsO}_4)_2(\text{OH})_4 \cdot (\text{H}_2\text{O})$, and

Liroconite $\text{Cu}_2\text{Al}(\text{AsO}_4)(\text{OH})_4 \cdot 4(\text{H}_2\text{O})$.

These vivid minerals range from greenish blue to slightly yellowish green.

Scheele's green is a chemically simpler, less brilliant, and less permanent, synthetic copper - arsenic pigment used for a rather short time before Paris Green was first prepared, which was approximately 1814. It was popular as a **wall paper** pigment, and would degrade, with moisture and moulds, to **arsine** gas. Paris Green may have also been used in wallpaper to some extent and may have also degraded similarly. Both pigments were once used in **printing ink** formulations.

The [ancient Romans](#) used one of them, possibly conichalcite, as a green pigment. The Paris Green paint used by the [Impressionists](#) is said to have been composed of relatively coarse particles. Later, the chemical was produced with increasingly small grinds and without carefully removing impurities; its permanence suffered. It is likely that it was ground more finely for use in watercolors and inks, too.

Schweizer's reagent

1 – Introduction :

Schweizer's reagent is the common name for the complex tetra ammine diaqua copper dihydroxide , $[\text{Cu} (\text{NH}_3)_4 (\text{H}_2\text{O})_2] (\text{OH})_2$. It is prepared by precipitating copper (II) hydroxide from an aqueous solution of copper sulfate using sodium hydroxide, then dissolving the precipitate in a solution of ammonium hydroxide. It forms a deep azure solution. If the solution is evaporated, it leaves blue, needle-like crystals.

Schweizer's reagent finds use in production of cellulose products such as rayon and cellophane, because wood - pulp, cotton fiber, and other natural cellulose sources are soluble in the solution. Dissolved cellulose precipitates when the solution is acidified.