Neptunium

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Neptunium is a chemical element with symbol **Np** and atomic number 93. A radioactive actinide metal, neptunium is the first transuranic element. Its position in the periodic table just after uranium, named after the planet Uranus, led to it being named after Neptune, the next planet beyond Uranus. A neptunium atom has 93 protons and 93 electrons, of which seven are valence electrons. Neptunium metal is silvery and tarnishes when exposed to air. The element occurs in three allotropic forms and it normally exhibits five oxidation states, ranging from +3 to +7. It is radioactive, poisonous, pyrophoric, and can accumulate in bones, which makes the handling of neptunium dangerous.

Although many false claims of its discovery were made over the years, the element was first synthesized by Edwin McMillan and Philip H. Abelson at the Berkeley Radiation Laboratory in 1940. Since then, most neptunium has been and still is produced by neutron irradiation of uranium in nuclear reactors. The vast majority is generated as a by-product in conventional nuclear power reactors. While neptunium itself has no commercial uses at present, it is widely used as a precursor for the formation of plutonium-238, used in radioisotope thermal generators to provide electricity for spacecraft. Neptunium has also been used in detectors of high-energy neutrons.

The most stable isotope of neptunium, neptunium-237, is a by-product of nuclear reactors and plutonium production. It, and the isotope neptunium-239, are also found in trace amounts in uranium ores due to neutron capture reactions and beta decay.[3]

Neptunium, $_{93}$Np

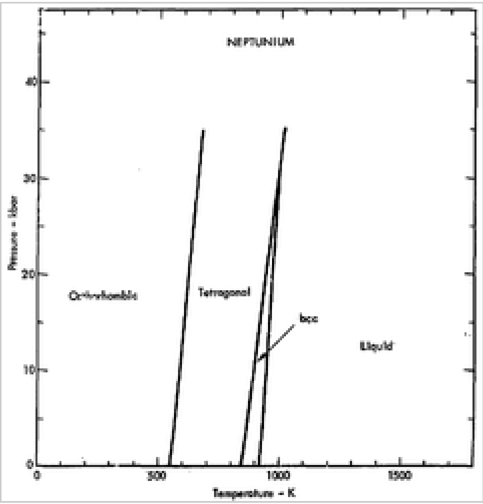
General properties	
Name, symbol	neptunium, Np
Pronunciation	UK /nɛpˈtjuːniəm/, US /nɛpˈtuːniəm/ *nep-TEW-nee-əm*, *nep-TOO-nee-əm*
Neptunium in the periodic table	
Atomic number (*Z*)	93
Group, block	group n/a, f-block
Period	period 7
Element category	□ actinide
Standard atomic weight (A_r)	(237)
Electron configuration	[Rn] $5f^4\ 6d^1\ 7s^2$
per shell	2, 8, 18, 32, 22, 9, 2
Physical properties	
Phase	solid
Melting point	912±3 K (639±3 °C, 1182±5 °F)

Characteristics

Physical

Neptunium is a hard, silvery, ductile, radioactive actinide metal. In the periodic table, it is located to the right of the actinide uranium, to the left of the actinide plutonium and below the lanthanide promethium.[4] Neptunium is a hard metal, having a bulk modulus of 118 GPa, comparable to that of manganese.[5] Neptunium metal is similar to uranium in terms of physical workability. When exposed to air at normal temperatures, it forms a thin oxide layer. This reaction proceeds more rapidly as the temperature increases.[4] Neptunium has been determined to melt at 639±3 °C: this low melting point, a property the metal shares with the neighboring element plutonium (which has melting point 639.4 °C), is due to the hybridization of the 5f and 6d orbitals and the formation of directional bonds in the metal.[6] The boiling point of neptunium is not empirically known and the usually given value of 4174 °C is extrapolated from the vapor pressure of the element. If accurate, this would give neptunium the largest liquid range of any element (3535 K passes between its melting and boiling points).[4][7]

Neptunium is found in at least three allotropes.[3] Some claims of a fourth allotrope have been made, but they are so far not proven.[4] This multiplicity of allotropes is common among the actinides. The crystal structures of neptunium, protactinium, uranium, and plutonium do not have clear analogs among the lanthanides and are more similar to those of the 3d transition metals.[6]



Phase diagram of neptunium

α-neptunium takes on an orthorhombic structure, resembling a highly distorted body-centered cubic structure.[9][10] Each neptunium atom is coordinated to four others and the Np–Np bond lengths are 260 pm.[11] It is the densest of all the actinides and the fifth-densest of all naturally occurring elements, behind only rhenium, platinum, iridium, and osmium.[7] α-neptunium has semimetallic properties, such as strong covalent bonding and a high electrical resistivity, and its metallic physical properties are closer to those of the metalloids than the true metals. Some allotropes of the other actinides also exhibit similar behaviour, though to a lesser degree.[12][13] The densities of different isotopes of neptunium in the alpha phase are expected to be observably different: α-^{235}Np should have density 20.303 g/cm^3; α-^{236}Np, density 20.389 g/cm^3; α-^{237}Np, density 20.476 g/cm^3.[14]

Boiling point	4447 K (4174 °C, 7545 °F) *(extrapolated)*
Density near r.t.	alpha: 20.45 g/cm^3[1] accepted standard value: 19.38 g/cm^3
Heat of fusion	5.19 kJ/mol
Heat of vaporization	336 kJ/mol
Molar heat capacity	29.46 J/(mol·K)

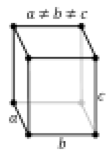
Vapor pressure

P (Pa)	**1**	**10**	**100**	**1 k**	**10 k**	**100 k**
at T (K)	2194	2437				

Atomic properties

Oxidation states	7, 6, **5**, 4, 3, 2 (an amphoteric oxide)
Electronegativity	Pauling scale: 1.36
Ionization energies	1st: 604.5 kJ/mol
Atomic radius	empirical: 155 pm
Covalent radius	190±1 pm

Miscellanea

Crystal structure	orthorhombic 
Thermal conductivity	6.3 W/(m·K)
Electrical resistivity	1.220 µΩ·m (at 22 °C)
Magnetic ordering	paramagnetic[2]

β-neptunium takes on a distorted tetragonal close-packed structure. Four atoms of neptunium make up a unit cell, and the Np–Np bond lengths are 276 pm.[11] γ-neptunium has a body-centered cubic structure and has Np–Np bond length of 297 pm. The γ form becomes less stable with increased pressure, though the melting point of neptunium also increases with pressure.[11] The β-Np/γ-Np/liquid triple point occurs at 725 °C and 3200 MPa.[11][15]

CAS Number	7439-99-8
History	
Naming	after planet Neptune, itself named after Roman god of the sea Neptune
Discovery	Edwin McMillan and Philip H. Abelson (1940)

Most stable isotopes of neptunium

iso	NA	half-life	DM	DE (MeV)	DP
^{235}**Np**	syn	396.1 d	α	5.192	^{231}Pa
			ε	0.124	^{235}U
^{236}**Np**	syn	1.54×10^{5} y	ε	0.940	^{236}U
			$β^{−}$	0.940	^{236}Pu
			α	5.020	^{232}Pa
^{237}**Np**	trace	2.144×10^{6} y	α	4.959	^{233}Pa
^{239}**Np**	trace	2.356 d	$β^{−}$	0.218	^{239}Pu

Alloys

Due to the presence of valence 5f electrons, neptunium and its alloys exhibit very interesting magnetic behavior, like many other actinides. These can range from the itinerant band-like character characteristic of the transition metals to the local moment behavior typical of scandium, yttrium, and the lanthanides. This stems from 5f-orbital hybridization with the orbitals of the metal ligands, and the fact that the 5f orbital is relativistically destabilized and extends outwards.[16] For example, pure neptunium is paramagnetic, $NpAl_3$ is ferromagnetic, $NpGe_3$ has no magnetic ordering, and $NpSn_3$ behaves fermionically.[16] Investigations are underway regarding alloys of neptunium with uranium, americium, plutonium, zirconium, and iron, so as to recycle long-lived waste isotopes such as neptunium-237 into shorter-lived isotopes more useful as nuclear fuel.[16]

One neptunium-based superconductor alloy has been discovered with formula $NpPd_5Al_2$. This occurrence in neptunium compounds is somewhat surprising because they often exhibit strong magnetism, which usually destroys superconductivity. The alloy has a tetragonal structure with a superconductivity transition temperature of −268.3 °C (4.9 K).[17][18]

Chemical

Neptunium has five ionic oxidation states ranging from +3 to +7 when forming chemical compounds, which can be simultaneously observed in solutions. It is the heaviest actinide that can lose all its valence electrons in a stable compound. The most stable state in solution is +5, but the valence +4 is preferred in solid neptunium compounds. Neptunium metal is very reactive. Ions of neptunium are prone to hydrolysis and formation of coordination compounds.[19]

Atomic

A neptunium atom has 93 electrons, arranged in the configuration $[Rn]5f^4 6d^1 7s^2$. This differs from the configuration expected by the Aufbau principle in that one electron is in the 6d subshell instead of being as expected in the 5f subshell. This is because of the similarity of the electron energies of the 5f, 6d, and 7s subshells. In forming compounds and ions, all the valence electrons may be lost, leaving behind an inert core of inner electrons with the electron configuration of the noble gas radon;[20] more commonly, only some of the valence electrons will be lost. The electron configuration for the tripositive ion Np^{3+} is $[Rn]\ 5f^4$, with the outermost 7s and 6d electrons lost first: this is exactly analogous to neptunium's lanthanide homolog promethium, and conforms to the trend set by the other actinides with their $[Rn]\ 5f^n$ electron configurations in the tripositive state. The first ionization potential of neptunium was measured to be at most (6.19 ± 0.12) eV in 1974, based on the assumption that the 7s electrons would ionize before 5f and 6d;[21] more recent measurements have refined this to 6.2657 eV.[22]

Isotopes

20 neptunium radioisotopes have been characterized with the most stable being ^{237}Np with a half-life of 2.14 million years, ^{236}Np with a half-life of 154,000 years, and ^{235}Np with a half-life of 396.1 days. All of the remaining radioactive isotopes have half-lives that are less than 4.5 days, and the majority of these have half-lives that are less than 50 minutes. This element also has at least four meta states, with the most stable being ^{236m}Np with a half-life of 22.5 hours.[23]

The isotopes of neptunium range in atomic weight from 225.0339 u (^{225}Np) to 244.068 u (^{244}Np).[23] Most of the isotopes that are lighter than the most stable one, ^{237}Np, decay primarily by electron capture although a sizable number, most notably ^{229}Np and ^{230}Np, also exhibit various levels of decay via alpha emission to become protactinium. ^{237}Np itself, being the beta-stable isobar of mass number 237, decays almost exclusively by alpha emission into ^{233}Pa. All of the known isotopes except one that are heavier than this decay exclusively via beta emission.[23][24] The lone exception, ^{240m}Np, exhibits a rare (>0.12%) decay by isomeric transition in addition to the beta emission.[23] ^{237}Np eventually decays to form bismuth-209 and thallium-205, unlike most other common heavy nuclei which decay into isotopes of lead. This decay chain is known as the neptunium series.[17][25]

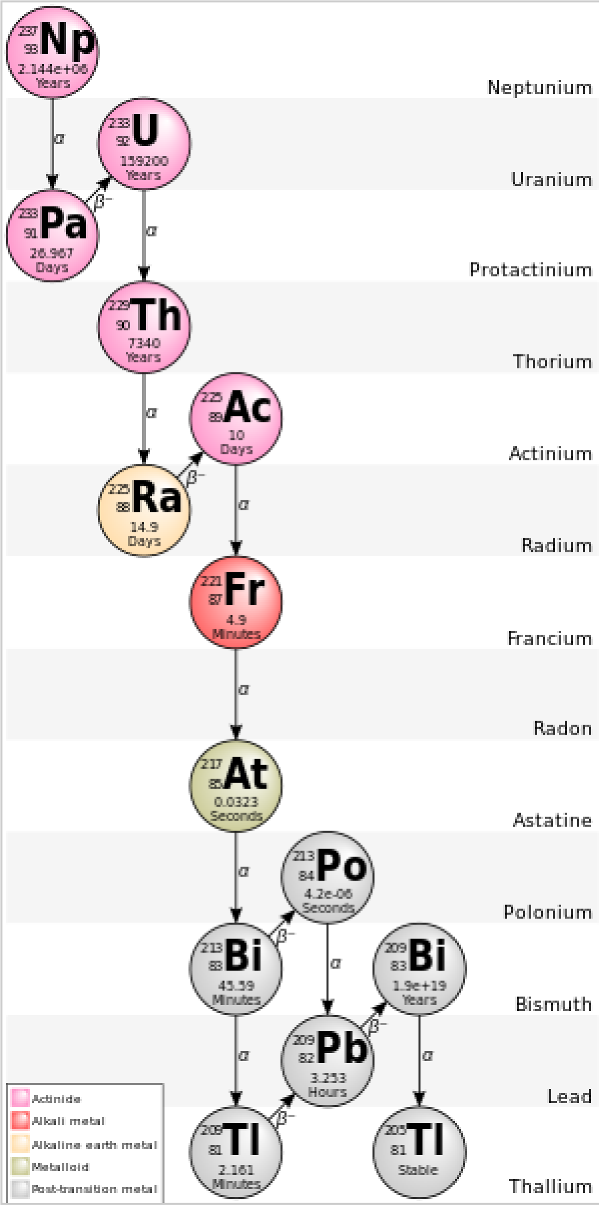
The isotopes neptunium-235, -236, and -237 are predicted to be fissile;[14] only neptunium-237's fissionability has been experimentally shown, with the critical mass being about 60 kg, only about 10 kg more than that of the commonly used uranium-235.[26] Calculated values of the critical masses of neptunium-235, -236, and -237 respectively are 66.2 kg, 6.79 kg, and 63.6 kg: the neptunium-236 value is even lower than that of plutonium-239. In particular ^{236}Np also has a low neutron cross section.[14] Despite this, a neptunium atomic bomb has never been built:[26] uranium and plutonium have lower critical masses than ^{235}Np and ^{237}Np, and ^{236}Np is difficult to purify as it is not found in quantity in spent nuclear fuel[24] and is nearly impossible to separate in any significant quantities from its parent ^{237}Np.[27]

Occurrence

Since all isotopes of neptunium have half-lives that are many times shorter than the age of the Earth, any primordial neptunium should have decayed by now. After only about 80 million years, the concentration of even the longest lived isotope, ^{237}Np, would have been reduced to less than one-trillionth (10^{-12}) of its original amount;[28] and even if the whole Earth had initially been made of pure ^{237}Np (and ignoring that this would be well over its critical mass of 60 kg), 2100 half-lives would have passed since the formation of the Solar System, and thus all of it would have decayed. Thus neptunium is present in nature only in negligible amounts produced as intermediate decay products of other isotopes.[19]

Trace amounts of the neptunium isotopes neptunium-237 and -239 are found naturally as decay products from transmutation reactions in uranium ores.[3][29] In particular, ^{239}Np and ^{237}Np are the most common of these isotopes; they are directly formed from neutron capture by uranium-238 atoms. These neutrons come from the spontaneous fission of uranium-238, naturally neutron-induced fission of uranium-235, cosmic ray spallation of nuclei, and light elements absorbing alpha particles and emitting a neutron.[28] The half-life of ^{239}Np is very short, although the detection of its much longer-lived daughter ^{239}Pu in nature in 1951 definitively established its natural occurrence.[28] In 1952, ^{237}Np was identified and isolated from concentrates of uranium ore from the Belgian Congo: in these minerals, the ratio of neptunium-237 to uranium is less than or equal to about 10^{-12} to 1.[28][30][31]

Most neptunium (and plutonium) now encountered in the environment is due to atmospheric nuclear explosions that took place between the detonation of the first atomic bomb in 1945 and the ratification of the Partial Nuclear Test Ban Treaty in 1963. The total amount of neptunium released by these explosions and the few atmospheric tests that have been carried out since 1963 is estimated to be around 2500 kg. The overwhelming majority of this is composed of the long-lived isotopes ^{236}Np and ^{237}Np since even the moderately long-lived ^{235}Np (half-life 396 days) would have decayed to less than one-billionth (10^{-9}) its original concentration over the intervening decades. An additional very small amount of neptunium, created by neutron irradiation of natural



The $4n + 1$ decay chain of neptunium-237, commonly called the "neptunium series" uranium in nuclear reactor cooling water, is released when the water is discharged into rivers or lakes.[28][30][32] The concentration of ^{237}Np in seawater is approximately 6.5×10^{-5} millibecquerels per liter: this concentration is between 0.1% and 1% that of plutonium.[28]

Once in the environment, neptunium generally oxidizes fairly quickly, usually to the +4 or +5 state. Regardless of its oxidation state, the element exhibits a much greater mobility than the other actinides, largely due to its ability to readily form aqueous solutions with various other elements. In one study comparing the diffusion rates of neptunium(V), plutonium(IV), and americium(III) in sandstone and limestone, neptunium penetrated more than ten times as well as the other elements. Np(V) will also react efficiently in pH levels greater than 5.5 if there are no carbonates present and in these conditions it has also been observed to readily bond with quartz. It has also been observed to bond well with goethite, ferric oxide colloids, and several clays including kaolinite and smectite. Np(V) does not bond as readily to soil particles in mildly acidic conditions as its fellow actinides americium and curium by nearly an order of magnitude. This behavior enables it to migrate rapidly through the soil while in solution without becoming fixed in place, contributing further to its mobility.[30][33] Np(V) is also readily absorbed by concrete, which because of the element's radioactivity is a consideration that must be addressed when building nuclear waste storage facilities. When absorbed in concrete, it is reduced to Np(IV) in a relatively short period of time. Np(V) is also reduced by humic acid if it is present on the surface of goethite, hematite, and magnetite. Np(IV) is absorbed efficiently by tuff, granodiorite, and bentonite; although uptake by the latter is most pronounced in mildly acidic conditions. It also exhibits a strong tendency to bind to colloidal particulates, an effect that is enhanced when in soil with a high clay content. The behavior provides an additional aid in the element's observed high mobility.[30][33][34][35]

Source

- Wikipedia: Neptunium (https://en.wikipedia.org/wiki/Neptunium)