

# Hafnium

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**Hafnium** is a chemical element with symbol **Hf** and atomic number 72. A lustrous, silvery gray, tetravalent transition metal, hafnium chemically resembles zirconium and is found in zirconium minerals. Its existence was predicted by Dmitri Mendeleev in 1869, though it was not identified until 1923, making it the penultimate stable element to be discovered (rhenium was identified two years later). Hafnium is named after *Hafnia*, the Latin name for Copenhagen, where it was discovered.<sup>[3][4]</sup>

Hafnium is used in filaments and electrodes. Some semiconductor fabrication processes use its oxide for integrated circuits at 45 nm and smaller feature lengths. Some superalloys used for special applications contain hafnium in combination with niobium, titanium, or tungsten.

Hafnium's large neutron capture cross-section makes it a good material for neutron absorption in control rods in nuclear power plants, but at the same time requires that it be removed from the neutron-transparent corrosion-resistant zirconium alloys used in nuclear reactors.

## Characteristics

### Physical characteristics



Hafnium bits

Hafnium is a shiny, silvery, ductile metal that is corrosion-resistant and chemically similar to zirconium<sup>[5]</sup> (due to not only to its having the same number of valence electrons and being in the same group, but also to relativistic effects). The physical properties of hafnium metal samples are markedly affected by zirconium impurities, especially the nuclear properties, as these two elements are among the most difficult to separate because of their chemical similarity.<sup>[5]</sup>

### Hafnium, $_{72}\text{Hf}$



Spectral lines of hafnium (400–700 nm)

#### General properties

**Name, symbol** hafnium, Hf

**Appearance** steel gray

#### Hafnium in the periodic table

**Atomic number** (*Z*) 72

**Group, block** group 4, d-block

**Period** period 6

**Element category** □ transition metal

**Standard atomic weight** ( $\pm$ ) (*A*<sub>r</sub>) 178.49(2)<sup>[1]</sup>

**Electron configuration** [Xe] 4f<sup>14</sup> 5d<sup>2</sup> 6s<sup>2</sup>  
per shell 2, 8, 18, 32, 10, 2

#### Physical properties

**Phase** solid

**Melting point** 2506 K (2233 °C, 4051 °F)

**Boiling point** 4876 K (4603 °C, 8317 °F)

**Density** near r.t. 13.31 g/cm<sup>3</sup>

A notable physical difference between these metals is their density, with zirconium having about one-half the density of hafnium. The most notable nuclear properties of hafnium are its high thermal neutron-capture cross-section and that the nuclei of several different hafnium isotopes readily absorb two or more neutrons apiece.<sup>[5]</sup> In contrast with this, zirconium is practically transparent to thermal neutrons, and it is commonly used for the metal components of nuclear reactors – especially the cladding of their nuclear fuel rods.

## Chemical characteristics



Hafnium dioxide

Hafnium reacts in air to form a protective film that inhibits further corrosion. The metal is not readily attacked by acids but can be oxidized with halogens or it can be burnt in air. Like its sister metal zirconium, finely divided hafnium can ignite spontaneously in air, producing an effect similar to that obtained in Dragon's Breath.<sup>[6]</sup> The metal is resistant to concentrated alkalis.

The chemistry of hafnium and zirconium is so similar that the two cannot be separated on the basis of differing chemical reactions. The melting points and boiling points of the compounds and the solubility in solvents are the major differences in the chemistry of these twin elements.<sup>[7]</sup>

## Isotopes

At least 34 isotopes of hafnium have been observed, ranging in mass number from 153 to 186.<sup>[8][9]</sup> The five stable isotopes are in the range of 176 to 180. The radioactive isotopes' half-lives range from only 400 ms for <sup>153</sup>Hf,<sup>[9]</sup> to 2.0 petayears (10<sup>15</sup> years) for the most stable one, <sup>174</sup>Hf.<sup>[8]</sup>

The nuclear isomer <sup>178m2</sup>Hf was at the center of a controversy for several years regarding its potential use as a weapon.

|                             |                      |
|-----------------------------|----------------------|
| when liquid, at m.p.        | 12 g/cm <sup>3</sup> |
| <b>Heat of fusion</b>       | 27.2 kJ/mol          |
| <b>Heat of vaporization</b> | 648 kJ/mol           |
| <b>Molar heat capacity</b>  | 25.73 J/(mol·K)      |


### Vapor pressure

| P (Pa)   | 1    | 10   | 100  | 1 k  | 10 k | 100 k |
|----------|------|------|------|------|------|-------|
| at T (K) | 2689 | 2954 | 3277 | 3679 | 4194 | 4876  |

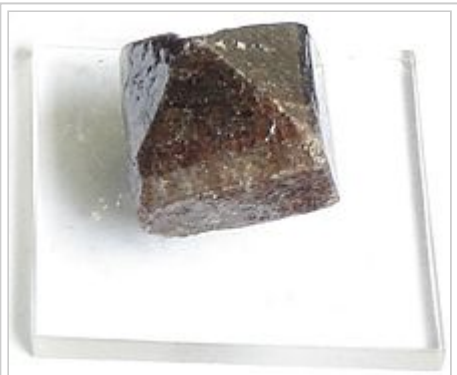
### Atomic properties

|                            |   |
|----------------------------|---|
| <b>Oxidation states</b>    | <b>4</b> , 3, 2, 1, −2 (an amphoteric oxide)              |
| <b>Electronegativity</b>   | Pauling scale: 1.3  |
| <b>Ionization energies</b> | 1st: 658.5 kJ/mol<br>2nd: 1440 kJ/mol<br>3rd: 2250 kJ/mol |
| <b>Atomic radius</b>       | empirical: 159 pm   |
| <b>Covalent radius</b>     | 175±10 pm   |

### Miscellanea

|                                   |   |
|-----------------------------------|---|
| <b>Crystal structure</b>          | hexagonal close-packed (hcp)  |
| <b>Speed of sound</b><br>thin rod | 3010 m/s (at 20 °C)   |
| <b>Thermal expansion</b>          | 5.9 μm/(m·K) (at 25 °C)   |
| <b>Thermal conductivity</b>       | 23.0 W/(m·K)  |
| <b>Electrical resistivity</b>     | 331 nΩ·m (at 20 °C)   |
| <b>Magnetic ordering</b>          | paramagnetic <sup>[2]</sup>   |
| <b>Young's modulus</b>            | 78 GPa  |

Occurrence



Zircon crystal (2×2 cm) from Tocantins, Brazil

Hafnium is estimated to make up about 5.8 ppm of the Earth's upper crust by mass. It does not exist as a free element on Earth, but is found combined in solid solution with zirconium in natural zirconium compounds such as zircon,  $\text{ZrSiO}_4$ , which usually has about 1 – 4% of the Zr replaced by Hf. Rarely, the Hf/Zr ratio increases during crystallization to give the isostructural mineral "hafnon"  $(\text{Hf,Zr})\text{SiO}_4$ , with atomic  $\text{Hf} > \text{Zr}$ .<sup>[10]</sup> An old (obsolete) name for a variety of zircon containing unusually high Hf content is *alvite*.<sup>[11]</sup>

A major source of zircon (and hence hafnium) ores is heavy mineral sands ore deposits, pegmatites, particularly in Brazil and Malawi, and carbonatite intrusions, particularly the Crown Polymetallic Deposit at Mount Weld, Western Australia. A potential source of hafnium is trachyte tuffs containing rare zircon-hafnium silicates eudialyte or armstrongite, at Dubbo in New South Wales, Australia.<sup>[12]</sup>

Hafnium reserves have been infamously estimated to last under 10 years by one source if the world population increases and demand grows.<sup>[13]</sup> In reality, since hafnium occurs with zirconium, hafnium can always be a byproduct of zirconium extraction to the extent that the low demand requires.

External links

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

| <b>Shear modulus</b>                   | 30 GPa   |                             |                |          |                   |
|--|--|-----------------------------|----------------|----------|-------------------|
| <b>Bulk modulus</b>                    | 110 GPa  |                             |                |          |                   |
| <b>Poisson ratio</b>                   | 0.37   |                             |                |          |                   |
| <b>Mohs hardness</b>                   | 5.5  |                             |                |          |                   |
| <b>Vickers hardness</b>                | 1520–2060 MPa  |                             |                |          |                   |
| <b>Brinell hardness</b>                | 1450–2100 MPa  |                             |                |          |                   |
| <b>CAS Number</b>                      | 7440-58-6  |                             |                |          |                   |
| <b>History</b>                         |  |                             |                |          |                   |
| <b>Naming</b>                          | after <i>Hafnia</i> . Latin for: Copenhagen, where it was discovered |                             |                |          |                   |
| <b>Prediction</b>                      | Dmitri Mendeleev (1869)  |                             |                |          |                   |
| <b>Discovery and first isolation</b>   | Dirk Coster and George de Hevesy (1922)                              |                             |                |          |                   |
| <b>Most stable isotopes of hafnium</b> |  |                             |                |          |                   |
| iso                                    | NA   | half-life                   | DM             | DE (MeV) | DP                |
| <b><sup>172</sup>Hf</b>                | syn  | 1.87 y                      | ε              | 0.350    | <sup>172</sup> Lu |
| <b><sup>174</sup>Hf</b>                | 0.16%  | 2×10 <sup>15</sup> y        | α              | 2.495    | <sup>170</sup> Yb |
| <b><sup>176</sup>Hf</b>                | 5.26%  | is stable with 104 neutrons |                |          |                   |
| <b><sup>177</sup>Hf</b>                | 18.60%   | is stable with 105 neutrons |                |          |                   |
| <b><sup>178</sup>Hf</b>                | 27.28%   | is stable with 106 neutrons |                |          |                   |
| <b><sup>178m2</sup>Hf</b>              | syn  | 31 y                        | IT             | 2.446    | <sup>178</sup> Hf |
| <b><sup>179</sup>Hf</b>                | 13.62%   | is stable with 107 neutrons |                |          |                   |
| <b><sup>180</sup>Hf</b>                | 35.08%   | is stable with 108 neutrons |                |          |                   |
| <b><sup>182</sup>Hf</b>                | syn  | 8.9×10 <sup>6</sup> y       | β <sup>−</sup> | 0.373    | <sup>182</sup> Ta |