

= Antimony =

Antimony is a chemical element with symbol Sb (from Latin : stibium) and atomic number 51 . A lustrous gray metalloid , it is found in nature mainly as the sulfide mineral stibnite (Sb_2S_3) . Antimony compounds have been known since ancient times and were used for cosmetics ; metallic antimony was also known , but it was erroneously identified as lead upon its discovery . In the West , it was first isolated by Vannoccio Biringuccio and described in 1540 , although in primitive cultures its powder has been used to cure eye ailments , as also for eye shadow , since time immemorial , and is often referred to by its Arabic name , kohl .

For some time , China has been the largest producer of antimony and its compounds , with most production coming from the Xikuangshan Mine in Hunan . The industrial methods to produce antimony are roasting and reduction using carbon or direct reduction of stibnite with iron .

The largest applications for metallic antimony are as alloying material for lead and tin and for lead antimony plates in lead acid batteries . Alloying lead and tin with antimony improves the properties of the alloys which are used in solders , bullets and plain bearings . Antimony compounds are prominent additives for chlorine and bromine containing fire retardants found in many commercial and domestic products . An emerging application is the use of antimony in microelectronics .

= = Characteristics = =

= = = Properties = = =

Antimony is in the nitrogen group (group 15) and has an electronegativity of 2 .05 . As expected from periodic trends , it is more electronegative than tin or bismuth , and less electronegative than tellurium or arsenic . Antimony is stable in air at room temperature , but reacts with oxygen if heated , to form antimony trioxide , Sb_2O_3 .

Antimony is a silvery , lustrous gray metalloid that has a Mohs scale hardness of 3 . Thus pure antimony is too soft to make hard objects ; coins made of antimony were issued in China 's Guizhou province in 1931 , but because of their rapid wear , their minting was discontinued . Antimony is resistant to attack by acids .

Four allotropes of antimony are known : a stable metallic form and three metastable forms (explosive , black and yellow) . Elemental antimony is a brittle , silver white shiny metalloid . When slowly cooled , molten antimony crystallizes in a trigonal cell , isomorphic with the gray allotrope of arsenic . A rare explosive form of antimony can be formed from the electrolysis of antimony trichloride . When scratched with a sharp implement , an exothermic reaction occurs and white fumes are given off as metallic antimony is formed ; when rubbed with a pestle in a mortar , a strong detonation occurs . Black antimony is formed upon rapid cooling of vapor derived from metallic antimony . It has the same crystal structure as red phosphorus and black arsenic , it oxidizes in air and may ignite spontaneously . At 100°C , it gradually transforms into the stable form . The yellow allotrope of antimony is the most unstable . It has only been generated by oxidation of stibine (SbH_3) at 90°C . Above this temperature and in ambient light , this metastable allotrope transforms into the more stable black allotrope .

Elemental antimony adopts a layered structure (space group $R\bar{3}m$ No. 166) in which layers consist of fused ruffled six membered rings . The nearest and next nearest neighbors form an irregular octahedral complex , with the three atoms in the same double layer being slightly closer than the three atoms in the next . This relatively close packing leads to a high density of 6.697 g/cm^3 , but the weak bonding between the layers leads to the low hardness and brittleness of antimony .

= = = Isotopes = = =

Antimony has two stable isotopes : ^{121}Sb with a natural abundance of 57 % and ^{123}Sb with a natural abundance of 42 % . It also has 35 radioisotopes , of which the longest lived is ^{125}Sb with a half life of 275 years . In addition , 29 metastable states have been characterized . The most stable of these is $^{120\text{m}}\text{Sb}$ with a half life of 576 days . Isotopes that are lighter than the stable ^{123}Sb tend to decay by β^+ decay , and those that are heavier tend to decay by β^- decay , with some exceptions .

== Occurrence ==

The abundance of antimony in the Earth 's crust is estimated at 0.2 to 0.5 parts per million , comparable to thallium at 0.5 parts per million and silver at 0.07 ppm . Even though this element is not abundant , it is found in over 100 mineral species . Antimony is sometimes found natively (e.g. on Antimony Peak) , but more frequently it is found in the sulfide stibnite (Sb_2S_3) which is the predominant ore mineral .

== Compounds ==

Antimony compounds are often classified according to their oxidation state : Sb (III) and Sb (V) . The + 5 oxidation state is more stable .

== Oxides and hydroxides ==

Antimony trioxide (Sb

O_3) is formed when antimony is burnt in air . In the gas phase , this compound exists as Sb

O_3 , but it polymerizes upon condensing . Antimony pentoxide (Sb

O_5) can only be formed by oxidation by concentrated nitric acid . Antimony also forms a mixed

@-@ valence oxide , antimony tetroxide (Sb

O_4) , which features both Sb (III) and Sb (V) . Unlike oxides of phosphorus and arsenic , these various oxides are amphoteric , do not form well @-@ defined oxoacids and react with acids to form antimony salts .

Antimonous acid Sb (OH)

3 is unknown , but the conjugate base sodium antimonite ([Na

3SbO_3^-]) forms upon fusing sodium oxide and Sb

O_3 . Transition metal antimonites are also known . Antimonic acid exists only as the hydrate HSb (

O_4) , forming salts containing the antimonate anion Sb (OH) ?

6 . Dehydrating metal salts containing this anion yields mixed oxides .

Many antimony ores are sulfides , including stibnite (Sb

2S) , pyrargyrite (Ag

3SbS_3) , zinkenite , jamesonite , and boulangerite . Antimony pentasulfide is non @-@ stoichiometric and features antimony in the + 3 oxidation state and S @-@ S bonds . Several thioantimonides are known , such as [Sb

6S] 2 ? and [Sb

8S
13] 2 ? .

== Halides ==

Antimony forms two series of halides : SbX

3 and SbX

5 . The trihalides SbF

3 , SbCl

3 , SbBr

3 , and SbI

3 are all molecular compounds having trigonal pyramidal molecular geometry .

The trifluoride SbF

3 is prepared by the reaction of Sb

2O

3 with HF :

Sb

2O

3 + 6 HF ? 2 SbF

3 + 3 H

2O

It is Lewis acidic and readily accepts fluoride ions to form the complex anions SbF ?

4 and SbF₂ ?

5 . Molten SbF

3 is a weak electrical conductor . The trichloride SbCl

3 is prepared by dissolving Sb

2S

3 in hydrochloric acid :

Sb

2S

3 + 6 HCl ? 2 SbCl

3 + 3 H

2S

The pentahalides SbF

5 and SbCl

5 have trigonal bipyramidal molecular geometry in the gas phase , but in the liquid phase , SbF

5 is polymeric , whereas SbCl

5 is monomeric . SbF

5 is a powerful Lewis acid used to make the superacid fluoroantimonic acid (" H₂SbF₇ ") .

Oxyhalides are more common for antimony than arsenic and phosphorus . Antimony trioxide dissolves in concentrated acid to form oxoantimonyl compounds such as SbOCl and (SbO)

2SO

4 .

== Antimonides , hydrides , and organoantimony compounds ==

Compounds in this class generally are described as derivatives of Sb₃ ? . Antimony forms antimonides with metals , such as indium antimonide (InSb) and silver antimonide (Ag₃Sb) . The alkali metal and zinc antimonides , such as Na₃Sb and Zn₃Sb₂ , are more reactive . Treating these antimonides with acid produces the unstable gas stibine , SbH

3 :

Sb₃ ? + 3 H + ? SbH

3

Stibine can also be produced by treating Sb_3 + salts with hydride reagents such as sodium borohydride. Stibine decomposes spontaneously at room temperature. Because stibine has a positive heat of formation, it is thermodynamically unstable and thus antimony does not react with hydrogen directly.

Organoantimony compounds are typically prepared by alkylation of antimony halides with Grignard reagents. A large variety of compounds are known with both Sb (III) and Sb (V) centers, including mixed chloro - organic derivatives, anions, and cations. Examples include $\text{Sb}(\text{C}_6\text{H}_5)_3$ (triphenylstibine), $\text{Sb}_2(\text{C}_6\text{H}_5)_4$ (with an Sb - Sb bond), and cyclic $[\text{Sb}(\text{C}_6\text{H}_5)]_n$. Pentacoordinated organoantimony compounds are common, examples being $\text{Sb}(\text{C}_6\text{H}_5)_5$ and several related halides.

= = History = =

Antimony (III) sulfide, Sb_2S_3 , was recognized in predynastic Egypt as an eye cosmetic (kohl) as early as about 3100 BC, when the cosmetic palette was invented.

An artifact, said to be part of a vase, made of antimony dating to about 3000 BC was found at Telloh, Chaldea (part of present - day Iraq), and a copper object plated with antimony dating between 2500 BC and 2200 BC has been found in Egypt. Austen, at a lecture by Herbert Gladstone in 1892 commented that " we only know of antimony at the present day as a highly brittle and crystalline metal, which could hardly be fashioned into a useful vase, and therefore this remarkable ' find ' (artifact mentioned above) must represent the lost art of rendering antimony malleable. "

Moorey was unconvinced the artifact was indeed a vase, mentioning that Selimkhanov, after his analysis of the Tello object (published in 1975), " attempted to relate the metal to Transcaucasian natural antimony " (i.e. native metal) and that " the antimony objects from Transcaucasia are all small personal ornaments. " This weakens the evidence for a lost art " of rendering antimony malleable. "

The Roman scholar Pliny the Elder described several ways of preparing antimony sulfide for medical purposes in his treatise Natural History. Pliny the Elder also made a distinction between " male " and " female " forms of antimony; the male form is probably the sulfide, while the female form, which is superior, heavier, and less friable, has been suspected to be native metallic antimony.

The Roman naturalist Pedanius Dioscorides mentioned that antimony sulfide could be roasted by heating by a current of air. It is thought that this produced metallic antimony.

The first description of a procedure for isolating antimony is in the book De la pirotechnia of 1540 by Vannoccio Biringuccio; this predates the more famous 1556 book by Agricola, De re metallica. In this context Agricola has been often incorrectly credited with the discovery of metallic antimony. The book Currus Triumphalis Antimonii (The Triumphal Chariot of Antimony), describing the preparation of metallic antimony, was published in Germany in 1604. It was purported to have been written by a Benedictine monk, writing under the name Basilius Valentinus, in the 15th century; if it were authentic, which it is not, it would predate Biringuccio.

The metal antimony was known to German chemist Andreas Libavius in 1615 who obtained it by adding iron to a molten mixture of antimony sulfide, salt and potassium tartrate. This procedure produced antimony with a crystalline or starred surface.

With the advent of challenges to phlogiston theory it was recognized that antimony is an element forming sulfides, oxides, and other compounds, as is the case with other metals.

The first natural occurrence of pure antimony in the Earth 's crust was described by the Swedish scientist and local mine district engineer Anton von Swab in 1783; the type - sample was collected from the Sala Silver Mine in the Bergslagen mining district of Sala, Västmanland, Sweden.

= = = Etymology = = =

The ancient words for antimony mostly have , as their chief meaning , kohl , the sulfide of antimony

The Egyptians called antimony *mꜣdmt* ; in hieroglyphs , the vowels are uncertain , but there is an Arabic tradition that the word is *mesdemet* . The Greek word , *stimmi* , is probably a loan word from Arabic or from Egyptian *stm*

and is used by Attic tragic poets of the 5th century BC ; later Greeks also used *stibi* , as did Celsus and Pliny , writing in Latin , in the first century AD . Pliny also gives the names *stim* [sic] , *larbaris* , *alabaster* , and the " very common " *platyophthalmos* , " wide @-@ eye " (from the effect of the cosmetic) . Later Latin authors adapted the word to Latin as *stibium* . The Arabic word for the substance , as opposed to the cosmetic , can appear as *ithmid* , *athmoud* , *othmod* , or *uthmod* . Littré suggests the first form , which is the earliest , derives from *stimmida* , an accusative for *stimmi* .

The use of Sb as the standard chemical symbol for antimony is due to Jöns Jakob Berzelius , who used this abbreviation of the name *stibium* . The medieval Latin form , from which the modern languages and late Byzantine Greek take their names for antimony , is *antimonium* . The origin of this is uncertain ; all suggestions have some difficulty either of form or interpretation . The popular etymology , from *anti* @-@ *monachos* or French *antimoine* , still has adherents ; this would mean " monk @-@ killer " , and is explained by many early alchemists being monks , and antimony being poisonous .

Another popular etymology is the hypothetical Greek word *antimonos* , " against aloneness " , explained as " not found as metal " , or " not found unalloyed " . Lippmann conjectured a hypothetical Greek word *anthemonion* , which would mean " floret " , and cites several examples of related Greek words (but not that one) which describe chemical or biological efflorescence .

The early uses of *antimonium* include the translations , in 1050 ? 1100 , by Constantine the African of Arabic medical treatises . Several authorities believe *antimonium* is a scribal corruption of some Arabic form ; Meyerhof derives it from *ithmid* ; other possibilities include *athimar* , the Arabic name of the metalloid , and a hypothetical as @-@ *stimmi* , derived from or parallel to the Greek .

= = Production = =

= = = Top producers and production volumes = = =

The British Geological Survey (BGS) reported that in 2005 , China was the top producer of antimony with an approximately 84 % world share , followed at a distance by South Africa , Bolivia and Tajikistan . Xikuangshan Mine in Hunan province has the largest deposits in China with an estimated deposit of 2 @.@ 1 million metric tons .

In 2010 , according to the US Geological Survey , China accounted for 88 @.@ 9 % of total antimony production with South Africa , Bolivia and Russia sharing the second place .

However , Roskill Consulting estimates for primary production show that in 2010 China held a 76 @.@ 75 % share of world supply with 120 @,@ 462 tonnes (90 @,@ 000 tonnes of reported and 30 @,@ 464 tonnes of un @-@ reported production) , followed by Russia (4 @.@ 14 % share , 6 @,@ 500 tonnes of production) , Myanmar (3 @.@ 76 % share , 5 @,@ 897 tonnes) , Canada (3 @.@ 61 % share , 5 @,@ 660 tonnes) , Tajikistan (3 @.@ 42 % share , 5 @,@ 370 tonnes) and Bolivia (3 @.@ 17 % share , 4 @,@ 980 tonnes) .

Roskill estimates that secondary production globally in 2010 was 39 @,@ 540 tonnes .

Antimony was ranked first in a Risk List published by the British Geological Survey in the second half of 2011 . The list provides an indication of the relative risk to the supply of chemical elements or element groups required to maintain the current British economy and lifestyle .

Also , antimony was identified as one of 12 critical raw materials for the EU in a report published in 2011 , primarily due to the lack of supply outside China .

Reported production of antimony in China fell in 2010 and is unlikely to increase in the coming

years , according to the Roskill report . No significant antimony deposits in China have been developed for about ten years , and the remaining economic reserves are being rapidly depleted . The world 's largest antimony producers , according to Roskill , are listed below :

== Reserves ==

According to statistics from the USGS , current global reserves of antimony will be depleted in 13 years . However , the USGS expects more resources will be found .

== Production process ==

The extraction of antimony from ores depends on the quality of the ore and composition of the ore . Most antimony is mined as the sulfide ; lower @-@ grade ores are concentrated by froth flotation , while higher @-@ grade ores are heated to 500 ? 600 ° C , the temperature at which stibnite melts and is separated from the gangue minerals . Antimony can be isolated from the crude antimony sulfide by a reduction with scrap iron :

Sb

2S

3 + 3 Fe ? 2 Sb + 3 FeS

The sulfide is converted to an oxide and advantage is often taken of the volatility of antimony (III) oxide , which is recovered from roasting . This material is often used directly for the main applications , impurities being arsenic and sulfide . Isolating antimony from its oxide is performed by a carbothermal reduction :

2 Sb

2O

3 + 3 C ? 4 Sb + 3 CO

2

The lower @-@ grade ores are reduced in blast furnaces while the higher @-@ grade ores are reduced in reverberatory furnaces .

== Applications ==

About 60 % of antimony is consumed in flame retardants , and 20 % is used in alloys for batteries , plain bearings and solders .

== Flame retardants ==

Antimony is mainly used as its trioxide in making flame @-@ proofing compounds . It is nearly always used in combination with halogenated flame retardants , with the only exception being in halogen @-@ containing polymers . The formation of halogenated antimony compounds is the cause for the flame retarding effect of antimony trioxide , due to reaction of these compounds with hydrogen atoms and probably also with oxygen atoms and OH radicals , thus inhibiting fire . Markets for these flame @-@ retardant applications include children 's clothing , toys , aircraft and automobile seat covers . It is also used in the fiberglass composites industry as an additive to polyester resins for such items as light aircraft engine covers . The resin will burn while a flame is held to it but will extinguish itself as soon as the flame is removed .

== Alloys ==

Antimony forms a highly useful alloy with lead , increasing its hardness and mechanical strength . For most applications involving lead , varying amounts of antimony are used as alloying metal . In lead ? acid batteries , this addition improves the charging characteristics and reduces generation of unwanted hydrogen during charging . It is used in antifriction alloys (such as Babbitt metal) , in

bullets and lead shot , cable sheathing , type metal (for example , for linotype printing machines) , solder (some " lead @-@ free " solders contain 5 % Sb) , in pewter , and in hardening alloys with low tin content in the manufacturing of organ pipes .

= = = Other applications = = =

Three other applications make up nearly all the rest of the consumption . One of these uses is as a stabilizer and a catalyst for the production of polyethyleneterephthalate . Another application is to serve as a fining agent to remove microscopic bubbles in glass , mostly for TV screens ; this is achieved by the interaction of antimony ions with oxygen , interfering the latter from forming bubbles . The third major application is the use as pigment .

Antimony is being increasingly used in the semiconductor industry as a dopant for heavily doped n @-@ type silicon wafers in the production of diodes , infrared detectors , and Hall @-@ effect devices . In the 1950s , tiny beads of a lead @-@ antimony alloy were used to dope the emitters and collectors of n @-@ p @-@ n alloy junction transistors with antimony . Indium antimonide is used as a material for mid @-@ infrared detectors .

Few biological or medical applications exist for antimony . Treatments principally containing antimony are known as antimonials and are used as emetics . Antimony compounds are used as antiprotozoan drugs . Potassium antimonyl tartrate , or tartar emetic , was once used as an anti @-@ schistosomal drug from 1919 on . It was subsequently replaced by praziquantel . Antimony and its compounds are used in several veterinary preparations like anthiomaline or lithium antimony thiomalate , which is used as a skin conditioner in ruminants . Antimony has a nourishing or conditioning effect on keratinized tissues , at least in animals .

Antimony @-@ based drugs , such as meglumine antimoniate , are also considered the drugs of choice for treatment of leishmaniasis in domestic animals . Unfortunately , as well as having low therapeutic indices , the drugs are poor at penetrating the bone marrow , where some of the Leishmania amastigotes reside , and so cure of the disease ? especially the visceral form ? is very difficult . Elemental antimony as an antimony pill was once used as a medicine . It could be reused by others after ingestion and elimination .

In the heads of some safety matches , antimony (III) sulfide is used . Antimony @-@ 124 is used together with beryllium in neutron sources ; the gamma rays emitted by antimony @-@ 124 initiate the photodisintegration of beryllium . The emitted neutrons have an average energy of 24 keV . Antimony sulfides have been shown to help stabilize the friction coefficient in automotive brake pad materials .

Antimony also is used in the making of bullets and bullet tracers . This element is also used in paint and glass art crafts and as opacifier in enamel .

= = Precautions = =

The effects of antimony and its compounds on human and environmental health differ widely . The massive antimony metal does not affect human and environmental health . Inhalation of antimony trioxide (and similar poorly soluble Sb (III) dust particles such as antimony dust) is considered harmful and suspected of causing cancer . However , these effects are only observed with female rats and after long @-@ term exposure to high dust concentrations . The effects are hypothesized to be attributed to inhalation of poorly soluble Sb particles leading to impaired lung clearance , lung overload , inflammation and ultimately tumour formation , not to exposure to antimony ions (OECD , 2008) . Antimony chlorides are corrosive to skin . The effects of antimony are not comparable to arsenic ; this might be caused by the significant differences of uptake , metabolism and excretion between arsenic and antimony .

For oral absorption , ICRP (1994) recommended values of 10 % for tartar emetic and 1 % for all other antimony compounds . Dermal absorption for metals is estimated at most 1 % (HERAG , 2007) . Inhalation absorption of antimony trioxide and other poorly soluble Sb (III) substances (such as antimony dust) is estimated at 6 @-@ 8 % (OECD , 2008) , whereas a value < 1 % is derived for

Sb (V) substances . Antimony (V) is not quantitatively reduced to antimony (III) in the cell , and both species exist simultaneously .

Antimony is mainly excreted from the human body via urine . Antimony and its compounds do not cause acute human health effects , with the exception of antimony potassium tartrate (" tartar emetic ") , a prodrug that is intentionally used to treat leishmaniasis patients .

Prolonged skin contact with antimony dust may cause dermatitis . However , it was agreed at the European Union level that the skin rashes observed are not substance @-@ specific , but most probably due to a physical blocking of sweat ducts (ECHA / PR / 09 / 09 , Helsinki , 6 July 2009) . Antimony dust may also be explosive when dispersed in the air ; when in a bulk solid it is not combustible .

Antimony is incompatible with strong acids , halogenated acids , and oxidizers ; when exposed to newly formed hydrogen it may form stibine (SbH₃) .

The 8 hour time weighted average (TWA) is set at 0 @.@ 5 mg / m³ by the American Conference of Governmental Industrial Hygienists and by the Occupational Safety and Health Administration (OSHA) as a legal permissible exposure limit (PEL) in the workplace . The National Institute for Occupational Safety and Health (NIOSH) has set a recommended exposure limit (REL) of 0 @.@ 5 mg / m³ as an 8 hour TWA . Antimony compounds are used as catalysts for polyethylene terephthalate (PET) production . Some studies report minor antimony leaching from PET bottles into liquids , but levels are below drinking water guidelines . Antimony concentrations in fruit juice concentrates were somewhat higher (up to 44 @.@ 7 µg / L of antimony) , but juices do not fall under the drinking water regulations . The drinking water guidelines are :

World Health Organization : 20 µg / L

Japan : 15 µg / L

United States Environmental Protection Agency , Health Canada and the Ontario Ministry of Environment : 6 µg / L

EU and German Federal Ministry of Environment : 5 µg / L

The TDI proposed by WHO is 6 µg antimony per kilogram of body weight . The IDLH (immediately dangerous to life and health) value for antimony is 50 mg / m³ .