

# Technetium

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**Technetium** 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 such 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 *τεχνητός*, 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.

## Characteristics

### Physical properties

Technetium is a silvery-gray radioactive metal with an appearance similar to platinum, commonly obtained as a gray powder.<sup>[19]</sup> The crystal structure of the pure metal is hexagonal close-packed. Atomic technetium has characteristic

## Technetium, <sup>43</sup>Tc



### General properties

<b>Name, symbol</b>	technetium, Tc
<b>Appearance</b>	shiny gray metal

### Technetium in the periodic table

<b>Atomic number</b> ( <i>Z</i> )	43
<b>Group, block</b>	group 7, d-block
<b>Period</b>	period 5
<b>Element category</b>	<span>☐</span> transition metal
<b>Standard atomic weight</b> ( <i>A</i> <sub>r</sub> )	[98]
<b>Electron configuration</b>	[Kr] 4d <sup>5</sup> 5s <sup>2</sup>
per shell	2, 8, 18, 13, 2

### Physical properties

<b>Phase</b>	solid
<b>Melting point</b>	2430 K (2157 °C, 3915 °F)
<b>Boiling point</b>	4538 K (4265 °C, 7709 °F)
<b>Density</b> near r.t.	11 g/cm <sup>3</sup>

emission lines at these wavelengths of light: 363.3 nm, 403.1 nm, 426.2 nm, 429.7 nm, and 485.3 nm.<sup>[20]</sup>

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.<sup>[21]</sup> Pure, metallic, single-crystal technetium becomes a type-II superconductor at temperatures below 7.46 K.<sup>[note 2][22]</sup> Below this temperature, technetium has a very high magnetic penetration depth, greater than any other element except niobium.<sup>[23]</sup>

## 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.<sup>[24]</sup> 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.<sup>[25]</sup> Technetium dissolves in aqua regia, nitric acid, and concentrated sulfuric acid, but it is not soluble in hydrochloric acid of any concentration.<sup>[19]</sup>

Technetium can catalyse the destruction of hydrazine by nitric acid, and this property is due to its multiplicity of valencies.<sup>[26]</sup> 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,<sup>[27]</sup> and required a process modification.

## Hydride and oxides

The reaction of technetium with hydrogen produces the negatively charged hydride  $\text{TcH}_9^{2-}$  ion, which has the same type of crystal structure as (in other words, it is isostructural with)  $\text{ReH}_9^{2-}$ . It consists of a trigonal prism with a

<b>Heat of fusion</b>	33.29 kJ/mol
<b>Heat of vaporization</b>	585.2 kJ/mol
<b>Molar heat capacity</b>	24.27 J/(mol·K)

### Vapor pressure (extrapolated)

P (Pa)	1	10	100	1 k	10 k	100 k
at T (K)	2727	2998	3324	3726	4234	4894

### Atomic properties

<b>Oxidation states</b>	<b>7</b> , 6, 5, <b>4</b> , 3, <sup>[1]</sup> 2, 1, <sup>[1]</sup> $-1$ , $-3$ (a strongly acidic oxide)
<b>Electronegativity</b>	Pauling scale: 1.9
<b>Ionization energies</b>	1st: 702 kJ/mol 2nd: 1470 kJ/mol 3rd: 2850 kJ/mol
<b>Atomic radius</b>	empirical: 136 pm
<b>Covalent radius</b>	147±7 pm

### Miscellanea

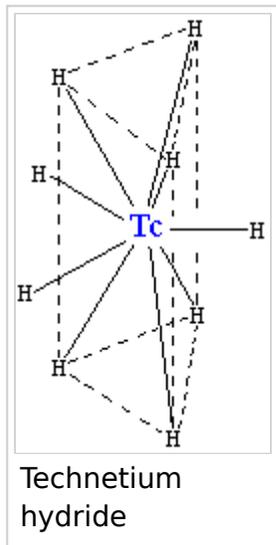
<b>Crystal structure</b>	hexagonal close-packed (hcp)
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<b>Speed of sound</b> thin rod	16,200 m/s (at 20 °C)
<b>Thermal expansion</b>	7.1 $\mu\text{m}/(\text{m}\cdot\text{K})$ <sup>[2]</sup> (at r.t.)
<b>Thermal conductivity</b>	50.6 W/(m·K)
<b>Electrical resistivity</b>	200 n $\Omega$ ·m (at 20 °C)
<b>Magnetic ordering</b>	Paramagnetic
<b>CAS Number</b>	7440-26-8

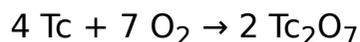
### History

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<sup>+</sup>) or potassium (K<sup>+</sup>) ions.<sup>[28]</sup>



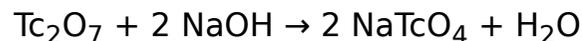
Metallic technetium slowly tarnishes in moist air<sup>[25]</sup> and, in powder form, burns in oxygen. Two oxides have been observed: TcO<sub>2</sub> and Tc<sub>2</sub>O<sub>7</sub>. Under oxidizing conditions, which tend to strip electrons from atoms, technetium(VII) exists as the pertechnetate ion, TcO<sub>4</sub><sup>-</sup>.<sup>[21][25]</sup>

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.<sup>[29]</sup>

Technetium heptoxide is the precursor to sodium pertechnetate.<sup>[30]</sup>



Black-colored technetium dioxide (TcO<sub>2</sub>) can be produced by reduction of heptoxide with technetium or hydrogen.<sup>[31]</sup>

Pertechnetic acid (HTcO<sub>4</sub>) is produced by reacting Tc<sub>2</sub>O<sub>7</sub> with water or oxidizing acids, such as nitric acid, concentrated sulfuric acid, aqua regia, or a mixture of nitric and hydrochloric acids.<sup>[32]</sup> 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 TcO<sub>3</sub>(OH)(H<sub>2</sub>O)<sub>2</sub>.<sup>[33]</sup>

**Prediction** Dmitri Mendeleev (1871)

**Discovery and first isolation** Emilio Segrè and Carlo Perrier (1937)

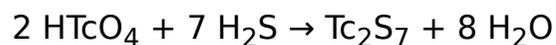
#### Most stable isotopes of technetium

iso	NA	half-life	DM	DE (MeV)	DP
<b><sup>95m</sup>Tc</b>	syn	61 d	ε	–	<sup>95</sup> Mo
			γ	0.204, 0.582, 0.835	–
			IT	0.0389, e	<sup>95</sup> Tc
<b><sup>96</sup>Tc</b>	syn	4.3 d	ε	–	<sup>96</sup> Mo
			γ	0.778, 0.849, 0.812	–
<b><sup>97</sup>Tc</b>	syn	2.6×10 <sup>6</sup> y	ε	–	<sup>97</sup> Mo
<b><sup>97m</sup>Tc</b>	syn	91 d	IT	0.965, e	<sup>97</sup> Tc
<b><sup>98</sup>Tc</b>	syn	4.2×10 <sup>6</sup> y	β <sup>-</sup>	0.4	<sup>98</sup> Ru
			γ	0.745, 0.652	–
<b><sup>99</sup>Tc</b>	trace	2.111×10 <sup>5</sup> y	β <sup>-</sup>	0.294	<sup>99</sup> Ru
<b><sup>99m</sup>Tc</b>	syn	6.01 h	IT	0.142, 0.002	<sup>99</sup> Tc
			γ	0.140	–

The pertechnetate (tetroxidotechnetate) anion  $\text{TcO}_4^-$  consists of a tetrahedron with oxygens in the corners and a technetium atom in the center. Unlike permanganate ( $\text{MnO}_4^-$ ), 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.<sup>[34]</sup>

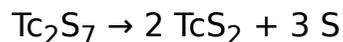
### Sulfides, selenides, and tellurides

Technetium forms various sulfides.  $\text{TcS}_2$  is obtained by direct reacting technetium with elemental sulfur, while  $\text{Tc}_2\text{S}_7$  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  $\text{Mo}_3(\mu^3\text{-S})(\text{S}_2)_6^{2-}$ .<sup>[35]</sup>

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

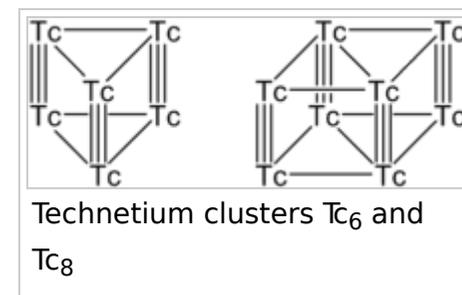
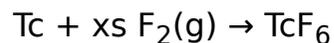


Analogous reactions occur with selenium and tellurium.<sup>[36]</sup>

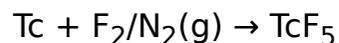
### Halides and oxyhalides

Technetium reacts with the Group XVII halogen elements (F, Cl, Br, I) to form various binary technetium halides ranging in oxidation state from Tc(II) to Tc(VII). Technetium halides exhibit different structure types, such as molecular octahedral complexes, extended chains, layered sheets, and metal clusters arranged in a three-dimensional network.<sup>[37]</sup> These compounds can be synthesized using standard solid-state reactions, and their chemistries are similar to those formed by neighboring transition metals, such as molybdenum, ruthenium, rhenium, and platinum. Technetium halides and oxyhalides are volatile at elevated temperatures, which allows them to be utilized for chemical separations.<sup>[22]</sup>

There are two binary technetium fluorides that are known:  $\text{TcF}_6$  and  $\text{TcF}_5$ . Both compounds can be synthesized at elevated temperatures from the reaction of technetium metal with elemental fluorine:



If the reaction is performed with a mixture of  $F_2/N_2(g)$ , then the pentafluoride can be isolated:



Typically these reactions are performed using a flowing gas setup equipped for handling fluorine.

Quantum chemical DFT calculations have suggested that, like rhenium, the tetra- and heptafluoride  $TcF_4$  and  $TcF_7$  should exist, although they have not yet been isolated experimentally.

## Clusters and organic complexes

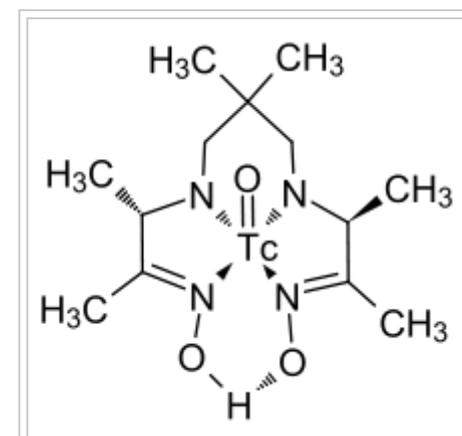
Several technetium clusters are known, including  $Tc_4$ ,  $Tc_6$ ,  $Tc_8$  and  $Tc_{13}$ .<sup>[38][39]</sup> The more stable  $Tc_6$  and  $Tc_8$  clusters have prism shapes where vertical pairs of Tc atoms are connected by triple bonds and the planar atoms by single bonds. Every technetium atom 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.<sup>[40]</sup>

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.<sup>[42]</sup> 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,<sup>[43][44]</sup> 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.<sup>[45]</sup>

A technetium complex<sup>[note 3]</sup> 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.<sup>[46]</sup>

## 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.<sup>[25]</sup> 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,<sup>[47]</sup> and odd numbered elements have fewer stable isotopes.



Organic complex of technetium<sup>[41]</sup>

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.<sup>[48]</sup> Thirty other radioisotopes have been characterized with mass numbers ranging from 85 to 118.<sup>[48]</sup> 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).<sup>[49]</sup>

The primary decay mode for isotopes lighter than technetium-98 (<sup>98</sup>Tc) is electron capture, producing molybdenum ( $Z = 42$ ).<sup>[48]</sup> For technetium-98 and heavier isotopes, the primary mode is beta emission (the emission of an electron or positron), producing ruthenium ( $Z = 44$ ), with the exception that technetium-100 can decay both by beta emission and electron capture.<sup>[48][50]</sup>

Technetium also has numerous nuclear isomers, which are isotopes with one or more excited nucleons. Technetium-97m (<sup>97m</sup>Tc; 'm' stands for metastability) is the most stable, with a half-life of 91 days (0.0965 MeV).<sup>[49]</sup> This is followed by technetium-95m (half-life: 61 days, 0.03 MeV), and technetium-99m (half-life: 6.01 hours, 0.142 MeV).<sup>[49]</sup> Technetium-99m emits only gamma rays and decays to technetium-99.<sup>[49]</sup>

Technetium-99 (<sup>99</sup>Tc) is a major product of the fission of uranium-235 (<sup>235</sup>U), making it the most common and most readily available isotope of technetium. One gram of technetium-99 produces  $6.2 \times 10^8$  disintegrations a second (that is, 0.62 GBq/g).<sup>[21]</sup>

## Source

- Wikipedia: Technetium (<https://en.wikipedia.org/wiki/Technetium>)