

= Protactinium =

Protactinium or protoactinium ( former name ) is a chemical element with symbol Pa and atomic number 91 . It is a dense , silvery @-@ gray metal which readily reacts with oxygen , water vapor and inorganic acids . It forms various chemical compounds where protactinium is usually present in the oxidation state + 5 , but can also assume + 4 and even + 2 or + 3 states . The average concentrations of protactinium in the Earth 's crust is typically on the order of a few parts per trillion , but may reach up to a few parts per million in some uraninite ore deposits . Because of its scarcity , high radioactivity and high toxicity , there are currently no uses for protactinium outside of scientific research , and for this purpose , protactinium is mostly extracted from spent nuclear fuel .

Protactinium was first identified in 1913 by Kasimir Fajans and Oswald Helmuth Göhring and named brevium because of the short half @-@ life of the specific isotope studied , namely protactinium @-@ 234 . A more stable isotope (  $^{231}\text{Pa}$  ) of protactinium was discovered in 1917 / 18 by Otto Hahn and Lise Meitner , and they chose the name proto @-@ actinium , but then the IUPAC named it finally protactinium in 1949 and confirmed Hahn and Meitner as discoverers . The new name meant " parent of actinium " and reflected the fact that actinium is a product of radioactive decay of protactinium . It is noted that John Arnold Cranston ( working with Frederick Soddy and Ada Hitchens ) is also credited with discovering the most stable isotope in 1915 but delayed his announcement due to being called up for service in the First World War .

The longest @-@ lived and most abundant ( nearly 100 % ) naturally occurring isotope of protactinium , protactinium @-@ 231 , has a half @-@ life of 32 @,@ 760 years and is a decay product of uranium @-@ 235 . Much smaller trace amounts of the short @-@ lived nuclear isomer protactinium @-@ 234m occur in the decay chain of uranium @-@ 238 . Protactinium @-@ 233 results from the decay of thorium @-@ 233 as part of the chain of events used to produce uranium @-@ 233 by neutron irradiation of thorium @-@ 232 . It is an undesired intermediate product in thorium @-@ based nuclear reactors and is therefore removed from the active zone of the reactor during the breeding process . Analysis of the relative concentrations of various uranium , thorium and protactinium isotopes in water and minerals is used in radiometric dating of sediments which are up to 175 @,@ 000 years old and in modeling of various geological processes .

= = History = =

In 1871 , Dmitri Mendeleev predicted the existence of an element between thorium and uranium . The actinide element group was unknown at the time . Therefore , uranium was positioned below tungsten , and thorium below zirconium , leaving the space below tantalum empty and , until the 1950s , periodic tables were published with this structure . For a long time chemists searched for eka @-@ tantalum as an element with similar chemical properties to tantalum , making a discovery of protactinium nearly impossible . Tantalum 's heavier analogue was later found to be the transuranic element dubnium .

In 1900 , William Crookes isolated protactinium as an intensely radioactive material from uranium ; however , he could not characterize it as a new chemical element and thus named it uranium @-@ X ( UX ) . Crookes dissolved uranium nitrate in ether , the residual aqueous phase contains most of the 234

90Th and 234

91Pa . His method was still used in the 1950s to isolate 234

90Th and 234

91Pa from uranium compounds . Protactinium was first identified in 1913 , when Kasimir Fajans and Oswald Helmuth Göhring encountered the isotope  $^{234}\text{Pa}$  during their studies of the decay chains of uranium @-@ 238 : 238

92U ? 234

90Th ? 234

91Pa ? 234

92U . They named the new element brevium ( from the Latin word , brevis , meaning brief or short )

because of its short half @-@ life , 6 @.@ 7 hours for 234

91Pa . In 1917 / 18 , two groups of scientists , Otto Hahn and Lise Meitner of Germany and Frederick Soddy and John Cranston of Great Britain , independently discovered another isotope of protactinium , 231Pa having much longer half @-@ life of about 32 @.@ 000 years . Thus the name brevium was changed to protoactinium as the new element was part of the decay chain of uranium @-@ 235 before the actinium ( from Greek : ?????? = protos meaning first , before ) . For ease of pronunciation , the name was shortened to protactinium by the IUPAC in 1949 . The discovery of protactinium completed one of the last gaps in the early versions of the periodic table , proposed by Mendeleev in 1869 , and it brought to fame the involved scientists .

Aristid von Grosse produced 2 milligrams of Pa<sub>2</sub>O<sub>5</sub> in 1927 , and in 1934 first isolated elemental protactinium from 0 @.@ 1 milligrams of Pa<sub>2</sub>O<sub>5</sub> . He used two different procedures : in the first one , protactinium oxide was irradiated by 35 keV electrons in vacuum . In another method , called the van Arkel ? de Boer process , the oxide was chemically converted to a halide ( chloride , bromide or iodide ) and then reduced in a vacuum with an electrically heated metallic filament :



In 1961 , the United Kingdom Atomic Energy Authority ( UKAEA ) produced 125 grams of 99 @.@ 9 % pure protactinium by processing 60 tonnes of waste material in a 12 @-@ stage process , at a cost of about 500 @.@ 000 USD . For many years , this was the world 's only significant supply of protactinium , which was provided to various laboratories for scientific studies . Oak Ridge National Laboratory in the US provided protactinium at a cost of about 280 USD / gram .

= = Isotopes = =

Twenty @-@ nine radioisotopes of protactinium have been discovered , the most stable being 231Pa with a half @-@ life of 32 @.@ 760 years , 233Pa with a half @-@ life of 27 days , and 230Pa with a half @-@ life of 17 @.@ 4 days . All of the remaining isotopes have half @-@ lives shorter than 1 @.@ 6 days , and the majority of these have half @-@ lives less than 1 @.@ 8 seconds . Protactinium also has two nuclear isomers , 217mPa ( half @-@ life 1 @.@ 2 milliseconds ) and 234mPa ( half @-@ life 1 @.@ 17 minutes ) .

The primary decay mode for isotopes of protactinium lighter than ( and including ) the most stable isotope 231Pa ( i.e. , 212Pa to 231Pa ) is alpha decay and the primary mode for the heavier isotopes ( i.e. , 232Pa to 240Pa ) is beta decay . The primary decay products of isotopes of protactinium lighter than ( and including ) 231Pa are actinium isotopes and the primary decay products for the heavier isotopes of protactinium are uranium isotopes .

= = Occurrence = =

Protactinium is one of the rarest and most expensive naturally occurring elements . It is found in the form of two isotopes ? 231Pa and 234Pa , with the isotope 234Pa occurring in two different energy states . Nearly all natural protactinium is protactinium @-@ 231 . It is an alpha emitter and is formed by the decay of uranium @-@ 235 , whereas the beta radiating protactinium @-@ 234 is produced as a result of uranium @-@ 238 decay . Nearly all uranium @-@ 238 ( 99 @.@ 8 % ) decays first to the 234mPa isomer .

Protactinium occurs in uraninite ( pitchblende ) at concentrations of about 0 @.@ 3 @-@ 3 parts 231Pa per million parts ( ppm ) of ore . Whereas the usual content is closer to 0 @.@ 3 ppm ( e.g. in Jáchymov , Czech Republic ) , some ores from the Democratic Republic of the Congo have about 3 ppm . Protactinium is homogeneously dispersed in most natural materials and in water , but at much lower concentrations on the order of one part per trillion , that corresponds to the radioactivity of 0 @.@ 1 picocuries ( pCi ) / g . There is about 500 times more protactinium in sandy soil particles than in water , even the water present in the same sample of soil . Much higher ratios of 2 @.@ 000 and above are measured in loam soils and clays , such as bentonite .

= = In nuclear reactors = =

Two major protactinium isotopes,  $^{231}\text{Pa}$  and  $^{233}\text{Pa}$ , are produced from thorium in nuclear reactors; both are undesirable and are usually removed, thereby adding complexity to the reactor design and operation. In particular,  $^{232}\text{Th}$  via  $(n, 2n)$  reactions produces  $^{231}\text{Th}$  which quickly (half-life 25 min, 5 hours) decays to  $^{231}\text{Pa}$ . The last isotope, while not a transuranic waste, has a long half-life of 32,760 years and is a major contributor to the long term radiotoxicity of spent nuclear fuel.

Protactinium-233 is formed upon neutron capture by  $^{232}\text{Th}$ . It further either decays to uranium-233 or captures another neutron and converts into the non-fissile uranium-234.  $^{233}\text{Pa}$  has a relatively long half-life of 27 days and high cross section for neutron capture (the so-called "neutron poison"). Thus instead of rapidly decaying to the useful  $^{233}\text{U}$ , a significant fraction of  $^{233}\text{Pa}$  converts to non-fissile isotopes and consumes neutrons, degrading the reactor efficiency. To avoid this,  $^{233}\text{Pa}$  is extracted from the active zone of thorium molten salt reactors, during their operation, so that it only decays to  $^{233}\text{U}$ . This is achieved using several meters tall columns of molten bismuth with lithium dissolved in it. In a simplified scenario, lithium selectively reduces protactinium salts to protactinium metal which is then extracted from the molten salt cycle, and bismuth is merely a carrier. It is chosen because of its low melting point ( $271^\circ\text{C}$ ), low vapor pressure, good solubility for lithium and actinides, and immiscibility with molten halides.

== Preparation ==

Before the advent of nuclear reactors, protactinium was separated for scientific experiments from uranium ores. Nowadays, it is mostly produced as an intermediate product of nuclear fission in thorium high-temperature reactors:

<formula> (The times are half-lives.)

Protactinium metal can be prepared by reduction of its fluoride with calcium fluoride, lithium or barium at a temperature of  $1300 - 1400^\circ\text{C}$ .

== Physical and chemical properties ==

Protactinium is an actinide which is positioned in the periodic table to the left of uranium and to the right of thorium, and many of its physical properties are intermediate between those two actinides. So, protactinium is more dense and rigid than thorium but is lighter than uranium, and its melting point is lower than that of thorium and higher than that of uranium. The thermal expansion, electrical and thermal conductivities of these three elements are comparable and are typical of post-transition metals. The estimated shear modulus of protactinium is similar to that of titanium. Protactinium is a metal with silvery-gray luster that is preserved for some time in air. Protactinium easily reacts with oxygen, water vapor and acids, but not with alkalis.

At room temperature, protactinium crystallizes in body-centered tetragonal structure which can be regarded as distorted body-centered cubic lattice; this structure does not change upon compression up to 53 GPa. The structure changes to face-centered cubic (fcc) upon cooling from high temperature, at about  $1200^\circ\text{C}$ . The thermal expansion coefficient of the tetragonal phase between room temperature and  $700^\circ\text{C}$  is  $9 - 9 \times 10^{-6}/^\circ\text{C}$ .

Protactinium is paramagnetic and no magnetic transitions are known for it at any temperature. It becomes superconductive at temperatures below  $1 - 4\text{ K}$ . Protactinium tetrachloride is paramagnetic at room temperature but turns ferromagnetic upon cooling to 182 K.

Protactinium exists in two major oxidation states, +4 and +5, both in solids and solutions, and the +3 and +2 states were observed in some solid phases. As the electron configuration of the neutral atom is  $[\text{Rn}] 5f^2 6d^1 7s^2$ , the +5 oxidation state corresponds to the low-energy (and thus favored)  $5f^0$  configuration. Both +4 and +5 states easily form hydroxides in water with the predominant ions being  $\text{Pa}(\text{OH})_3^+$ ,  $\text{Pa}(\text{OH})_2^+$ ,  $\text{Pa}(\text{OH})^+$

3 and  $\text{Pa}(\text{OH})_4$ , all colorless. Other known protactinium ions include  $\text{PaCl}_2^+$ ,  $\text{PaSO}_2^+$ ,  $\text{PaF}_3^+$ ,  $\text{PaF}_2^+$ ,  $\text{PaF}^+$ ,  $\text{PaF}_2^+$ ,  $\text{PaF}_3^+$ , and  $\text{PaF}_3$ .

== Chemical compounds ==

Here  $a$ ,  $b$  and  $c$  are lattice constants in picometers,  $N$  is space group number and  $Z$  is the number of formula units per unit cell; fcc stands for the face centered cubic symmetry. Density was not measured directly but calculated from the lattice parameters.

== Oxides and oxygen containing salts ==

Protactinium oxides are known for the metal oxidation states +2, +4 and +5. The most stable is white pentoxide  $\text{Pa}_2\text{O}_5$ , which can be produced by igniting protactinium(V) hydroxide in air at a temperature of 500 °C. Its crystal structure is cubic, and the chemical composition is often non-stoichiometric, described as  $\text{PaO}_{2.25}$ . Another phase of this oxide with orthorhombic symmetry has also been reported. The black dioxide  $\text{PaO}_2$  is obtained from the pentoxide by reducing it at 1550 °C with hydrogen. It is not readily soluble in either dilute or concentrated nitric, hydrochloric or sulfuric acids, but easily dissolves in hydrofluoric acid. The dioxide can be converted back to pentoxide by heating in oxygen containing atmosphere to 1100 °C. The monoxide  $\text{PaO}$  has only been observed as a thin coating on protactinium metal, but not in an isolated bulk form.

Protactinium forms mixed binary oxides with various metals. With alkali metals  $A$ , the crystals have a chemical formula  $\text{APaO}_3$  and perovskite structure, or  $\text{A}_3\text{PaO}_4$  and distorted rock salt structure, or  $\text{A}_7\text{PaO}_6$  where oxygen atoms form a hexagonal close packed lattice. In all these materials, protactinium ions are octahedrally coordinated. The pentoxide  $\text{Pa}_2\text{O}_5$  combines with rare earth metal oxides  $\text{R}_2\text{O}_3$  to form various nonstoichiometric mixed oxides, also of perovskite structure.

Protactinium oxides are basic; they easily convert to hydroxides and can form various salts, such as sulfates, phosphates, nitrates, etc. The nitrate is usually white but can be brown due to radiolytic decomposition. Heating the nitrate in air at 400 °C converts it to the white protactinium pentoxide. The polytrioxophosphate  $\text{Pa}(\text{PO}_3)_4$  can be produced by reacting difluoride sulfate  $\text{PaF}_2\text{SO}_4$  with phosphoric acid ( $\text{H}_3\text{PO}_4$ ) under inert gas atmosphere. Heating the product to about 900 °C eliminates the reaction by-products such as hydrofluoric acid, sulfur trioxide and phosphoric anhydride. Heating to higher temperatures in an inert atmosphere decomposes  $\text{Pa}(\text{PO}_3)_4$  into the diphosphate  $\text{Pa}_2\text{P}_2\text{O}_7$ , which is analogous to diphosphates of other actinides. In the diphosphate, the  $\text{PO}_3$  groups form pyramids of  $C_{2v}$  symmetry. Heating  $\text{Pa}_2\text{P}_2\text{O}_7$  in air to 1400 °C decomposes it into the pentoxides of phosphorus and protactinium.

== Halides ==

Protactinium(V) fluoride forms white crystals where protactinium ions are arranged in pentagonal bipyramids and coordinated by 7 other ions. The coordination is the same in protactinium(V) chloride, but the color is yellow. The coordination changes to octahedral in the brown protactinium(V) bromide and is unknown for protactinium(V) iodide. The protactinium coordination in all its tetrahalides is 8, but the arrangement is square antiprismatic in protactinium(IV) fluoride and dodecahedral in the chloride and bromide. Brown colored protactinium(III) iodide has been reported where protactinium ions are 8 coordinated in a bicapped trigonal prismatic arrangement.

Protactinium ( V ) fluoride and protactinium ( V ) chloride have a polymeric structure of monoclinic symmetry . There , within one polymeric chain , all the halide atoms lie in one graphite @-@ like plane and form planar pentagons around the protactinium ions . The coordination 7 of protactinium originates from the 5 halide atoms and two bonds to protactinium atoms belonging to the nearby chains . These compounds easily hydrolyze in water . The pentachloride melts at 300 ° C and sublimates at even lower temperatures .

Protactinium ( V ) fluoride can be prepared by reacting protactinium oxide with either bromine pentafluoride or bromine trifluoride at about 600 ° C , and protactinium ( IV ) fluoride is obtained from the oxide and a mixture of hydrogen and hydrogen fluoride at 600 ° C ; a large excess of hydrogen is required to remove atmospheric oxygen leaks into the reaction .

Protactinium ( V ) chloride is prepared by reacting protactinium oxide with carbon tetrachloride at temperature of 200 ? 300 ° C. The by @-@ products ( such as  $\text{PaOCl}_3$  ) are removed by fractional sublimation . Reduction of protactinium ( V ) chloride with hydrogen at about 800 ° C yields protactinium ( IV ) chloride ? a yellow @-@ green solid which sublimes in vacuum at 400 ° C ; it can also be obtained directly from protactinium dioxide by treating it with carbon tetrachloride at 400 ° C.

Protactinium bromides are produced by the action of aluminium bromide , hydrogen bromide , carbon tetrabromide or a mixture of hydrogen bromide and thionyl bromide on protactinium oxide . An alternative reaction is between protactinium pentachloride and hydrogen bromide or thionyl bromide . Protactinium ( V ) bromide has two similar monoclinic forms , one is obtained by sublimation at 400 ? 410 ° C and another by sublimation at slightly lower temperature of 390 ? 400 ° C.

Protactinium iodides result from the oxides and aluminium iodide or ammonium iodide heated to 600 ° C. Protactinium ( III ) iodide was obtained by heating protactinium ( V ) iodide in vacuum . As with oxides , protactinium forms mixed halides with alkali metals . Among those , most remarkable is  $\text{Na}_3\text{PaF}_8$  where protactinium ion is symmetrically surrounded by 8 F ? ions which form a nearly perfect cube .