

= Palladium =

Palladium is a chemical element with symbol Pd and atomic number 46 . It is a rare and lustrous silvery @-@ white metal discovered in 1803 by William Hyde Wollaston . He named it after the asteroid Pallas , which was itself named after the epithet of the Greek goddess Athena , acquired by her when she slew Pallas . Palladium , platinum , rhodium , ruthenium , iridium and osmium form a group of elements referred to as the platinum group metals (PGMs) . These have similar chemical properties , but palladium has the lowest melting point and is the least dense of them .

More than half the supply of palladium and its congener platinum is used in catalytic converters , which convert as much as 90 % of the harmful gases in automobile exhaust (hydrocarbons , carbon monoxide , and nitrogen dioxide) into harmless substances (nitrogen , carbon dioxide and water vapor) . Palladium is also used in electronics , dentistry , medicine , hydrogen purification , chemical applications , groundwater treatment , and jewelry . Palladium is a key component of fuel cells , which react hydrogen with oxygen to produce electricity , heat , and water .

Ore deposits of palladium and other PGMs are rare . The most extensive deposits have been found in the norite belt of the Bushveld Igneous Complex covering the Transvaal Basin in South Africa , the Stillwater Complex in Montana , United States , the Thunder Bay District of Ontario , Canada , and the Norilsk Complex in Russia . Recycling is also a source , mostly from scrapped catalytic converters . The numerous applications and limited supply sources result in considerable investment interest .

= = Characteristics = =

Palladium belongs to group 10 in the periodic table , but the configuration in the outermost electron shells is atypical for group 10 (see also niobium (41) , ruthenium (44) , and rhodium (45)) . Fewer electron shells are filled than the elements directly preceding it (a phenomenon unique to palladium) . The valence shell has eighteen electrons ? ten more than the eight found in the valence shells of the noble gases from neon onward .

Palladium is a soft silver @-@ white metal that resembles platinum . It is the least dense and has the lowest melting point of the platinum group metals . It is soft and ductile when annealed and is greatly increased in strength and hardness when cold @-@ worked . Palladium dissolves slowly in concentrated nitric acid , in hot , concentrated sulfuric acid , and when finely ground , in hydrochloric acid .

Common oxidation states of palladium are 0 , + 1 , + 2 and + 4 . Relatively few compounds are known with palladium unambiguously in the + 3 oxidation state , though such compounds have been proposed as intermediates in many palladium @-@ catalyzed cross @-@ coupling reactions . Palladium (VI) was first observed in 2002 .

Palladium films with defects produced by alpha particle bombardment at low temperature exhibit superconductivity having $T_c = 3 \text{ @.} 2 \text{ K}$.

= = = Isotopes = = =

Naturally occurring palladium is composed of seven isotopes , six of which are stable . The most stable radioisotopes are ^{107}Pd with a half @-@ life of 6 @. 5 million years (found in nature) , ^{103}Pd with 17 days , and ^{100}Pd with 3 @. 63 days . Eighteen other radioisotopes have been characterized with atomic weights ranging from 90 @. 94948 (64) u (^{91}Pd) to 122 @. 93426 (64) u (^{123}Pd) . These have half @-@ lives of less than thirty minutes , except ^{101}Pd (half @-@ life : 8 @. 47 hours) , ^{109}Pd (half @-@ life : 13 @. 7 hours) , and ^{112}Pd (half @-@ life : 21 hours) .

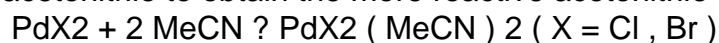
For isotopes with atomic mass unit values less than that of the most abundant stable isotope , ^{106}Pd , the primary decay mode is electron capture with the primary decay product being rhodium . The primary mode of decay for those isotopes of Pd with atomic mass greater than 106 is beta decay with the primary product of this decay being silver .

Radiogenic ^{107}Ag is a decay product of ^{107}Pd and was first discovered in 1978 in the Santa Clara meteorite of 1976. The discoverers suggest that the coalescence and differentiation of iron @-@ cored small planets may have occurred 10 million years after a nucleosynthetic event. ^{107}Pd versus Ag correlations observed in bodies, which have been melted since accretion of the solar system, must reflect the presence of short @-@ lived nuclides in the early solar system.

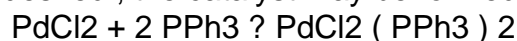
= = Compounds = =

Palladium does not react with oxygen at standard temperatures (and thus does not tarnish in air). Palladium heated to 800°C will produce a layer of palladium (II) oxide (PdO). It tarnishes lightly in a moist atmosphere containing sulfur. Palladium primarily exists in the 0, + 2, and + 4 oxidation states, though + 4 is comparatively rare. One major example of palladium (IV) is hexachloropalladate (IV), $[\text{PdCl}_6]^{2-}$.

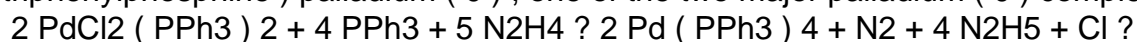
Elemental palladium reacts with chlorine to give palladium (II) chloride; it dissolves in nitric acid and precipitates palladium (II) acetate on addition of acetic acid. These two compounds and the bromide are reactive and relatively inexpensive, making them convenient entry points to palladium chemistry. All three are not monomeric; the chloride and bromide often must be refluxed in acetonitrile to obtain the more reactive acetonitrile complex monomers, for example:



Palladium (II) chloride is the principal starting material for many other palladium catalysts. It is used to prepare heterogeneous palladium catalysts: palladium on barium sulfate, palladium on carbon, and palladium chloride on carbon. It reacts with triphenylphosphine in coordinating solvents to give bis (triphenylphosphine) palladium (II) dichloride, a useful catalyst. Where desired, the catalyst may be formed in situ.



Reduction of this phosphine complex with hydrazine with more phosphine gives tetrakis (triphenylphosphine) palladium (0), one of the two major palladium (0) complexes:



The other major palladium (0) complex, tris (dibenzylideneacetone) dipalladium (0) ($\text{Pd}_2(\text{dba})_3$), is prepared by reducing sodium tetrachloropalladate in the presence of dibenzylideneacetone.

Mixed valence palladium complex of $\text{Pd}_4(\text{CO})_4(\text{OAc})_4$ and $\text{Pd}(\text{acac})_2$ forms an infinite Pd chain structure, with alternatively interconnected $\text{Pd}_4(\text{CO})_4(\text{OAc})_4$ and $\text{Pd}(\text{acac})_2$ units.

The many reactions catalyzed by palladium compounds are collectively known as palladium @-@ catalyzed coupling reactions. Prominent examples include the Heck, Suzuki, and Stille reactions. Palladium (II) acetate, tetrakis (triphenylphosphine) palladium (0) ($\text{Pd}(\text{PPh}_3)_4$), and tris (dibenzylideneacetone) dipalladium (0) ($\text{Pd}_2(\text{dba})_3$) serve either as catalysts or as starting materials for catalysts.

= = History = =

William Hyde Wollaston noted the discovery of a new noble metal in July 1802 in his lab @-@ book and named it palladium in August of the same year. Wollaston purified enough of the material and offered it, without naming the discoverer, in a small shop in Soho in April 1803. After harsh criticism from Richard Chenevix that palladium is an alloy of platinum and mercury, Wollaston anonymously offered a reward of 20 British pounds for 20 grains of synthetic palladium alloy. Chenevix received the Copley Medal in 1803 after he published his experiments on palladium. Wollaston published the discovery of rhodium in 1804 and mentions some of his work on palladium. He disclosed that he was the discoverer of palladium in a publication in 1805.

It was named by Wollaston in 1802 after the asteroid Pallas, which had been discovered two months earlier. Wollaston found palladium in crude platinum ore from South America by dissolving the ore in aqua regia, neutralizing the solution with sodium hydroxide, and precipitating platinum as ammonium chloroplatinate with ammonium chloride. He added mercuric cyanide to form the

compound palladium (II) cyanide , which was heated to extract palladium metal .

Palladium chloride was at one time prescribed as a tuberculosis treatment at the rate of 0 .065 g per day (approximately one milligram per kilogram of body weight) . This treatment had many negative side effects , and was later replaced by more effective drugs .

Most palladium is used for catalytic converters in the automobile industry . In the run up to year 2000 , the Russian supply of palladium to the global market was repeatedly delayed and disrupted because for political reasons , the export quota was not granted on time . The ensuing market panic drove the price to an all time high of \$ 1100 per troy ounce in January 2001 . Around that time , the Ford Motor Company , fearing that automobile production would be disrupted by a palladium shortage , stockpiled the metal . When prices fell in early 2001 , Ford lost nearly US \$ 1 billion .

World demand for palladium increased from 100 tons in 1990 to nearly 300 tons in 2000 . The global production of palladium from mines was 222 tonnes in 2006 according to the United States Geological Survey . Many are concerned about a steady supply of palladium in the wake of Russia 's military maneuvers in Ukraine , partly as sanctions could hamper Russian palladium exports ; any restrictions on Russian palladium exports would exacerbate what is already expected to be a large palladium deficit in 2014 .

= = Occurrence = =

With a 44 % world share of palladium in 2007 , Russia was the top producer , followed by South Africa with 40 % . Canada with 6 % and the U.S. with 5 % are the other substantial producers of palladium .

Palladium can be found as a free metal alloyed with gold and other platinum group metals in placer deposits of the Ural Mountains , Australia , Ethiopia , North and South America . For the production of palladium , these deposits play only a minor role . The most important commercial sources are nickel copper deposits found in the Sudbury Basin , Ontario , and the Norilsk ? Talnakh deposits in Siberia . The other large deposit is the Merensky Reef platinum group metals deposit within the Bushveld Igneous Complex South Africa . The Stillwater igneous complex of Montana and the Roby zone ore body of the Lac des Îles igneous complex of Ontario are the two other sources of palladium in Canada and the United States . Palladium is found in the rare minerals cooperite and polarite .

Palladium is also produced in nuclear fission reactors and can be extracted from spent nuclear fuel (see synthesis of precious metals) , though this source for palladium is not used . None of the existing nuclear reprocessing facilities are equipped to extract palladium from the high level radioactive waste .

= = Applications = =

The largest use of palladium today is in catalytic converters . Palladium is also used in jewelry , dentistry , watch making , blood sugar test strips , aircraft spark plugs , surgical instruments , and electrical contacts . Palladium is also used to make professional transverse (concert or classical) flutes . As a commodity , palladium bullion has ISO currency codes of XPD and 964 . Palladium is one of only four metals to have such codes , the others being gold , silver and platinum . Because it absorbs hydrogen , palladium is a key component of the controversial cold fusion experiments that began in 1989 .

= = = Catalysis = = =

When it is finely divided , as with palladium on carbon , palladium forms a versatile catalyst ; it speeds hydrogenation , dehydrogenation , and petroleum cracking . A large number of carbon carbon bonding reactions in organic chemistry (such as the Heck reaction and Suzuki coupling) are facilitated by palladium compound catalysts . (See Palladium Compounds and palladium catalyzed coupling reactions .)

When dispersed on conductive materials , palladium is an excellent electrocatalyst for oxidation of primary alcohols in alkaline media . In 2010 , palladium catalysed organic reactions were recognised by the Nobel Prize in Chemistry . Palladium is also a versatile metal for homogeneous catalysis , used in combination with a broad variety of ligands for highly selective chemical transformations . A 2008 study showed that palladium is an effective catalyst for carbon-fluoride bonds .

Palladium is essential to the Lindlar catalyst , also called Lindlar 's Palladium .

== Electronics ==

The second greatest application of palladium in electronics is in multilayer ceramic capacitors in which palladium (and palladium-silver alloy) is used for electrodes . Palladium (sometimes alloyed with nickel) is used for component and connector plating in consumer electronics and in soldering materials . The electronic sector consumed 1 07 million troy ounces (33 2 tonnes) of palladium in 2006 , according to a Johnson Matthey report .

== Technology ==

Hydrogen easily diffuses through heated palladium , and membrane reactors with Pd membranes are used in the production of high purity hydrogen . Palladium is used in palladium-hydrogen electrodes in electrochemical studies . Palladium (II) chloride readily catalyzes carbon monoxide gas to carbon dioxide and is useful in carbon monoxide detectors .

== Hydrogen storage ==

Palladium readily absorbs hydrogen at room temperatures , forming palladium hydride PdH_x with x less than 1 . While this property is common to many transition metals , palladium has a uniquely high absorption capacity and does not lose its ductility until x approaches 1 . This property has been investigated in designing an efficient , inexpensive , and safe hydrogen fuel storage medium , though palladium itself is currently prohibitively expensive for this purpose . The content of hydrogen in palladium can be linked to magnetic susceptibility , which decreases with the increase of hydrogen and becomes zero for PdH_{0.62}. At any higher ratio , the solid solution becomes diamagnetic .

== Dentistry ==

Palladium is used in small amounts (about 0-5 %) in some alloys of dental amalgam to decrease corrosion and increase the metallic lustre of the final restoration .

== Jewelry ==

Palladium has been used as a precious metal in jewelry since 1939 as an alternative to platinum in the alloys called " white gold " , where the naturally white color of palladium does not require rhodium plating . Palladium is much less dense than platinum . Similar to gold , palladium can be beaten into leaf as thin as 100 nm (1 ? 250 000 in) . Unlike platinum , palladium may discolor at temperatures above 400 ° C (752 ° F) ; it is relatively brittle .

Palladium is one of the three most popular alloying metals in white gold (nickel and silver can also be used) . Palladium-gold is more expensive than nickel-gold , but seldom causes allergic reactions (though certain cross-allergies with nickel may occur) .

When platinum was declared a strategic government resource during World War II , many jewelry bands were made out of palladium . As recently as September 2001 , palladium was more expensive than platinum and rarely used in jewelry because of the technical difficulty of casting . Currently , the casting problem has been resolved and use in jewelry has increased because

platinum has increased in price while palladium decreased .

Prior to 2004 , the principal use of palladium in jewelry was the manufacture of white gold . In early 2004 , when gold and platinum prices rose steeply , China began fabricating volumes of palladium jewelry , consuming 37 tonnes in 2005 . Changes in the relative price of platinum after 2008 lowered demand for palladium to 17 @. @ 4 tonnes in 2009 .

In January 2010 , hallmarks for palladium were introduced by assay offices in the United Kingdom , and hallmarking became mandatory for all jewelry advertising pure or alloyed palladium . Articles can be marked as 500 , 950 , or 999 parts of palladium per thousand of the alloy .

Fountain pen nibs made from gold are sometimes plated with palladium when a silver (rather than gold) appearance is desired . Sheaffer has used palladium plating for decades , either as an accent on otherwise gold nibs or coverING the gold completely .

= = = Photography = = =

In the platinotype printing process , photographers make fine @-@ art black @-@ and @-@ white prints using platinum or palladium salts . Often used with platinum , palladium provides an alternative to silver .

= = Toxicity = =

Palladium is a metal with low toxicity . It is poorly absorbed by human body when digested . Plants such as the water hyacinth are killed by low levels of palladium salts , but most other plants tolerate it , although tests show that at levels above 0 @. @ 0003 % growth is affected . High doses of palladium could be poisonous ; tests on rodents suggest it may be carcinogenic , no clear evidence indicates the element harms humans .

= = Precautions = =

Finely divided palladium metal can be pyrophoric . As a platinum @-@ group metal , the bulk material is quite inert . Although contact dermatitis has been reported , the amount of data on the effects of exposure to palladium is limited . It has been shown that people with an allergic reaction to palladium also react to nickel , making it advisable to avoid the use of dental alloys containing palladium on those so allergic .

Some palladium is emitted with the exhaust gases of cars with catalytic converters . Between 4 and 108 ng / km of palladium particulate is released by such cars , while the total uptake from food is estimated to be less than 2 µg per person a day . The second possible source of palladium is dental restoration , from which the uptake of palladium is estimated to be less than 15 µg per person per day . People working with palladium or its compounds might have a considerably greater uptake . For soluble compounds such as palladium chloride , 99 % is eliminated from the body within 3 days .

The median lethal dose (LD50) of soluble palladium compounds in mice is 200 mg / kg for oral and 5 mg / kg for intravenous administration .