

= Osmium =

Osmium (from Greek osme , " smell ") is a chemical element with symbol Os and atomic number 76 . It is a hard , brittle , bluish white transition metal in the platinum group that is found as a trace element in alloys , mostly in platinum ores . Osmium is the densest naturally occurring element , with a density of 22.59 g / cm^3 . Its alloys with platinum , iridium , and other platinum group metals are employed in fountain pen nibs , electrical contacts , and other applications where extreme durability and hardness are needed .

= = Characteristics = =

= = = Physical properties = = =

Osmium has a blue gray tint and is the densest stable element , slightly denser than iridium . Calculations of density from the X ray diffraction data may produce the most reliable data for these elements , giving a value of $22.562 \pm 0.009 \text{ g / cm}^3$ for iridium versus $22.587 \pm 0.009 \text{ g / cm}^3$ for osmium .

Osmium is a hard but brittle metal that remains lustrous even at high temperatures . It has a very low compressibility . Correspondingly , its bulk modulus is extremely high , reported between 395 and 462 GPa , which rivals that of diamond (443 GPa) . The hardness of osmium is moderately high at 4 GPa . Because of its hardness , brittleness , low vapor pressure (the lowest of the platinum group metals) , and very high melting point (the fourth highest of all elements) , solid osmium is difficult to machine , form , or work .

= = = Chemical properties = = =

Osmium forms compounds with oxidation states ranging from -2 to $+8$. The most common oxidation states are $+2$, $+3$, $+4$, and $+8$. The $+8$ oxidation state is notable for being the highest attained by any chemical element aside from iridium 's $+9$ and is encountered only in xenon , ruthenium , hassium , iridium , plutonium , and curium (uncertain) . The oxidation states -1 and -2 represented by the two reactive compounds

$2[\text{Os}$

$4(\text{CO})$

$13]$ and Na

$2[\text{Os}(\text{CO})$

$4]$ are used in the synthesis of osmium cluster compounds .

The most common compound exhibiting the $+8$ oxidation state is osmium tetroxide . This toxic compound is formed when powdered osmium is exposed to air . It is a very volatile , water soluble , pale yellow , crystalline solid with a strong smell . Osmium powder has the characteristic smell of osmium tetroxide . Osmium tetroxide forms red osmates OsO_4

$4(\text{OH})_2$

upon reaction with a base . With ammonia , it forms the nitrido osmates OsO_3N

3N . Osmium tetroxide boils at 130°C and is a powerful oxidizing agent . By contrast , osmium dioxide (OsO_2) is black , non volatile , and much less reactive and toxic .

Only two osmium compounds have major applications : osmium tetroxide for staining tissue in electron microscopy and for the oxidation of alkenes in organic synthesis , and the non volatile osmates for organic oxidation reactions .

Osmium pentafluoride (OsF_5) is known , but osmium trifluoride (OsF_3) has not yet been synthesized . The lower oxidation states are stabilized by the larger halogens , so that the trichloride , tribromide , triiodide , and even diiodide are known . The oxidation state $+1$ is known only for osmium iodide (OsI) , whereas several carbonyl complexes of osmium , such as triosmium dodecacarbonyl ($\text{Os}_3(\text{CO})_{12}$)

3 (CO)

12) , represent oxidation state 0 .

In general , the lower oxidation states of osmium are stabilized by ligands that are good π -donors (such as amines) and π -acceptors (heterocycles containing nitrogen) . The higher oxidation states are stabilized by strong σ - and π -donors , such as O_2 and N_3 .

Despite its broad range of compounds in numerous oxidation states , osmium in bulk form at ordinary temperatures and pressures resists attack by all acids and alkalis , including aqua regia .

== Isotopes ==

Osmium has seven naturally occurring isotopes , six of which are stable : ^{184}Os , ^{187}Os , ^{188}Os , ^{189}Os , ^{190}Os , and (most abundant) ^{192}Os . ^{186}Os undergoes alpha decay with such a long half life ($2.0 \pm 1.1 \times 10^{15}$ years) that for practical purposes it can be considered stable . Alpha decay is predicted for all seven naturally occurring isotopes , but it has been observed only for ^{186}Os , presumably due to very long half lives . It is predicted that ^{184}Os and ^{192}Os can undergo double beta decay but this radioactivity has not been observed yet .

^{187}Os is the daughter of ^{187}Re (half life 4.56×10^{10} years) and is used extensively in dating terrestrial as well as meteoric rocks (see rhenium - osmium dating) . It has also been used to measure the intensity of continental weathering over geologic time and to fix minimum ages for stabilization of the mantle roots of continental cratons . This decay is a reason why rhenium - rich minerals are abnormally rich in ^{187}Os . However , the most notable application of Os isotopes in geology has been in conjunction with the abundance of iridium , to characterise the layer of shocked quartz along the Cretaceous - Paleogene boundary that marks the extinction of the dinosaurs 66 million years ago .

== History ==

Osmium was discovered in 1803 by Smithson Tennant and William Hyde Wollaston in London , England . The discovery of osmium is intertwined with that of platinum and the other metals of the platinum group . Platinum reached Europe as platina (" small silver ") , first encountered in the late 17th century in silver mines around the Chocó Department , in Colombia . The discovery that this metal was not an alloy , but a distinct new element , was published in 1748 . Chemists who studied platinum dissolved it in aqua regia (a mixture of hydrochloric and nitric acids) to create soluble salts . They always observed a small amount of a dark , insoluble residue . Joseph Louis Proust thought that the residue was graphite . Victor Collet - Descotils , Antoine François , comte de Fourcroy , and Louis Nicolas Vauquelin also observed the black residue in 1803 , but did not obtain enough material for further experiments .

In 1803 , Smithson Tennant analyzed the insoluble residue and concluded that it must contain a new metal . Vauquelin treated the powder alternately with alkali and acids and obtained a volatile new oxide , which he believed to be of this new metal , which he named ptene , from the Greek word $\pi\tau\epsilon\nu\omicron\varsigma$ (ptēnos) for winged . However , Tennant , who had the advantage of a much larger amount of residue , continued his research and identified two previously undiscovered elements in the black residue , iridium and osmium . He obtained a yellow solution (probably of $[\text{Os}(\text{OH})_2\text{O}_4]^{2-}$) by reactions with sodium hydroxide at red heat . After acidification he was able to distill the formed OsO_4 . He named it osmium after Greek osme meaning " a smell " , because of the ashy and smoky smell of the volatile osmium tetroxide . Discovery of the new elements was documented in a letter to the Royal Society on June 21 , 1804 .

Uranium and osmium were early successful catalysts in the Haber process , the nitrogen fixation reaction of nitrogen and hydrogen to produce ammonia , giving enough yield to make the process economically successful . At the time , a group at BASF led by Carl Bosch bought most of the world 's supply of osmium to use as a catalyst . Shortly thereafter , in 1908 , cheaper catalysts based on iron and iron oxides were introduced by the same group for the first pilot plants , removing the need for the expensive and rare osmium .

Nowadays osmium is obtained primarily from the processing of platinum and nickel ores .

= = Occurrence = =

Osmium is the least abundant stable element in Earth 's crust with an average mass fraction of 50 parts per trillion in the continental crust .

Osmium is found in nature as an uncombined element or in natural alloys ; especially the iridium ? osmium alloys , osmiridium (osmium rich) , and iridosmium (iridium rich) . In nickel and copper deposits , the platinum group metals occur as sulfides (i.e. , (Pt , Pd) S) , tellurides (e.g. , PtBiTe) , antimonides (e.g. , PdSb) , and arsenides (e.g. , PtAs₂) ; in all these compounds platinum is exchanged by a small amount of iridium and osmium . As with all of the platinum group metals , osmium can be found naturally in alloys with nickel or copper .

Within Earth 's crust , osmium , like iridium , is found at highest concentrations in three types of geologic structure : igneous deposits (crustal intrusions from below) , impact craters , and deposits reworked from one of the former structures . The largest known primary reserves are in the Bushveld igneous complex in South Africa , though the large copper ? nickel deposits near Norilsk in Russia , and the Sudbury Basin in Canada are also significant sources of osmium . Smaller reserves can be found in the United States . The alluvial deposits used by pre @-@ Columbian people in the Chocó Department , Colombia are still a source for platinum group metals . The second large alluvial deposit was found in the Ural Mountains , Russia , which is still mined .

= = Production = =

Osmium is obtained commercially as a by @-@ product from nickel and copper mining and processing . During electrolysis of copper and nickel , noble metals such as silver , gold and the platinum group metals , together with non @-@ metallic elements such as selenium and tellurium settle to the bottom of the cell as anode mud , which forms the starting material for their extraction . In order to separate the metals , they must first be brought into solution . Several methods are available depending on the separation process and the composition of the mixture ; two representative methods are fusion with sodium peroxide followed by dissolution in aqua regia , and dissolution in a mixture of chlorine with hydrochloric acid . Osmium , ruthenium , rhodium and iridium can be separated from platinum , gold and base metals by their insolubility in aqua regia , leaving a solid residue . Rhodium can be separated from the residue by treatment with molten sodium bisulfate . The insoluble residue , containing Ru , Os and Ir , is treated with sodium oxide , in which Ir is insoluble , producing water @-@ soluble Ru and Os salts . After oxidation to the volatile oxides , RuO₄

4 is separated from OsO₄

4 by precipitation of (NH₄)₃RuCl₆ with ammonium chloride .

After it is dissolved , osmium is separated from the other platinum group metals by distillation or extraction with organic solvents of the volatile osmium tetroxide . The first method is similar to the procedure used by Tennant and Wollaston . Both methods are suitable for industrial scale production . In either case , the product is reduced using hydrogen , yielding the metal as a powder or sponge that can be treated using powder metallurgy techniques .

Neither the producers nor the United States Geological Survey published any production amounts for osmium . Estimations of the United States consumption date published from 1971 , which gives a consumption in the United States of 2000 troy ounces (62 kg) , would suggest that the production is still less than 1 ton per year . In 2012 , the estimated US production of osmium was 75 kg .

= = Applications = =

Because of the volatility and extreme toxicity of its oxide , osmium is rarely used in its pure state , but is instead often alloyed with other metals . Those alloys are utilized in high @-@ wear applications . Osmium alloys such as osmiridium are very hard and , along with other platinum @-@

group metals , are used in the tips of fountain pens , instrument pivots , and electrical contacts , as they can resist wear from frequent operation . They were also used for the tips of phonograph styli during the late 78 rpm and early " LP " and " 45 " record era , circa 1945 to 1955 . Although very durable compared to steel and chromium needle points , osmium alloy tips wore out far more rapidly than competing but costlier sapphire and diamond tips and were discontinued .

Osmium tetroxide has been used in fingerprint detection and in staining fatty tissue for optical and electron microscopy . As a strong oxidant , it cross links lipids mainly by reacting with unsaturated carbon - carbon bonds and thereby both fixes biological membranes in place in tissue samples and simultaneously stains them . Because osmium atoms are extremely electron dense , osmium staining greatly enhances image contrast in transmission electron microscopy (TEM) studies of biological materials . Those carbon materials have otherwise very weak TEM contrast (see image) . Another osmium compound , osmium ferricyanide (OsFeCN) , exhibits similar fixing and staining action .

The tetroxide and a related compound potassium osmate are important oxidants for chemical synthesis , despite being very poisonous . For the Sharpless asymmetric dihydroxylation , which uses osmate for the conversion of a double bond into a vicinal diol , Karl Barry Sharpless won the Nobel Prize in Chemistry in 2001 . OsO_4 is very expensive for this use , so KMnO_4 is often used instead , even though the yields are less for this cheaper chemical reagent .

In 1898 an Austrian chemist Auer von Welsbach developed the Osram lamp with a filament made of osmium , which he introduced commercially in 1902 . After only a few years , osmium was replaced by the more stable metal tungsten . Tungsten has the highest melting point among all metals , and using it in light bulbs increases the luminous efficacy and life of incandescent lamps .

The light bulb manufacturer Osram (founded in 1906 , when three German companies , Auer Gesellschaft , AEG and Siemens & Halske , combined their lamp production facilities) derived its name from the elements of osmium and Wolfram (the latter is German for tungsten) .

Like palladium , powdered osmium effectively absorbs hydrogen atoms . This could make osmium a potential candidate for a metal hydride battery electrode . However , osmium is expensive and would react with potassium hydroxide , the most common battery electrolyte .

Osmium has high reflectivity in the ultraviolet range of the electromagnetic spectrum ; for example , at 600 Å osmium has a reflectivity twice that of gold . This high reflectivity is desirable in space based UV spectrometers , which have reduced mirror sizes due to space limitations . Osmium coated mirrors were flown in several space missions aboard the Space Shuttle , but it soon became clear that the oxygen radicals in the low Earth orbit are abundant enough to significantly deteriorate the osmium layer .

The only known clinical use of osmium appears to be for synovectomy in arthritic patients in Scandinavia . It involves the local administration of osmium tetroxide (OsO_4) , which is a highly toxic compound . The lack of reports of long term side effects suggest that osmium itself can be biocompatible , although this depends on the osmium compound administered . In 2011 , osmium (VI) and osmium (II) compounds were reported to show anticancer activity in vivo , it indicated a promising future for using osmium compounds as anticancer drugs .

= = Precautions = =

Finely divided metallic osmium is pyrophoric and reacts with oxygen at room temperature , forming volatile osmium tetroxide . Some osmium compounds are also converted to the tetroxide if oxygen is present . This makes osmium tetroxide the main source of contact with the environment .

Osmium tetroxide is highly volatile and penetrates skin readily , and is very toxic by inhalation , ingestion , and skin contact . Airborne low concentrations of osmium tetroxide vapor can cause lung congestion and skin or eye damage , and should therefore be used in a fume hood . Osmium tetroxide is rapidly reduced to relatively inert compounds by polyunsaturated vegetable oils , such as corn oil .

= = Price = =

Osmium is usually sold as a minimum 99.99 % pure powder . Like other precious metals , it is measured by troy weight and by grams . Its price in 2012 was about \$ 400 per troy ounce (or about \$ 13,000 per kilogram) , depending on the quantity and its supplier .