Zinc

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1 - Introduction :

Zinc (pronounced / zɪŋk /, from German: *Zink* and also known as **spelter**) is a metallic chemical element with the symbol **Zn** and atomic number 30. It is a first-row transition metal in group 12 of the periodic table. Zinc is chemically similar to magnesium because its ion is of similar size and its only common oxidation state is +2. Zinc is the 24th most abundant element in the Earth's crust and has five stable isotopes. The most exploited zinc ore is sphalerite, or zinc sulfide; the largest exploitable deposits are found in Australia, Canada and the United States. Zinc production includes froth flotation of the ore , roasting and final extraction by electricity.

Brass, which is an alloy of copper and zinc , has been used since at least the 10th century BC. Impure zinc metal was not produced in large scale until the 13 th century in India, while the metal was unknown to Europe until the end of the 16th century. Alchemists burned zinc in air to form what they called "philosopher's wool" or "white snow." The element was probably named by the alchemist Paracelsus after the German word *Zinke*. German chemist Andreas Sigismund Marggraf is normally given credit for discovering pure metallic zinc in a 1746 experiment. Work by Luigi Galvani and Alessandro Volta uncovered the electrochemical properties of zinc by 1800. Corrosion-resistant zinc plating of steel is the major application for zinc. Other applications are in batteries and alloys, such as brass. A variety of zinc compounds are commonly used, such as zinc chloride (in deodorants), zinc pyrithione (anti-dandruff shampoos), zinc sulfide (in luminescent paints), and zinc methyl or zinc diethyl in the organic laboratory.

Zinc is an essential mineral of "exceptional biologic and public health importance". Zinc deficiency affects about 2 billion people in the developing world and is associated with many diseases . In children it causes growth retardation, delayed sexual maturation, infection susceptibility, and diarrhea, contributing to the death of about 800,000 children worldwide per year. Enzymes with a zinc atom in the reactive center are widespread in biochemistry, such as alcohol dehydrogenase in humans. Consumption of excess zinc can cause ataxia, lethargy and copper deficiency.

Name, symbol, number	Zinc , Zn , 30
Element Category	Transition metal

Group , period , block	12 , 4 , d
Atomic Weigt	65.5
Density	7.14 g ·cm^{3}
Liquid density at m.p.	6.57 g · cm^{3}
Melting Point	787.15 °C
Boiling Point	1665 ° C
Heat of Fusion	7.32 kJ · mol^{-1}
Heat of Vaporization	123.6 kJ · mol^{-1}
Specific heat capacity (25 ° C)	25.470 J·mol^{-1}·K^{-1}
Oxidation states	+ 2 , + 1 , 0 (amphoteric oxide)
Electro negativity	1.65 (Pauling scale)
Ionization energies	1st : 906.4 kJ·mol^{-1} 2nd : 1733.3 kJ·mol^{-1} 3rd : 3833 kJ·mol^{-1}
Covalent Radius	122 ± 4 pm
Van der Waals radius	139 pm
Crystal Structure	Hexagonal
Magnetic Ordering	Diamagnetic
Electrical Resistivity	(20 °C) 59.0 nΩ·m
Thermal Conductivity	(300 K) 116 W·m^{-1}·K^{-1}
Thermal Expansion	(25 °C) 30.2 µm·m^{-1}·K^{-1}
Speed of Sound	3850 m·s^{-1}
Poisson Ratio	0.25
Mohs Hardness	2.5

2 . Characteristics

2 . 1 . Physical

Zinc, also referred to in nonscientific contexts as *spelter*, is a bluish - white, lustrous, diamagnetic metal, though most common commercial grades of the metal have a dull finish. It is some what less dense than iron and has a hexagonal crystal structure.

The metal is hard and brittle at most temperatures but becomes malleable between 100 and 150 °C . Above 210 °C, the metal becomes brittle again and can be pulverized by beating. Zinc is a fair conductor of electricity. For a metal, zinc has relatively low melting (420 °C) and boiling points (900 °C) . Its melting point is the lowest of all the transition metals aside from mercury and cadmium.

Many alloys contain zinc, including brass, an alloy of zinc and copper. Other metals long known to form binary alloys with zinc are aluminium, antimony, bismuth, gold, iron, lead, mercury, silver, tin, magnesium, cobalt, nickel, tellurium and sodium. While neither zinc nor zirconium are ferro magnetic, their alloy $Zr\ Zn_2$ exhibits ferro magnetism below 35 K.

2 . 2 . Occurrence

Zinc makes up about 75 ppm (0.007 %) of the Earth's crust, making it the 24 th most abundant element there. Soil contains 5 – 770 ppm of zinc with an average of 64 ppm. Sea water has only 30 ppb zinc and the atmosphere contains 0.1 – 4 $\mu g / m^3$.

The element is normally found in association with other base metals such as copper and lead in ores. Zinc is a chalcophile (" sulfur loving ") , meaning the element has a low affinity for oxygen and prefers to bond with sulfur in highly insoluble sulfides. Chalcophiles formed as the crust solidified under the reducing conditions of the early Earth's atmosphere. Sphalerite, which is a form of zinc sulfide, is the most heavily mined zinc-containing ore because its concentrate contains 60–62 % zinc.

Other minerals from which zinc is extracted include smithsonite (zinc carbonate) , hemimorphite (zinc silicate) , wurtzite (another zinc sulfide), and sometimes hydrozincite (basic zinc carbonate) . With the exception of wurtzite, all these other minerals were formed as a result of weathering processes on the primordial zinc sulfides .

World zinc resources total about 1.8 billion metric tons. Nearly 200 million metric tons were economically viable in 2008 ; adding marginally economic and subeconomic reserves to that number, a total reserve base of 500 million metric tons has been identified. Large deposits are in Australia, Canada and the United States. At the current rate of consumption, these reserves are estimated to be depleted sometime between 2027 and 2055 . About 346 teragrams (each teragram is equivalent to a megatonne) have been extracted throughout history to 2002, and one estimate found that about 109 teragrams of that remains in - use .

2 . 3 . Isotopes of zinc

Five isotopes of zinc occur in nature. ^{64}Zn is the most abundant isotope (48.63 % natural abundance). This isotope has such a long half - life, at 4.3×10^{18} y, that its radioactivity can be ignored.[20] Similarly, ^{70}Zn (0.6 %), with a half life of 1.3×10^{16} y is not usually considered to be radioactive. The other isotopes found in nature are ^{66}Zn (28 %) , ^{67}Zn (4 %) and ^{68}Zn (19 %).

Twenty - five radioisotopes have been characterized. ^{65}Zn, which has a half - life of 243.66 days, is the most long-lived isotope, followed by ^{72}Zn with a half-life of 46.5 hours. Zinc has 10 nuclear isomers. ^{69m}Zn has the longest half - life, 13.76 h.[18] The superscript *m* indicates a meta stable isotope. The nucleus of a metastable isotope is in an excited state and will return to the ground state by emitting a photon in the form of a gamma ray. ^{61}Zn has three excitated states and ^{73}Zn has two. The isotopes ^{65}Zn, ^{71}Zn, ^{77}Zn and ^{78}Zn each have only one excited state . The most common decay mode of an isotope of zinc with a mass number lower than 64 is electron capture. The decay product resulting from electron capture is an isotope of copper .

$$n30\ Zn + e^- \rightarrow n29\ Cu$$

The most common decay mode of an isotope of zinc with mass number higher than 64 is beta decay (β^-) , which produces an isotope of gallium .

$$n30\ Zn \rightarrow n31\ Ga + e^- + \nu_e$$

3 . Compounds and chemistry of zinc

3 . 1 . Reactivity

Zinc has an electron configuration of $[Ar]3d^{10}4s^2$ and is a member of the group 12 of the periodic table. It is a moderately reactive metal and strong reducing agent. The surface of the pure metal tarnishes quickly, eventually forming a protective passivating layer of the basic zinc carbonate, $Zn_5 (OH)_6 CO_3$, by reaction with atmospheric carbon dioxide. This layer helps prevent further reaction with air and water.

Zinc burns in air with a bright bluish - green flame, giving off fumes of zinc oxide. Zinc reacts readily with acids, alkalis and other non - metals. Extremely pure zinc reacts only slowly at room temperature with acids. Strong acids, such as hydrochloric or sulphuric acid, can remove the passivating layer and subsequent reaction with water releases hydrogen gas .

The chemistry of zinc is dominated by the +2 oxidation state. When compounds in this oxidation state are formed the outer shell *s* electrons are lost, which yields a bare zinc ion with the electronic configuration $[Ar]3d^{10}$. This allows for the formation of four covalent bonds by accepting four electron pairs and thus obeying the octet rule. The stereochemistry is therefore tetrahedral and the bonds may be described as being formed from sp^3 hybrid orbitals on the zinc ion. In aqueous solution an octa hedral complex, $[Zn (H_2O)_6]^{2+}$ is the predominant species . The volatilization of zinc in combination with zinc chloride at temperatures above 285 °C indicates the formation of $Zn_2 Cl_2$, a zinc compound with a +1 oxidation state. No compounds of zinc in oxidation states other than +1 or +2 are known. Calculations indicate that a zinc compound with the oxidation state of +4 is unlikely to exist.

Zinc chemistry is similar to the chemistry of the late first-row transition metals, nickel and copper though it has a filled d -shell, so its compounds are diamagnetic and mostly colorless. The ionic radii of zinc and magnesium happen to be nearly identical. Because of this some of their salts have the same crystal structure and in circumstances where ionic radius is a determining factor zinc and magnesium chemistries have much in common. Other wise there is little similarity. Zinc tends to form bonds with a greater degree of covalency and it forms much more stable complexes with N - and S - donors. Complexes of zinc are mostly 4 - or 6 - coordinate although 5 -coordinate complexes are known.

3 . 2 . Compounds

1 - Zinc chloride

Binary compounds of zinc are known for most of the metalloids and all the nonmetals except the noble gases. The oxide ZnO is a white powder that is nearly insoluble in neutral aqueous solutions, but is amphoteric, dissolving in both strong basic and acidic solutions. The other chalco genides (Zn S, Zn Se, and Zn Te) have varied applications in electronics and optics. Pnicto genides (Zn_3N_2 , Zn_3P_2 , Zn_3As_2 and Zn_3Sb_2) , the peroxide ($Zn\ O_2$), the hydride (ZnH_2) , and the carbide (ZnC_2) are also known. Of the four halides, ZnF_2 has the most ionic character, whereas the others ($ZnCl_2$, $ZnBr_2$, and ZnI_2) have relatively low melting points and are considered to have more covalent character.

2 - Basic zinc acetate

In weak basic solutions containing Zn^{2+} ions, the hydroxide $Zn\ (OH)_2$ forms as a white precipitate In stronger alkaline solutions, this hydroxide is dissolved to form zincates ($[\ Zn\ (OH)_4\ ]^{2-}$) .The nitrate $Zn\ (NO_3)_2$, chlorate $Zn\ (ClO_3)_2$, sulfate $Zn\ SO_4$, phosphate $Zn_3\ (PO_4)_2$, molybdate $Zn\ MoO_4$, cyanide $Zn(CN)_2$, arsenite $Zn(AsO_2)_2$, arsenate $Zn(AsO_4)_2{\bullet}8H_2O$ and the chromate $Zn\ CrO_4$ (one of the few colored zinc compounds) are a few examples of other common inorganic compounds of zinc . One of the simplest examples of an organic compound of zinc is the acetate ($Zn\ (\ O_2C\ CH_3\ )_2$) .

Organozinc compounds are those that contain zinc-carbon covalent bonds. Diethylzinc ($(\ C_2H_5\ )_2\ Zn$) is a reagent in synthetic chemistry. It was first reported in 1848 from the reaction of zinc and ethyl iodide, and is the first compound known to contain a metal -

carbon sigma bond. Deca methyl dizincocene contains a strong zinc - zinc bond at room temperature .

4 . History

4 . 1 . Ancient use

Various isolated examples of the use of impure zinc in ancient times have been discovered. A possibly prehistoric statuette containing 87.5 % zinc was found in a Dacian archaeological site in Transylvania (modern Romania) . Ornaments made of alloys that contain 80 – 90 % zinc with lead, iron, antimony, and other metals making up the remainder, have been found that are 2500 years old.[11] The Berne zinc tablet is a votive plaque dating to Roman Gaul made of an alloy that is mostly zinc .

Zinc ores were used to make the zinc - copper alloy brass many centuries prior to the discovery of zinc as a separate element. Palestinian brass from the 14 th to 10 th centuries BC contains 23 % zinc. The Book of Genesis, written between the 10th and 5th centuries BC, mentions Tubalcain as an "instructor in every artificer in brass and iron" (Genesis 4 : 22) . Knowledge of how to produce brass spread to Ancient Greece by the 7 th century BC but few varieties were made.

The manufacture of brass was known to the Romans by about 30 BC. They made brass by heating powdered calamine (zinc silicate or carbonate), charcoal and copper together in a crucible. The resulting calamine brass was then either cast or hammered into shape and was used in weaponry. Some coins struck by Romans in the Christian era are made of what is probably calamine brass. In the West, impure zinc was known from antiquity to exist in the remnants in melting ovens, but it was usually discarded, as it was thought to be worthless . References to medicinal uses of zinc are in the Charaka Samhita, which is believed to have been written as early as 300 BC in India. The zinc mines and smelter of Zawar, near Udaipur in India, were active about 100 years before that and produced an estimated million tonnes of metallic zinc and zinc oxide from the 12 th to 16 th centuries. The Rasaratna Samuccaya, written in approximately the year 800, mentions two types of zinc - containing ores ; one used for metal extraction and another used for medicinal purposes.

4 . 2 . Early studies and naming

Zinc was distinctly recognized as a metal under the designation of *Fasada* in the medical Lexicon ascribed to the Hindu king Madanapala and written about the year 1374. Smelting and extraction of impure zinc by reducing calamine with wool and other organic substances was accomplished in the 13th century in India. The Chinese did not learn of the technique until the 17 th century .

Alchemists burned zinc metal in air and collected the resulting zinc oxide on a condenser. Some alchemists called this zinc oxide *lana philosophica,* Latin for "philosopher's wool", because it collected in wooly tufts while others thought it looked like white snow and named it *ninx album*.

The name of the metal was probably first used by Paracelsus, a Swiss - born German alchemist, who referred to the metal as "zincum" or " zinken" in his book *Liber Mineralium II*, in the 16th century. The word is probably derived from the German *Zinke*, and supposedly meant "tooth-like, pointed or jagged" (metallic zinc crystals have a needle-like appearance). A second possibility is that the word is derived from the Persian word سنگ *seng* meaning stone. The metal was also called Indian tin , tutanego , calamine, and spinter.

German metallurgist Andreas Libavius received a quantity of what he called "calay" of Malabar from a cargo ship captured from the Portuguese in 1596. Libavius described the properties of the sample, which may have been zinc. Zinc was regularly imported to Europe from the Orient in the 17th and early 18th centuries, but was at times very expensive.

4 . 3 . Isolation of the pure element

The isolation of metallic zinc in the West may have been achieved independently by several people . Postlewayt's *Universal Dictionary*, a contemporary source giving technological information in Europe , did not mention zinc before 1751 but the element was studied before then .

Flemish metallurgist P.M. de Respour reported that he extracted metallic zinc from zinc oxide in 1668. By the turn of the century, Étienne François Geoffroy described how zinc oxide condenses as yellow crystals on bars of iron placed above zinc ore being smelted. In Britain, John Lane is said to have carried out experiments to smelt zinc, probably at Landore, prior to his bankruptcy in 1726.

In 1738, William Champion patented in Great Britain a process to extract zinc from calamine in a vertical retort style smelter.[61] His technology was somewhat similar to that used at Zawar zinc mines in Rajasthan but there is no evidence that he visited the Orient . Champion's process was used through 1851.

German chemist Andreas Marggraf normally gets credit for discovering pure metallic zinc even though Swedish chemist Anton von Swab distilled zinc from calamine four years before. In his 1746 experiment , Marggraf heated a mixture of calamine and charcoal in a closed vessel without copper to obtain a metal. This procedure became commercially practical by 1752.

4 . 4 . Later work

William Champion's brother, John, patented a process in 1758 for calcining zinc sulfide into an oxide usable in the retort process . Prior to this only calamine could be used to produce zinc. In 1798, Johann Christian Ruberg improved on the smelting process by building the first horizontal retort smelter. Jean-Jacques Daniel Dony built a different kind of horizontal zinc smelter in Belgium, which processed even more zinc .

Italian doctor Luigi Galvani discovered in 1780 that connecting the spinal cord of a freshly dissected frog to an iron rail attached by a brass hook caused the frog's leg to twitch . He incorrectly thought he had discovered an ability of nerves and muscles to create electricity and called the effect " animal electricity " . The galvanic cell and the process of galvanization were both named for Luigi Galvani and these discoveries paved the way for electrical batteries, galvanization and cathodic protection.

Galvani's friend , Alessandro Volta , continued researching this effect and invented the Voltaic pile in 1800. The basic unit of Volta's pile was a simplified galvanic cell, which is made of a plate of copper and a plate of zinc connected to each other externally and separated by an electrolyte. These were stacked in series to make the Voltaic cell, which in turn produced electricity by directing electrons from the zinc to the copper and allowing the zinc to corrode.

The non - magnetic character of zinc and its lack of color in solution delayed discovery of its importance to biochemistry and nutrition. This changed in 1940 when carbonic anhydrase, an enzyme that scrubs carbon dioxide from blood, was shown to have zinc in its active site. The digestive enzyme carboxypeptidase became the second known zinc - containing enzyme in 1955.

5 . Production

5 . 1 . Mining and processing

Zinc is the fourth most common metal in use, trailing only iron, aluminium, and copper with an annual production of about 10 million tonnes. The world's largest zinc producer is Nyrstar, a merger of the Australian OZ Minerals and the Belgian Umicore. About 70 % of the world's zinc originates from mining, while the remaining 30 % comes from recycling secondary zinc. Commercially pure zinc is known as Special High Grade, often abbreviated *SHG* , and is 99.995 % pure.

World wide, 95 % of the zinc is mined from sulfidic ore deposits, in which sphalerite ZnS is nearly always mixed with the sulfides of copper, lead and iron. There are zinc mines throughout the world, with the main mining areas being China, Australia and Peru. China produced over one - fourth of the global zinc output in 2006.

Zinc metal is produced using extractive metallurgy. After grinding the ore, froth flotation, which selectively separates minerals from gangue by taking advantage of differences in their hydrophobicity, is used to get an ore concentrate. A final concentration of zinc of about 50 % is reached by this process with the remainder of the concentrate being sulphur (32 %) , iron (13 %) , and SiO_2 (5 %) .

Roasting converts the zinc sulfide concentrate produced during processing to zinc oxide :

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$$

Top 10 zinc producing countries in 2006		
Rank	Country	tonnes
1	China	2,600,000
2	Australia	1,338,000
3	Peru	1,201,794
4	United States	727,000
5	Canada	710,000
6	Mexico	480,000
7	Ireland	425,700
8	India	420,800
9	Kazakhstan	400,000
10	Sweden	192,400

The sulfur dioxide is used for the production of sulfuric acid , which is necessary for the leaching process . If deposits of zinc carbonate, zinc silicate or zinc spinel, like the Skorpion Deposit in Namibia are used for zinc production the roasting can be omitted . For further processing two basic methods are used : pyrometallurgy or electrowinning. Pyrometallurgy processing reduces zinc oxide with carbon or carbon monoxide at 950 °C (1,740 °F) into the metal, which is distilled as zinc vapor . The zinc vapor is collected in a condenser. The below set of equations demonstrate this process :

$$2\ ZnO + C \rightarrow 2\ Zn + CO_2$$
$$2\ ZnO + 2\ CO \rightarrow 2\ Zn + 2\ CO_2$$

Electro winning processing leaches zinc from the ore concentrate by sulfuric acid :

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$

After this step electrolysis is used to produce zinc metal.

5 . 2 . Environmental impact

The production for sulfidic zinc ores produces large amounts of sulfur dioxide and cadmium vapor. Smelter slag and other residues of process also contain significant amounts of heavy metals. About 1,100,000 tones of metallic zinc and 130,000 tonnes of lead were mined and smelted in the Belgian towns of La Calamine and Plombières between 1806 and 1882 . The dumps of the past mining operations leach significant amounts of zinc and cadmium, and, as a result, the sediments of the Geul River contain significant amounts of heavy metals . About two thousand years ago emissions of zinc from mining and smelting totaled 10,000 tones a year. After increasing 10 - fold from 1850, zinc emissions peaked at 3.4 mega tones per year in the 1980s and declined to 2.7 mega tones in the 1990s, although a 2005 study of the Arctic troposphere found that the concentrations there did not reflect the decline. Anthropogenic and natural emissions occur at a ratio of 20 to 1.

Levels of zinc in rivers flowing through industrial or mining areas can be as high as 20 ppm. Effective sewage treatment greatly reduces this ; treatment along the Rhine, for example, has decreased zinc levels to 50 ppb. Concentrations of zinc as low as 2 ppm adversely affects the amount of oxygen that fish can carry in their blood .

The zinc works at Lutana , is the largest exporter in Tasmania , generating 2.5 % of the state's GDP. It produces over 250000 tons of zinc per year. The Zinc works were historically responsible for high heavy metal levels in the Derwent River

Soils contaminated with zinc through the mining of zinc - containing ores, refining, or where zinc - containing sludge is used as fertilizer, can contain several grams of zinc per kilogram (several %) of dry soil. Levels of zinc in excess of 500 ppm in soil interfere with the ability of plants to absorb other essential metals, such as iron and manganese. Zinc levels of 2000 ppm to 180,000 ppm (18 %) have been recorded in some soil samples .

6 . Applications

6 . 1 . Anti - corrosion and batteries

The metal is most commonly used as an anti-corrosion agent . Galvanization, which is the coating of iron or steel to protect the metals against corrosion, is the most familiar form of using zinc in this way. In 2006 in the United States, 56 % or 773,000 tones of the zinc metal was used for galvanization, while worldwide 47 % was used for this purpose.

Zinc is more reactive than iron or steel and thus will attract almost all local oxidation until it completely corrodes away. A protective surface layer of oxide and carbonate $Zn_5 (OH)_6 CO_3)_2$ forms as the zinc corrodes . This protection lasts even after the zinc layer is scratched but degrades through time as the zinc corrodes away. The zinc is applied electrochemically or as molten zinc by hot - dip galvanizing or spraying. Galvanization is used on chain-link fencing, guard rails, suspension bridges, lightposts, metal roofs, heat exchangers, and car bodies.

The relative reactivity of zinc and its ability to attract oxidation to itself also makes it a good sacrificial anode in cathodic protection. Cathodically protecting (CP) buried pipelines requires a solid piece of zinc to be connected by a conductor to a steel pipe. Zinc acts as the anode (negative terminus) by slowly corroding away as it passes electric current to the steel pipeline. Zinc is also used to cathodically protect metals that are exposed to sea water from corrosion. A zinc disc attached to a ship's iron rudder will slowly corrode while the rudder stays unattacked . Other similar uses include a plug of zinc attached to a propeller or the metal protective guard for the keel of the ship .

With an electrochemical potential of − 0.7618 volts , zinc makes a good material for the negative terminus or anode in batteries. Powdered zinc is used in this way in alkaline batteries and sheets of zinc metal form the cases for and act as anodes in zinc - carbon batteries .

6 . 2 . Alloys

A widely used alloy of zinc is **brass**, in which copper is alloyed with any where from 3 % to 45 % zinc, depending upon the type of brass. Brass is generally more ductile and stronger than copper and has superior corrosion resistance. These properties make it useful in communication equipment, hardware, musical instruments, and water valves.

Other widely used alloys that contain zinc include **nickel silver**, type writer metal , soft and aluminum solder , and commercial bronze . Zinc is also used in contemporary pipe organs as a substitute for the traditional lead /t in alloy in pipes. Alloys of 85 – 88 % zinc, 4 – 10 % copper, and 2 – 8 % aluminium find limited use in certain types of machine bearings. Zinc is the primary metal used in making American one cent coins since 1982 . The zinc core is coated with a thin layer of copper to give the impression of a copper coin. In 1994, 33,200 tones of zinc were used to produce 13.6 billion pennies in the United States.

Alloys of primarily zinc with small amounts of copper, aluminium, and magnesium are useful in die casting as well as spin casting, especially in the automotive, electrical, and hardware industries. These alloys are marketed under the name Zamak. An example of this is zinc aluminium. The low melting point together with the low viscosity of the alloy makes the production of small and intricate shapes possible. The low working temperature leads to rapid cooling of the cast products and therefore fast assembly is possible. Another alloy, marketed under the name Prestal, contains 78 % zinc and 22 % aluminium and is reported to be nearly as strong as steel but as malleable as plastic. This super plasticity of the alloy allows it to be molded using die casts made of ceramics and cement.

Similar alloys with the addition of a small amount of lead can be cold - rolled into sheets. An alloy of 96 % zinc and 4 % aluminium is used to make stamping dies for low production run applications for which ferrous metal dies would be too expensive. In building facades, roofs or other applications in which zinc is used as sheet metal and for methods such as deep drawing, roll forming or bending, zinc alloys with titanium and copper are used. Unalloyed zinc is too brittle for these kinds of manufacturing processes .

Cadmium zinc telluride (CZT) is a semi conductive alloy that can be divided into an array of small sensing devices. These devices are similar to an integrated circuit and can detect the energy of incoming gamma ray photons . When placed behind an absorbing mask, the CZT sensor array can also be used to determine the direction of the rays. Zinc is used as the anode or fuel of the zinc-air battery/fuel cell providing the basis of the theorized zinc economy .

6 . 3 . Other industrial uses

Roughly one quarter of all zinc output, in the United States (2006) , is consumed in the form of zinc compounds; a variety of which are used industrially. Zinc oxide is widely used as a white pigment in paints, and as a catalyst in the manufacture of rubber. It is also used as a heat disperser for the rubber and acts to protect its polymers from ultra violet radiation (the same UV protection is conferred to plastics containing zinc oxide) . The semiconductor properties of zinc oxide make it useful in varistors and photocopying products. The zinc zinc - oxide cycle is a two step thermochemical process based on zinc and zinc oxide for hydrogen production .

Zinc chloride is often added to lumber as a fire retardant and can be used as a wood preservative. It is also used to make other chemicals. Zinc methyl ($Zn(CH_3)_2$) is used in a number of organic syntheses. Zinc sulfide (Zn S) is used in luminescent pigments such as on the hands of clocks , X - ray and television screens, and luminous paints. Crystals of ZnS are used in lasers that operate in the mid – infra red part of the spectrum . Zinc sulphate is a chemical in dyes and pigments. Zinc pyrithione is used in antifouling paints .

Zinc powder is some times used as a propellant in model rockets. When a compressed mixture of 70 % zinc and 30 % sulfur powder is ignited there is a violent chemical reaction . This produces zinc sulfide, together with large amounts of hot gas, heat, and light. Zinc sheet metal is used to make zinc bars.

Zinc has been proposed as a salting material for nuclear weapons (cobalt is another, better - known salting material) . A jacket of isotopically enriched Zn – 64 , irradiated by the intense high - energy neutron flux from an exploding thermonuclear weapon, would transmute into the radioactive isotope Zn - 65 with a half - life of 244 days and produce massive gamma radiation, significantly increasing the radio -activity of the weapon's fallout for several days. Such a weapon is not known to have ever been built, tested, or used. Zn - 65 is also used as a tracer to study how alloys that contain zinc wear out, or the path and the role of zinc in organisms.

Zinc dithiocarbamate complexes are used as agricultural fungicides, these include Zineb, Metiram, Propineb and Ziram. Zinc naphthenate is used as wood preservative .

6 . 4 . Medicinal

Zinc is included in most single tablet over - the - counter daily vitamin and mineral supplements. It is believed to possess antioxidant properties, which protect against premature aging of the skin and muscles of the body, although studies differ as to its effectiveness. Zinc also helps speed up the healing process after an injury. Zinc gluconate glycine and zinc acetate are used in throat lozenges or tablets to reduce the duration and the severity of cold symptoms. Preparations include zinc oxide, zinc acetate and zinc gluconate.

Zinc gluconate is one compound used for the delivery of zinc as a dietary supplement .

Zinc preparations can protect against sun burn in the summer and wind burn in the winter . Applied thinly to a baby's diaper area (perineum) with each diaper change, it can protect against diaper rash .

The Age - Related Eye Disease Study determined that zinc can be part of an effective treatment for age - related macular degeneration. Zinc supplementation is an effective treatment for acrodermatitis enteropathica, a genetic disorder affecting zinc absorption that was previously fatal to babies born with it.

Zinc lactate is used in tooth paste to prevent halitosis . Zinc pyrithione is widely applied in shampoos because of its anti - dandruff function. Zinc ions are effective antimicrobial agents even at low concentrations. Gastroenteritis is strongly attenuated by ingestion of zinc, and this effect could be due to direct antimicrobial action of the zinc ions in the gastrointestinal tract, or to the absorption of the zinc and re-release from immune cells (all granulocytes secrete zinc) , or both .

7 . Biological role

Zinc is an essential trace element, necessary for plants , animals, and micro organisms. Zinc is found in nearly 100 specific enzymes (other sources say 300) , serves as structural ions in transcription factors and is stored and transfered in metallothioneins. It is " typically the second most abundant transition metal in organisms " after iron and it is the only metal which appears in all enzyme classes

The human body has 2 - 4 grams of zinc distributed throughout the body. Most zinc is in the brain, muscle, bones, kidney, and liver, with the highest concentrations in the prostate and parts of the eye. Semen is particularly rich in zinc, which is a key factor in prostate gland function and reproductive organ growth.

In humans zinc plays "ubiquitous biological roles". It interacts with " a wide range of organic ligands " and has a role in the metabolism of RNA and DNA, signal transduction, and gene expression. It also regulates apoptosis and can " modulate brain excitability ". A 2006 study estimated that about 10% of human proteins (2800) potentially bind zinc in addition to hundreds which transport and traffic zinc; a similar *in silico* study in the plant *Arabidopsis thaliana* found 2367 zinc - related proteins .

7 . 1 . Enzymes

Zinc is a good Lewis acid, making it a useful catalytic agent in hydroxylation and other enzymatic reactions. The metal also has a flexible coordination geometry, which allows proteins using it to rapidly shift conformations to perform biological reactions. Two examples of zinc - containing enzymes are carbonic anhydrase and carboxypeptidase, which are vital to the processes of carbon dioxide (CO_2) regulation and digestion of proteins, respectively.

In vertebrate blood, carbonic anhydrase converts CO_2 into bicarbonate and the same enzyme transforms the bicarbonate back into CO_2 for exhalation through the lungs.[136] Without this enzyme, this conversion would occur about one million times slower at the normal blood pH of 7 or would require a pH of 10 or more. The non-related β - carbonic anhydrase is required in plants for leaf formation, the synthesis of indole acetic acid (auxin) and anaerobic respiration (alcoholic fermentation) .

Carboxy peptidase cleaves peptide linkages during digestion of proteins . A coordinate covalent bond is formed between the terminal peptide and a C = O group attached to zinc, which gives the carbon a positive charge. This helps to create a hydrophobic pocket on the enzyme near the zinc, which attracts the non - polar part of the protein being digested.

7 . 2 . Other proteins

Zinc serves a purely structural role in zinc fingers, twists and clusters. Zinc fingers form parts of some transcription factors, which are proteins that recognize DNA base sequences during the replication and transcription of DNA. Each of the nine or ten Zn^{2+} ions in a zinc finger helps maintain the finger's structure by coordinately binding to four amino acids in the transcription factor. The transcription factor wraps around the DNA helix and uses its fingers to accurately bind to the DNA sequence.

In blood plasma, zinc is bound to and transported by albumin (60 % , low – affinity) and transferrin (10 %) . Since transferrin also transports iron, excessive iron reduces zinc absorption, and vice - versa. A similar reaction occurs with copper. The concentration of zinc in blood plasma stays relatively constant regardless of zinc intake. Cells in the salivary gland, prostate, immune system and intestine use zinc signaling as one way to communicate with other cells.

Zinc may be held in metallothionein reserves within microorganisms or in the intestines or liver of animals . Metallothionein in intestinal cells is capable of adjusting absorption of zinc by 15 – 40 % . However, inadequate or excessive zinc intake can be harmful; excess zinc particularly impairs copper absorption because metallothionein absorbs both metals.

7 . 3 . Dietary intake

In the U.S., the Recommended Dietary Allowance (RDA) is 8 mg / day for women and 11 mg / day for men. Median intake in the U.S. around 2000 was 9 mg / day for women and 14 mg / day in men . Red meats , especially beef , lamb and liver have some of the highest concentrations of zinc in food .

The concentration of zinc in plants varies based on levels of the element in soil. When there is adequate zinc in the soil, the food plants that contain the most zinc are wheat (germ and bran) and various seeds (sesame , poppy , alfalfa , celery , mustard) . Zinc is also found in beans, nuts, almonds, whole grains, pumpkin seeds, sunflower seeds and blackcurrant. Soil conservation is needed to make sure that crop rotation will not deplete the zinc in soil .

Other sources include fortified food and dietary supplements, which come in various forms. A 1998 review concluded that zinc oxide, one of the most common supplements in the United States, and zinc carbonate are nearly insoluble and poorly absorbed in the body. This review cited studies which found low plasma zinc concentrations after zinc oxide and zinc carbonate were consumed compared with those seen after consumption of zinc acetate and sulfate salts. However, harmful excessive supplementation is a problem among the relatively affluent, and should probably not exceed 20 mg/day in healthy people, although the U.S. National Research Council set a Tolerable Upper Intake of 40 mg / day.

For fortification, however, a 2003 review recommended zinc oxide in cereals as cheap, stable, and as easily absorbed as more expensive forms. A 2005 study found that various compounds of zinc, including oxide and sulfate, did not show statistically significant differences in absorption when added as fortificants to maize tortillas.

7 . 4 . Deficiency of Zinc

Zinc deficiency is usually due to insufficient dietary intake, but can be associated with malabsorption, acrodermatitis enteropathica, chronic liver disease, chronic renal disease, sickle cell disease, diabetes, malignancy, and other chronic illnesses.[2] Symptoms of mild zinc deficiency are diverse . Clinical out comes include depressed growth, diarrhea, impotence and delayed sexual maturation, alopecia, eye and skin lesions, impaired appetite, altered cognition, host defense properties, defects in carbohydrate utilization, and reproductive teratogenesis. Mild zinc deficiency depresses immunity, although so does excessive zinc. Animals with a diet deficient in zinc require twice as much food to attain the same weight gain as animals given sufficient zinc.

Groups at risk for zinc deficiency include the elderly, vegetarians, and those with renal insufficiency. There is a paucity of adequate zinc biomarkers, and the most widely used indicator, plasma zinc, has poor sensitivity and specificity. Diagnosing zinc deficiency is a persistent challenge.

Nearly 2 billion people in the developing world are deficient in zinc . In children it causes an increase in infection and diarrhea, contributing to the death of about 800,000 children worldwide per year. The World Health Organization advocates zinc supplementation for severe malnutrition and diarrhea.[156] Zinc supplements help prevent disease and reduce mortality, especially among children with low birth weight or stunted growth. However, zinc supplements should not be administered alone, since many in the developing world have several deficiencies, and zinc interacts with other micronutrients.

Zinc deficiency is plants' most common crop micronutrient deficiency; it is particularly common in high - pH soils. Zinc - deficient soil is cultivated in the cropland of about half of Turkey and India, a third of China, and most of Western Australia, and substantial responses to zinc fertilization have been reported in these areas. Plants that grow in soils that are zinc-deficient are more susceptible to disease. Zinc is primarily added to the soil through the weathering of rocks, but humans have added zinc through fossil fuel combustion, mine waste, phosphate fertilizers, limestone, manure, sewage sludge, and particles from galvanized surfaces. Excess zinc is toxic to plants, although zinc toxicity is far less widespread .

8 . Precautions

8 . 1 . Toxicity

Even though zinc is an essential requirement for good health, excess zinc can be harmful. Excessive absorption of zinc suppresses copper and iron absorption . The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish . The Free Ion Activity Model is well-established in the literature, and shows that just micromolar amounts of the free ion kills some organisms. A recent example showed 6 micromolar killing 93 % of all *Daphnia* in water.

The free zinc ion is a powerful Lewis acid up to the point of being corrosive. Stomach acid contains hydrochloric acid, in which metallic zinc dissolves readily to give corrosive zinc chloride. Swallowing a post - 1982 American one cent piece (97.5 % zinc) can cause damage to the stomach lining due to the high solubility of the zinc ion in the acidic stomach .

There is evidence of induced copper deficiency at low intakes of 100–300 mg Zn/d; a recent trial had higher hospitalizations among elderly men taking 80 mg / day. The USDA RDA is 15 mg Zn / d. Even lower levels, closer to the RDA, may interfere with the utilization of copper and iron or to adversely affect cholesterol. Levels of zinc in excess of 500 ppm in soil interferes with the ability of plants to absorb other essential metals, such as iron and manganese.

There is also a condition called the zinc shakes or " zinc chills " that can be induced by the inhalation of freshly formed zinc oxide formed during the welding of galvanized materials.

The U.S. Food and Drug Administration (FDA) has stated that zinc damages nerve receptors in the nose, which can cause anosmia. Reports of anosmia were also observed in the 1930s when zinc preparations were used in a failed attempt to prevent polio infections. On June 16, 2009 the FDA said that consumers should stop using zinc - based intranasal cold products and ordered their removal from store shelves. The FDA said the loss of smell can be life-threatening because people with impaired smell cannot detect leaking gas or smoke and cannot tell if food has spoiled before they eat it .

8 . 2 . Poisoning

In 1982, the United States Mint began minting pennies coated in copper but made primarily of zinc . With the new zinc pennies, there is the potential for zinc toxicosis, which can be fatal. One reported case of chronic ingestion of 425 pennies (over 1 kg of zinc) resulted in death due to gastrointestinal bacterial and fungal sepsis, while another patient, who ingested 12 grams of zinc, only showed lethargy and ataxia (gross lack of coordination of muscle movements) . Several other cases have been reported of humans suffering zinc intoxication by the ingestion of zinc coins .

Pennies and other small coins are sometimes ingested by dogs, resulting in the need for medical treatment to remove the foreign body. The zinc content of some coins can cause zinc toxicity, which is commonly fatal in dogs, where it causes a severe hemolytic anemia, and also liver or kidney damage ; vomiting and diarrhea are possible symptoms. Zinc is highly toxic in parrots and poisoning can often be fatal. The consumption of fruit juices stored in galvanized cans has resulted in mass parrot poisonings with zinc .

Zinc minerals

1 - Adamite

Yellow-green adamite in limonite

Category	Arsenate mineral
Chemical Formula	Zn_2 As O_4 OH
Dana classification	Olivenite Group
Color	Pale yellow, honey-yellow, brownish yellow, reddish; rarely white, colorless, blue, pale green to green, may be zoned;
Crystal habit	Wedge-like prisms typically in druses and radiating clusters - also smooth botryoidal masses.
Crystal system	Orthorhombic Dipyramidal H-M Symbol (2/m 2/m 2/m) Space Group : Pnnm
Mohs scale hardness	3.5
Luster	Vitreous
Streak	white to pale green
Specific gravity	4.32– 4.48 measured
Optical properties	Biaxial (+/-)
Refractive index	n_α=1.708 - 1.722, n_β=1.742 - 1.744,

	n_γ=1.763 - 1.773
Birefringence	$\delta = 0.055$
Other characteristics	May fluoresce and phosphoresce lemon-yellow under SW and LW UV

1 – Introduction :

Adamite is a zinc arsenate hydroxide mineral, Zn_2AsO_4OH. It is a mineral that typically occurs in the oxidized or weathered zone above zinc ore occurrences. Pure adamite is colorless, but usually it possess yellow color due to Fe compounds admixture. Tints of green also occur and are connected with copper substitutions in the mineral structure. Olivenite is a copper arsenate that is isostructural with adamite and there is considerable substitution between zinc and copper resulting in an intermediate called *cupro adamite*. Zincolivenite is a recently discovered mineral being an intermediate mineral with formula Cu Zn (AsO_4) (OH). Manganese, cobalt, and nickel also substitute in the structure. An analogous zinc phosphate, *tarbuttite*, is known.

Adamite on limonite from the Gold Hill District Tooele County, Utah, USA - Scale at bottom is approx. 2.5 cm.

2 - Occurrence :

Adamite occurs as a secondary mineral in the oxidized zone of zinc- and arsenic-bearing hydrothermal mineral deposits. It occurs in association with smithsonite, hemimorphite, scorodite, olivenite, calcite, quartz and iron and manganese oxides.

The yellow to bright lime-green colored crystals and druze along with its distinctive fluorescence make adamite a favorite among mineral collectors. Found in Mapimi, Mexico; Greece; and California and Utah in the United States.

Adamite was named after the French mineralogist Gilbert-Joseph Adam (1795-1881). It was first described in 1866 for an occurrence at the type locality of Chañarcillo, Copiapó Province, Atacama Region, Chile.

2 – Aurichalcite

 *Needle Crystals of Aurichalcite from Nevada, USA*	 *Aurichalcite in gossan*	 *Aurichalcite, , Banner District, Gila County, Arizona, USA*

1 - Aurichalcite is a carbonate mineral, usually found as a secondary mineral in copper and zinc deposits. Its chemical formula is $(Zn,Cu)_5(CO_3)_2(OH)_6$. The zinc to copper ratio is about 5:4.

Category	Carbonate mineral
Chemical Formula	$(Zn,Cu)_5[(OH)_3\|CO_3]_2$
Strunz Classification	05.BA.15
Crystal Symmetry	Monoclinic 2/m
Unit cell	a = 13.82 Å, b = 6.419 Å, c = 5.29 Å; β = 101.04°; Z=2
Color	Pale green, greenish blue, sky-blue ; colorless to pale blue, pale green in transmitted light
Crystal habit	Typically in tufted divergent sprays or spherical aggregates, may be in thick crusts; rarely columnar, laminated or granular

Crystal system	Monoclinic-prismatic
Twinning	Observed in X-ray patterns
Fracture	Uneven
Mohs scale hardness	2
Luster	Pearly, silky
Streak	Light blue
Diaphaneity	Transparent
Specific gravity	3.96
Optical properties	Biaxial (-)
Refractive index	$n_\alpha = 1.655$ $n_\beta = 1.740$ $n_\gamma = 1.744$
Birefringence	0.0890
Pleochroism	Weak colorless to pale green
2V angle	Measured: 1° to 4°, Calculated: 22°

2 - Occurrence

Auricalcite typically occurs in the oxidized zone of copper and zinc deposits. Associated minerals include: rosasite, smithsonite, hemimorphite, hydrozincite, malachite and azurite.

It was first described in 1839 by Bottger who named the mineral for its zinc and copper content after the Greek όρειχαλκος, for "mountain brass" or "mountain copper", the name of a fabulous metal. The type locality is the Loktevskoye Mine, Upper Loktevka River, Rudnyi Altai, Altaiskii Krai, Western Siberia, Russia.

3 - Calamine (mineral)

Calamine is a historic name for an ore of zinc. The name *calamine* was derived from the Belgian town of Kelmis, whose French name is "La Calamine", which is home to a zinc mine. In the 18th and 19th century large ore mines could be found near the German village of Breinigerberg.

During the late 18th century it was discovered that what had been thought to be one ore was actually two distinct minerals :

- Zinc carbonate $Zn\,CO_3$ or smithsonite and
- Zinc silicate $Zn_4\,Si_2\,O_7\,(OH)_2 \cdot H_2O$ or hemimorphite.

The two minerals are usually very similar in appearance and can only be distinguished through chemical analysis. The first person to separate the minerals was the British chemist and mineralogist James Smithson in 1803. In the mining industry the term calamine is still used to refer to both minerals indiscriminately.

In mineralogy calamine is no longer considered a valid term. It has been replaced by smithsonite and hemimorphite in order to distinguish it from the pinkish mixture of zinc oxide (ZnO) and iron (III) oxide (Fe_2O_3) used in calamine lotion.

Until the 18th century, *calamine* was essential for the production of brass since metallic zinc does not exist in nature and no technique was known to produce it. Brass produced using calamine is called calamine brass.

4 - Chaidamuite

1 – Introducion :

Chaidamuite is a sulfate mineral that was first found in Xitieshan mine south of Mt. Qilianshan in the Chaidamu basin, Qinghai (Chinghai) Province, China. It is named from locality and is a hydrated sulfate containing a hydroxyl and four dihydrogen monoxide molecules. It a secondary mineral possibly formed due to mining process.

Category	Sulfate minerals
Chemical Formula	$ZnFe^{3+}(SO_4)_2(OH)\cdot4(H_2O)$
Crystal symmetry	Triclinic pedial 1 – pseudo monoclinic
Unit cell	a = 7.309(2) Å, b = 7.202(2) Å, c = 9.691(3) Å; α = 89.64(3)°, β = 105.89(1)°, γ = 91.11(1)°; Z = 2
Color	Brown to yellow-brown
Crystal system	Triclinic
Mohs scale hardness	2.5 – 3
Luster	Vitreous
Streak	Pale yellow
Diaphaneity	Translucent
Optical properties	Biaxial (+)
Refractive index	$n_\alpha = 1.632$ $n_\beta = 1.640$ $n_\gamma = 1.688$

Pleochroism	Strong : X = pale yellow , colorless; Y = pale yellow ; Z = Brownish yellow

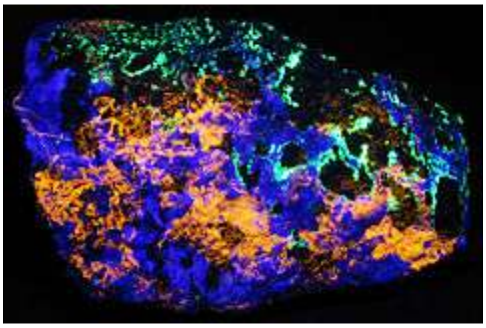
2 - Composition

Chemistry : Zn $Fe^{3+}(SO_4)_2$ (OH)·$4H_2O$

3 - Structure :

The crystal structure has been determined by the Patterson method and Fourier syntheses and refined by the full-matrix least-squares method to an R factor of 0.032, using 2833 independent reflections. In the structure, a zigzag chain consists of [Fe(1)O_5(OH)] and [Fe(2)O_5(OH)] octahedra sharing the OH corners, and an octahedral-tetrahedral chain running parallel to the b axis consists of the zigzag chain of Fe octahedra and (SO_4) tetrahedra sharing four pairs of octahedral corners on either side of the zigzag chains. These chains are cross-linked by the isolated [Zn(1)O_2(H_2O)$_4$] and [Zn(2)O_2(H_2O)$_4$] octahedra into corrugated sheets parallel to the (100) plane. Adjacent sheets are hydrogen bonded through water molecules (Li, et al 1990).

5 – Clinohedrite



Clinohedrite coating hardystonite, franklinite with willemite reaction rims. Franklin, New Jersey. Orange fluorescence under UV.

Clinohedrite is a rare silicate mineral. Its chemical composition is a hydrous calcium-zinc silicate; $CaZn(SiO)_4{\cdot}H_2O$. It crystallizes in the monoclinic system and typically occurs as veinlets and fracture coatings. It is commonly colorless, white to pale amethyst in color. It has perfect cleavage and the crystalline habit has a brilliant luster. It has a Mohs hardness of 5.5 and a specific gravity of 3.28 - 3.33.

Under short wave ultraviolet light it fluoresces a rich orange color. It is frequently associated with minerals such as hardystonite (fluoresces violet blue), esperite (fluoresces bright yellow), calcite (fluoresces orange-red), franklinite (non-fluorescent) and willemite (fluoresces green).

Clinohedrite was found primarily at the Franklin zinc mines in New Jersey, the type locality, but has also been reported from the Christmas mine, Gila County, Arizona, [1] and the Western Quinling gold belt, Gansu Province, China.

It was first described in 1898 and was named for its crystal morphology from the Greek *klino* for incline, and *hedra* for face.

Category	Silicate mineral
Chemical Formula	$CaZn(SiO)_4{\cdot}H_2O$
Crystal symmetry	Monoclinic point group m
Unit cell	a = 5.09 Å ,

	b = 15.82 Å , c = 5.38 Å ; β = 103.39° ; Z = 4
Color	Colorless to brown surface coating, clear to pale pink to amethystine crystals
Crystal habit	Thin to thick or platey surface and fracture coatings, in vugs or cavities, rarely as crusts of crystals - prismatic to tabular, may be wedge-shaped
Mohs scale hardness	5.5
Luster	Brilliant , glassy; pearly
Streak	white
Specific gravity	3.28 - 3.33
Optical properties	Biaxial (-)
Refractive index	n_α = 1.662 n_β = 1.667 n_γ = 1.669
Ultraviolet fluorescence	UV = orange
Other characteristics	Strongly pyroelectric

6 – Descloizite

Superb spear-point bladed crystals of Descloizite, Berg Aukas, Namibia. Size 3.6 x 3.1 x .9 cm.

Descloizite specimen from Berg Aukas (Berg Aukus), Namibia, 9.5 x 8.9 x 4.9 cm]]

1 – Introduction :

Descloizite is a rare mineral species consisting of basic lead and zinc vanadate, $(Pb,Zn)_2(OH)VO_4$, crystallizing in the orthorhombic system and isomorphous with olivenite.

The color is deep cherry-red to brown or black, and the crystals are transparent or translucent with a greasy lustre; the streak is orange-yellow to brown; specific gravity 5.9 to 6.2; hardness 31/2. A variety known as cuprodescloizite is dull green in color; it contains a considerable amount of copper replacing zinc and some arsenic replacing vanadium. Appreciable gallium and germanium may also be incorporated into the crystal structure.

Category	Vanadate mineral
Chemical Formula	$(Pb,Zn)_2VO_4OH$
Crystal symmetry	Orthorhombic (2/m 2/m 2/m) - dipyramidal
Unit cell	a = 7.593 Å, b = 6.057 Å,

	c = 9.416 Å; Z = 4
Color	Brownish red, red-orange, reddish to blackish brown, nearly black
Crystal habit	Zoned tabular crystals common, encrustations and plumose aggregates
Crystal system	Orthorhombic
Cleavage	None
Fracture	Irregular, sub - conchoidal
Tenacity	Brittle
Mohs scale hardness	3 - 3.5
Luster	Greasy
Streak	Orange to brownish red
Diaphaneity	Transparent to opaque
Specific gravity	6.1 - 6.2
Optical properties	Biaxial (-)
Refractive index	$n_\alpha = 2.185$ $n_\beta = 2.265$ $n_\gamma = 2.350$

2 - Discovery and occurrence :

It was discovered in the Sierra de Córdoba deposit in Córdoba, Argentina in 1854 and named in honor of the French mineralogist Alfred Des Cloizeaux. It occurs as small prismatic or pyramidal crystals, usually forming drusy crusts and stalactitic aggregates; also as fibrous encrusting masses with a mammillary surface.

Descloizite occurs in oxidised portions of veins of lead ores in association with pyromorphite, vanadinite, wulfenite, mottramite, mimetite and cerussite.

The Otavi Mountainland of northern Namibia was once considered home to the greatest vanadium deposits in the world, including those at Berg Aukas, Abenab, Baltika and Uitsab.[4] Descloizite and mottramite were the main ore minerals in each of these deposits, which are now exhausted. Other localities are the Sierra de Cordoba in Argentina; Lake Valley in Sierra County, New Mexico; Arizona; Phoenixville in Pennsylvania and Kappel (Eisen-Kappel) near Klagenfurt in Carinthia.

7 – Goslarite

Goslarite is a hydrous zinc sulfate mineral with formula: $ZnSO_4 \cdot 7H_2O$. It is a secondary mineral which develops after primary zinc minerals within the zone of oxidation and in old sphalerite mine workings. It is unstable at the surface and dehydrates readily. It is transparent to translucent and variable in color, ranging from colorless, green, blue to brown. It crystallizes in the orthorhombic system and forms acicular crystals, stalactitic forms and massive clumps. It has a Mohs hardness of 2 - 2.5 and a low specific gravity of only 2. Related minerals include epsomite ($MgSO_4 \cdot 7H_2O$) and morenosite ($NiSO_4 \cdot 7H_2O$).

Goslarite was first described in 1847 for an occurrence in Rammelsberg mines near Goslar, Harz Mountains, Germany.

8 – Hardystonite

Hardystonite in plane light, same sample as in fluorescent light image above right

Hardystonite is fluorescing blue in this Franklin Furnace specimen. Red is calcite, and green is willemite (size: 7.0 x 6.0 x 3.2 cm)

Hardystonite is a rare calcium zinc silicate mineral first described from the Franklin, New Jersey, USA zinc deposits. It often contains lead, which was detrimental to the zinc smelting process, so it was not a useful ore mineral. Like many of the famous Franklin minerals, hardystonite responds to short wave ultraviolet (254 nm wavelength) light, emitting a fluorescence from dark purple to bright violet blue. In daylight, it is white to gray to light pink in color, sometimes with a vitreous or greasy luster. It is very rarely found as well formed crystals, and these are usually rectangular in appearance and rock-locked.

Hardystonite has a chemical composition of $Ca_2ZnSi_2O_7$. It is frequently found with willemite (fluoresces green), calcite (fluoresces red), and clinohedrite (fluoresces orange). Hardystonite can be found altered to clinohedrite $CaZn(SiO_4)\cdot H_2O$ through direct hydrothermal alteration.[5] Other minerals often associated with hardystonite are franklinite, diopside, andradite garnet, and esperite (fluoresces yellow).

It was first described in 1899 by J.E. Wolff, when the New Jersey Zinc Company mines were located in what was called Franklin Furnace, in Hardyston Township, New Jersey.

Category	Silicate mineral
Chemical Formula	$Ca_2ZnSi_2O_7$
Crystal symmetry	Tetragonal 4 2m scalenohedral
Unit cell	a = 7.8287(16) Å, c = 5.0140(2) Å; Z = 2
Color	light brownish white, pale greyish-white, very pale pink
Crystal habit	Massive granular
Crystal system	Tetragonal
Mohs scale hardness	3 - 4
Luster	vitreous, resinous, greasy, dull
Diaphaneity	Transparent to translucent
Specific gravity	3.396 – 3.443
Optical properties	Uniaxial (-)
Refractive index	$n_\omega = 1.672$ $n_\varepsilon = 1.661$
Ultraviolet fluorescence	purple to violet blue in short wave ultraviolet light
Alters to	hydrothermal alteration to clinohedrite

9 - Hemimorphite

Hemimorphite from Mapimi, Durango, Mexico

1 – Introduction :

Hemimorphite, is a sorosilicate mineral which has been mined from days of old from the upper parts of zinc and lead ores, chiefly associated with smithsonite. It was often assumed to be the same mineral and both were classed under the same name of calamine. In the second half of the 18th century it was discovered that there were two different minerals under the heading of calamine - a zinc carbonate and a zinc silicate, which often closely resembled each other.

The silicate was the more rare of the two, and was named hemimorphite because of the hemimorph development of its crystals. This unusual form, which is typical of only a few minerals, means that the crystals are terminated by dissimilar faces. Hemimorphite most commonly forms crystalline crusts and layers, also massive, granular, rounded and reniform aggregates, concentrically striated, or finely needle-shaped, fibrous or stalactitic, and rarely fan-shaped clusters of crystals.

Some specimens show strong green fluorescence in shortwave ultraviolet light (253.7 nm) and weak light pink fluorescence in longwave UV.

Category	Silicate mineral
Chemical Formula	$Zn_4Si_2O_7(OH)_2 \cdot H_2O$
Crystal symmetry	Orthorhombic mm2
Unit cell	a = 8.367(5) Å, b = 10.73Å, c = 5.155(3) Å; Z = 2
Color	White, blue, greenish
Crystal habit	Polar crystals, with different or hemimorphic ends. Also *coxcomb* masses, mammillary, stalactitic, or massive
Crystal system	Ortho rhombic pyramidal
Fracture	Uneven to conchoidal
Tenacity	Brittle
Mohs scale hardness	4.5 - 5
Luster	Vitreous, adamantine, rarely silky
Streak	White
Diaphaneity	Transparent to translucent
Specific gravity	3.516 - 3.525
Optical properties	Biaxial (+)
Refractive index	n_α = 1.614 n_β = 1.617 n_γ = 1.636
2V angle	Measured: 46°, calculated: 44°
Solubility	Soluble in acid

2 – Occurrence :

Hemimorphite "spray" of crystals from Durango, Mexico (size: 2.9 x 2.1 x 2.0 cm)

Hemimorphite most frequently occurs as the product of the oxidation of the upper parts of sphalerite bearing ore bodies, accompanied by other secondary minerals which form the so- called *iron cap* or *gossan*. Hemimorphite is an important ore of zinc and contains up to 54.2 % of the metal.

Blue vug filling hemimorphite from Wenshan, Yunnan Province, China (size: 9.2 x 4.8 x 3.1 cm)

The regions on the Belgian-German border are well known for their deposits of hemimorphite of metasomatic origin, especially Vieille Montagne in Belgium and Aachen in Germany. Other deposits are near Tarnovice in upper Silesia, Poland; near Phoenixville, Pennsylvania; the Missouri lead-zinc district; Elkhorn, Montana; Leadville, Colorado; and Organ Mountains, New Mexico in the United States; and in several localities in North Africa. Further hemimorphite occurrences are the Padaeng deposit near Mae Sod in western Thailand; Sardinia; Nerchinsk, Siberia; Cave del Predil, Italy; Bleiberg, Carinthia, Austria; Matlock, Derbyshire, England.

10 – Herbertsmithite

Herbertsmithite from Caracoles, Sierra Gorda District, Tocopilla Province, Chile. Size: 4.5 x 4.4 x 2.7 cm.

Herbertsmithite is a mineral with chemical structure $ZnCu_3(OH)_6Cl_2$. It is named after the mineralogist Herbert Smith and was first found in 1972 in Chile. A polymorph of kapellasite and closely related to paratacamite, is generally found in and around Anarak, Iran, hence its other name, Anarakite. Herbertsmithite is associated with copper mineralizations in syenitic porphyries and granites.

Herbertsmithite has a vitreous lustre and is fairly transparent with a light-green to blue green color. Herbertsmithite has a Mohs hardness of between 3 and 3.5 and is known to have a brittle tenacity. The crystal's density has been calculated at 3.76 g / cm^3.

Herbertsmithite is of some interest to solid state physics in scientific research into string-net liquids and quantum spin liquids due to its Kagome lattice structure.

Category	Copper minerals Zinc minerals Halide minerals
Chemical Formula	$Zn\ Cu_3(OH)_6Cl_2$
Color	Light green, blue-green

Crystal system	Trigonal
Cleavage	Distinct to good
Tenacity	Brittle
Mohs scale hardness	3 - 3½
Luster	Vitreous
Streak	Light green
Diaphaneity	Transparent
Density	3.76

11 - Hydrozincite

Hydrozincite

Hydrozincite, also known as **zinc bloom**, is a white carbonate mineral consisting of $Zn_5(CO_3)_2(OH)_6$. It is usually found in massive rather than crystalline form.

It occurs as an oxidation product of zinc ores and as post mine incrustations. It occurs associated with smithsonite, hemimorphite, willemite, cerussite, aurichalcite, calcite and limonite.

It was first described in 1853 for an occurrence in Bad Bleiberg, Carinthia, Austria and named for its chemical content.

Category	Carbonate mineral
Chemical Formula	$Zn_5(CO_3)_2(OH)_6$
Crystal symmetry	Monoclinic prismatic H–M Symbol 2 /m
Unit cell	a = 13.58 Å, b = 6.28 Å, c = 5.41 Å; β = 95.51°, Z = 2
Color	White to grey, stained pale pink, or pale yellow or brown; colourless in transmitted light.

Crystal habit	Lathlike or bladed crystals uncommon, in fibrous, stalactitic, reniform, pisolitic aggregates; also earthy, chalky, massive
Crystal system	Monoclinic
Mohs scale hardness	2 - 2½
Luster	Silky, pearly, dull, earthy
Streak	White
Diaphaneity	Transparent, translucent
Specific gravity	3.5 - 4
Optical properties	Biaxial (-)
Refractive index	$n_\alpha = 1.630$ $n_\beta = 1.642$ $n_\gamma = 1.750$
Dispersion	relatively strong
Ultraviolet fluorescence	Fluoresces pale blue to lilac under UV
Solubility	Readily soluble in acids.

12 – Phosphophyllite

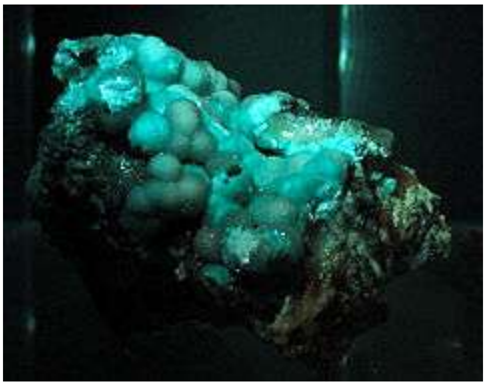
Phosphophyllite is a rare mineral composed of hydrated zinc phosphate. Its name derives from its chemical composition (phosphate) and the Greek word for "leaf", *phyllon*, a reference to its cleavage . It is highly prized by collectors for its rarity and for its delicate bluish green colour. Phosphophyllite is rarely cut because it is fragile and brittle, and large crystals are too valuable to be broken up.

The finest phosphophyllite crystals come from Potosí, Bolivia, but it is no longer mined there. Other sources include New Hampshire, USA and Hagendorf, Bavaria, Germany. It is often found in association with the minerals chalcopyrite and triphylite.

Category	Phosphate minerals
Chemical Formula	hydrated zinc phosphate $Zn_2 Fe (PO_4)_2 \bullet 4H_2O$
Molar mass	448.40 g mol^{-1}
Color	Blue - green to colourless
Crystal habit	prismatic
Crystal system	monoclinic
Twinning	common

Fracture	conchoidal
Mohs scale hardness	3.5
Luster	vitreous
Streak	white
Diaphaneity	transparent
Specific gravity	3.1
Refractive index	1.59 - 1.62
Birefringence	0.021
Common impurities	Mn

13 – Rosasite



Blue velvety mass lining a cavity

Rosasite is a carbonate mineral with minor potential for use as a zinc and copper ore. Chemically, it is a copper zinc carbonate hydroxide with a copper to zinc ratio of 3:2, occurring in the secondary oxidation zone of copper-zinc deposits. It was originally discovered in 1908 in the Rosas mine in Sardinia, Italy, and is named after the location. Fibrous blue-green rosasite crystals are usually found in globular aggregates, often associated with red limonite and other colourful minerals. It is very similar to aurichalcite, but can be distinguished by its superior hardness.

Category	Carbonate mineral
Chemical Formula	(Cu,Zn)$_2$(CO]sub>3)(OH)$_2$
Crystal symmetry	Monoclinic prismatic H–M Symbol 2/m Space group P21/a
Unit cell	a = 12.873(3) Å, b = 9.354(3) Å, c = 3.156(2) Å; β = 110.36(3)°; Z = 4
Color	Blue, bluish green, green
Crystal habit	Acicular crystals as radiating fibrous clusters; botryoidal; mammillary; encrustations

Crystal system	Monoclinic
Fracture	Splintery, fibrous
Tenacity	Brittle
Mohs scale hardness	4
Luster	Silky, vitreous to dull
Streak	Light blue or green
Specific gravity	4 - 4.2
Optical properties	Biaxial (-)
Refractive index	n_α = 1.672 - 1.688 n_β = 1.796 - 1.830 n_γ = 1.811 - 1.831
Birefringence	δ = 0.139 - 0.143
Pleochroism	Strong: X = pale emerald green or colourless; Y = dark emerald green or pale blue; Z = dark emerald green or pale blue
2V angle	Measured : 33°
Solubility	Effervesces in cold, dilute hydrochloric acid
Nickeloan rosasite	Dark green

14 – Smithsonite

A specimen of smithsonite
from Kelly mine, Socorro County, New Mexico, USA .

Smithsonite, or **zinc spar**, is zinc carbonate ($ZnCO_3$), a mineral ore of zinc. Historically, smithsonite was identified with hemimorphite before it was realised that they were two distinct minerals. The two minerals are very similar in appearance and the term calamine has been used for both, leading to some confusion. The distinct mineral smithsonite was named in 1832 by François Sulpice Beudant in honor of English chemist and mineralogist, James Smithson (c.1765-1829), whose bequest established the Smithsonian Institution and who first identified the mineral in 1802.

Smithsonite is a variably colored trigonal mineral which only rarely is found in well formed crystals. The typical habit is as earthy botryoidal masses. It has a Mohs hardness of 4.5 and a specific gravity of 4.4 to 4.5.

Smithsonite occurs as a secondary mineral in the weathering or oxidation zone of zinc-bearing ore deposits. It sometimes occurs as replacement bodies in carbonate rocks and as such may constitute zinc ore. It commonly occurs in association with hemimorphite, willemite, hydrozincite, cerussite, malachite, azurite, aurichalcite and anglesite. It forms two limited solid solution series, with substitution of manganese leading to rhodochrosite, and with iron, leading to siderite.

Category	Carbonate mineral
Chemical Formula	$ZnCO_3$
Crystal symmetry	Trigonal 3 2/m
Unit cell	a = 4.6526(7) Å, c = 15.0257(22) Å; Z = 6
Color	White, grey, yellow, green to apple-green, blue, pink, purple, bluish grey, and brown
Crystal habit	Uncommon as crystals, typically botryoidal, reniform, spherulitic; stalactitic, earthy, compact massive
Crystal system	Trigonal - Hexagonal Scalenohedral
Twinning	None observed
Mohs scale hardness	4.5
Luster	Vitreous , may be pearly
Streak	White
Diaphaneity	Translucent
Specific gravity	4.4 - 4.5
Optical properties	Uniaxial (-)
Refractive index	n_ω = 1.842 - 1.850 n_ε = 1.619 - 1.623
Birefringence	δ = 0.223 - 0.227
Ultraviolet fluorescence	May fluoresce pale green or pale blue under UV

Pink botryoidal smithsonite from Choix, 6.8 x 5.8 x 3.3 cm

Botryoidal smithsonite from Choix, Sinaloa, Mexico, 18.8 x 11.6 x 4.0 cm

 *Cuprian smithsonite on dolomite, Tsumeb, 4.4 x 4 x 3 cm*	 *Crystals of slightly pink cobaltoan smithsonite, Tsumeb, 6.8 x 4.6 x 3.7 cm*

15 – Sphalerite

 *Another sphalerite sample*	 *Sphalerite on dolomite from the Tri-State District, Jasper County, Missouri, USA*

Contents

1 – Introduction :

Sphalerite ((Zn,Fe)S) is a mineral that is the chief ore of zinc. It consists largely of zinc sulfide in crystalline form but almost always contains variable iron. When iron content is high it is an opaque black variety, **marmatite**. It is usually found in association with galena, pyrite, and other sulfides along with calcite, dolomite, and fluorite. Miners have also been known to refer to sphalerite as **zinc blende** and **black - jack**.

Category	Sulfide mineral
Chemical Formula	(Zn,Fe)S
Color	Brown, yellow, red, green, black.

Crystal habit	Euhedral crystals – occurs as well-formed crystals showing good external form. Granular – generally occurs as anhedral to subhedral crystals in matrix.
Crystal system	Isometric hextetrahedral (4 3m)
Fracture	Uneven to conchoidal
Mohs scale hardness	3.5 - 4
Luster	Adamantine, resinous, greasy
Streak	brownish white, pale yellow
Diaphaneity	Transparent to translucent, opaque when iron-rich
Specific gravity	3.9 – 4.2
Optical properties	Isotropic
Refractive index	$n_\alpha = 2.369$
Other characteristics	non-radioactive, non-magnetic, fluorescent and triboluminescent.

2 – Chemistry :

The mineral crystallizes in the cubic crystal system. In the crystal structure, zinc and sulfur atoms are tetrahedrally coordinated. The structure is closely related to the structure of diamond. The hexagonal analog is known as the wurtzite structure. The lattice constant for zinc sulfide in the zincblende crystal structure is 0.541 nm, calculated from geometry and ionic radii of 0.074 nm (zinc) and 0.184 nm (sulfide). It forms ABCABC layers.

3 – Varieties :

Its color is usually yellow, brown, or gray to gray-black, and it may be shiny or dull. Its luster is adamantine, resinous to submetallic for high iron varieties. It has a yellow or light brown streak, a Mohs hardness of 3.5 – 4, and a specific gravity of 3.9 – 4.1. Some specimens have a red iridescence within the gray - black crystals; these are called "ruby sphalerite." The pale yellow and red varieties have very little iron and are translucent. The darker more opaque varieties contain more iron. Some specimens are also fluorescent in ultraviolet light. The refractive index of sphalerite (as measured via sodium light, 589.3 nm) is 2.37. Sphalerite crystallizes in the isometric crystal system and possesses perfect dodecahedral cleavage. Gemmy, pale specimens from Franklin, New Jersey are highly fluorescent orange and/or blue under longwave ultraviolet light and are known as *cleiophane*, an almost pure ZnS variety.

Sharp, tetrahedral sphalerite crystals with minor associated chalcopyrite from the Idarado Mine, Telluride, Ouray District, Colorado, USA (size: 2.3×2.3×1.2 cm)

4 – Occurrence :

Sphalerite is the major ore of zinc and is found in thousands of locations worldwide.

Sources of high quality crystals include :

- Freiberg, Saxony, and Neudorf, Harz Mountains of Germany
- the Lengenbach Quarry, Binntal, Valais, Switzerland, has produced colorless crystals
- Horni Slavkov (Schlaggenwald) and Pribram, Czech Republic
- From Rodna, Romania
- Transparent green to opaque black Madan, Smolyan Province, Rhodope Mountains, Bulgaria;

- Transparent crystals in the Aliva mine, Picos de Europa Mountains, Cantabria [Santander] Province, Spain
- In England, from Alston Moor, Cumbria
- At Dalnegorsk, Primorskiy Kray, Russia
- From Watson Lake, Yukon Territory, Canada
- In the USA
  - the Tri-State district including deposits near Baxter Springs, Cherokee County, Kansas; Joplin, Jasper County, Missouri and Picher, Ottawa County, Oklahoma
  - From the Elmwood mine, near Carthage, Smith County, Tennessee
  - the Eagle mine, Gilman district, Eagle County, Colorado
- In Mexico, from Santa Eulalia and Naica, Chihuahua, and Cananea, Sonora
- Huaron, Casapalca, and Huancavelica, Peru

5 - Gemstone use :

Gemmy, 1.8 cm, twinned, cherry-red sphalerite crystal from Hunan Province, China

Crystals of suitable size and transparency have been fashioned into gemstones, usually featuring the brilliant cut to best display sphalerite's high dispersion of 0.156 (B-G interval)—over three times that of diamond. Freshly cut gems have an adamantine luster. Owing to the softness and fragility the gems are often left unset as collector's or museum pieces (although some have been set into pendants). Gem-quality material is usually a yellowish to honey brown, red to orange, or green.

16 – Staurolite

Staurolite from Pestsovye Keivy, Keivy Mountains, Kola Peninsula, Murmanskaja Oblast', Northern Region, Russia, 2.5 x 2.2 x 1 cm

Contents :

- 1 Introdution
- 2 Properties
- 3 Name
- 4 Occurrence
- 5 Use

1 – Introduction :

Staurolite is a red brown to black, mostly opaque, nesosilicate mineral with a white streak.

Category	Silicate mineral
Chemical Formula	$(Fe^{2+},Mg,Zn)_{1.5-2}Al_9[O_6\|(OH,O)_2\|(SiO_4)_4]$
Crystal symmetry	Monoclinic 2/m
Unit cell	a = 7.86 Å, b = 16.6 Å, c = 5.65 Å; β = 90.45°; Z=2
Color	Dark reddish brown to blackish brown,

	yellowish brown, rarely blue; pale golden yellow in thin section
Crystal habit	Commonly in prismatic crystals
Crystal system	Monoclinic - Prismatic; Pseudo-orthorhombic
Twinning	Commonly as 60° twins, less common as 90° cruciform twins
Fracture	Subconchoidal
Tenacity	Brittle
Mohs scale hardness	7 - 7.5
Luster	Subvitreous to resinous
Streak	White to grayish
Diaphaneity	Transparent to opaque
Specific gravity	3.74 - 3.83 meas. 3.686 calc.
Optical properties	Biaxial (+)
Refractive index	$n_\alpha = 1.736 - 1.747$ $n_\beta = 1.740 - 1.754$ $n_\gamma = 1.745 - 1.762$
Birefringence	$\delta = 0.009 - 0.015$
Pleochroism	Pleochroism: X = colorless; Y = pale yellow; Z = golden yellow
2V angle	Measured: 88°, Calculated: 84° to 88°
Dispersion	r > v; weak

2 – Properties :

It crystallizes in the monoclinic crystal system, has a Mohs hardness of 7 to 7.5 and a rather complex chemical formula:

$(Fe,Mg,Zn)_2Al_9(Si,Al)_4O_{20}(OH)_4$. Iron, magnesium and zinc occur in variable ratios.

Staurolite from Madagascar

A special property of staurolite is that it often occurs twinned in a characteristic cross-shape. In handsamples, macroscopically visible staurolite crystals are of prismatic shape. They are often larger than the surrounding minerals and are then called porphyroblasts.

In thin sections staurolite is commonly twinned and shows lower first order birefringence similar to quartz, with the twinning displaying optical continuity. It can be identified in metamorphic rocks by its swiss cheese appearance (with poikilitic quartz) and often mantled porphyroblastic character.

3 – Name :

The name is derived from the Greek, *stauros* for cross and *lithos* for stone in reference to the common twinning.

4 - Occurrence :

Staurolite is a regional metamorphic mineral of intermediate to high grade. It occurs with almandine garnet, micas, kyanite; as well as albite, biotite, and sillimanite in gneiss and schist of regional metamorphic rocks.

It is the official state mineral of the U.S. state of Georgia and is also to be found in the Lepontine Alps in Switzerland.

Staurolite is also found in Fairy Stone State Park in Patrick County, Virginia. The park is named for a local name for staurolite from a legend in the area.

5 - Use :

Staurolite is one of the index minerals that are used to estimate the temperature, depth, and pressure at which a rock undergoes metamorphism.

17 – Tsumcorite

Tsumcorite from the Tsumeb Mine, Namibia

Contents

1 – Introduction :

Tsumcorite is a rare hydrated lead arsenate mineral that was discovered in 1971, and reported by Geier, Kautz and Muller. It was named after the **TSUM**eb **COR**poration mine at Tsumeb, in Namibia, in recognition of the Corporation's support for mineralogical investigations of the orebody at its Mineral Research Laboratory.

Category	Arsenate minerals
Chemical formula	$PbZnFe^{2+}(AsO_4)_2.H_2O$
Crystal symmetry	Monoclinic prismatic (2/m)
Unit cell	a = 9.124 Å, b = 6.329 Å, c = 7.577 Å; β = 115.3°; Z = 2

Molar mass	624 g
Color	Yellow-brown, red-brown, orange
Crystal habit	Radiating, fibrous crusts
Crystal system	Monoclinic
Twinning	Common, on a unknown law
Mohs scale hardness	4½
Luster	Vitreous
Streak	Yellow
Diaphaneity	Translucent
Specific gravity	5.2
Optical properties	Biaxial
Refractive index	n_α = 1.87–1.91 n_β = 1.89–1.93 n_γ = 1.92–1.96
Pleochroism	Weak, yellow to yellow-green
2V angle	67 – 83.5°
Solubility	Dissolves in HCl

2 - Unit cell

Tsumcorite belongs to the monoclinic crystal class 2/m, which means that it has a twofold axis of symmetry along the b axis and a mirror plane perpendicular to this, in the plane containing the a and c axes. The a and c axes are inclined to each other at angle β = 115.3°. The unit cell parameters are a = 9.124 Å to 9.131 Å, b = 6.326 Å to 6.329 Å and c = 7.577 Å to 7.583 Å.

There are two formula units per unit cell (Z = 2), and the space group is C2/m, meaning that the cell is a C- face centred lattice, with lattice points in the center of the C face as well as at the corners of the cell. The structure is related to the brackebushite group structure.

3 - Mineral series :

Tsumcorite belongs to the helmutwinklerite group,[1] whose members are :

- tsumcorite $PbZnFe^{2+}(AsO_4)_2.H_2O$
- helmutwinklerite $PbZn_2(AsO_4)_2.2H_2O$
- thometzekite $PbCu^{2+}{}_2(AsO_4)_2.2H_2O$
- mawbyite $PbFe^{3+}{}_2(AsO_4)_2(OH)_2$

Tsumcorite forms a series with helmutwinklerite as Zn replaces the Fe^{2+}, with thometzekite as Cu replaces the Zn and Fe^{2+}, and also with mawbyite.

4 - Crystal habit and Properties :

Crystals are prismatic, elongated along the b axis, or wedge-shaped. They occur in radiating sheaves and spherulites, and as fibrous crusts or earthy and powdery material. Cleavage is good perpendicular to the c axis, and twinning is common.

Tsumcorite is yellow – brown , red - brown or orange in color, and it is one of the few minerals that have a yellow streak (orpiment and crocoite are two others). It is translucent, with a vitreous luster, and dichroic yellow to yellow-greenn. The optical class is biaxial and the refractive indices are approximately equal to 1.90.

The mineral is moderately hard, with a Mohs hardness of 4½, between fluorite and apatite , and quite heavy, due to the lead content, with specific gravity 5.2, which is more than baryte but less than cerussite . It dissolves in hydrochloric acid and it is not radioactive.

5 - Occurrence and Associations :

Tsumcorite is a rare secondary mineral in the oxidized zone of some arsenic-bearing hydrothermal lead-zinc deposits .

The type locality is the Tsumeb Mine, Tsumeb, Otjikoto Region, Namibia, where it is associated with willemite, smithsonite, mimetite, scorodite, anglesite, arseniosiderite, beaverite, beudantite, carminite, ludlockite, o'danielite, zincroselite, stranskiite and leiteite. At the Puttapa Mine in Australia it occurs with adamite, mimetite, smithsonite, goethite and quartz. At the Kintore Open Cut, Broken Hill, Australia it occurs with segnitite, beudantite, carminite and mawbyite.

18 – Warikahnite


Warikahnite, *Tsumeb mine*, *Namibia*, 0.9 x 0.4 x 0.1 cm


Warikahnite, *Tsumeb mine*, *Namibia*, 0.6 x 0.4 x 0.1 cm

1 – Introduction :

Warikahnite is a rare zinc arsenate mineral. It occurs in the second oxidation zone of the Tsumeb mine in Namibia on corroded tennantite . It is associated with adamite, stranskiite, koritnigite, claudetite, tsumcorite, and ludlockite . It has also been found at Lavrion, Greece and Plaka, Greece as microscopic white needles.

Category	Arsenate Zinc minerals
Chemical Formula	$Zn_3(AsO_4)_2 \cdot 2H_2O$
Molar mass	510 g mol^{-1}
Color	Pale yellow to colorless; honey-yellow ; orange
Crystal habit	Acicular; Radial
Crystal system	Triclinic - Pinacoidal
Fracture	Brittle
Mohs scale hardness	2
Luster	Vitreous, waxy
Streak	White

Diaphaneity	Transparent
Specific gravity	4.28
Optical properties	Biaxial (+)
Refractive index	nα = 1.747 nβ = 1.753 nγ = 1.768

2 - Discovery :

Warikahnite was discovered by Clive Queit at Tsumeb mine and was first described in 1979 by Keller, Hess, and Dunn . The name "warikahnite" honors WAlter RIchard KAHN, who was born in 1911. He was from Bayersoien, Germany, and he was a dealer and collector that specialized in Tsumeb minerals . He was honored due to his support of research into rare secondary minerals. The type material is located at the University of Stuttgart, the Smithsonian Institution, and Harvard University.

3 - Chemical composition :

Warikahnite has the chemical formula $Zn_3(AsO_4)_2 \bullet 2H_2O$. Loss of water can occur at 365°C, and it can be dissolved by hot HCl or HNO_3.[4]

19 – Willemite

Willemite variety troostite from *New Jersey*

Willemite with *franklinite* from *New Jersey*

1 – Introduction :

Willemite is a zinc silicate mineral (Zn_2SiO_4) and a minor ore of zinc. It is highly fluorescent (green) under shortwave ultraviolet light. It occurs in all different colors in daylight, in fibrous masses, solid brown masses ("troostite"), and apple green gemmy masses . It was discovered in 1830 and named after William I of the Netherlands.

Category	Zinc Silicate mineral
Chemical Formula	Zn_2SiO_4
Color	Colorless to white, gray, flesh-red, dark brown, honey-yellow, apple-green, blue
Crystal habit	Fibrous, botryoidal to massive
Crystal system	Trigonal Rhombohedral 33
Fracture	Irregular to conchoidal
Mohs scale hardness	5.5
Luster	Vitreous to resinous
Diaphaneity	Transparent to opaque

Specific gravity	3.9 - 4.2
Optical properties	Uniaxial (+)
Refractive index	nω = 1.691 - 1.694 nε = 1.719 - 1.725
Other characteristics	Strongly fluorescent - may be phosphorescent

2 - Formation and associated minerals :

Willemite is usually formed as an alteration of previously existing sphalerite ore bodies, and is usually associated with limestone. It occurs in many places, but is best known from Arizona and the zinc, iron, manganese deposits at Franklin and Sterling Hill Mines in New Jersey. It often occurs with red zincite (zinc oxide) and franklinite $(Fe,Mn,Zn)(Fe,Mn)_2O_4$ (an iron rich zinc mineral occurring in sharp black isometric octahedral crystals and masses). Franklinite and zincite are not fluorescent.

3 – Uses :

Artificial willemite was used as the basis of first generation fluorescent tube phosphors. Doped with manganese-II, it fluoresces with a broad white emission band. Some versions had some of the zinc replaced with beryllium. In the 1940s it was largely replaced by the second generation halophosphors based on the fluorapatite structure. These, in turn have been replaced by the third generation TriPhosphors.

30 – Wurtzite

1 – Introduction :

Wurtzite is a zinc iron sulfide mineral ((Zn,Fe)S) a less frequently encountered mineral form of sphalerite. The iron content is variable up to eight percent. It is trimorphous with matraite and sphalerite.

It occurs in hydrothermal deposits associated with sphalerite, pyrite, chalcopyrite, barite and marcasite. It also occurs in low-temperature clay-ironstone concretions.

It was first described in 1861 for an occurrence in the San José Mine, Oruro City, Cercado Province, Oruro Department, Bolivia, and named for French chemist Charles-Adolphe Wurtz.[2] It has widespread distribution. In Europe it is reported from Příbram, Czech Republic; Hesse, Germany; and Liskeard, Cornwall, England. In the US it is reported from Litchfield County, Connecticut; Butte, Silver Bow County, Montana; at Frisco, Beaver County, Utah; and from the Joplin district, Jasper County, Missouri.

Category	Sulfide mineral
Chemical Formula	(Zn,Fe)S
Color	Brownish black, Orange brown, Reddish brown, Black.

Crystal habit	Radial clusters and colloform crusts and masses. Also as tabular crystals
Crystal system	Hexagonal dihexagonal pyramidal H-M symbol (6mm) Space group : $P6_3mc$
Fracture	Uneven - irregular
Mohs scale hardness	3.5 - 4
Luster	Resinous, brilliant submetallic on crystal faces
Streak	light brown
Diaphaneity	Translucent
Specific gravity	4.10
Optical properties	Uniaxial (+)
Refractive index	$n_\omega = 2.356$ $n_\varepsilon = 2.378$
Other characteristics	Nonmagnetic, non-radioactive

3 - Wurtzite structure :

The wurtzite group includes : Cadmoselite CdSe, Greenockite CdS, Mátraite ZnS and Rambergite MnS, in addition to wurtzite.

Its crystal structure is called the wurtzite crystal structure, to which it lends its name. This structure is a member of the hexagonal crystal system and consists of tetrahedrally coordinated zinc and sulfur atoms that are stacked in an ABABAB pattern.

The unit cell parameters of wurtzite are (-2H polytype):[2]

- $a = b = 3.82$ Å = 382 pm
- $c = 6.26$ Å = 626 pm
- $V = 79.11$ Å^3
- $Z = 2$

21 - Zinc chloride hydroxide monohydrate

Contents

1 – Introduction :

Zinc chloride hydroxide monohydrate is a zinc hydroxy compound with chemical formula $Zn_5(OH)_8Cl_2 \cdot H_2O$. It is often referred to as tetrabasic zinc chloride (TBZC), basic zinc chloride, zinc hydroxychloride, or zinc oxychloride. It is a colorless crystalline solid insoluble in water. Simonkolleite has been shown to be a desirable nutritional supplement for animals.

IUPAC name : Zinc chloride hydroxide monohydrate	
Other names : Tetrabasic zinc chloride hydrate , Basic zinc chloride , Zinc hydroxychloride, Zinc oxychloride , Micronutrients TBZC	

Molecular Formula	$Zn_5(OH)_8Cl_2 \cdot H_2O$
Molar Mass	552
Appearance	White crystalline solid
Density	3.3 g / cm^3
Solubility in water	Insoluble in water, pH 6.9
Solubility	Insoluble in organic solvents
Crystal structure	Hexagonal
Coordination geometry	Octahedral and Tetrahedral
Flash point	non flammable

2 - Natural occurrence :

The naturally occurring mineral form, *simonkolleite,* was described as a new mineral in 1985 for samples collected at Richelsdorf, Germany. It is a rare secondary mineral formed by weathering of zinc-bearing slag, and is associated with native zinc, hydrocerussite, diaboleite, zincite and hydrozincite. It is named after Werner Simon and Kurt Kolle, Mineral collectors of Cornberg, near Michelsdorf who submitted the samples for investigation. Simonkolleite is frequently found as a corrosion product of Zn-bearing metals.

3 – Structure :

Simonkolleite is rhombohedral, space group R3m. There are two crystallographically distinct zinc sites in Simonkolleite, both of which are fully occupied by zinc. The Zn (1) site is coordinated by six hydroxyl (OH) groups in an octahedral geometry [$Zn(OH)_6$]. The Zn(2) site is coordinated by three OH groups, and one Cl atom in a tetrahedral geometry [$Zn(OH)_3Cl$]. The [$Zn(OH)_6$] octahedra form an edge-sharing dioctahedral sheet similar to that observed in dioctahedral micas. On each site of the vacant octahedron, a [$Zn(OH)_3Cl$] tetrahedron is attached to three anions of the sheet and points away from the sheet. Intercalated between adjacent sheets are interstitial water (H_2O) groups. The sheets are held together by hydrogen bonding from OH groups of one sheet to Cl anions of adjacent sheets, and to interstitial H_2O groups. The $[Zn(OH)_6]$ octahedra have four long equatorial bonds (at 2.157Å) and two short apical bonds (at 2.066Å). This apical shortening is a result of the bond-valence requirements of the coordinating OH groups and the connectivity of polyhedra in the structure. The equatorial OH groups [O(1)H] are coordinated by two Zn(1) cations and one Zn(2) cation, whereas the apical OH groups [O(2)H] are coordinated by three Zn(1) cations. As Zn(1) is six-coordinated and Zn(2) is four-coordinated, the local bond-valence requirements require the Zn(1)-O(1) bonds to be considerably longer than the Zn(1)-O(2) bonds. The $[Zn(OH)_3Cl]$ tetrahedron has three short Zn(2)-O(1) bonds (at 1.950Å) and one long Zn(2)-Cl bond (2.312Å) (Figure 1) .

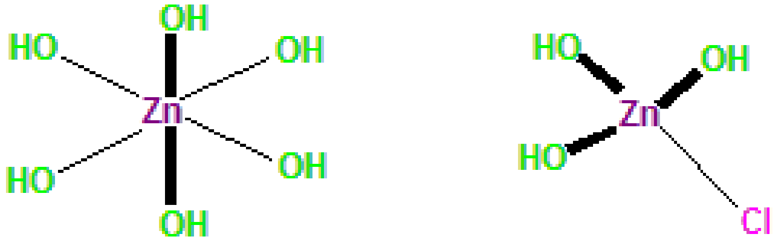


Figure 1. Zn coordination and bonding in Simonkolleite

4 – Properties :

Simonkolleite is colorless, forms tabular hexagonal crystal up to 1 mm in diameter, and has perfect cleavage parallel to (001).

Thermal stability studies have shown that simonkolleite decomposes to ZnO at several stages upon heating (eq. 1-3) . The decomposition starts with loss of a single mole of the lattice water. Further dehydration at 165 ~ 210 °C produces a mixture of ZnO and an intermediate Zn(OH)Cl. At 210 ~ 300 °C, the intermediate Zn(OH)Cl decomposes to ZnO and $ZnCl_2$. At higher temperature, volatilization of zinc chloride occurs, leaving a final residue of zinc oxide.

$$Zn_5(OH)_8Cl_2(H_2O) \xrightarrow{110 \sim 165\ ^{\circ}C} Zn_5(OH)_8Cl_2 + H_2O \qquad \text{(eq.1)}$$

$$Zn_5(OH)_8Cl_2 \xrightarrow{165 \sim 210\ ^{\circ}C} 2Zn(OH)Cl + ZnO + H_2O \qquad \text{(eq.2)}$$

$$2Zn(OH)Cl \xrightarrow{210 \sim 300\ ^{\circ}C} ZnCl_2 + ZnO + H_2O \qquad \text{(eq.3)}$$

Interestingly, the dehydrated mixture (Zn(OH)Cl and ZnO) is easily rehydrated and converted back to simonkoellete upon exposure to cool moist air (eq.4).

$$Zn_5(OH)_8Cl_2(H_2O) \underset{\text{Cool in moist air}}{\overset{180\ ^{\circ}C}{\rightleftharpoons}} 2Zn(OH)Cl + 3ZnO + 4H_2O \qquad \text{(eq.4)}$$

Simonkolleite is virtually insoluble in water and organic solvents, soluble in mineral acids yielding the corresponding zinc salts (eq. 5), soluble in ammonia, amine and EDTA solutions under complex formation. It can easily be converted to zinc hydroxide by reacting with sodium hydroxide (eq. 6). Its pH in water is 6.9 measured by EPA method SW846-9045.

$Zn_5(OH)_8Cl_2 \cdot (H_2O) + 8\ HCl \rightarrow 5ZnCl_2 + 9H_2O$ (eq.5)

$Zn_5(OH)_8Cl_2 \cdot (H_2O) + 2NaOH \rightarrow$
$5Zn(OH)_2 + 2NaCl + H_2O$ (eq.6)

5 - Preparation :

5 – 1 - From hydrolysis of $ZnCl_2$:

Basic zinc chloride can be prepared by hydrolysis of a $ZnCl_2$ solution in the presence of a base such as sodium hydroxide or ammonia (eq. 7- 8) .

$5ZnCl_2 + 8NaOH + H_2O \rightarrow Zn_5(OH)_8Cl_2 \cdot (H_2O) + 8NaCl$ (eq.7)

$5ZnCl_2 + 8NH_3 + 9H_2O \rightarrow Zn_5(OH)_8Cl_2 \cdot (H_2O) + 8NH_4Cl$ (eq.8)

Simonkolleite nonodisks with a width of 40 nm have been successfully synthesized via a hydrothermal method using zinc chloride and ammonia as the starting materials.

5 – 2 - From reaction of $ZnCl_2$ with ZnO :

Basic zinc chloride can be synthesized from the reaction of a $ZnCl_2$ solution with ZnO (eq.9).

$ZnCl_2 + 4ZnO + 5H_2O \rightarrow Zn_5(OH)_8Cl_2 \cdot (H_2O)$ (eq.9) can be synthesized from nano - sized ZnO particles aged in aqueous $ZnCl_2$ solution at 6 ~ 140 ^oC for 48h. Elevating the aging temperature increases the crystallinity of basic zinc chloride.

6 – Applications :

6 – 1 - As a feed additive and nutrition supplement for animals :

Zinc is an essential trace element for all animals. It is found in all organs and tissues of the body, with bone, muscle, liver, kidney, and skin accounting for the majority of body zinc. Zinc is commonly added to diets for animals in a supplemental form, usually as inorganic feed-grade zinc oxide or zinc sulfate hydrate, or one of the organic zinc chelates and complexes. In several experiments, zinc oxide has been shown to be less bioavailable for poultry and pigs than reagent - grade or feed - grade zinc sulfate; however, the sulfate forms are highly water soluble and thus also hygroscopic under humid conditions .

Tetrabasic zinc chloride (Simonkolleite) , a zinc hydroxy mineral, is a new form of zinc nutrition supplement for animals. When TBZC is made by a crystallization process (Micronutrients TBZC), it excludes contaminating ions, providing a product with greater purity and fewer dust particles than occurs with precipitation. The result is a crystalline solid that is essentially insoluble in water, non-hygroscopic, un-reactive in most foods or feedstuffs, and yet highly bioavailable.

Since TBZC is neutral and water insoluble, it has excellent palatability and very low interactions with other ingredients in a food mixture compared to zinc chloride, zinc sulfate or chelated forms of the metal. It also avoids the problems with caking.

It has been shown that the relative zinc bioavailability for chicks in TBZC is two to three times higher than that in Waselz-processed ZnO.

Research studies performed at universities and feed industry have all indicated that TBZC has a higher bioavailability relative to zinc sulfate, with values ranging from 102 to 111% . Four studies comparing TBZC to zinc oxide as a growth promoter all indicate improved weight gain and feed conversion at lower levels using TBZC . Testing in vitro has shown better antimicrobial activity with TBZC than both zinc sulfate and zinc oxide . Investigation on growth performance and some physiological parameters in the digestive tract of weanling piglets has shown that TBZC stimulated the synthesis and secretion of pancreatic chymotrypsin and may promote intestinal health.

6 – 2 - As a stabilizing agent in nutritional and fungicidal compositions :

Basic zinc chloride has been used as a stabilizing agent in nutritional and fungicidal compositions for application to the foliage of growing plants.

6 – 3 - As a Zn supplementation to metalloprotease therapy :

Tetrabasic zinc chloride has been used as a Zn supplementation for increasing responsiveness to therapeutic metalloproteases, including increasing and/or maximizing responsiveness and preventing botulinum and tetanus toxin resistance due to a functional deficiency of zinc.

6 – 4 - In oral compositions :

Basic zinc chloride has been used as a therapeutically active agent in oral compositions for the care of teeth.

6 – 5 - In coating compositions :

Basic zinc chloride, in combination with water - soluble alkali metal silicate, is used to coat substrates normally infested by algae, such as concrete roofing tiles and other silicate - containing building materials, to prevent or minimize algal infestation that imparts a dark, unsightly appearance .

A Zn-based plating layer formed by basic zinc chloride and Mg has been shown to display excellent corrosion resistance.

6 – 6 - In color development materials :

Basic zinc chloride is one of the three components to prepare color development materials used for pressure sensitive copying papers and thermo sensitive recording papers.

22 – Zincite

Natural crystalline zincite, Franklin, New Jersey

Zincite is the mineral form of zinc oxide (ZnO). Its crystal form is rare in nature; a notable exception to this is at the Franklin and Sterling Hill Mines in New Jersey, an area also famed for its many fluorescent minerals. It has a hexagonal crystal structure and a color that depends on the presence of impurities. The zincite found at Franklin Furnace is red - colored (mostly due to iron and manganese) and associated with willemite and franklinite.

Zincite crystals can be grown artificially, and synthetic zincite crystals are available as a by - product of zinc smelting. Synthetic crystals can be colorless or can range in color from dark red, orange, or yellow to light green.

Synthetic zincite crystals

Both natural and synthetic zincite crystals are significant for their early use as semiconductor crystal detectors in the early development of crystal radios before the advent of vacuum tubes. As an early radio detector it was used in conjunction with another mineral, chalcopyrite, and this combination was known as the cat's-whisker detector.

Category	Oxide mineral
Chemical Formula	(Zn , Mn) O
Color	Yellow - orange to deep red, rarely yellow, green, colorless
Crystal habit	Disseminated – occurs in small, distinct particles dispersed in matrix.
Crystal system	Hexagonal dihexagonal pyramidal 6 mm
Fracture	Conchoidal
Tenacity	Brittle
Mohs scale hardness	4
Luster	Subadamantine to resinous
Streak	Yellowish orange
Diaphaneity	Translucent, transparent in thin fragments
Specific gravity	5.64 – 5.68
Optical properties	Uniaxial (+)
Refractive index	$n_\omega = 2.013$, $n_\varepsilon = 2.029$

Zinc alloys

I . Brass
II . Nickel silver

I . Brass

Brass die, along with zinc and copper samples.

Contents

1 – Introduction :

Brass is an alloy of copper and zinc ; the proportions of zinc and copper can be varied to create a range of brasses with varying properties.

In comparison, bronze is principally an alloy of copper and tin. Bronze does not necessarily contain tin, and a variety of alloys of copper, including alloys with arsenic, phosphorus, aluminium, manganese, and silicon, are commonly termed "bronze". The term is applied to a variety of brasses and the distinction is largely historical .

Brass is a substitutional alloy. It is used for decoration for its bright gold-like appearance; for applications where low friction is required such as locks, gears, bearings, doorknobs, ammunition, and valves; for plumbing and electrical applications; and extensively in musical instruments such as horns and bells for its acoustic properties. It is also used in zippers. Because it is softer than most other metals in general use, brass is often used in situations where it is important that sparks not be struck, as in fittings and tools around explosive gases.

Brass has a muted yellow color which is somewhat similar to gold. It is relatively resistant to tarnishing, and is often used as decoration and for coins. In antiquity, polished brass was often used as a mirror.

2 - Lead content :

To enhance the mach inability of brass, lead is often added in concentrations of around 2 %. Since lead has a lower melting point than the other constituents of the brass, it tends to migrate towards the grain boundaries in the form of globules as it cools from casting. The pattern the globules form on the surface of the brass increases the available lead surface area which in turn affects the degree of leaching. In addition, cutting operations can smear the lead globules over the surface. These effects can lead to significant lead leaching from brasses of comparatively low lead content.

Silicon is an alternative to lead; however, when silicon is used in a brass alloy, the scrap must never be mixed with leaded brass scrap because of contamination and safety problems. b

In October 1999 the California State Attorney General sued 13 key manufacturers and distributors over lead content. In laboratory tests, state researchers found the average brass key, new or old, exceeded the California Proposition 65 limits by an average factor of 19, assuming handling twice a day. In April 2001 manufacturers agreed to reduce lead content to 1.5 %, or face a requirement to warn consumers about lead content. Keys plated with other metals are not affected by the settlement, and may continue to use brass alloys with higher percentage of lead content.

Also in California, lead-free materials must be used for "each component that comes into contact with the wetted surface of pipes and pipe fittings, plumbing fittings and fixtures." On January 1, 2010, the maximum amount of lead in "lead-free brass" in California was reduced from 4 % to 0.25 % lead. The common practice of using pipes for electrical grounding is discouraged, as it accelerates lead corrosion.

3 - Corrosion - resistant brass for harsh environments :

Brass sampling cock with stainless steel handle.

The so called dezincification resistant (DZR or DR) brasses are used where there is a large corrosion risk and where normal brasses do not meet the standards. Applications with high water temperatures, chlorides present or deviating water qualities (soft water) play a role. DZR-brass is excellent in water boiler systems. This brass alloy must be produced with great care, with special attention placed on a balanced composition and proper production temperatures and parameters to avoid long - term failures.

4 - Germicidal / antimicrobial applications :

The copper in brass makes brass germicidal. Depending upon the type and concentration of pathogens and the medium they are in, brass kills these microorganisms within a few minutes to eight hours of contact.

The bactericidal properties of brass have been observed for centuries and were confirmed in the laboratory in 1983. Subsequent experiments by research groups around the world reconfirmed the antimicrobial efficacy of brass, as well as copper and other copper alloys. Extensive structural membrane damage to bacteria was noted after being exposed to copper.

In 2007, U.S. Department of Defense's Telemedicine and Advanced Technologies Research Center (TATRC) began to study the antimicrobial properties of copper alloys, including four brasses (C87610, C69300, C26000, C46400) in a multi-site clinical hospital trial conducted at the Memorial Sloan-Kettering Cancer Center (New York City), the Medical University of South Carolina, and the Ralph H. Johnson VA Medical Center (South Carolina) . Commonly-touched items, such as bed rails, over-the-bed tray tables, chair arms, nurse's call buttons, IV poles, etc. were retrofitted with antimicrobial copper alloys in certain patient rooms (i.e., the "coppered" rooms) in the Intensive Care Unit (ICU). Early results disclosed in 2011 indicate that the coppered rooms demonstrated a 97% reduction in surface pathogens versus the non-coppered rooms. This reduction is the same level achieved by "terminal" cleaning regimens conducted after patients vacate their rooms. Furthermore, of critical importance to health care professionals, the preliminary results indicated that patients in the coppered ICU rooms had a 40.4 % lower risk of contracting a hospital acquired infection versus patients in non-coppered ICU rooms . The U.S. Department of Defense investigation contract, which is ongoing, will also evaluate the effectiveness of copper alloy touch surfaces to prevent the transfer of microbes to patients and the transfer of microbes from patients to touch surfaces, as well as the potential efficacy of copper - alloy based components to improve indoor air quality.

In the U.S., the Environmental Protection Agency regulates the registration of antimicrobial products. After extensive antimicrobial testing according to the Agency's stringent test protocols, 355 copper alloys, including many brasses, were found to kill more than 99.9 % of methicillin-resistant *Staphylococcus aureus* (MRSA), *E. coli* O157:H7, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Enterobacter aerogenes*, and vancomycin-resistant *Enterococci* (VRE) within two hours of contact. Normal tarnishing was found to not impair antimicrobial effectiveness.

Antimicrobial tests have also revealed significant reductions of MRSA as well as two strains of epidemic MRSA (EMRSA-1 and EMRSA-16) on brass (C24000 with 80 % Cu) at room temperature (22 degrees Celsius) within three hours. Complete kills of the pathogens were observed within 4 ½ hours. These tests were performed under wet exposure conditions. The kill timeframes, while impressive, are nevertheless longer than for pure copper, where kill timeframes ranged between 45 to 90 minutes.

A novel assay that mimics dry bacterial exposure to touch surfaces was developed because this test method is thought to more closely replicate real world touch surface exposure conditions. In these conditions, copper alloy surfaces were found to kill several million Colony Forming Units of *Escherichia coli* within minutes. This observation, and the fact that kill timeframes shorten as the percentage of copper in an alloy increases, is proof that copper is the ingredient in brass and other copper alloys that kills the microbes.

The mechanisms of antimicrobial action by copper and its alloys, including brass, is a subject of intense and ongoing investigation. It is believed that the mechanisms are multifaceted and include the following:

1) Potassium or glutamate leakage through the outer membrane of bacteria;

2) Osmotic balance disturbances;

3) Binding to proteins that do not require or utilize copper;

4) Oxidative stress by hydrogen peroxide generation.

Research is being conducted at this time to determine whether brass, copper, and other copper alloys can help to reduce cross contamination in public facilities and reduce the incidence of nosocomial infections (hospital acquired infections) in healthcare facilities.

Also, due to its antimicrobial / algaecidal properties that prevent bio fouling, in conjunction with its strong structural and corrosion-resistant benefits for marine environments, brass alloy netting cages are currently being deployed in commercial-scale aquaculture operations in Asia, South America, and the USA .

5 - Season cracking :

Cracking in brass caused by ammonia attack

Brass is susceptible to stress corrosion cracking, especially from ammonia or substances containing or releasing ammonia. The problem is sometimes known as season cracking after it was first discovered in brass cartridge cases used for rifle ammunition during the 1920s in the Indian Army. The problem was caused by high residual stresses from cold forming of the cases during manufacture, together with chemical attack from traces of ammonia in the atmosphere. The cartridges were stored in stables and the ammonia concentration rose during the hot summer months, so initiating brittle cracks. The problem was resolved by annealing the cases, and storing the cartridges else where.

6 - Brass types :

- **Admiralty brass** contains 30 % zinc, and 1% tin which inhibits dezincification in many environments.
- **Aich's alloy** typically contains 60.66 % copper, 36.58 % zinc, 1.02 % tin, and 1.74 % iron. Designed for use in marine service owing to its corrosion resistance, hardness and toughness. A characteristic application is to the protection of ships' bottoms,

but more modern methods of cathodic protection have rendered its use less common. Its appearance resembles that of gold.

- **Alpha brasses** with less than 35 % zinc, are malleable, can be worked cold, and are used in pressing, forging, or similar applications. They contain only one phase, with face - centered cubic crystal structure.
- **Prince's metal** or **Prince Rupert's metal** is a type of alpha brass containing 75 % copper and 25 % zinc. Due to its beautiful yellow color, it is used as an imitation of gold. The alloy was named after Prince Rupert of the Rhine.
- **Alpha-beta brass** (Muntz metal), also called **duplex brass**, is 35 – 45 % zinc and is suited for hot working. It contains both α and β' phase ; the β'-phase is body - centered cubic and is harder and stronger than α. Alpha-beta brasses are usually worked hot.
- **Aluminium brass** contains aluminium, which improves its corrosion resistance. It is used for seawater service and also in Euro coins (Nordic gold) .
- **Arsenical brass** contains an addition of arsenic and frequently aluminium and is used for boiler fireboxes.
- **Beta brasses**, with 45 – 50 % zinc content, can only be worked hot, and are harder, stronger, and suitable for casting.
- **Cartridge brass** is a 30 % zinc brass with good cold working properties. Used for ammunition cases.
- **Common brass**, or **rivet brass**, is a 37 % zinc brass, cheap and standard for cold working.
- **DZR brass** is dezincification resistant brass with a small percentage of arsenic.
- **Gilding metal** is the softest type of brass commonly available. An alloy of 95 % copper and 5 % zinc , gilding metal is typically used for ammunition "jackets", e.g. full metal jacket bullets.
- **High brass** contains 65 % copper and 35 % zinc, has a high tensile strength and is used for springs, screws, and rivets.
- **Leaded brass** is an alpha-beta brass with an addition of lead. It has excellent machine ability.

- **Lead - free brass** as defined by California Assembly Bill AB 1953 contains "not more than 0.25 percent lead content".
- **Low brass** is a copper - zinc alloy containing 20 % zinc with a light golden color and excellent ductility; it is used for flexible metal hoses and metal bellows.
- **Manganese brass** is a brass most notably used in making golden dollar coins in the United States. It contains roughly 70% copper, 29 % zinc, and 1.3 % manganese.
- **Muntz metal** is about 60 % copper, 40 % zinc and a trace of iron, used as a lining on boats.
- **Nickel brass** is composed of 70 % copper, 24.5 % zinc and 5.5% nickel used to make pound coins in the pound sterling currency.
- **Naval brass**, similar to admiralty brass, is 40% zinc and 1% tin.
- **Nordic gold**, used in 10 , 20 and 50 cts euro coins, contains 89 % copper, 5 % aluminium, 5 % zinc, and 1% tin.
- **Red brass** is both an American term for the copper-zinc-tin alloy known as gunmetal, and an alloy which is considered both a brass and a bronze. It typically contains 85 % copper, 5% tin, 5% lead, and 5 % zinc. Red brass is also an alternative name for *copper alloy C23000*, which is composed of 14 –16% zinc, 0.05% iron and lead, and the remainder copper. It may also refer to ounce metal, another copper-zinc-tin alloy.
- **Rich low brass** (Tombac) is 15 % zinc. It is often used in jewelry applications.
- **Tonval brass** (also called CW617N or CZ122 or OT58) is a copper-lead-zinc alloy. It is not recommended for seawater use, being susceptible to dezincification.
- **White brass** contains more than 50% zinc and is too brittle for general use. The term may also refer to certain types of nickel silver alloys as well as Cu – Zn - Sn alloys with high proportions (typically 40 % +) of tin and/or zinc, as well as predominantly zinc casting alloys with copper additive.
- **Yellow brass** is an American term for 33 % zinc brass.

7 – History :

Although forms of brass have been in use since prehistory , its true nature as a copper-zinc alloy was not understood until the post medieval period because the zinc vapor which reacted with copper to make brass was not recognized as a metal . The King James Bible makes many references to "brass". The Shakespearean English form of the word 'brass' can mean any bronze alloy, or copper, rather than the strict modern definition of brass. The earliest brasses may have been natural alloys made by smelting zinc-rich copper ores. By the Roman period brass was being deliberately produced from metallic copper and zinc minerals using the cementation process and variations on this method continued until the mid 19th century. It was eventually replaced by speltering, the direct alloying of copper and zinc metal which was introduced to Europe in the 16th century.

7 - 1 - Early copper zinc alloys :

In West Asia and the Eastern Mediterranean early copper zinc alloys are now known in small numbers from a number of third Millennium BC sites in the Aegean, Iraq, the United Arab Emirates, Kalmikia, Turkmenistan and Georgia and from 2nd Millennium BC sites in West India, Uzbekistan, Iran, Syria, Iraq and Palestine.[48] However, isolated examples of copper - zinc alloys are known in China from as early as the 5th Millennium BC.

The compositions of these early "brass" objects are very variable and most have zinc contents of between 5 % and 15% wt which is lower than in brass produced by cementation . These may be "natural alloys" manufactured by smelting zinc rich copper ores in reducing conditions. Many have similar tin contents to contemporary bronze arte facts and it is possible that some copper-zinc alloys were accidental and perhaps not even distinguished from copper. How ever the large number of copper-zinc alloys now known suggests that at least some were deliberately manufactured and many have zinc contents of more than 12 % wt which would have resulted in a distinctive golden color.

By the 8th–7th century BC Assyrian cuneiform tablets mention the exploitation of the "copper of the mountains" and this may refer to "natural" brass. *Oreichalkos*, the Ancient Greek translation of this term, was later adapted to the Latin *aurichalcum* meaning "golden copper" which became the standard term for brass. In the 4th century BC Plato knew *oreichalkos* as rare and nearly as valuable as gold and Pliny describes how *aurichalcum* had come from Cypriot ore deposits which had been exhausted by the 1st century AD.

7 - 2 - Brass making in the Roman World :

During the later part of first Millennium BC the use of brass spread across a wide geographical area from Britain and Spain in the west to Iran, and India in the east. This seems to have been encouraged by exports and influence from the Middle - East and eastern Mediterranean where deliberate production of brass from metallic copper and zinc ores had been introduced. The 4th century BC writer Theopompus , quoted by Strabo, describes how heating earth from Andeira in Turkey produced "droplets of false silver", probably metallic zinc, which could be used to turn copper into oreichalkos . In the 1st century BC the Greek Dioscorides seems to have recognised a link between zinc minerals and brass describing how Cadmia (zinc oxide) was found on the walls of furnaces used to heat either zinc ore or brass and explaining that it can then be used to make brass.[61]

By the first century BC brass was available in sufficient supply to use as coinage in Phrygia and Bithynia,[62] and after the Augustan currency reform of 23 BC it was also used to make Roman *dupondii* and *sestertii*. The uniform use of brass for coinage and military equipment across the Roman world may indicate a degree of state involvement in the industry, and brass even seems to have been deliberately boycotted by Jewish communities in Palestine because of its association with Roman authority.

Brass was produced by the cementation process where copper and zinc ore are heated together until zinc vapor is produced which reacts with the copper. There is good archaeological evidence for this process and crucibles used to produce brass by cementation have been found on Roman period sites including Xanten and Nidda in Germany, Lyon in France and at a number of sites in Britain. They vary in size from tiny acorn sized to large amphorae like vessels but all have elevated levels of zinc on the interior and are lidded. They show no signs of slag or metal prills suggesting that zinc minerals were heated to produce zinc vapor which reacted with metallic copper in a solid state reaction. The fabric of these crucibles is porous, probably designed to prevent a build up of pressure, and many have small holes in the lids which may be designed to release pressure or to add additional zinc minerals near the end of the process. Dioscorides mentioned that zinc minerals were used for both the working and finishing of brass, perhaps suggesting secondary additions.

Brass made during the early Roman period seems to have varied between 20 % to 28 % wt zinc . The high content of zinc in coinage and brass objects declined after the first century AD and it has been suggested that this reflects zinc loss during recycling and thus an interruption in the production of new brass . How ever it is now thought this was probably a deliberate change in composition and overall the use of brass increases over this period making up around 40 % of all copper alloys used in the Roman world by the 4th century AD.

7 - 3 - Brass making in the medieval period :

Baptism of Christ on the 12th century Baptismal font at St Bartholomew's Church, Liège.

Little is known about the production of brass during the centuries immediately after the collapse of the Roman Empire. Disruption in the trade of tin for bronze from Western Europe may have contributed to the increasing popularity of brass in the east and by the 6th –7th centuries AD over 90 % of copper alloy arte facts from Egypt were made of brass. However other alloys such as low tin bronze were also used and they vary depending on local cultural attitudes, the purpose of the metal and access to zinc, especially between the Islamic and Byzantine world . Conversely the use of true brass seems to have declined in Western Europe during this period in favour of gunmetals and other mixed alloys but by the end of the first Millennium AD brass arte facts are found in Scandinavian graves in Scotland , brass was being used in the manufacture of coins in Northumbria and there is archaeological and historical evidence for the production of brass in Germany and The Low Countries areas rich in calamine ore which would remain important centres of brass making throughout the medieval period , especially Dinant – brass objects are still collectively known as *dinanterie* in French. The Baptismal font at St Bartholomew's Church, Liège in modern Belgium (before 1117) is an outstanding masterpiece of Romanesque brass casting.

The cementation process continued to be used but literary sources from both Europe and the Islamic world seem to describe variants of a higher temperature liquid process which took places in open topped crucibles . Islamic cementation seems to have used zinc oxide known as *tutiya* or tutty rather than zinc ores for brass making resulting in a metal with lower iron impurities . A number of Islamic writers and the 13th century Italian Marco Polo describe how this was obtained by sublimation from zinc ores and condensed onto clay or iron bars, archaeological examples of which have been identified at Kush in Iran . It could then be used for brass making or medicinal purposes. In 10th century Yemen al - Hamdani described how spreading al - iglimiya, probably zinc oxide, onto the surface of molten copper produced tutiya vapor which then reacted with the metal. The 13th century Iranian writer al - Kashani describes a more complex process whereby *tutiya* was mixed with raisins and gently roasted before being added to the surface of the molten metal. A temporary lid was added at this point presumably to minimize the escape of zinc vapor.

In Europe a similar liquid process in open topped crucibles took place which was probably less efficient than the Roman process and the use of the term tutty by Albertus Magnus in the 13th century suggests influence from Islamic technology. The 12th century German monk Theophilus described how preheated crucibles were one sixth filled with powdered calamine and charcoal then topped up with copper and charcoal before being melted, stirred then filled again. The final product was cast, then again melted with calamine. It has been suggested that this second melting may have taken place at a lower temperature to allow more zinc to be absorbed . Albertus Magnus noted that the "power" of both calamine and tutty could evaporate and described how the addition of powdered glass could create a film to bind it to the metal. German brass making crucibles are known from Dortmund dating to the 10th century AD and from Soest and Schwerte in Westphalia dating to around the 13th century confirm Theophilus' account as they are open topped, although ceramic discs from Soest may have served as loose lids which may have been used to reduce zinc evaporation , and have slag on the interior resulting from a liquid process.

7 – 4 - Brass making in Renaissance and post medieval Europe :

The Renaissance saw important changes to both the theory and practice of brass making in Europe. By the 15th century there is evidence for the renewed use of lidded cementation crucibles at Zwickau in Germany . These large crucibles were capable of producing c.20 kg of brass . There are traces of slag and pieces of metal on the interior. Their irregular composition suggesting that this was a lower temperature not entirely liquid process . The crucible lids had small holes which were blocked with clay plugs near the end of the process presumably to maximize zinc absorption in the final stages . Triangular crucibles were then used to melt the brass for casting .

16th century technical writers such as Biringuccio , Ercker and Agricola described a variety of cementation brass making techniques and came closer to understanding the true nature of the process noting that copper became heavier as it changed to brass and that it became more golden as additional calamine was added . Zinc metal was also becoming more commonplace By 1513 metallic zinc ingots from India and China were arriving in London and pellets of zinc condensed in furnace flues at the Rammelsberg in Germany were exploited for cementation brass making from around 1550.

Eventually it was discovered that metallic zinc could be alloyed with copper to make brass; a process known as speltering and by 1657 the German chemist Johann Glauber had recognized that calamine was "nothing else but un melt able zinc" and that zinc was a "half ripe metal " . How ever some earlier high zinc, low iron brasses such as the 1530 Wightman brass memorial plaque from England may have been made by alloying copper with *zinc* and include traces of cadmium similar those found in some zinc ingots from China.

However the cementation process was not abandoned and as late as the early 19th century there are descriptions of solid state cementation in a domed furnace at around 900 – 950 degrees Celsius and lasting up to 10 hours. The European brass industry continued to flourish into the post medieval period buoyed by innovations such as the 16th century introduction of water powered hammers for the production of battery wares. By 1559 the Germany city of Aachen alone was capable of producing 300,000 cwt of brass per year . After several false starts during the 16th and 17th centuries the brass industry was also established in England taking advantage of abundant supplies of cheap copper smelted in the new coal fired reverberatory furnace . In 1723 Bristol brass maker Nehemiah Champion patented the use of granulated copper, produced by pouring molten metal into cold water . This increased the surface area of the copper helping it react and zinc contents of up to 33 % wt were reported using this new technique.

In 1738 Nehemiah's son William Champion patented a technique for the first industrial scale distillation of metallic zinc known as *distillation per descencum* or "the English process."[107][108] This local zinc was used in speltering and allowed greater control over the zinc content of brass and the production of high zinc copper alloys which would have been difficult or impossible to produce using cementation, for use in expensive objects such as scientific instruments, clocks, brass buttons and costume jewellery. How ever Champion continued to use the cheaper calamine cementation method to produce lower zinc brass and the archaeological remains of bee-hive shaped cementation furnaces have been identified at his works at Warmley . By the mid late 18th century developments in cheaper zinc distillation such as John-Jaques Dony's horizontal furnaces in Belgium and the reduction of tariffs on zinc as well as demand for corrosion resistant high zinc alloys increased the popularity of speltering and as a result cementation was largely abandoned by the mid 19th century.

II - Nickel Silver

"German silver" hair comb by Bruce Caesar (Pawnee), Oklahoma, 1984

Contents

1 – Introduction :

Nickel silver, also known as **German silver**, **Argentann**, **new silver**, **nickel brass**, **albata**, , or **alpacca**, is a copper alloy with nickel and often zinc. The usual formulation is 60 % copper , 20 % nickel and 20 % zinc. Nickel silver is named for its silvery appearance, but it contains no elemental silver unless plated. The name "German silver" refers to its development by 19th-century German metalworkers in imitation of the Chinese alloy known as **paktong** All modern, commercially important nickel silvers (such as those standardized under ASTM B122) contain significant amounts of zinc, and are sometimes considered a subset of brass.

2 – Uses :

Nickel silver first became popular as a base metal for silver-plated cutlery and other silver ware , notably the electro plated wares called EPNS (electro - plated nickel silver) . It is used in zippers, better-quality keys, costume jewellery , for making musical instruments (e.g., cymbals, saxophones), and is preferred for the track in electrically powered model railway layouts, as its oxide is conductive. It is widely used in the production of coins (e.g. Portuguese escudo and the former GDR marks) . Its industrial and technical uses include marine fittings and plumbing fixtures for its corrosion resistance, and heating coils for its high electrical resistance

In the 19th century, particularly after 1868, Plains Indian jewelers were able to easily acquire sheets of German silver. They used them to cut, stamp, and cold hammer a wide range of accessories and horse gear. Continuing into the present, Plains metalsmiths have used German silver for pendants, pectorals, bracelets, armbands, hair plates, *conchas*, earrings, belt buckles, necktie slides, stickpins, *dush-tuhs*, and tiaras . Nickel silver is the metal of choice among contemporary Kiowa and Pawnee metal smiths in Oklahoma.

Early in the twentieth century, German silver was used by automobile manufacturers before the advent of steel sheet metal, i.e., the famous Rolls Royce Silver Ghost of 1907. After about 1920, its use became widespread for pocketknife bolsters, due to its machine ability and corrosion resistance. Prior to this point, the most common metal was iron.

Musical instruments, including the flute, saxophone, trumpet, and French horn, can be made of nickel silver. For example, some leading saxophone manufacturers, such as Keilwerth , Selmer, P.Mauriat, Yanagisawa, and Yamaha, offer saxophones made of nickel silver, though these are far rarer than traditional brass bodied saxophones. It is said to produce a bright and powerful sound quality; an additional benefit is that nickel silver does not require a lacquer finish. It is the most commonly used material for woodwind keys. Most clarinets, oboes and similar wind instruments have nickel silver keys, normally silver plated. It is used to produce the tubes (called staples) onto which oboe reeds are tied. It was used in the construction of the National tri cone resophonic guitar. The frets of guitar, mandolin, banjo, bass, and related string instruments are typically made of nickel silver.

3 – Toxicity :

According to the *Merck Manual*, prolonged contact of copper alloys with acidic food or beverages (including boiling milk) can leach out the copper and cause toxicity. Long term, low doses can lead to cirrhosis.

4 – History :

Nickel silver was first known and used in China. It became known in the west from imported wares called *bai-tong* or *pakfong* (literally "white copper") , for which the silvery metal colour was used to imitate sterling silver. According to Berthold Laufer, it was identical with *khar sini*, one of the seven metals recognized by Jābir ibn Hayyān.

In the 18th century, researchers found it was a copper – nickel - zinc alloy . In 1770 the Suhl (Germany) metal works were able to produce a similar alloy. In 1823 a German competition was held to perfect the production process: the goal was to develop an alloy that possessed the closest visual similarity to silver. The brothers Henniger in Berlin and Ernst August Geitner in Schneeberg independently achieved this goal. The manufacturer Berndorf named the trademark brand *Alpacca*, which became widely known in northern Europe for nickel silver. About the same time in 1832, a form of German silver was also developed in Birmingham, England .

After 1840, the development of electroplating caused nickel silver to become widely used. It formed an ideal, strong and bright substrate for the plating process. It was also used un plated in applications such as cheaper grades of cutlery.

5 - Fraudulent uses :

Counterfeiters have used nickel silver to produce coins and medallions purporting to be silver rounds, generally in an attempt to trick unsuspecting buyers into paying prices based on the spot price of silver. The metal has also been used to produce counterfeit Morgan dollars.

Counterfeit Morgan Dollar (right) compared to a genuine American Silver Eagle (left)

Nickel silver fraud has included the production of replica bullion bars, marked "Nickel Silver" or "German Silver", in weights of one troy ounce. They are sold without notification that they contain no elemental silver.

Zinc Compounds

Contents

1 – Introduction :

Compounds of zinc are chemical compounds containing the element zinc which is a member of the group 12 of the periodic table. The oxidation state of most compounds is the group oxidation state of +2. Zinc may be classified as a post-transition main group element with zinc (II) having much chemical behaviour in common with copper (II). Many salts of zinc (II) are isomorphous with salts of magnesium (II) due to the ionic radii of the cations being almost the same. Zinc forms many complexes; metallo - proteins containing zinc are widespread in biological systems.

2 - General characteristics :

Zinc atoms have an electronic configuration of $[Ar]3d^{10}4s^2$. When compounds in the +2 oxidation state are formed the *s* electrons are lost, so the bare zinc ion has the electronic configuration $[Ar]3d^{10}$. This allows for the formation of four covalent bonds by accepting four electron pairs and thus obeying the octet rule. The stereochemistry is tetrahedral and the bonds may be described as being formed from sp^3 hybrid orbitals on the zinc ion. Examples occur in the oxide, ZnO, (calamine) and sulfide, ZnS, (zinc blende) in which the oxide and sulfide ions are also tetrahedrally bound to four zinc ions. Many complexes, such as $ZnCl_4^{2-}$, are tetrahedral.

Tetrahedrally coordinated zinc is found in metallo- enzymes such as carbonic anhydrase. However 6-coordinate complexes can also be formed by using empty 4d orbitals to form sp^3d^2 hybrid orbitals. The ion $[Zn(H_2O)_6]^{2+}$, which is present when a zinc salt is dissolved in water, has an octahedral structure.

Many zinc (II) salts are isomorphous (have the same type of crystal structure) with the corresponding salts of magnesium (II) which results from the fact that Zn^{2+} and Mg^{2+} have almost identical ionic radii. This comes about because of the d - block contraction. Whilst calcium is somewhat larger than magnesium, there is a steady decrease in size as atomic number increases from calcium to zinc. By chance it is the ionic radius of zinc that is almost equal to that of magnesium. In most other respects the chemistry of zinc(II) most closely resembles the chemistry of copper(II), its neighbour in the periodic table, in which there is less electron. However, whereas Cu^{2+} is classed as a transition metal ion by virtue of its electronic configuration, $[Ar]3d^9$, in which there is an incomplete *d*-shell, Zn^{2+} is best considered to be an ion of a post-transition main group element. The IUPAC periodic table places zinc in the d - block.

Some compounds with zinc in the oxidation state +1 are known. The compounds have the formula RZn_2R and they contain a Zn — Zn bond analogous to the metal-metal bond in mercury(I) ion, Hg_2^{2+}. In this respect zinc is similar to magnesium where low valent compounds containing a Mg — Mg bond have been characterized.

No compounds of zinc in oxidation states other than +1 or +2 are known. Calculations indicate that a zinc compound with the oxidation state of +4 is unlikely to exist . Although higher oxidation states are more stable with the heavier elements of a group, the compound HgF_4 was only characterized at 4 K in a neon/argon matrix

2 – 1 - Colour and magnetism :

Zinc compounds, like those of main group elements, are mostly colourless. Exceptions occur when the compound contains a coloured anion or ligand. Zinc selenide , Zn Se , however, is yellow, due to charge-transfer transitions and zinc telluride, ZnTe is brown for the same reason. Zinc oxide turns yellow when heated due to the loss of some oxygen atoms and formation of a defect structure.

Compounds containing zinc and no other metal are all diamagnetic.

3 - Reactivity of the metal :

Zinc is a strong reducing agent with a standard redox potential of -0.76 V. Pure zinc tarnishes rapidly in air, eventually forming a passive layer of basic zinc carbonate, $Zn_5(OH)_6CO_3$. The reaction of zinc with water is prevented by the passive layer. When this layer is penetrated by acids such as hydrochloric acid and sulfuric acid the reaction proceeds with the evolution of hydrogen gas.[1][10]

$$Zn(s) + 2H^+ (aq) \rightarrow Zn^{2+} (aq) + H_2 \uparrow$$

The hydrogen ion is reduced by accepting an electron from the reducing agent. The zinc metal is oxidized. Amalgamation with mercury, as in the Jones reductor also destroys the passive layer. Zinc reacts with alkalis as with acids. It reacts directly with oxidising non-metals such as chalcogens and halogens to form binary compounds.

4 - Binary compounds :

Zinc oxide, Zn O , is the most important manufactured compound of zinc, with a wide variety of uses.[2] It crystallizes with the Wurtzite structure. It is amphoteric , dissolving in acids to give the aqueous Zn^{2+} ion and in alkali to give the tetrahedral hydroxo complex, $[Zn(OH)_4]^{2-}$. Zinc hydroxide, $Zn(OH)_2$ is also amphoteric.

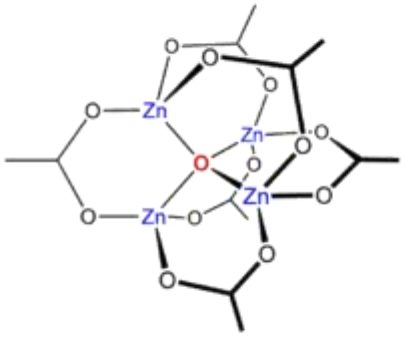
Zinc sulfide, ZnS , crystallizes in two closely related structures, the Zinc blende structure and the Wurtzite structure which are common structures of compounds with the formula MA. Both Zn and S are tetra hedrally coordinated by the other ion. A useful property of ZnS is its phosphorescence .The other chalcogenides, ZnSe, and ZnTe, have applications in electronics and optics.

Of the four halides ZnF_2 has the most ionic character, whereas the others, $ZnCl_2$, $ZnBr_2$, and ZnI_2, have relatively low melting points and are considered to have more covalent character . The pnictogenides Zn_3N_2 (notable for its high melting point) , Zn_3P_2, Zn_3As_2 and Zn_3Sb_2, have various applications . Other binary compounds of zinc include the peroxide ZnO_2 , the hydride ZnH_2, and the carbide ZnC_2.

4 – 1 - Salts :

The nitrate $Zn(NO_3)_2$ (used as oxidizing agent, the chlorate $Zn(ClO_3)_2$, the sulfate $ZnSO_4$ (known as "white vitriol"), the phosphate $Zn_3(PO_4)_2$ (used as primer pigment), the molybdate $ZnMoO_4$ (used as white pigment), , the chromate $ZnCrO_4$ (one of the few colored zinc compounds), the arsenite $Zn(AsO_2)_2$ (colorless powder) and the arsenate octa hydrate $Zn(AsO_4)_2$•$8H_2O$ (white powder, also referred to as koettigite are a few examples of other common inorganic compounds of zinc. The latter two compounds are both used in insecticides and wood preservatives . One of the simplest examples of an organic compound of zinc is the acetate $Zn(O_2CCH_3)_2$, which has several medicinal applications. Zinc salts are usually fully dissociated in aqueous solution. Exceptions occur when the anion can form a complex, such as in the case of zinc sulfate, where the complex $[Zn(H_2O)_n(SO_4)]$ may be formed, (log K = ca. 2.5) .

5 - Complexes :



Structure of solid basic zinc acetate, $[Zn_4(\mu^4\text{-}O)(\eta^2\text{-}O_2CCH_3)_6]$

The most common structure of zinc complexes is tetrahedral which is clearly connected with the fact that the octet rule is obeyed in these cases. Nevertheless, octahedral complexes comparable to those of the transition elements are not rare. Zn^{2+} is a class A acceptor in the classification of Ahrland, Chatt and Davies , and so forms stronger complexes with the first-row donor atoms oxygen or nitrogen than with second-row sulfur or phosphorus. In terms of HSAB theory Zn^{2+} is a hard acid.

In aqueous solution an octahedral complex, $[Zn(H_2O)_6]^{2+}$ is the predominant species . Aqueous solutions of zinc salts are mildly acidic because the aqua-ion is subject to hydrolysis with a $pK_a$of around 5, depending on conditions .

$$[Zn(H_2O)_6]^{2+} \rightleftharpoons [Zn(H_2O)_5(OH)]^{+} + H^{+}$$

Hydrolysis explains why basic salts such as basic zinc acetate and basic zinc carbonate, $Zn_3(OH)_4(CO_3).H_2O$ are easy to obtain. The reason for the hydrolysis is the high electrical charge density on the zinc ion, which pulls electrons away from an OH bond of a coordinated water molecule and releases a hydrogen ion. The polarizing effect of Zn^{2+} is part of the reason why zinc is found in enzymes such as carbonic anhydrase.

No fluoro complexes are known, but complexes with the other halides and with pseodo halides, $[ZnX_3]^-$ and $[ZnX_4]^{2-}$ can be prepared. The case of the thio cyanate complex illustrates the class A character of the zinc ion as it is the N-bonded isomer, $[Zn(NCS)_4]^{2-}$in contrast to $[Cd(SCN)_4]^{2-}$ which is S-bonded. Being a class-A acceptor does not preclude the formation of complexes with sulfur donors, as is shown by zinc dithiophosphate and the zinc finger complex (below).

The acetyla cetonate complex, $Zn(acac)_2$ is interesting. As the ligand is bi dentate a tetrahedral structure might be expected. However, the compound is in fact a trimer, $Zn_3(acac)_6$ in which each Zn ion is coordinated by five oxygen atoms in a distorted trigonal bi pyramidal structure . Other 5-coordinate structures can be engineered by choosing ligands which have specific stereo chemical requirements. For example, ter pyridine , which is a tridentate ligand forms the complex $[Zn(terpy)Cl_2]$. Another example would involve a tripodal ligand such as Tris(2-aminoethyl)amine. The compound zinc cyanide, $Zn(CN)_2$, is not 2-coordinate. It adopts a polymeric structure consisting of tetrahedral zinc centers linked by bridging cyanide ligands. The cyanide group shows head to tail disorder with any zinc atom having between 1 and 4 carbon atom neighbours and the remaining being nitrogen atoms. These two examples illustrate the difficulty of sometimes relating structure to stoichiometry.

A coordination number of 2 occurs in the amide $Zn(NR^1R^2)_2$ (R^1=CMe_3, R^2=$SiMe_3$); the ligand is so bulky that there is not enough space for more than two of them .

6 - Bio – complexes :

A very large number of metallo - enzymes contain zinc(II). Also many proteins contain zinc for structural reasons. The zinc ion is invariably 4-coordinate with at least three ligands that are amino-acid side-chains. The imidazole nitrogen of a histidine side-chain is a common ligand. The following are typical examples of the two kinds of zinc-protein complexes.

In the active site of resting Carbonic anhydrase a zinc ion is coordinated by three histidine residues. The fourth position is occupied by a water molecule, which is strongly polarized as in hydrolysis (see above). When carbon dioxide enters the active site, it subject to nucleophilic attack by the oxygen atom which carries a partial negative charge, or indeed a full negative charge if the water molecule is dissociated. The CO_2 is rapidly converted into a bicarbonate ion.

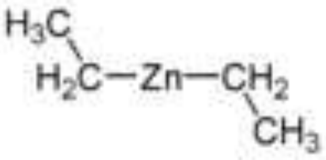
$$[(\text{-hys})_3Zn(H_2O)]^{2+} + CO_2 \rightarrow [(\text{-hys})_3Zn]^{2+} + HCO_3^- + H^+$$

Some peptidases , such as Glutamate carboxy peptidase II are thought to act in a similar way, with the zinc ion promoting the formation of a nucleophilic reagent.

The zinc finger motif is a rigid substructure in a protein which facilitates the binding of the protein to another molecule such as DNA. In this case all four coordination positions are occupied by the hystidine and cysteine residues. The tetrahedral geometry around the zinc ion constrains an α helix fragment and an anti parallel β sheet fragment to a particular orientation with respect to each other.

The magnesium ion, which has a higher concentration in biological fluids, cannot perform these functions as its complexes are much weaker than those of zinc.

7 - Organo metallic compounds



Diethylzinc

Organozinc compounds contain zinc — carbon covalent bonds. Diethylzinc ($(C_2H_5)_2Zn$) was first reported in 1848. It was made by reaction of zinc and ethyl iodide and is the first compound known to contain a metal — carbon sigma bond . For a long time it was a mystery why copper (II) did not form an analogous compound. It was not until the 1980s that the reason was found: the zinc compound does not undergo the Beta-hydride elimination reaction whereas the compound of the transition metal copper does so. Alkyl and aryl zinc compounds are contain the linear C — Zn — C motif. Because the zinc centre is coordinatively unsaturated the compound are powerful electrophiles . In fact the low-molecular weight compounds will ignite spontaneously on contact with air and are immediately destroyed by reaction with water molecules. The use of zinc alkyls has been largely superseded by the use of the more easily handled Grignard reagents. This demonstrates yet another connection between the chemistries of zinc and magnesium.

Zinc cyanide, $Zn\ (CN)_2$, is used as a catalyst in some organic reactions.

Organo metallic compounds of zinc (I) contain M — M bonds. deca methyl dizincocene is now known.

Zinc Acetate

Contents

1 – Introduction :

Zinc acetate is the chemical compound with the formula $Zn(O_2CCH_3)_2$, which commonly occurs as a dihydrate $Zn(O_2CCH_3)_2(H_2O)_2$. Both the hydrate and the anhydrous forms are colorless solids that are commonly used in chemical synthesis and as dietary supplements. Zinc acetates are prepared by the action of acetic acid on zinc carbonate or zinc metal. When used as a food additive, it has the E number E650.

IUPAC name : Zinc acetate	
Other names : Acetic acid Zinc salt , Acetic acid Zinc (II) salt , Di carbomethoxy zinc , Zinc diacetate	
Molecular Formula	$C_4H_{10}O_6Zn$ (dihydrate)
Molar mass	219.50 g / mol (dihydrate) 183.50 g / mol (anhydrous)
Appearance	White solid (all forms)

Density	1.735 g / cm^3 (dihydrate)
Melting Point	Decomposes 237 °C (dihydrate loses water at 100 °C)
Boiling Point	decomp.
Solubility in water	43 g /100 mL (20 °C, dehydrate)
Solubility	soluble in alcohol
Coordination geometry	Octa hedral (dihydrate)
Molecular shape	tetrahedral
Main hazards	mildly toxic

2 - Basic properties and structures :

The acetate group is capable of binding to metal ions in a variety of ways through its two oxygen atoms and several connectivities are observed for the various hydrates of zinc acetate. Anhydrous zinc acetate adopts a polymeric structure consisting of zinc coordinated to four oxygen atoms in a tetrahedral environment, each tetrahedron being connected to neighbors by the acetate groups. The acetate ligands are not bidentate. In contrast, most metal diacetates feature metals in octahedral coordination with bidentate acetate groups. In zinc acetate dihydrate the zinc is octahedral, wherein both acetate groups are bidentate.

2 – 1 - Basic zinc acetate :

Heating $Zn(CH_3CO_2)_2$ in a vacuum results in loss of acetic anhydride, leaving a residue of "basic zinc acetate," with the formula $Zn_4O(CH_3CO_2)_6$. This cluster compound has the tetrahedral structure shown below. This species closely resembles the corresponding beryllium compound, although it is slightly expanded with Zn-O distances ~1.97 vs ~1.63 Å for $Be_4O (OAc)_6$.

3 - Applications :

3 – 1 - Dietary and medicinal applications :

Zinc acetate is used as a dietary supplement and in lozenges used to treat the common cold. Zinc acetate alone is thought to be a more effective treatment than zinc gluconate.

Zinc acetate can also be used to treat zinc deficiencies. As an oral daily supplement it is used to inhibit the body's absorption of copper as part of the treatment for Wilson's disease. Zinc acetate is also sold as an astringent in the form of an ointment, a topical lotion; or combined with an antibiotic such as erythromycin for the topical treatment of acne. Furthermore Zinc acetate is commonly sold as a topical anti-itch ointment.

In chewing gum , zinc acetate is a breath freshener and plaque inhibitor .

3 – 2 - Industrial applications :

Industrial applications include wood preserving, manufacturing other zinc salts, polymers, manufacture of ethylene acetate, as a dye mordant, and analytical reagent.

Zinc acetate is a precursor via a sol - gel route to the transparent semi conductor zinc oxide.

Zinc Ammonium Chloride

Zinc ammonium chloride is commonly known as Flux, and is used for galvanizing steel. It is 60 % ammonium chloride and 40 % zinc chloride in it. The pH of zinc ammonium chloride should be 4.2.

Zinc ammonium chloride is not to be confused with zinc ammonium carbonate.

Zinc ammonium chloride is not necessarily 60:40 ratio of Ammonium chloride and Zinc Chloride as stated by the writer above. The ratio is varied as per type of usage for the flux. However 60:40 is a more running grade of zinc ammonium chloride. Apart from ammonium chloride and zinc chloride, it also contains galvanizing additives like glycerol, sodium dichromate, borax, etc. For a good write up of zinc ammonium chloride one may visit Zinc Ammonium Chloride Flux

Zinc Borate

Zinc borate is an inorganic compound, a borate of zinc. It is a white crystalline or amorphous powder insoluble in water. Its toxicity is low. Its melting point is 980 °C.

Several variants of zinc borate exist, differing by the zinc / boron ratio and the water content :

- Zinc borate Fire brake ZB ($2ZnO \cdot 3\ B_2O_3 \cdot 3.5H_2O$),
- Zinc borate Fire brake 500 ($2ZnO \cdot 3\ B_2O_3$),
- Zinc borate Fire brake 415 ($4ZnO \cdot B_2O_3 \cdot H_2O$),
- ZB-467 ($4ZnO \cdot 6B_2O_3 \cdot 7H_2O$),
- ZB-223 ($2ZnO \cdot 2B_2O_3 \cdot 3H_2O$),

The hydrated variants lose water between 290 – 415 °C.

Zinc borate is primarily used as a flame retardant in plastics and cellulose fibers, paper, rubbers and textiles. It is also used in paints, adhesives, and pigments. As a flame retardant, it can replace antimony trioxide as a synergist in both halogen - based and halogen-free systems . It is an anti - dripping and char - promoting agent, and suppresses the afterglow. In electrical insulator plastics it suppresses arcing and tracking.

In halogen - containing systems, zinc borate is used together with antimony trioxide and alumina tri hydrate. It catalyzes formation of char and creates a protective layer of glass. Zinc catalyzes the release of halogens by forming zinc halides and zinc oxy halides.

In halogen - free system, zinc borate can be used together with alumina tri hydrate, magnesium hydroxide, red phosphorus, or ammonium poly phosphate. During burning the plastics, a porous borate ceramics is formed that protects the underlying layers. In presence of silica, borosilicate glass can be formed at plastic burning temperatures.

Zinc borate is used in poly vinyl chloride , poly olefins, poly amides, epoxy resins, poly esters, thermoplastic elastomers , rubbers, etc. It is also used in some intumescent systems.

Zinc borate has synergistic effect with zinc phosphate or barium borate as a corrosion inhibitor pigment.

Zinc borate acts as a broad - spectrum fungicide in plastics and wood products.

Zinc borate can be used as a flux in some ceramics. In electrical insulators it improves the ceramics properties.

Nano powder zinc borate can be used for the applications above, and also for improving the frictional properties of lubricating oils.

Zinc Bromide

1 – Introduction :

Zinc bromide ($ZnBr_2$) is a chemical compound of zinc and bromine. Its shares many properties with zinc chloride, $ZnCl_2$, namely a high solubility in water forming acidic solutions, and solubility in organic solvents. It is hygroscopic and forms a hydrate $ZnBr_2.2H_2O$. $ZnBr_2$ can be prepared by reacting (double displacement) barium bromide and zinc sulfate to produce the insoluble barium sulfate along with zinc bromide or the reaction of HBr and zinc metal :

$$BaBr_2 + ZnSO_4 \rightarrow BaSO_4 + ZnBr_2$$
$$Zn + 2\,HBr \rightarrow ZnBr_2 + H_2$$

The structure of crystalline $ZnBr_2$ has the same unusual structure as ZnI_2. Zinc atoms are tetra hedrally coordinated, and groups of four of these tetra hedra share three vertices to form “super- tetra hedra” of composition $\{Zn_4Br_{10}\}$, which are linked by their vertices to form a three dimensional structure. Molecular, vapour phase, $ZnBr_2$ is linear in accordance with VSEPR theory with a Zn-Br bond length of 221 pm . The di hydrate $ZnBr_2.2H_2O$ also has a usual structure and should be formulated as $Zn(H_2O)_6\ Zn_2Br_6$, where the $Zn_2Br_6^{2-}$ ion has bromine bridges linking the two zinc atoms, and has a similar structure to the dimeric form of aluminium bromide, Al_2Br_6 .

IUPAC name : Zinc bromide	
Other names : Zinc (II) bromide , Zinc di bromide	
Molecular Formula	$ZnBr_2$
Molar Mass	225 g / mol
Appearance	white crystalline powder hygroscopic
Density	4.20 g / cm^3 (20 °C) 4.22 g / cm^3 (25 °C)

Melting point	394 °C
Boiling point	697 °C
Solubility in water	311 g / 100 mL (0 °C) 447 g / 100 mL (20 °C) 538 g / 100 mL (100 °C)
Solubility	very soluble in alcohol , ether , acetone , tetra hydro furan
Refractive index (n_D)	1.5452
EU Index	Not listed
Flash point	Non - flammable

2 - Uses

- Organic chemistry as a Lewis acid.
- As a transparent shield against radiation . Two glass panes filled with a strong aqueous solution of zinc bromide has a very high density, which can then be used as a window on a hot cell. This type of window has the advantage over lead glass in that it will not darken as a result of exposure to radiation. All glass will darken slowly over time due to radiation, however this is especially true in a hot cell, where exceptional levels of radiation are present. The advantage of an aqueous salt solution is that any radiation damage will last less than a millisecond, so the shield will undergo self-repair.
- The Zinc bromide battery .
- Used in oil and natural gas wells to displacing drilling mud when transitioning from the drilling phase to the completion phase or in well work over operations. The extremely heavy dense brine solution gives the fluid it's weight of 20 pounds/gallon, which makes it especially useful in holding back flammable oil and gas particles in high pressure wells. How ever, the high acidity and osmilarity cause high corrosion and handling problems. Crews must be issued slicker suits and rubber boots because the salt in the fluid removes water from live tissue, leather boots, and gloves via osmosis. The HSE concerns must be weighed carefully against it's advantages when using this fluid.

Zinc Chlorate

Zinc chlorate ($Zn(ClO_3)_2$) is an inorganic chemical compound used as a oxidizing agent in explosives.

IUPAC Name : Zinc chlorate	
Other Names : Chloric acid zinc salt	
Molecular Formula	$Zn(ClO_3)_2$
Molar Mass	232 g / mol
Appearance	Yellow hygroscopic crystals
Density	2.15 g / cm^3
Melting point	60°C (decomposes)
Solubility in water	200 g / 100 mL (20 °C)

Zinc Chloride

Contents

1 – Introduction :

Zinc chloride is the name of chemical compound with the formula $ZnCl_2$ and its hydrates. Zinc chlorides, of which nine crystalline forms are known, are colorless or white and highly soluble in water. $ZnCl_2$ itself is hygroscopic and even deliquescent. Samples should there fore be protected from sources of moisture , including the water vapor present in ambient air. Zinc chloride finds wide application in textile processing, metallurgical fluxes, and chemical synthesis. No mineral with this chemical composition is known although a very rare mineral, simonkolleite , $Zn_5(OH)_8Cl_2 \cdot H_2O$, is known.

Other Names	*Zinc (II) chloride* *Zinc dichloride* *Butter of zinc*
Molecular Formula	$ZnCl_2$
Molar mass	*136.5 g / mol*
Appearance	*White crystalline solid hygroscopic*

Odor	*Odorless*
Density	*2.907 g / cm^3*
Melting Point	*292 °*
Boiling Point	*756 °C*
Solubility in Water	*432 g / 100 mL (25 °C)*
Solubility	*soluble in ethanol , glycerol and acetone*
Solubility in alcohol	*430 g / 100 mL*
Crystal structure	*Four forms known : hexagonal δ - form is most stable when anhydrous*
EU classification	*Harmful (Xn)* *Corrosive (C)* *Dangerous for the environment (N)*
LD50	*350 mg / kg , rat (oral)*

2 - Structure and properties :

Four crystalline forms, (polymorphs) , of $Zn\ Cl_2$ are known, and in each case the Zn^{2+} ions are trigonal planar coordinated to four chloride ions . The pure anhydrous orthorhombic form rapidly changes to one of the other forms on exposure to the atmosphere and a possible explanation is that the presence of OH^{-} facilitates the rear rangement . Rapid cooling of molten $Zn\ Cl_2$ gives a glass, that is, a rigid amorphous solid and this ability has been related to the structure in the melt .

The covalent character of the anhydrous material is indicated by its relatively low melting point of 275 °C . Further evidence for covalency is provided by the high solubility of the dichloride in ethereal solvents where it forms adducts with the formula $Zn\ Cl_2\ L_2$, where L = ligand such as $O\ (\ C_2H_5\ )_2$. In the gas phase , $Zn\ Cl_2$ molecules are linear with a bond length of 205 pm .

Molten $Zn\ Cl_2$ has a high viscosity at its melting point and a comparatively low electrical conductivity that increases markedly with temperature . A raman spectra study of the melt indicated the presence of polymeric structures and a neutron scattering study indicated the presence of tetrahedral { $Zn Cl_4$ } complexes .

2 – 1 : Hydrates

Five hydrates of zinc chloride are known , $Zn Cl_2 (H_2O)_n$ where n = 1, 1.5, 2.5, 3 and 4 . The tetra hydrate $Zn Cl_2(H_2O)_4$ crystallizes from aqueous solutions of zinc chloride .

3 - Preparation and Purification

Anhydrous $ZnCl_2$ can be prepared from zinc and hydrogen chloride .

$$Zn + 2 HCl \rightarrow ZnCl_2 + H_2$$

Hydrated forms and aqueous solutions may be readily prepared similarly by treating Zn metal with hydrochloric acid. Zinc oxide and zinc sulfide react with HCl :

$$Zn S (s) + 2 H Cl \rightarrow Zn Cl_2 (aq) + H_2 S (g)$$

Unlike many other elements, zinc essentially exists in only one oxidation state, 2+ , which simplifies purification of the chloride .

Commercial samples of zinc chloride typically contain water and products from hydrolysis as impurities. Such samples may be purified by recrystallization from hot dioxane . Anhydrous samples can be purified by sublimation in a stream of hydrogen chloride gas, followed by heating the sub mlimate to 400 °C in a stream of dry nitrogen gas . Finally, the simplest method relies on treating the zinc chloride with thionyl chloride.

4 - Reactions

Molten anhydrous $Zn Cl_2$ at 500 - 700 °C dissolves zinc metal and on rapid cooling of the melt a yellow diamagnetic glass is formed which Raman studies indicate contain the Zn_2^{+2} ion .

A number of salts containing the tetra chloro zincate anion, $Zn\ Cl_2^{-4}$, are known. " Caulton's reagent ," $V_2\ Cl_3$ (thf $)_6$ $Zn_2\ Cl_6$ is an example of a salt containing $Zn_2\ Cl_2^{-6}$. The compound $Cs_3\ Zn\ Cl_5$ contains tetra hedral $Zn\ Cl_2^{-4}$ and Cl^- anions . No compounds containing the $Zn\ Cl_4^{-6}$ ion have been characterized.

Whilst zinc chloride is very soluble in water, solutions cannot be considered to contain simply solvated Zn^{2+} ions and Cl^- ions, $Zn\ Cl_x\ H_2O_{(4-x)}$ species are also present .

Aqueous solutions of $Zn\ Cl_2$ are acidic : a 6 M aqueous solution has a pH of 1. The acidity of aqueous $Zn\ Cl_2$ solutions relative to solutions of other Zn^{2+} salts is due to the formation of the tetrahedral chloro aqua complexes where the reduction in coordination number from 6 to 4 further reduces the strength of the O - H bonds in the solvated water molecules .

In alkali solution in the presence of OH^- ion various zinc hydroxy chloride anions are present in solution . e.g : $Zn\ OH_3\ Cl^{2-}$, $Zn\ OH_2\ Cl_2^{-2}$, $Zn\ OH\ Cl_2^{-3}$, and $Zn_5\ OH_2\ Cl_3 \cdot H_2O$ (simonkolleite) precipitates .

When ammonia is bubbled through a solution of zinc chloride the hydroxide does not precipitate , instead compounds containing complexed ammonia (ammines) are produced , $Zn\ (NH_3)_4\ Cl_2 \cdot H_2O$ and on concentration $Zn\ Cl_2\ (\ NH_3\ )_2$.

The former contains the $Zn\ (NH_3)_6^{\ 2+}$ ion and the latter is molecular with a distorted tetra hedral geometry . The species in aqueous solution have been investigated and show that $Zn\ (NH_3)_4^{\ 2+}$ is the main species present with $Zn\ (NH_3)_3\ Cl^+$ also present at lower NH_3 : Zn ratio .

Aqueous zinc chloride reacts with zinc oxide to form an amorphous cement which was first investigated in the 1855 by Sorel,who later he went on to investigate the related magnesium oxychloride cement which bears his name .

When hydrated zinc chloride is heated , one obtains a residue of Zn (OH) Cl e.g :

$$\text{Zn Cl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Zn Cl (OH)} + \text{HCl} + \text{H}_2\text{O}$$

The compound $Zn\ Cl_2 \cdot ½\ HCl \cdot H_2O$ may be prepared by careful precipitation from a solution of $Zn\ Cl_2$ acidified with HCl and it contains a polymeric anion $(Zn_2Cl_5^{\,-})_n$ with balancing mono hydrated hydronium ions , $H_5\ O_2^+$ ions .

The formation of highly reactive anhydrous HCl gas formed when zinc chloride hydrates are heated is the basis of qualitative inorganic spot tests . The use of zinc chloride as a flux , some times in a mixture with ammonium chloride, involves the production of HCl and its subsequent reaction with surface oxides. Zinc chloride forms two salts with ammonium chloride, $(NH_4)\ Zn\ Cl_4$ and $(NH_4)_3\ Cl\ Zn\ Cl_4$, which decompose on heating liberating HCl just as zinc chloride hydrate does. The action of zinc chloride/ammonium chloride fluxes, for example, in the hot dip galvanizing process produces H_2 gas and ammonia fumes .

Cellulose dissolves in aqueous solutions of $Zn\ Cl_2$ and zinc - cellulose complexes have been detected . Cellulose also dissolves in molten $Zn\ Cl_2$ hydrate and carboxylation and acetylation performed on the cellulose polymer .

Thus, although many zinc salts have different formulas and different crystal structures, these salts behave very similarly in aqueous solution. For example, solutions prepared from any of the polymorphs of $Zn\ Cl_2$ as well as other halides (bromide , iodide) and the sulfate can often be used interchangeably for the preparation of other zinc compounds . Illustrative is the preparation of zinc carbonate :

$$\text{Zn Cl}_2\text{ (aq)} + \text{Na}_2\text{ CO}_3\text{ (aq)} \rightarrow \text{Zn CO}_3\text{ (s)} + 2\text{ NaCl (aq)}$$

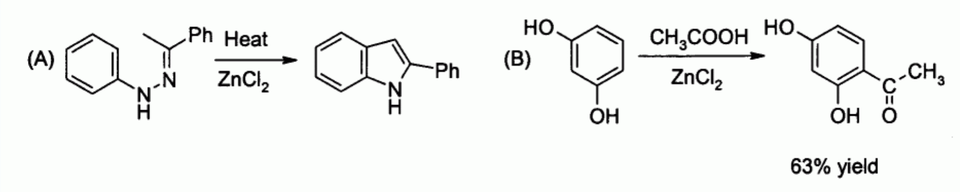
5 - Applications

5 – 1 : As a metallurgical flux

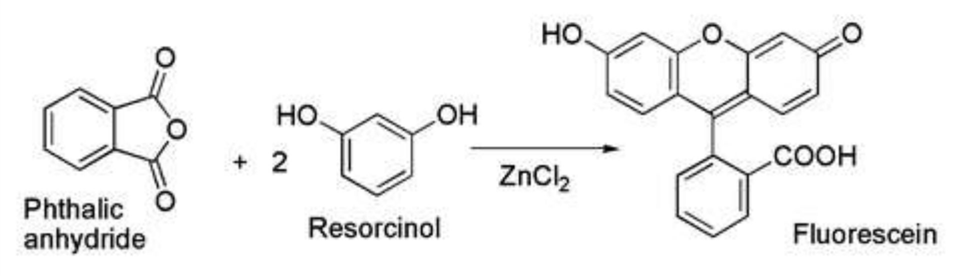
Zinc chloride has the ability to attack metal oxides (MO) to give derivatives of the formula M Zn O Cl_2 . This reaction is relevant to the utility of Zn Cl_2 as a flux for soldering - it dissolves oxide coatings exposing the clean metal surface . Fluxes with Zn Cl_2 as an active ingredient are some times called " Tinner's Fluid ". Typically this flux was prepared by dissolving zinc foil in dilute hydro chloric acid until the liquid ceased to evolve hydrogen ; for this reason , such flux was once known as **killed spirits** . Because of its corrosive nature, this flux is not suitable for situations where any residue cannot be cleaned away, such as electronic work. This property also leads to its use in the manufacture of magnesia cements for dental fillings and certain mouthwashes as an active ingredient.

5 – 2 : In organic synthesis

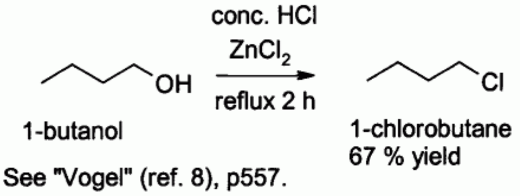
In the laboratory, zinc chloride finds wide use, principally as a moderate - strength Lewis acid . It can catalyse (A) the Fischer indole synthesis , and also (B) Friedel - Crafts acylation reactions involving activated aromatic rings ·



Related to the latter is the classical preparation of the dye fluorescein from phthalic anhydride and resorcinol, which involves a Friedel - Crafts acylation . This transformation has in fact been accomplished using even the hydrated Zn Cl_2 sample shown in the picture above .

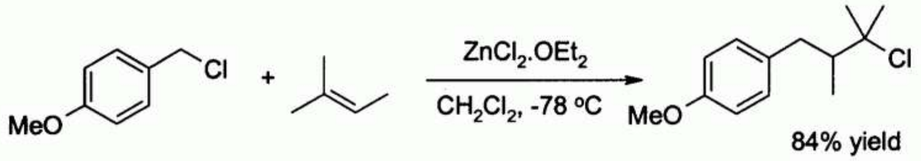


Hydro chloric acid alone reacts poorly with primary alcohols and secondary alcohols , but a combination of HCl with $ZnCl_2$ (known together as the " Lucas reagent ") is effective for the preparation of alkyl chlorides. Typical reactions are conducted at 130 °C. This reaction probably proceeds via an S_N2 mechanism with primary alcohols but S_N1 pathway with secondary alcohols .



See "Vogel" (ref. 8), p557.

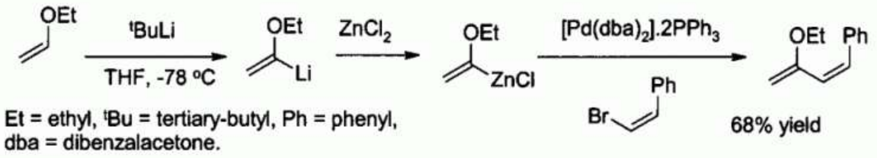
Zinc chloride also activates benzylic and allylic halides towards substitution by weak nucleophiles such as alkenes :



E. Bauml et al., Tetrahedron Letters, 29, 6925 (1988)

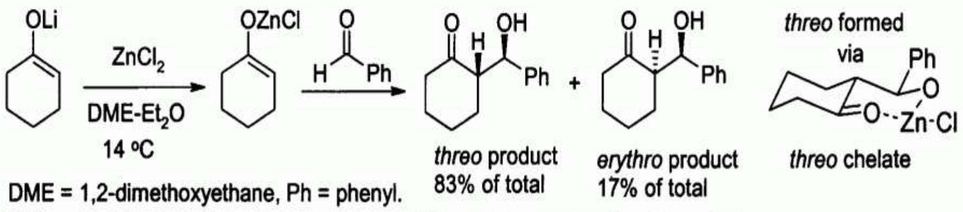
In similar fashion, Zn Cl_2 promotes selective Na B H_3 CN reduction of tertiary , allylic or benzylic halides to the corresponding hydrocarbons .

Zinc chloride is also a useful starting reagent for the synthesis of many organozinc reagents, such as those used in the palladium catalysed Negishi coupling with aryl halides or vinyl halides . In such cases the organozinc compound is usually prepared by transmetallation from an organolithium or a Grignard reagent, for example :



Et = ethyl, tBu = tertiary-butyl, Ph = phenyl, dba = dibenzalacetone.

Zinc enolates , prepared from alkali metal enolates and $ZnCl_2$, provide control of stereochemistry in aldol condensation reactions due to chelation on to the zinc . In the example shown below, the *threo* product was favored over the *erythro* by a factor of 5 : 1 when $ZnCl_2$ in DME / ether was used . The chelate is more stable when the bulky phenyl group is pseudo-equatorial rather than pseudo-axial, i.e., *threo* rather than *erythro*.



DME = 1,2-dimethoxyethane, Ph = phenyl.

Without $ZnCl_2$, the lithium enolate gives roughly equal amounts of each product.

H. O. House et al., *Journal of the American Chemical Society*, **95**, 3310 (1973).

5 – 3 : In textile processing

Concentrated aqueous solutions of zinc chloride (more than 64 % weight / weight zinc chloride in water) have the interesting property of dissolving starch , silk , and cellulose . Thus , such solutions cannot be filtered through standard filter papers. Relevant to its affinity for these materials , $ZnCl_2$ is used as a fire proofing agent and in fabric " refresheners " such as Febreze .

5 – 4 : Smoke bombs

Smoke bombs (" HC ") contain zinc oxide and hexa chloro ethane which when ignited react to form zinc chloride smoke .

5 – 5 : Finger print detection :

Ninhydrin reacts with amino acids and amines to form a coloured compound “ Ruhemann’s purple ” (RP) . Spraying with a zinc chloride solution forms a 1 : 1 complex (RP) $ZnCl(H_2O)_2$ which is more readily detected as it fluoresces better than Ruhemann’s purple .

5 – 6 : Disinfectant

Historically a dilute aqueous solution of zinc chloride was used as a disinfectant under the name " Burnett ' s Disinfecting Fluid " .

6 - Safety considerations

Zinc chloride is a skin and respiratory irritant according to its MSDS . Precautions that apply to anhydrous $Zn Cl_2$ are those applicable to other anhydrous metal halides, i.e . hydrolysis can be exothermic and contact should be avoided. Concentrated solutions are acidic and corrosive and specifically attack cellulose and silk as Lewis acids .

Zinc chromate

B-25 Mitchell bombers, painted with Zinc Chromate undercoat, being assembled, 1942

Zinc chromate, $Zn\,Cr\,O_4$, is a chemical compound containing the chromate anion, appearing as odorless yellow solid powder. It is used industrially in chromate conversion coatings, having been developed by Ford Motor Company in 1920s. Exposure to zinc chromate can cause tissue ulceration and cancer.

Its use as a corrosion resistant agent was applied to aluminium alloy parts first in commercial aircraft, and then in military ones. During the 1940 and 1950s it was typically found as the "paint" in the wheel wells of retractable landing gear on U.S. military aircraft, not because of its glaring yellow-green color symbolizing anything, but to protect the aluminium from corrosion.

When used as a pigment, it is known as Zinc Yellow, Buttercup Yellow or Yellow 36 . It is rarely used in art anymore.

Zinc chromate putty was used as sealant in addition to two O-rings between sections of the failed solid rocket booster on Space Shuttle Challenger, contributing to the loss of the shuttle.

IUPAC Name : Zinc chromate	
Molecular Formula	$Zn\,Cr\,O_4$
Molar Mass	181.5 g / mol
Appearance	Yellow - green crystals
Density	3.43 g / cm^3

Melting Point	316 °C
Boiling Point	732 °C
Solubility in water	insoluble
Hazards	
EU classification	not listed
U.S. Permissible exposure limit (PEL)	0.1 mg / m^3
LD_{50}	0.5 to 5 g/kg

Zinc cyanide

Contents

1 – Introduction :

Zinc cyanide is the inorganic compound with the formula Zn(CN)$_2$. It is a white solid that is used mainly for electroplating zinc but also has more specialized applications for the synthesis of organic compounds.

Molecular Formula	$C_2 N_2 Zn$
Molar mass	117.5 g / mol
Appearance	white powder
Density	1.852 g / cm^3, solid
Melting point	800 °C (decomposes)
Solubility in water	0.00005 g / 100 mL (20 °C)
Solubility	attacked by alkalies , KCN , ammonia
Hazards	
EU classification	not listed
LD$_{50}$	100 mg / kg, rat (intra peritoneal)

2 - Structure , properties , synthesis :

The structure features the zinc in the familiar tetrahedral coordination environment, all linked by bridging cyanide ligands. The structure consists of two "interpenetrating" structures. Such motifs are sometimes called "expanded diamondoid" structures because the interconnecting atoms are tetrahedral but instead of being directly linked as in diamond, the atoms are separated by additional bonds. Some forms of Si O$_2$ adopts a similar structures, wherein the tetrahedral Si centres are linked by oxides. The cyanide group shows head to tail disorder with any zinc atom having between 1 and 4 carbon neighbors , and the remaining being nitrogen atoms. It shows one of the largest negative coefficients of thermal expansion (exceeding the previous record holder, zirconium tungstate).

Typical for an inorganic polymer, $Zn(CN)_2$ is insoluble in most solvents. The solid dissolves in, or more precisely, is degraded by, aqueous solutions of basic ligands such as hydroxide, ammonia, and additional cyanide to give anionic complexes.

$Zn(CN)_2$ is fairly easy to make because combining aqueous solutions of cyanide and zinc ions. For commercial applications, some effort is made to avoid halide impurities by using zinc acetates.[1] Zinc cyanide is a byproduct of certain gold extraction methods. To isolate gold from aqueous gold cyanide, some procedures call for the addition of zinc:

$$2\ [Au(CN)_2]^- + Zn \rightarrow 2\ Au + Zn(CN)_2 + 2\ CN^-$$

3 - Applications :

The main application of $Zn(CN)_2$ is for electroplating of zinc from aqueous solutions containing additional cyanide.

3 – 1 - Organic synthesis :

$Zn(CN)_2$ is employed as a catalyst for the cyanosilylation of aldehydes and ketones .

It is also used to introduce the formyl group in organic synthesis. 2-Hydroxy-1-naphthaldehyde has been prepared from 2-naphthol, zinc cyanide, and anhydrous hydrogen chloride.

Zinc ferrite

Zinc ferrites are a series of synthetic inorganic compounds of zinc and iron (ferrite) with the general formula of $Zn_xFe_{3-x}O_4$. Zinc ferrite compounds can be prepared by aging solutions of $Zn(NO_3)_2$, $Fe(NO_3)_3$, and tri ethanol amine in the presence and in the absence of hydrazine , or reacting iron oxides and zinc oxide at high temperature. Spinel (Zn, Fe) Fe_2O_4 appears as a tan-colored solid that is insoluble in water, acids, or diluted alkali . Because of their high opacity .

zinc ferrites can be used as pigments, especially in applications requiring heat stability. For example, zinc ferrite prepared from yellow iron oxide can be used as a substitute for applications in temperatures above 177 °C . When added to high corrosion - resistant coatings , the corrosion protection increases with an increase in the concentration of zinc ferrite . A recent investigation shows that the zinc ferrite, which is paramagnetic in the bulk form, becomes ferri magnetic in nano crystalline thin film format . A large room temperature magnetization and narrow ferro magnetic resonance line width have been achieved by controlling thin films growth conditions.

Zinc fluoride

1 – Introduction :

Zinc fluoride (ZnF_2) is an inorganic chemical compound. It is encountered as the anydrous form and also as the tetra hydrate, $ZnF_2.4H_2O$ (rhombohedral crystal structure) . It has a high melting point and has the rutile structure containing 6 coordinate zinc, which suggests appreciable ionic character in its chemical bonding . Unlike the other zinc halides , $ZnCl_2$, $ZnBr_2$ and ZnI_2 , it is not very soluble in water .

Other names :	Zinc di fluoride
Molecular Formula	$Zn\ F_2$
Molar mass	103.5 g / mol (anhydrous) 175. 5 g / mol (tetra hydrate)
Appearance	white needles , hygroscopic
Density	4.95 g / cm^3 (anhydrous) 2.30 g / cm^3 (tetra hydrate)
Melting Point	872 °C (anhydrous) 100 °C, decomp (tetra hydrate)
Boiling Point	1500 °C (anhydrous)
Solubility in water	.000052 g / 100 mL (anhydrous) 1.52 g / 100 mL, 20 °C (tetra hydrate)
Solubility	sparingly soluble in HCl , HNO_3 , ammonia
Crystal structure	tetragonal (anhydrous), *tP6*
Space group	$P4_2/mnm$, No. 136
Hazards	
EU Index	Not listed

2 - Preparation and reactions :

Zinc fluoride can be synthesized several ways.

1. Reaction of a fluoride salt with zinc chloride, to yield zinc fluoride and a chloride salt, in aqueous solution .
2. The reaction of zinc metal with fluorine gas .
3. Reaction of hydrofluoric acid with zinc, to yield hydrogen gas (H_2) and zinc fluoride (ZnF_2) .

Zinc fluoride can be hydrolysed by hot water to form the zinc hydroxy fluoride , Zn(OH)F .

Zinc Hydroxide

Zinc hydroxide $Zn(OH)_2$ is an inorganic chemical compound. It also occurs naturally as 3 rare minerals: wülfingite (orthorhombic), ashoverite and sweetite (both tetragonal).

Like the hydroxides of other metals, such as lead, aluminium, beryllium, tin and chromium, zinc hydroxide (and zinc oxide), is amphoteric. Thus it will dissolve readily in a dilute solution of a strong acid, such as HCl, and also in a solution of an alkali such as sodium hydroxide.

It can be prepared by adding sodium hydroxide solution, but not in excess, to a solution of any zinc salt. A white precipitate will be seen :

$$Zn^{2+} + 2OH^{-} \rightarrow Zn(OH)_2.$$

If excess sodium hydroxide is added, the precipitate of zinc hydroxide will dissolve, forming a colorless solution of zincate ion :

$$Zn(OH)_2 + 2OH^{-} \rightarrow Zn(OH)_4^{2-}.$$

This property can be used as a test for zinc ions in solution, but it is not exclusive, since aluminum and lead compounds behave in a very similar manner. Unlike the hydroxides of aluminum and lead, zinc hydroxide also dissolves in aqueous ammonia to form a colourless, water-soluble ammine complex.

One major use is as an absorbent in surgical dressings.

IUPAC name ; Zinc hydroxide	
Molecular Formula	$Zn(OH)_2$
Molar mass	99.5 g / mol
Appearance	white powder
Density	3.053 g/cm^3, solid

Melting point	125 °C (decomposition)
Solubility in water	slightly soluble
Solubility product, K_{sp}	3.0×10^{-17}
Solubility in alcohol	insoluble
Hazards	
EU Index	not listed
Flash point	Non-flammable

Zinc Nitrate

$NaNO_3$

Zinc nitrate is a highly deliquescent substance which is usually prepared by dissolving zinc in nitric acid. It can be used as a mordant in dyeing. An example reaction gives a precipitate of zinc carbonate :

$Zn(NO_3)_2 + Na_2CO_3 \rightarrow ZnCO_3 + 2\ NaNO_3$.

Conditions/substances to avoid are : reducing agents , organic materials, metal powders , heat and flame , cyanides , sodium hypo phosphite , tin (IV) chloride, phosphorus, thio cyanates , carbon , and sulfur. Its relative molecular mass is 189.

Zinc nitrate is soluble in both water and alcohol.

IUPAC Name :	Zinc nitrate
Molecular Formula	$Zn\ (\ NO_3\ )_2$
Molar Mass	189.5 g / mol (anhydrous) 297.5 g / mol (hexa hydrate)
Appearance	Colorless , deliquescent crystals
Density	2.065 g / cm^3 (hexa hydrate)
Melting point	110 °C (anhydrous) 45.5 °C (tri hydrate) 36.4 °C (hexa hydrate)
Boiling point	~125 °C, decomp (hexa hydrate)
Solubility in water	327 g / 100 mL , 40 °C (tri hydrate) 184.3 g / 100 ml, 20 °C (hexa hydrate)
Solubility	very soluble in alcohol
Hazards	
EU Index	Not listed
Main hazards	Oxidant , may explode on heating
Flash point	Non - flammable

Zinc Nitride

1 – Introduction :

Zinc nitride ($Zn_3 N_2$) is an inorganic compound of zinc and nitrogen. In pure form, it is cubic in structure .

Molecular Formula	$Zn_3 N_2$
Molar Mass	224. 5 g / mol
Appearance	gray powder
Density	6.22 g / cm³, solid
Solubility in water	insoluble (decomposes)
Crystal structure	Cubic, cI80
Space group	Ia-3, No. 206[1][2]
Hazards	
EU classification	not listed

2 - Chemical properties :

Zinc nitride can be obtained by thermally decomposing zinc amide (zinc di amine) in an anaerobic environment, at temperatures in excess of 200 °C . The by - product of the reaction is ammonia.

$$3Zn\ (NH_2)_2 \rightarrow Zn_3\ N_2 + 4NH_3$$

It can also be formed by heating zinc to 315 °C in a current of ammonia; the by-product is hydrogen gas .

$$3Zn + 2NH_3 \rightarrow Zn_3N_2 + 3H_2$$

Zinc nitride reacts violently with water to form ammonia and zinc oxide .

$$Zn_3N_2 + 3H_2O \rightarrow 3ZnO + 2NH_3$$

It is soluble in hydrochloric acid and "reversibly reacts with lithium electrochemically". Like magnesium nitride (Mg_3N_2) and lithium nitride (Li_3N) , it has a high melting point.

Zinc Oxide

Contents

1 – Introduction :

Zinc oxide is an inorganic compound with the formula ZnO . It usually appears as a white powder, nearly insoluble in water. The powder is widely used as an additive into numerous materials and products including plastics, ceramics, glass, cement, rubber (e.g. car tyres) , lubricants , paints, ointments, adhesives, sealants, pigments, foods (source of Zn nutrient), batteries, ferrites, fire retardants, first aid tapes, etc. ZnO is present in the Earth crust as a mineral zincite; however, most ZnO used commercially is produced synthetically .

In materials science, ZnO is often called a II-VI semiconductor because zinc and oxygen belong to the 2nd and 6th groups of the periodic table, respectively. This semiconductor has several favorable properties : good transparency , high electron mobility , wide band gap , strong room - temperature luminescence, etc. Those properties are already used in emerging applications for transparent electrodes in liquid crystal displays and in energy - saving or heat - protecting windows , and electronic applications of ZnO as thin-film transistor and light - emitting diode are forth coming as of 2009 .

Other Names	Zinc white - Calamine
Molecular Formula	Zn O
Molar Mass	81.5 g / mol
Appearance	White solid
Odor	Odorless
Density	5.606 g / cm^3
Melting point	1975 °C (decomposes)
Boiling point	2360 °C
Solubility in water	0.16 mg /100 mL (30 °C)
Refractive index (n_D)	2.0041
EU classification	Dangerous for the environment (**N**)

2 - Chemical properties

ZnO occurs as white powder known as zinc white or as the mineral zincite. The mineral usually contains a certain amount of manganese and other elements and is of yellow to red color.[2] Crystalline zinc oxide is thermo chromic , changing from white to yellow when heated and in air reverting to white on cooling.[3] This color change is caused by a very small loss of oxygen at high temperatures to form the non- stoichio metric $Zn_{1+x}O$, where at 800 °C , $x = 0.00007$.

Zinc oxide is an amphoteric oxide. It is nearly insoluble in water and alcohol, but it is soluble in (degraded by) most acids, such as hydrochloric acid :

$$ZnO + 2\,HCl \rightarrow ZnCl_2 + H_2O$$

Bases also degrade the solid to give soluble zincates:

$$ZnO + 2NaOH + H_2O \rightarrow Na_2(Zn(OH)_4)$$

Zn O reacts slowly with fatty acids in oils to produce the corresponding carboxylates, such as oleate or stearate . Zn O forms cement - like products when mixed with a strong aqueous solution of zinc chloride and these are best described as zinc hydroxy chlorides . This cement was used in dentistry .

Zn O also forms cement - like products when treated with phosphoric acid ; related materials are used in dentistry . A major component of zinc phosphate cement produced by this reaction is hopeite , $Zn_3(PO_4)_2 \cdot 4H_2O$.

Zn O decomposes into zinc vapor and oxygen only at around 1975 °C , reflecting its considerable stability . Heating with carbon converts the oxide into the metal, which is more volatile than the oxide .

$$ZnO + C \rightarrow Zn + CO$$

Zinc oxide can react violently with aluminum and magnesium powders , with chlorinated rubber and linseed oil on heating causing fire and explosion hazard . It reacts with hydrogen sulfide to give the sulfide : this reaction is used commercially in removing H_2S using ZnO powder (e.g., as deodorant) .

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

When ointments containing Zn O and water are melted and exposed to ultra violet light , hydrogen peroxide is produced .

3 - Physical properties

3 – 1 : Crystal structure

Zinc oxide crystallizes in three forms : hexagonal wurtzite, cubic zinc blende , and the rarely observed cubic rock salt . The wurtzite structure is most stable at ambient conditions and thus most common . The zinc blende form can be stabilized by growing Zn O on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetra hedral. The rock salt (Na Cl – type) structure is only observed at relatively high pressures about 10 Gpa .

Hexagonal and zinc blende polymorphs have no inversion symmetry (reflection of a crystal relatively any given point does not transform it into itself) . This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zinc blende ZnO , and in pyro electricity of hexagonal Zn O .

The hexagonal structure has a point group 6 mm (Hermann - Mauguin notation) or C_{6v} (Schoenflies notation) , and the space group is $P6_3mc$ or C_{6v}^4 . The lattice constants are a = 3.25 Å and c = 5.2 Å ; their ratio $c / a \sim 1.60$ is close to the ideal value for hexagonal cell $c / a = 1.633$. As in most II - VI materials, the bonding in Zn O is largely ionic, which explains its strong piezo electricity. Due to the polar Zn - O bonds , zinc and oxygen planes bear electric charge (positive and negative, respectively) . Therefore , to maintain electrical neutrality, those planes reconstruct at atomic level in most relative materials, but not in Zn O - its surfaces are atomically flat, stable and exhibit no reconstruction. This anomaly of Zn O is not fully explained yet .

3 – 2 : Mechanical properties

Zn O is a relatively soft material with approximate hardness of 4.5 on the Mohs scale . Its elastic constants are smaller than those of relevant III - V semi conductors , such as Ga N . The high heat capacity and heat conductivity, low thermal expansion and high melting temperature of Zn O are beneficial for ceramics .

Among the tetra hedrally bonded semiconductors, it has been stated that Zn O has the highest piezoelectric tensor or at least one comparable to that of Ga N and Al N . This property makes it a technologically important material for many piezo electrical applications , which require a large electro mechanical coupling.

3 – 3 : Electronic properties

Zn O has a relatively large direct band gap of ~3.3 eV at room temperature ; therefore, pure Zn O is colorless and transparent. Advantages associated with a large band gap include higher breakdown voltages, ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation. The band gap of Zn O can further be tuned from ~3 – 4 eV by its alloying with magnesium oxide or cadmium oxide .

Most Zn O has *n* - type character, even in the absence of intentional doping . Non stoichiometry is typically the origin of n - type character, but the subject remains controversial . An alternative explanation has been proposed, based on theoretical calculations , that unintentional substitutional hydrogen impurities are responsible . Controllable n-type doping is easily achieved by substituting Zn with group - III elements such as Al, Ga, In or by substituting oxygen with group - VII elements chlorine or iodine .

Reliable p - type doping of Zn O remains difficult . This problem originates from low solubility of p - type dopants and their compensation by abundant n - type impurities. This problem is observed with GaN and Zn Se . Measurement of p-type in " intrinsically " n - type material is complicated by the inhomogeneity of samples .

Current limitations to p - doping does not limit electronic and optoelectronic applications of Zn O , which usually require junctions of n - type and p - type material. Known p-type dopants include group - I elements Li , Na , K ; group - V elements N , P and As ; as well as copper and silver . However, many of these form deep acceptors and do not produce significant p - type conduction at room temperature .

Electron mobility of ZnO strongly varies with temperature and has a maximum of ~2000 cm^2 / (V·s) at ~80 K . Data on hole mobility are scarce with values in the range 5 -30 cm^2 / V·s.

4 - Production

For industrial use , Zn O is produced at levels of 10^5 tons per year by three main processes :

4 – 1 : Indirect (French) process

Metallic zinc is melted in a graphite crucible and vaporized at temperatures above 907 °C (typically around 1000 °C) . Zinc vapor instantaneously reacts with the oxygen in the air to give Zn O , accompanied by a drop in its temperature and bright luminescence . Zinc oxide particles are transported into a cooling duct and collected in a bag house. This indirect method was popularized by Le Claire (France) in 1844 and there fore is commonly known as the French process. Its product normally consists of agglomerated zinc oxide particles with an average size of 0.1 to a few micrometers. By weight, most of the world's zinc oxide is manufactured via French process . Major applications involve industries related to rubber , varistors, sunscreens, paints, healthcare, and poultry nutrients Recent developments involve acicular nanostructures (rods, wires , tripods , tetrapods , plates) synthesized using a modified French process known as catalyst - free combust - oxidized mesh (CFCOM) process . Acicular nanostructures usually have micro meter - length nano rods with nano metric diameters (below 100 nm) .

4 – 2 : Direct (American) process

In the direct process , the starting material is various contaminated zinc composites , such as zinc ores or smeleter by – products . It is reduced by heating with a carbon additive (e.g. antracite) to produce zinc vapor , which is then oxidized as in the indirect process . Because of the lower purity of the source material , the final product is also of lower quality in the direct process as compared to the indirect one .

4 – 3 : Wet chemical process

Wet chemical processes start with purified zinc solutions, from which zinc carbonate or zinc hydroxide is precipitated. It is then filtered , washed , dried and calcined at temperatures ~ 800 °C .

4 – 4 : Laboratory synthesis

A large number of Zn O production methods exist for producing ZnO for scientific studies and electronic applications. These methods can be classified by the resulting Zn O form (bulk , thin film , nanowire) , temperature ("low" , that is close to room temperature or " high " , that is T ~ 1000 °C) , process type (vapor deposition or growth from solution) and other parameters .

Large single crystals (many cubic centimeters) are usually grown by the gas transport (vapor - phase deposition) , hydro thermal synthesis , or melt growth . However, because of high vapor pressure of Zn O , growth from the melt is problematic. Growth by gas transport is difficult to control, leaving the hydrothermal method as a preference. Thin films can be produced by chemical vapor deposition, metalorganic vapour phase epitaxy, electrodeposition, pulsed laser deposition, sputtering , sol - gel synthesis, spray pyrolysis , etc . Nanostructures can be obtained with most above - mentioned techniques, at certain conditions, and also with the vapor – liquid - solid method .

5 - Applications

The applications of zinc oxide powder are numerous, and the principal ones are summarized below. Most applications exploit the reactivity of the oxide as a precursor to other zinc compounds. For material science applications, zinc oxide has high refractive index, good thermal, binding, antibacterial and UV - protection properties. Consequently, it is added into various materials and products, including plastics, ceramics, glass, cement, rubber, lubricants , paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, fire retardants , etc .

5 – 1 : Rubber manufacture

About 50 % of Zn O use is in rubber industry. Zinc oxide along with stearic acid activates vulcanization, which otherwise may not occur at all . Zinc oxide and stearic acid are ingredients in the commercial manufacture of rubber goods. A mixture of these two compounds allows a quicker and more controllable rubber cure. Zn O is also an important additive to the rubber of car tyres. Vulcanization catalysts are derived from zinc oxide, and it considerably improves the thermal conductivity, which is crucial to dissipate the heat produced by the deformation when the tyre rolls . Zn O additive also protect rubber from fungi (see medical applications) and UV light.

5 – 2 : Concrete industry

Zinc oxide is widely used for concrete manufacturing. Addition of Zn O improves the processing time and the resistance of concrete against water .

5 – 3 : Medical

Zinc oxide as a mixture with about 0.5 % iron (III) oxide (Fe_2O_3) is called calamine and is used in calamine lotion . There are also two minerals , zincite and hemi morphite , which have been called calamine historically . When mixed with eugenol , a chelate , zinc oxide eugenol is formed which has restorative and prosthodontic applications in dentistry .

Reflecting the basic properties of Zn O , fine particles of the oxide have deodorizing and antibacterial action and for that reason are added into various materials including cotton fabric, rubber, food packaging, etc . Enhanced antibacterial action of fine particles compared to bulk material is not intrinsic to Zn O and is observed for other materials, such as silver .

Zinc oxide is widely used to treat a variety of other skin conditions, in products such as baby powder and barrier creams to treat diaper rashes, calamine cream, anti-dandruff shampoos, and antiseptic ointments . It is also a component in tape (called " zinc oxide tape ") used by athletes as a bandage to prevent soft tissue damage during workouts .

5 – 4 : Cigarette filters

Zinc oxide is a constituent of cigarette filters for removal of selected components from tobacco smoke . A filter consisting of charcoal impregnated with zinc oxide and iron oxide removes significant amounts of HCN and H_2S from tobacco smoke with out affecting its flavor .

5 – 5 : Food additive

Zinc oxide is added to many food products , e.g., break fast cereals, as a source of zinc, a necessary nutrient. (Other cereals may contain zinc sulfate for the same purpose) . Some prepackaged foods also include trace amounts of Zn O even if it is not intended as a nutrient .

5 – 6 : Pigment

Zinc white is used as a pigment in paints and is more opaque than lithopone , but less opaque than titanium dioxide . It is also used in coatings for paper. Chinese white is a special grade of zinc white used in artists' pigments. Because it reflects both UVA and UVB rays of ultraviolet light , zinc oxide can be used in ointments, creams, and lotions to protect against sunburn and other damage to the skin caused by ultra violet light) . It is the broadest spectrum UVA and UVB absorber that is approved for use as a sunscreen by the FDA , and is completely photo stable. It is also a main ingredient of mineral makeup .

5 – 7 : Coatings

Paints containing zinc oxide powder have long been utilized as anti corrosive coatings for various metals . They are especially effective for galvanized Iron . The latter is difficult to protect because its reactivity with organic coatings leads to brittleness and lack of adhesion . Zinc oxide paints however , retain their flexibility and adherence on such surfaces for many years .

Zn O highly n - type doped with Al , Ga or nitrogen is transparent and conductive (transparency ~90 %, lowest resistivity ~10^{-4} Ω cm) . ZnO : Al coatings are being used for energy - saving or heat - protecting windows . The coating lets the visible part of the spectrum in but either reflects the infrared (IR) radiation back into the room (energy saving) or does not let the IR radiation into the room (heat protection) , depending on which side of the window has the coating .

Various plastics, such as poly ethylene – naphthalate (PEN) , can be protected by applying zinc oxide coating . The coating reduces the diffusion of oxygen with PEN . Zinc oxide layers can also be used on poly carbonate (PC) in outdoor applications. The coating protects PC form solar radiation and decreases the oxidation rate and photo - yellowing of PC .

5 – 8 : Corrosion prevention in nuclear reactors

Zinc oxide depleted in the zinc isotope with the atomic mass 64 is used in corrosion prevention in nuclear pressurized water reactors. The depletion is necessary, because ^{64}Zn is transformed into radioactive ^{65}Zn under irradiation by the reactor neutrons .

6 - Potential applications

6 -1 : Electronics

Zn O has wide direct band gap (3.37 eV or 375 nm at room temperature) . There fore , its most common potential applications are in laser diodes and light emitting diodes (LEDs) . Some optoelectronic applications of Zn O overlap with that of Ga N, which has a similar band gap (~3.4 eV at room temperature) . Compared to

Ga N, Zn O has a larger exciton binding energy (~ 60 meV , 2.4 times of the room -temperature thermal energy) , which results in bright room -temperature emission from Zn O . Other properties of Zn O favorable for electronic applications include its stability to high-energy radiation and to wet chemical etching . Radiation resistance makes Zn O a suitable candidate for space applications .

The pointed tips of Zn O nanorods result in a strong enhancement of an electric field . Therefore, they can be used as field emitters .

Aluminium - doped Zn O layers are used as a transparent electrodes . The constituents Zn and Al are much cheaper and less poisonous compared to the generally used indium tin oxide (ITO) . One application which has begun to be commercially available is the use of Zn O as the front contact for solar cells or of liquid crystal displays .

Transparent thin - film transistors (TTFT) can be produced with Zn O . As field - effect transistors , they even may not need a p – n junction , thus avoiding the p - type doping problem of Zn O . Some of the field-effect transistors even use Zn O nano rods as conducting channels .

6 – 2 : Zinc oxide nano rod sensor

Zinc oxide nano rod sensors are devices detecting changes in electrical current passing through zinc oxide nano wires due to adsorption of gas molecules. Selectivity to hydrogen gas was achieved by sputtering Pd clusters on the nano rod surface. The addition of Pd appears to be effective in the catalytic dissociation of hydrogen molecules into atomic hydrogen, increasing the sensitivity of the sensor device. The sensor detects hydrogen concentrations down to 10 parts per million at room temperature, whereas there is no response to oxygen.

6 – 3 : Spintronics

Zn O has also been considered for spintronics applications: if doped with 1- 10 % of magnetic ions (Mn , Fe , Co , V , etc), Zn O could become ferro magnetic , even at room temperature. Such room temperature ferromagnetism in Zn O : Mn has been observed , but it is not clear yet whether it originates from the matrix itself or from Mn - containing precipitates .

6 – 4 : Piezo electricity

The piezo electricity in textile fibers coated in Zn O have been shown capable of " self - powering nano systems " with everyday mechanical stress generated by wind or body movements .

In 2008 the *Center for Nano structure Characterization* at the Georgia Institute of Technology reported producing an electricity generating device (called flexible charge pump generator) delivering alternating current by stretching and releasing zinc oxide wires . This mini - generator creates an oscillating voltage up to 45 millivolts, converting close to seven percent of the applied mechanical energy into electricity. Researchers used wires with lengths of 0.2 - 0.3 mm and diameters of three to five micrometers , but the device could be scaled down to nanometer size .

6 – 5 : Bio sensor

Zn O has high bio compatibility and fast electron transfer kinetics . Such features advocate the use of this material as a bio mimic membrane to immobilize and modify bio molecules .

7 - History

It is hardly possible to trace the first usage of zinc oxide – various zinc compounds were widely used by early humans, in various processed and unprocessed forms, as a paint or medicinal ointment, but their exact composition is uncertain.

The Romans produced considerable quantities of brass (an alloy of zinc and copper) as early as 200 BCE by a cementation process where copper was reacted with zinc oxide . The zinc oxide is thought to have been produced by heating zinc ore in a shaft furnace. This liberated metallic zinc as a vapor, which then ascended the flue and condensed as the oxide. This process was described by Dioscorides in the 1st century CE . Zinc oxide has also been recovered from zinc mines at Zawar in India, dating from the second half of the first millennium BCE. This was presumably also made in the same way and used to produce brass .

The use of zinc oxide as a treatment for skin conditions dates back to Avicenna's *The Canon of Medicine* (1025 CE) , which introduced it as a preferred treatment for a variety of skin conditions, including skin cancer. Though today it is no longer used for treating skin cancer, it is still widely used today to treat a variety of other skin conditions .

From the 12 th to the 16 th century zinc and zinc oxide were recognized and produced in India using a primitive form of the direct synthesis process . From India , zinc manufacture moved to China in the 17 th century . Zinc was recognized as a separate metal in Europe in 1546 . In 1743 , the first European zinc smelter was established in Bristol , United Kingdom .

The main usage of zinc oxide (zinc white) was again paints and additive to ointments . Zinc white was accepted as a watercolor by 1834 but it did not mix well with oil. This problem was quickly solved by optimizing the synthesis of ZnO. In 1845 , Le Claire in Paris was producing the oil paint on a large scale , and by 1850 , zinc white was being manufactured throughout Europe . The success of zinc white paint was due to its advantages over the traditional white lead: zinc white is essentially permanent in sunlight, it is not blackened by sulfur-bearing air, it is non - toxic and more economical. Because zinc white is so " clean " it is very valuable for making tints with other colors; however, it makes a rather brittle dry film when unmixed with other colors. For example, during the late 1890s and early 1900s , some artists used zinc white as a ground for their oil paintings . All those paintings developed cracks over the years .

In the recent times, most zinc oxide was used in the rubber industry (see applications above) . In the 1970s , the second largest application of Zn O was photo copying . High - quality Zn O produced by the " French process " was added into the photocopying paper as a filler. This application was however soon displaced .

8 - Safety

As a food additive , zinc oxide is on the U.S. FDA's generally recognized as safe , or GRAS, substances .

Zinc oxide itself is non - toxic ; however it is hazardous to breathe zinc oxide fumes, as generated when zinc or zinc alloys are melted and oxidized at high temperature. This problem occurs while melting brass because the melting point of brass is close to the boiling point of zinc . Exposure to zinc oxide in the air, which also occurs while welding galvanized (zinc plated) steel , can result in a nervous malady called metal fume fever. For this reason, typically galvanized steel is not welded, or the zinc is removed first .

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Zinc Oxide Eugenol

1 – Introduction :

Zinc oxide eugenol (ZOE) is a material created by the combination of zinc oxide and eugenol contained in oil of cloves. An acid-base reaction takes place with the formation of zinc eugenolate chelate. The reaction is catalyzed by water and is accelerated by the presence metal salts. ZOE can be used as a filling or cement material in dentistry . It is often used in dentistry when the decay is very deep or very close to the nerve or pulp chamber. Because the tissue inside the tooth, i. e. the pulp, reacts badly to the drilling stimulus (heat and vibration), it frequently becomes severely inflamed and precipitates a condition called acute or chronic pulpits . This condition usually leads to severe chronic tooth sensitivity or actual toothache and can then only be treated with the removal of the nerve (pulp) called root canal therapy. The placement of a ZOE "temporary" for a few to several days prior to the placement of the final filling usually prevents the sensitivity or toothache and there fore, most times, precludes the need for the expensive and time consuming root canal procedure. It is classified as an intermediate restorative material and has anaesthetic and anti bacterial properties. It is sometimes used in the management of dental caries as a "temporary filling". ZOE cements were introduced in the 1890s.

Zinc oxide eugenol is also used as an impression material during construction of complete dentures and are used in the mucostatic technique of taking impressions.

Zinc oxide eugenol is also used as an anti microbial additive in paint.

2 - Composition :

The chemical composition of ZOE is typically :

- Zinc oxide , ~ 69.0 %
- White rosin , ~ 29.3 %
- Zinc acetate , ~1.0 % (improves strength)
- Zinc stearate , ~ 0.7 % (acts as accelerator)
- Liquid (Eugenol , ~ 85 % , Olive oil ~15 %)

ZOE impression pastes are dispensed as two separate pastes. One tube contains zinc oxide and vegetable or mineral oil; the other contains eugenol and rosin. The vegetable or mineral oil acts as a plasticizer and aids in offsetting the action of the eugenol as an irritant.

Oil of cloves, which contains 70 % to 85 % eugenol, is some times used in preference to eugenol because it produces less burning sensation for patients when it contacts the soft tissues. The addition of rosin to the paste in the second tube facilitates the speed of the reaction and yields a smoother, more homogenous product.

Canada balsam and Peru balsam are often used to increase flow and improve mixing properties. If the mixed paste is too thin or lacks body before it sets, a filler (such as a wax) or an inert powder (such as kaolin, talc, or diatomaceous earth) may be added to one or both of the original pastes.

Zinc Peroxide

Zinc peroxide (ZnO_2) is a chemical compound used as a bleaching and curing agent. It appears as white to yellow powder. Perhaps its most important use is to promote cross - linking in carboxylated nitrile rubber and other elastomers . Another application of ZnO_2 is additive to antiseptic ointments. Zinc peroxide has also been used as an oxidant in explosives and pyrotechnic mixtures .

Zinc peroxide can be prepared by reacting ZnO or zinc acetate with hydrogen peroxide . It has cubic crystalline structure (same as FeS_2) , a bulk modulus of 174 GPa, and it is paramagnetic down to 5 K.

Other names : zinc dioxide , zinc bioxide	
Molecular Formula	$Zn\ O_2$
Molar Mass	97.5 g / mol
Appearance	White - yellowish powder
Density	1.57 g / cm^3
Melting point	212°C (decomposes)
Acidity (pK_a)	~7 (3 % solution)
Band gap	3.8 eV (indirect)
Crystal structure	Cubic

Zinc Phosphate

Zinc phosphate ($Zn_3(PO_4)_2$) is an inorganic chemical compound used as a corrosion resistant coating on metal surfaces either as part of an electro plating process or applied as a primer pigment . Zinc phosphate coats better on a crystalline structure than bare metal, so a seeding agent is often used as a pre treatment . One common agent is sodium pyro phosphate .

Natural forms of zinc phosphate include minerals hopeite and parahopeite, $Zn_3(PO_4)_2 \cdot 4H_2O$. A some what similar mineral is natural hydrous zinc phosphate called tarbuttite, $Zn_2(PO_4)(OH)$. Both are known from oxidation zones of Zn ore beds and were formed through oxidation of sphalerite by the presence of phosphate-rich solutions. The anhydrous form has not yet been found naturally.

Zinc phosphate is formed from zinc phosphate cement and used in dentistry. Zinc phosphate dental cement is one of the oldest and widely used cements, and is commonly used for luting permanent metal restorations and as a base for dental restorations. Zinc phosphate cement is used for cementation of inlays, crowns, bridges, and orthodontic appliances and occasionally as a temporary restoration. It is prepared by mixing zinc oxide and magnesium oxide powders with a liquid consisting principally of phosphoric acid, water, and buffers. It is the standard cement to measure against. It has the longest track record of use in dentistry. It is still commonly used; however, resin-modified glass ionomer cements are more convenient and stronger when used in a dental setting.

IUPAC name[hide]	
Zinc phosphate	
Molecular formula	$Zn_3 (PO_4)_2$
Molar mass	386 g / mol
Appearance	white crystals
Density	3.998 g / cm^3
Melting point	900 °C

Solubility in water	insoluble
Refractive index (n_D)	1.595
Crystal structure	monoclinic
Hazards	
EU Index	Not listed
Flash point	Non - flammable

Zinc phosphide

2 – Introduction :

Zinc phosphide (Zn_3P_2) is an inorganic chemical compound.

3 – Reactions :

Zinc phosphide can be prepared by the reaction of zinc with phosphorus :

$$3Zn + 2P \rightarrow Zn_3P_2$$

Zinc phosphide will react with water to produce phosphine (PH_3) and zinc hydroxide ($Zn(OH)_2$):

$$Zn_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Zn(OH)_2$$

3 - Rodenticide :

Metal phosphides have been used as rodenticides. A mixture of food and zinc phosphide is left where the rodents can eat it. The acid in the digestive system of the rodent reacts with the phosphide to generate the toxic phosphine gas. This method of vermin control has possible use in places where rodents immune to many of the common poisons have appeared. Other pesticides similar to zinc phosphide are aluminium phosphide and calcium phosphide.

Zinc phosphide is typically added to rodent baits in amount of around 0.75-2%. The baits have strong, pungent garlic-like odor characteristic for phosphine liberated by hydrolysis. The odor attracts rodents, but has a repulsive effect on other animals; birds, notably wild turkeys, are not sensitive to the smell. The baits have to contain sufficient amount of zinc phosphide in sufficiently attractive food in order to kill rodents in a single serving; a sublethal dose may cause aversion towards zinc - phosphide baits encountered by surviving rodents in the future.

Rodenticide - grade zinc phosphide usually comes as a black powder containing 75 % of zinc phosphide and 25% of antimony potassium tartrate , an emetic to cause vomiting if the material is accidentally ingested by humans or domestic animals. However, it is still effective against rats, mice, guinea pigs and rabbits, all of which do not have a vomiting reflex.

4 - Zinc phosphide use in New Zealand

The New Zealand Environmental Protection Authority has approved the import and manufacture of Microencapsulated Zinc Phosphide (MZP Paste) for the ground control of possums. The application was made by Pest Tech Limited, with support from Conn ovation Ltd, Lincoln University and the Animal Health Board. It will be used as an additional vertebrate poison in certain situations. Unlike 1080 poison, it cannot be used for aerial application.

Zinc stearate

1 – Introduction :

Zinc stearate ($Zn(C_{18}H_{35}O_2)_2$) is a zinc soap that repels water. It is insoluble in polar solvents such as alcohol and ether but soluble in aromatic hydrocarbons (e.g., benzene and chlorinated hydrocarbons) when heated. It is the most powerful mold release agent among all metal soaps. It contains no electrolyte and has a hydrophobic effect. Its main application areas are the plastics and rubber industry where it is used as a releasing agent and lubricant which can be easily incorporated.

IUPAC Name : zinc octadecanoate	
Other Names : zinc di stearate	
Molecular Formula	$C_{36} H_{70} O_4 Zn$
Molar Mass	632. 5 g mol^{-1}
Appearance	soft, white powder
Density	1.095 g / cm^3, solid
Melting point	120 -130 °C
Boiling point	decomposes
Solubility in water	insoluble
Solubility in benzene	slightly soluble
Hazards	
EU classification	Not listed
Flash point	277 °C
Auto ignition temperature	420 °C

2 - Applications :

- As a synergic stabilizer for Ba/Cd and Pb stabilizer systems.
- As a gloss imparting agent in paint industry.
- As a metal release agent in rubber, polyurethane and polyester processing system.

- As a die release agent in powder metallurgy.
- As a chief ingredient in "fanning powder", used by magicians performing card manipulation to decrease the friction between the cards.
- As a lubricant in cosmetics to improve texture.[1]
- As an activator system for rubber vulcanization by sulfur and accelerators

Zinc Sulfate

1 – Introduction :

Zinc sulfate is the inorganic compound with the formula $ZnSO_4$ as well as any of three hydrates. It was historically known as "white vitriol". It is a colorless solid that is a common source of soluble zinc ions.

IUPAC Name : Zinc Sulfate	
Other Names : White vitriol , Goslarite	
Molecular Formula	Zn SO_4
Molar mass	161.5 g / mol (anhydrous) 179.5 g / mol (mono hydrate) 287.5 g/ mol (hepta hydrate)
Appearance	white powder
Odor	odorless
Density	3.54 g/cm^3 (anhydrous) 2.072 g/cm^3 (hexahydrate)
Melting point	680 ºC decomp. (anhydrous) 100 °C (hepta hydrate) 70 °C, decomp (hexa hydrate)
Boiling point	740 °C (anhydrous) 280 °C, decomp (hepta hydrate)
Solubility in water	57.7 g/100 mL , anhydrous (20 °C)
Solubility	alcohols
Refractive index (n_D)	1.658 (anhydrous) , 1.4357 (hepta hydrate)
Hazards	
EU classification	Harmful (Xn) Dangerous for the environment (N)
Flash point	Non - flammable

2 - Production and reactivity :

Zinc sulfate and is produced by treating zinc with aqueous sulfuric acid :

$$Zn + H_2SO_4 + 7\ H_2O \rightarrow ZnSO_4(H_2O)_7 + H_2$$

Pharmaceutical grade zinc sulfate is produced from high purity zinc oxide:

$$ZnO + H_2SO_4 + 6\ H_2O \rightarrow ZnSO_4(H_2O)_7$$

In the laboratory, it can also be prepared by adding solid zinc to a copper (II) sulfate solution :

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$$

In aqueous solution, all forms of zinc sulfate behave identically. These aqueous solutions consist of the metal aquo complex $[Zn(H_2O)_6]^{2+}$ and SO_4^{2-} ions. Barium sulfate forms when these solutions are treated with solutions of barium ions :

$$ZnSO_4 + BaCl_2 \rightarrow BaSO_4 + ZnCl_2$$

With a reduction potential of -0.76, zinc(II) reduces only with difficulty.

3 - Applications :

The hydrates, especially the hepta hydrate, are the primary forms used commercially. The main application is as a coagulant in the production of rayon. It is also a precursor to the pigment lithopone. Zinc sulfate is used to supply zinc in animal feeds, fertilizers, and agricultural sprays. It is used as in electrolytes for zinc plating, as a mordant in dyeing, as a preservative for skins and leather and in medicine as an astringent and emetic.

4 - Minerals

As a mineral $ZnSO_4 \cdot 7H_2O$ is known as goslarite. Zinc sulfate occurs as several other minor minerals Zinc - melanterite $(Zn,Cu,Fe)SO_4 \cdot 7H_2O$ (structurally different from goslarite). Lower hydrates of zinc sulfate are rarely found in nature: $(Zn,Fe)SO_4 \cdot 6H_2O$ (bianchite), $(Zn,Mg)SO_4 \cdot 4H_2O$ (boyleite), and $(Zn,Mn)SO_4 \cdot H_2O$ (gunningite).

Zinc Sulfide

Contents

1 – Introduction :

Zinc sulfide (or zinc sulphide) is a inorganic compound with the formula ZnS. ZnS is the main form of zinc in nature, where it mainly occurs as the mineral sphalerite. Although the mineral is black owing to impurities, the pure material is white and is in fact used widely as a pigment.

Other Names : Zinc blende , Wurtzite	
Molecular Formula	Zn S
Molar Mass	97.5 g / mol
Density	4.090 g / cm^3
Melting Point	1185 °C (sublime)
Solubility in Water	negligible
Band gap	3.54 eV (cubic , 300 K) 3.91 eV (hexagonal , 300 K)
Structure	
Coordination geometry	Tetrahedral (Zn^{2+}) Tetrahedral (S^{2-})
Thermo chemistry	

Std enthalpy of formation $\Delta_f H^\circ_{298}$	−204.6 kJ/mol
Hazards	
EU Index	Not listed
Flash point	Non - flammable

2 - Structure of ZnS :

ZnS exists in two main forms, and this dualism is often a textbook example of polymorphism. In both polymorphs, the coordination geometry at Zn and S are tetrahedral. The more stable form cubic form is known also as zinc blende or sphalerite. The hexagonal form is known as the mineral Wurtzite , although it also can be produced synthetically. The transition from the sphalerite form to the Wurtzite form occurs at around 1020 °C. A tetragonal form is also known as the very rare mineral called polhemusite , with the formula (Zn , Hg) S .

3 – Applications :

3 – 1 - Luminescent Material :

Zinc sulfide, with addition of few ppm of suitable activator, is used as phosphor in many applications, from cathode ray tubes through x-ray screens to glow in the dark products. When silver is used as activator, the resulting color is bright blue, with maximum at 450 nm. Manganese yields an orange-red color at around 590 nm. Copper provides long glow time and the familiar glow-in-the-dark greenish color . Copper - doped zinc sulfide ("ZnS + Cu") is used also in electro luminescent panels. It also exhibits phosphorescence due to impurities on illumination with blue or ultra violet light.

3 – 2 - Optical material :

Zinc sulfide is also used as an infrared optical material, transmitting from visible wavelengths to over 12 micrometres. It can be used planar as an optical window or shaped into a lens. It is made as microcrystalline sheets by the synthesis from hydrogen sulfide gas and zinc vapour and sold as FLIR (Forward Looking IR) grade ZnS a pale milky yellow visibly opaque form. This material when hot iso statically pressed (HIPed) can be converted to a water - clear form known as **Cleartran** (trademark). Early commercial forms were marketed as **Irtran-2** but this designation is now obsolete.

3 – 3 – Pigment :

Zinc sulfide is a common pigment. When compounded with barium sulfate , zinc sulfide forms lithopone .

3 – 4 – Semi conductor properties :

Both sphalerite and wurtzite are intrinsic , wide - band gap semi conductors. It is a proto typical II-VI semi conductors and adopts structures related to many other semi conductors such as gallium arsenide. The cubic form has a band gap of 3.54 eV at 300 K whereas the hexagonal form has a band gap of 3.91 eV. It can be doped as both n - type semi conductor and p - type semi conductor.

3 – 5 – History :

The phosphorescence of ZnS was first reported by the French chemist Théodore Sidot in 1866. His findings were presented by A. E. Becquerel, who was renowned for the research on luminescence. ZnS was used by Ernest Rutherford and others in the early years of nuclear physics as a scintillation detector, because it emits light upon excitation by x - rays or electron beam, making it useful for X-ray screens and cathode ray tubes .

4 – Production :

Zinc sulfide is usually produced from waste materials from other applications. Typical sources include smelter, slag, and pickle liquors . It is also a by - product of the synthesis of ammonia from methane where zinc oxide is used to scavenge hydrogen sulfide impurities in the natural gas :

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

4 – 1 - Laboratory preparation :

It is easily produced by igniting a mixture of zinc and sulfur . Since zinc sulfide is insoluble in water, solutions containing Zn^{2+} salts readily form a precipitate ZnS in the presence of sulfide ions (e.g., from H_2S).

$$Zn^{2+} + S^{2-} \rightarrow ZnS$$

This reaction is the basis of a gravimetric analysis for zinc.

Zincate

1 – Introduction :

In chemistry the term **zincate** may refer to :

- a salt containing $Zn(OH)_4^{2-}$,also called the tetra hydroxo zincate ion . It is an ore of Zinc. Examples include calcium zincate Ca $Zn(OH)_4.2H_2O$, or $Na_2Zn(OH)_4$c’ or the polymeric anion $[Zn(OH)_3^-]$ in for example Na $Zn(OH)_3 \cdot H_2O$
- an alkali solution prepared from dissolving zinc metal, zinc hydroxide or zinc oxide which contains various anionic species such as $Zn(OH)_4^{2-}$. Such solutions are used in the plating industry.
- an oxide containing zinc and a less electronegative element e.g. Na_2ZnO_2 .
- a commercially available zinc supplement formulated as zinc sulfate .

2 - Zincate - plating processes :

In industry it can refer to the alkaline solutions used in a dipping (immersion) process to plate aluminium with zinc prior to electrolytic or electroless nickel plating. This immersion process is electroless (i.e. not electroplating) and involves the displacement of zinc from zincate by aluminum :

$$3\ Zn(OH)_4^{2-} + 2\ Al \rightarrow 3\ Zn + 2\ Al(OH)_4^- + 4\ OH^-$$

It can also refer to alkaline solutions used in electro plating of e.g. steel with zinc .

3 - Inorganic compound nomenclature

In the naming of inorganic compounds zincate is a suffix that indicates that a polyatomic anion contains a central zinc atom. Examples include tetra chloro zincate , $ZnCl_4^{2-}$, the tetra hydroxo zincate , $Zn(OH)_4^{2-}$ and tetra nitrato zincate, $Zn(NO_3)_4^{2-}$. More recent recommendations (2005), that are not widely used, would call the first two ions tetra chloride zincate (2−) and tetra hydroxide zincate(2−) respectively.

4 - Zincates aqueous chemistry :

It is now generally accepted that the ionic species in alkali solutions of ZnO or $Zn(OH)_2$ contain $Zn(OH)_4^{2-}$. Earlier Raman studies had been interpreted as indicating the existence of linear ZnO_2^{2-} ions .

Sodium Zincate

1 – Introduction :

Sodium zincate refers to anionic zinc oxides or hydroxides, depending on conditions. In the applications of these materials, the exact formula is not necessarily important and it is likely that aqueous zincate solutions consist of mixtures.\

IUPAC Name : sodium tetra hydroxide zincate (2−)	
Molecular formula	$Na_2Zn(OH)_4$
Molar mass	179.5 g / mol

2 - Hydroxy zincates :

Solutions of sodium zincate may be prepared by dissolving zinc, zinc hydroxide , or zinc oxide in an aqueous solution of sodium hydroxide . Simplified equations for these complex processes are:

$$ZnO + H_2O + 2\,NaOH \rightarrow Na_2Zn(OH)_4$$
$$Zn + 2\,H_2O + 2\,NaOH \rightarrow Na_2Zn(OH)_4 + H_2$$

From such solutions, one can crystallize salts of containing the anions $Zn(OH)_4^{2-}$, $Zn_2(OH)_6^{2-}$, and $Zn(OH)_6^{4-}$. $Na_2Zn(OH)_4$ consists of tetrahedral zincate ion and octahedral sodium cations. The salt $Sr_2Zn(OH)_6$ features zinc in an octahedral coordination sphere.

3 - Oxo zincates :

Related oxides are also known such as Na_2ZnO_2 , $Na_2Zn_2O_3$, $Na_{10}Zn_4O_9$.