

= Technetium =

Technetium (/ tɛkˈniːʃiəm /) is a chemical element with symbol Tc and atomic number 43 . It is the lightest element of which all isotopes are radioactive ; none are stable . Only one other element , promethium , is followed (in the periodic table) by elements with stable isotopes . Nearly all technetium is produced synthetically , and only minute amounts are found in the Earth 's crust . Naturally occurring technetium is a spontaneous fission product in uranium ore or the product of neutron capture in molybdenum ores . The chemical properties of this silvery gray , crystalline transition metal are intermediate between rhenium and manganese .

Many of technetium 's properties were predicted by Dmitri Mendeleev before the element was discovered . Mendeleev noted a gap in his periodic table and gave the undiscovered element the provisional name ekamanganese (Em) . In 1937 , technetium (specifically the technetium @-@ 97 isotope) became the first predominantly artificial element to be produced , hence its name (from the Greek ????????, meaning " artificial " , + -ium) .

Its short @-@ lived gamma ray @-@ emitting nuclear isomer ? technetium @-@ 99m ? is used in nuclear medicine for a wide variety of diagnostic tests . Technetium @-@ 99 is used as a gamma @-@ ray @-@ free source of beta particles . Long @-@ lived technetium isotopes produced commercially are by @-@ products of fission of uranium @-@ 235 in nuclear reactors and are extracted from nuclear fuel rods . Because no isotope of technetium has a half @-@ life longer than 4 @. @ 2 million years (technetium @-@ 98) , the 1952 detection of technetium in red giants , which are billions of years old , helped to prove that stars can produce heavier elements .

= = History = =

= = Search for element 43 = =

From the 1860s through 1871 , early forms of the periodic table proposed by Dmitri Mendeleev contained a gap between molybdenum (element 42) and ruthenium (element 44) . In 1871 , Mendeleev predicted this missing element would occupy the empty place below manganese and have similar chemical properties . Mendeleev gave it the provisional name ekamanganese (from eka- , the Sanskrit word for one) because the predicted element was one place down from the known element manganese .

= = Early mis @-@ identifications = =

Many early researchers , both before and after the periodic table was published , were eager to be the first to discover and name the missing element ; its location in the table suggested that it should be easier to find than other undiscovered elements .

= = Unreproducible results = =

German chemists Walter Noddack , Otto Berg , and Ida Tacke reported the discovery of element 75 and element 43 in 1925 , and named element 43 masurium (after Masuria in eastern Prussia , now in Poland , the region where Walter Noddack 's family originated) . The group bombarded columbite with a beam of electrons and deduced element 43 was present by examining X @-@ ray diffraction spectrograms . The wavelength of the X @-@ rays produced is related to the atomic number by a formula derived by Henry Moseley in 1913 . The team claimed to detect a faint X @-@ ray signal at a wavelength produced by element 43 . Later experimenters could not replicate the discovery , and it was dismissed as an error for many years . Still , in 1933 , a series of articles on the discovery of elements quoted the name masurium for element 43 . Whether the 1925 team actually did discover element 43 is still debated .

= = = Official discovery and later history = = =

The discovery of element 43 was finally confirmed in a December 1936 experiment at the University of Palermo in Sicily by Carlo Perrier and Emilio Segrè . In mid 1936 , Segrè visited the United States , first Columbia University in New York and then the Lawrence Berkeley National Laboratory in California . He persuaded cyclotron inventor Ernest Lawrence to let him take back some discarded cyclotron parts that had become radioactive . Lawrence mailed him a molybdenum foil that had been part of the deflector in the cyclotron .

Segrè enlisted his colleague Perrier to attempt to prove , through comparative chemistry , that the molybdenum activity was indeed from an element with the atomic number 43 . They succeeded in isolating the isotopes technetium 95m and technetium 97 . University of Palermo officials wanted them to name their discovery " panormium " , after the Latin name for Palermo , Panormus . In 1947 element 43 was named after the Greek word ??????? , meaning " artificial " , since it was the first element to be artificially produced . Segrè returned to Berkeley and met Glenn T. Seaborg . They isolated the metastable isotope technetium 99m , which is now used in some ten million medical diagnostic procedures annually .

In 1952 , astronomer Paul W. Merrill in California detected the spectral signature of technetium (specifically wavelengths of 403 nm , 423 nm , 426 nm , and 429 nm) in light from S type red giants . The stars were near the end of their lives , yet were rich in this short lived element , indicating that it was being produced in the stars by nuclear reactions . This evidence bolstered the hypothesis that heavier elements are the product of nucleosynthesis in stars . More recently , such observations provided evidence that elements are formed by neutron capture in the s process .

Since that discovery , there have been many searches in terrestrial materials for natural sources of technetium . In 1962 , technetium 99 was isolated and identified in pitchblende from the Belgian Congo in extremely small quantities (about 0.2 ng / kg) ; there it originates as a spontaneous fission product of uranium 238 . The Oklo natural nuclear fission reactor contains evidence that significant amounts of technetium 99 were produced and have since decayed into ruthenium 99 .

= = Characteristics = =

= = Physical properties = =

Technetium is a silvery gray radioactive metal with an appearance similar to platinum , commonly obtained as a gray powder . The crystal structure of the pure metal is hexagonal close packed . Atomic technetium has characteristic emission lines at these wavelengths of light : 363 nm , 403 nm , 426 nm , 429 nm , and 485 nm .

The metal form is slightly paramagnetic , meaning its magnetic dipoles align with external magnetic fields , but will assume random orientations once the field is removed . Pure , metallic , single crystal technetium becomes a type II superconductor at temperatures below 7.4 K. Below this temperature , technetium has a very high magnetic penetration depth , greater than any other element except niobium .

= = Chemical properties = =

Technetium is located in the seventh group of the periodic table , between rhenium and manganese . As predicted by the periodic law , its chemical properties are between those two elements . Of the two , technetium more closely resembles rhenium , particularly in its chemical inertness and tendency to form covalent bonds . Unlike manganese , technetium does not readily form cations (ions with a net positive charge) . Technetium exhibits nine oxidation states from -1 to $+7$, with $+4$, $+5$, and $+7$ being the most common . Technetium dissolves in aqua regia , nitric acid , and

concentrated sulfuric acid , but it is not soluble in hydrochloric acid of any concentration .

Technetium can catalyze the destruction of hydrazine by nitric acid , and this property is to its multiplicity of valencies . This caused a problem in the separation of plutonium from uranium in nuclear fuel processing , where hydrazine is used as a protective reductant to keep plutonium in the trivalent rather than the more stable tetravalent state . The problem was exacerbated by the mutually @-@ enhanced solvent extraction of technetium and zirconium at the previous stage , and required a process modification .

=== Hydride and oxides ===

The reaction of technetium with hydrogen produces the negatively charged hydride TcH_2^- ?

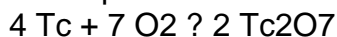
9 ion , which has the same type of crystal structure as (in other words , it is isostructural with) ReH_2^- ?

9 . It consists of a trigonal prism with a technetium atom in the center and six hydrogen atoms at the corners . Three more hydrogen atoms make a triangle lying parallel to the base and crossing the prism in its center . Although those hydrogen atoms are not equivalent geometrically , their electronic structure is almost the same . This complex has a coordination number of 9 (meaning that the technetium atom has nine neighbors) , which is the highest for a technetium complex . Two hydrogen atoms in the complex can be replaced by sodium (Na^+) or potassium (K^+) ions .

Metallic technetium slowly tarnishes in moist air and , in powder form , burns in oxygen . Two oxides have been observed : TcO_2 and Tc_2O_7 . Under oxidizing conditions , which tend to strip electrons from atoms , technetium (VII) exists as the pertechnetate ion , TcO_4^- ?

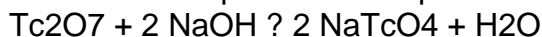
4 .

At temperatures of 400 ? 450 ° C , technetium oxidizes to form the pale @-@ yellow heptoxide :



This compound adopts a centrosymmetric structure with two types of Tc ? O bonds with 167 and 184 pm bond lengths , and 180 ° Tc ? O ? Tc angle .

Technetium heptoxide is the precursor to sodium pertechnetate :



Black @-@ colored technetium dioxide (TcO_2) can be produced by reduction of heptoxide with technetium or hydrogen .

Pertechnetic acid (HTcO_4) is produced by reacting Tc_2O_7 with water or oxidizing acids , such as nitric acid , concentrated sulfuric acid , aqua regia , or a mixture of nitric and hydrochloric acids . The resulting dark red , hygroscopic substance is a strong acid and easily donates protons . In concentrated sulfuric acid , Tc (VII) tetraoxidotechnetate anion converts to the octahedral form of technetic (VII) acid $\text{TcO}_3(\text{OH})(\text{H}_2\text{O})_2$.

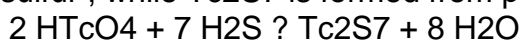
The pertechnetate (tetroxidotechnetate) anion TcO_4^- ?

4 consists of a tetrahedron with oxygens in the corners and a technetium atom in the center . Unlike permanganate (MnO_4^-)

4) , it is only a weak oxidizing agent . Pertechnetate is often used as a convenient water @-@ soluble source of technetium isotopes , such as $^{99\text{m}}\text{Tc}$, and as a catalyst .

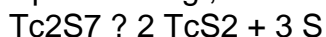
=== Sulfides , selenides , and tellurides ===

Technetium forms various sulfides . TcS_2 is obtained by direct reacting technetium with elemental sulfur , while Tc_2S_7 is formed from pertechnetic acid as follows :



In this reaction , technetium is reduced to Tc (IV) while excess sulfur forms a disulfide ligand . The produced technetium heptasulfide has a polymeric structure ($\text{Tc}_3(\mu_3\text{S})(\text{S}_2)_3\text{S}_6$)_n with a core similar to $\text{Mo}_3(\mu_3\text{S})(\text{S}_2)_6$? .

Upon heating , technetium heptasulfide decomposes into disulfide and elemental sulfur :



Analogous reactions occur with selenium and tellurium .

=== Clusters and organic complexes ===

Several technetium clusters are known, including Tc_4 , Tc_6 , Tc_8 and Tc_{13} . The more stable Tc_6 and Tc_8 clusters have prism shapes where vertical pairs of Tc atoms are connected by triple bonds and the planar atoms by single bonds. Every technetium atom makes six bonds, and the remaining valence electrons can be saturated by one axial and two bridging ligand halogen atoms such as chlorine or bromine.

Technetium forms numerous organic complexes, relatively well investigated because they are important for nuclear medicine. Technetium carbonyl ($Tc_2(CO)_{10}$) is a white solid. In this molecule, two technetium atoms are weakly bound to each other; each atom is surrounded by octahedra of five carbonyl ligands. The bond length between technetium atoms, 303 pm, is significantly larger than the distance between two atoms in metallic technetium (272 pm). Similar carbonyls are formed by technetium's congeners, manganese and rhenium.

A technetium complex with an organic ligand (shown in the figure on right) is commonly used in nuclear medicine. It has a unique Tc-O functional group (moiety) oriented perpendicularly to the plane of the molecule, where the oxygen atom can be replaced by a nitrogen atom.

=== Isotopes ===

Technetium, with atomic number (denoted Z) 43, is the lowest numbered element in the periodic table of which all isotopes are radioactive. The second lightest, exclusively radioactive element, promethium, has an atomic number of 61. Atomic nuclei with an odd number of protons are less stable than those with even numbers, even when the total number of nucleons (protons + neutrons) is even, and odd numbered elements have fewer stable isotopes.

The most stable radioactive isotopes are technetium-98 with a half life of 4.2 million years (Ma), technetium-97 with 2.6 Ma, and technetium-99 with 211,000 years. Thirty other radioisotopes have been characterized with mass numbers ranging from 85 to 118. Most of these have half lives that are less than an hour, the exceptions being technetium-93 (half life: 2.73 hours), technetium-94 (half life: 4.88 hours), technetium-95 (half life: 20 hours), and technetium-96 (half life: 4.3 days).