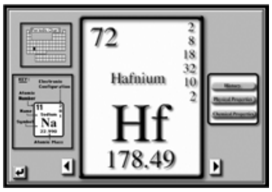
# Hafnium



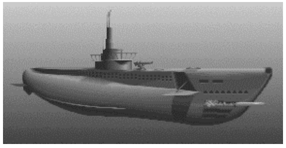
(Hafinia, Latin name for Copenhagen) Many years before its discovery in 1932 (credited to D. Coster and G. von Hevesey), Hafnium was thought to be present in various minerals and concentrations.

It was originally separated from zirconium by repeated recrystallization of the double ammonium or potassium fluorides.

Metallic hafnium was first prepared by van Arkel and deBoer by passing the vapor of the tetraiodide over a heated tungsten filament.

Almost all hafnium metal now produced is made by reducing the tetrachloride with magnesium or with sodium (Kroll Process).

Hafnium is resistant to concentrated bases, but at elevated temperatures reacts with oxygen, nitrogen, carbon , boron , sulfur , and silicon . Halogens react to form tetrahalides.



**Hafnium is used in:**
**-alloying with iron, titanium, niobium and other metals.**
**-nuclear control rods**
**-scavenging oxygen and nitrogen**
**-in gas-filled and incandescent lamps.**

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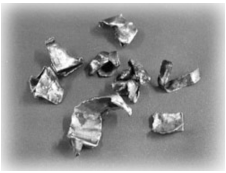
# Group 4: V, Nb, Ta

Discovered in 1803 by Andres Manuel del Rio and Nils Sefström

Named after "*Vanadis*", the goddess of beauty in Scandinavian mythology



The discovery of vanadium was claimed first by Andres Manuel del Rio (a Spanish mineralogist) at Mexico City in 1803.

He prepared a number of salts from a material contained in "brown lead" (now called vanadite, from a mine near Hidalgo in Northern Mexico). He found the colours reminiscent of those shown by chromium, so he called the element panchromium ("something which can take or have any colour"). He later renamed the element erythronium ("red") after noting that most of these salts turned red upon heating.

It seems he withdrew his claim after a Frenchman, Collett-Desotils, disputed. It was only 30 years later that it was shown that del Rio's work was, in fact, correct.

**Metallic vanadium was not made until 1867 when Henry Enfield Roscoe reduced vanadium chloride ($VCl_3$) with hydrogen gas to give vanadium metal and HCl.**

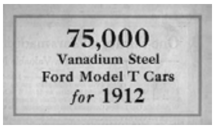
# Vanadium Applications

**Vanadium metal is important in a number of areas.**

**Its structural strength and neutron cross section properties makes it useful in nuclear applications.**

**The metal is used for producing rust-resistant springs and steels used for making tools.**

**About 80% of the vanadium now produced is used as ferrovanadium or as a steel additive.**



75,000
Vanadium Steel
Ford Model T Cars
*for* 1912

**Vanadium foil is used as a bonding agent in binding titanium to steel**

**The pentoxide $V_2O_5$ is used in ceramics and as a chemical catalyst.**

**Vanadium compounds are used for dyeing and printing fabrics.**

**A vanadium-gallium mixture is used in producing superconductive magnets.**

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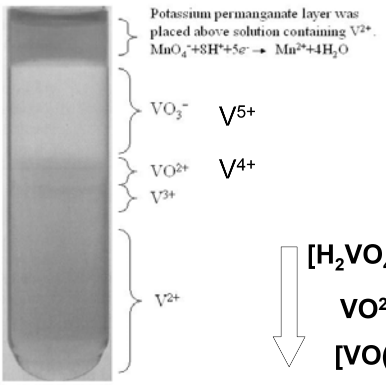
# Vanadium Chemistry

**Redox Chemistry**

Readily exists in four different oxidation states $d^{0-3}$

Oxidation states of vanadium



$V^{5+}$

$V^{4+}$

The same series of colours can be obtained using Zn metal as a reagent.

How does this reaction differ from the $KMnO_4$ reaction?

$$[H_2VO_4]^-_{(aq)} + 4H^+ + e^- \rightarrow VO^{2+}_{(aq)} + 3H_2O_{(l)}$$

$$VO^{2+}_{(aq)} + 4H^+ + e^- \rightarrow V^{3+}_{(aq)} + H_2O_{(l)}$$

$$[VO(OH_2)_5]^{2+}_{(aq)} + e^- \rightarrow [V(OH_2)_6]^{2+}_{(aq)}$$

Exposure of the final solution to air results in reoxidation to $V^{3+}$.

**Biological role**

Vanadium is essential to sea squirts (ascidians). The concentration of vanadium in sea squirts is a million times higher than in sea water as a consequence of their ability to concentrate vanadium.

Vanadium is a necessary part of the diet of rats and chicks, but only is very small amounts. Deficiencies cause reduced growth and impair reproduction.

**Reaction of vanadium with air**

Vanadium metal reacts with excess oxygen, $O_2$, upon heating to form vanadium(V) oxide, $V_2O_5$.

$$4V_{(s)} + 5O_{2(g)} \rightarrow 2V_2O_{5(s)} \text{ [yellow-orange]}$$

**Reaction of vanadium with water**

The surface of vanadium metal is protected by an oxide layer and does not reacts with water under normal conditions.

**Reaction of vanadium with the halogens**

Vanadium reacts with fluorine, $F_2$ upon warming to form vanadium(V) fluoride. The other vanadium pentahalides are unknown.

$$2V_{(s)} + 5F_{2(g)} \rightarrow 2VF_{5(l)} \text{ [colourless]}$$

**Reaction of vanadium with acids and bases**

Vanadium metal is resistant to attack by molten alkali.

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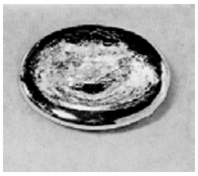
# Niobium



From the Greek word "*Niobe*" meaning "*daughter of Tantalus*" (tantalum is closely related to niobium in the periodic table)

## Discovered in 1801 in England by Charles Hatchett

A mineral (columbite) was sent to England in the 1750s by John Winthrop the Younger, the first goveror of Connecticut, USA.

Hatchett called the new element columbium.

Yet, he was not able to isolate the free element. There was then considerable confusion concerning the distinction between niobium and tantalum as they are so closely related.

This confusion was resolved by Heinrich Rose, who named niobium, and Marignac in 1846. The name niobium is now used in place of the original name "columbium".

The metal niobium was first prepared in 1864 by Blomstrand, who reduced the chloride by heating it in a hydrogen atmosphere.

**Reaction of niobium with air**
Niobium does not react with air under normal conditions. The surface of niobium metal is protected by a thin oxide layer.

**Reaction of niobium with water**
Niobium does not react with water under normal conditions. The surface of niobium metal is protected by a thin oxide layer.

**Reaction of niobium with the halogens**
Niobium does react with the halogens upon warming to form niobium(V) halides.

$$2Nb_{(s)} + 5F_{2(g)} \rightarrow NbF_{5(s)} \text{ [white]}$$

$$2Nb_{(s)} + 5Cl_{2(g)} \rightarrow NbCl_{5(l)} \text{ [yellow]}$$

$$2Nb_{(s)} + 5Br_{2(g)} \rightarrow NbBr_{5(s)} \text{ [orange]}$$

$$2Nb_{(s)} + 5I_{2(g)} \rightarrow NbI_{5(s)} \text{ [brass coloured]}$$

**Reaction of niobium with acids**
Niobium appears not to be attacked by many acids at room temperature but does dissolve in hydrofluoric acid, HF, or in a mixture of HF and nitric acid, $HNO_3$.

**Reaction of niobium with bases**
Niobium metal is largely resistant to attack by molten alkali but will dissolve slowly.

## Uses

It is a component of some stainless steels and also alloys with nonferrous metals. These alloys have good strength and other properties, and are used in pipeline construction.

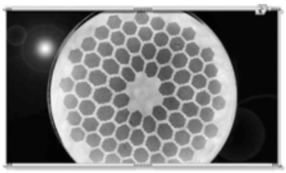
The metal has a low capture crosssection for thermal neutrons and so finds use in the nuclear industries.

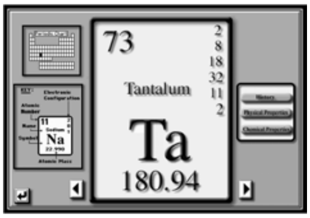
The metal is used in arc-welding rods for some grades of stainless steel.

It is used in advanced engineering systems such as those used in the Gemini space program.

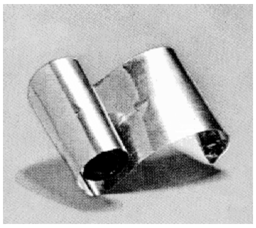
Some magnets contain niobium and superconductive magnets are made with Nb-Zr alloy wire.

Because of its bluish colour, niobium is apparently being used for "body art" products, such as navel rings.





# Tantalum



**Discovered by Anders Ekeberg in 1802**

From the Greek word "*Tantalos*" meaning "*father of Niobe*" (Greek mythology, **tantalum** is closely related to **niobium** in the periodic table)

In 1802 many chemists thought niobium and tantalum were the same same element. Primarily because of their chemical similarity. There was some question if perhaps tantalum was an allotrope of niobium.

Proof of the different elements arose when Rose, in 1844, and Marignac, in 1866, demonstrated that niobic and tantalic acids were different.

The first relatively pure tantalum was produced by von Bolton in 1907.

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# Isolation of Ta

Isolation of tantalum appears is complicated.

Tantalum minerals usually contain both niobium and tantalum.

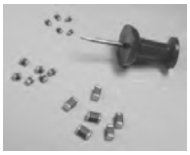
The similar chemical behavior of these two elements makes them difficult to separate.

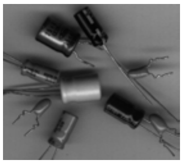
Tantalum is extracted from the ores by first fusing the ore with alkali, and then extracting the resultant mixture into hydrofluoric acid, HF.

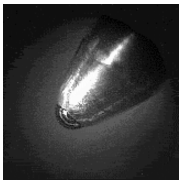
Current methodology involves the separation of tantalum from these acid solutions using a liquid-liquid extraction technique. In this process tantalum salts are extracted into the ketone MIBK (methyl isobutyl ketone, 4-methyl pentan-2-one). The niobium remains in the HF solution. This solvent extraction procedure yields 98% pure niobium oxide in one phase and a 99.5% pure tantalum oxide in another.

After conversion to the oxide, metallic tantalum can be made by reduction with sodium or carbon. Electrolysis of molten fluorides is also used.

# Applications of Ta







Tantalum is used to make steels with desirable properties such as high melting point, high strength, good ductility. These find use in aircraft and missile manufacture.

It is very inert and so useful in the chemical and nuclear industries to line reactors.

Tantalum wires were those used first for light bulbs (now tungsten is preferred).

The metal is immune to body liquids and the body tolerates the metal well. Therefore, tantalum has widespread use for surgical use. Examples of this include sutures and as cranial repair plates.

The metal is used in the electronics industry for capacitors.

The oxide is used to make special glass with a high index of refraction for camera lenses.

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# Where does Ta come from?

**Tantalum occus in nature in the minerals columbite and tantalite and euxenite.**

**Niobium and tantalum concentrates are found in Brazil, Canada, Africa, particularly Congo, Australia and Spain.**

**Tantalum is also obtained as a by product in the extraction of tin from mineral deposits in Malaysia and Nigeria.**

**Reaction of tantalum with air**

Tantalum does not react with air under normal conditions. The surface of tantalum metal is protected by a thin oxide layer.

**Reaction of tantalum with water**

Tantalum does not react with water under normal conditions. The surface of tantalum metal is protected by a thin oxide layer.

**Reaction of tantalum with the halogens**

Tantalum does react with the halogens upon warming to form tantalum(V) halides.

$$2Ta_{(s)} + 5F_{2(g)} \rightarrow TaF_{5(s)} \text{ [white]}$$

$$2Ta_{(s)} + 5Cl_{2(g)} \rightarrow TaCl_{5(l)} \text{ [white]}$$

$$2Ta_{(s)} + 5Br_{2(g)} \rightarrow TaBr_{5(s)} \text{ [pale yellow]}$$

$$2Ta_{(s)} + 5I_{2(g)} \rightarrow TaI_{5(s)} \text{ [black]}$$

**Reaction of tantalum with acids**

Tantalum appear not to be attacked by many acids at room temperature but does dissolve in hydrofluoric acid, HF, or oleum (a solution of sulphur trioxide, $SO_3$, in sulphuric acid, $H_2SO_4$, also known as fuming sulphuric acid).

**Reaction of tantalum with bases**

The metal is attacked by molten alkali.

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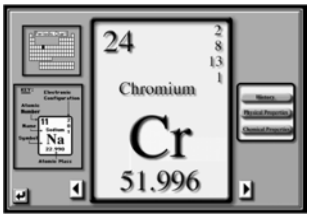
# Chromium



Discovered by Louis-Nicholas
Vauquelin in France 1797

Chromium is steel-gray, lustrous, hard, metallic, and takes a high polish.

Its compounds are toxic.

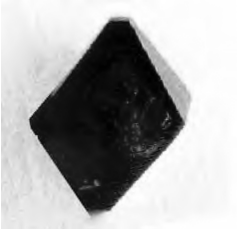
It is found as chromite ore.

Siberian red lead (crocoite, $PrCrO_4$) is a chromium ore prized as a red pigment for oil paints.

# Gem Stones

Emerald is a form of beryl (a beryllium aluminium silicate) which is green because of the inclusion of a little chromium into the beryl crystal lattice in place of some of the aluminium ions.

Traces of chromium incorporated into the crystal lattice of corundum (crystalline aluminium oxide, $Al_2O_3$) as a replacement for some of the $Al^{3+}$ ions results in another highly coloured gem stone, in this case the red ruby.



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# Isolation of Cr

Chromium is not typically prepared in the laboratory given its commercial availability.

The most common commercial source of chromium is the ore chromite, $FeCr_2O_4$.

Oxidation of this ore by air in molten alkali gives sodium chromate, $Na_2CrO_4$ in which the **chromium is in the +6 oxidation state**. This is converted to the Cr(III) oxide $Cr_2O_3$ by extraction into water, precipitation, and reduction with carbon. The oxide is then further reduced with aluminium or silicon to form chromium metal.

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$
$$2Cr_2O_3 + 3Si \rightarrow 4Cr + 3SiO_2$$

Another isolation is by electroplating processes. This involves the dissolution of $Cr_2O_3$ in sulphuric acid to give an electrolyte used for chromium electroplating.

**Reaction of chromium with air**
Chromium metal does not react with air or oxygen at room temperature.

**Reaction of chromium with water**
Chromium metal does not react with water at room temperature.

**Reaction of chromium with acids**
Chromium metal dissolves in dilute hydrochloric acid to form solutions containing the aquated Cr(II) ion together with hydrogen gas, $H_2$.

In practice, the Cr(II) is present as the complex ion $[Cr(OH_2)_6]^{2+}$. Similar results are seen for sulphuric acid but pure samples of chromium may be resistant to attack. **Chromium metal does not react with nitric acid, $HNO_3$ and in fact is passivated.**

$$Cr(s) + 2HCl(aq) \rightarrow Cr^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$$

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# Cr and halides

**Reaction of chromium with the halogens**

Chromium reacts directly with fluorine, $F_2$, at 400°C and 200-300 atmospheres to form chromium(VI) fluoride, $CrF_6$.

$$Cr(s) + 3F_2(g) \rightarrow CrF_6(s) \text{ [yellow]}$$

Under milder conditions, chromium(V) fluoride, $CrF_5$, is formed.

$$2Cr(s) + 5F_2(g) \rightarrow 2CrF_5(s) \text{ [red]}$$

Under still milder conditions, chromium metal reacts with the halogens fluorine, $F_2$, chlorine, $Cl_2$, bromine, $Br_2$, and iodine, $I_2$, to form the corresponding trihalides chromium(III) fluoride, $CrF_3$, chromium(III) chloride, $CrCl_3$, chromium(III) bromide, $CrBr_3$, or chromium(III) iodide, $CrI_3$.

$$2Cr(s) + 3F_2(g) \rightarrow 2CrF_3(s) \text{ [green]}$$

$$2Cr(s) + 3Cl_2(g) \rightarrow 2CrCl_3(s) \text{ [red-violet]}$$

$$2Cr(s) + 3Br_2(g) \rightarrow 2CrBr_3(s) \text{ [very dark green]}$$

$$2Cr(s) + 3I_2(g) \rightarrow 2CrI_3(s) \text{ [very dark green]}$$

## Where does Cr come from?

Chromium is not found as the free metal in nature.

The most important ore is chromite ($FeCr_2O_4$) and this is found in Turkey, USA, South Africa, Albania, Finland, Iran, Madagascar, Russia, Southern Rhodesia, Transvaal, Cuba, Brazil, Japan, India, Pakistan, and the Philippines.

Crocoite, $PbCrO_4$, is also a chromium mineral and this is found in Russia, Brazil, USA, and Tasmania.

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## Biology and the Movies

Chromium is an essential trace element and has a role in glucose metabolism. It seems to have an effect in the action of insulin. In anything other than trace amounts, chromium compounds should be regarded as highly toxic.

Erin
Brockovich

# Cr(VI)

# Chromium Applications

To harden steel, to manufacture stainless steel, and to form alloys

Plating to produce a hard, beautiful surface and to prevent corrosion.

Wide use as a catalyst

Dichromates such as $K_2Cr_2O_7$ are oxidising agents and are used in quantitative analysis and also in tanning leather

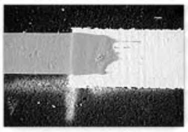
Lead chromate as chrome yellow is a pigment (DCC).

compounds are used in the textile industry as mordants

used by the aircraft and other industries for anodising aluminium

the refractory industry uses chromite for forming bricks and shapes, as it has a high melting point, moderate thermal expansion, and stable crystalline structure

tanning leather



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Historical information

Discovered by: Carl William Scheele

Discovered at: Sweden

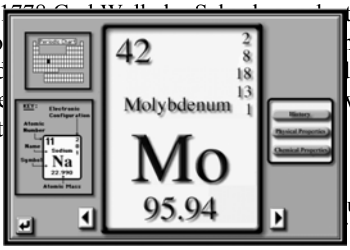
Discovered when: 1781

Mo

From the Greek word "molybdos" meaning "lead"

In … ted research on an ore now known as
mo … not contain lead as was suspected at the time
and … a new element that he called molybdenum
afte … was prepared in an impure form in 1782 by
Pet

… the free metal. The main ore is
… ulphide, $MoS_2$). Molybdenum is
… copper and tungsten production.



42

2
8
18
13
1

Molybdenum

Mo

95.94

Molybdenum is a silver/gray metal. Its name is derived from the Greek word "molybdaena", meaning "lead". The name was also used to describe galena and graphite, which have similar appearances in natural form. In 1778, Karl Scheele had been able to distinguish molybdenite from graphite by noting that molybdenite formed a white powder when treated with nitric acid, whereas graphite did not. Molybdenum metal was isolated and proven to be a new element in 1790 by P.J. Hjelm, drawing on the earlier work of Scheele.

In the 1800's, molybdenum was used primarily in dyes and the preparation of certain chemical compounds, but little else was done with it. However, in 1893 German chemists Sternberg and Deutsch developed an ecomomical process to produce 96% pure molybdenum metal. Although the product still contained 3% carbon, the sales price of $0.86 per pound generated interest in possible commercial uses. Tests designed to evaluate molybdenum's ability to replace tungsten as an additive in tool steel were unsuccessful, primarily because of sulphur and phosphorus impurities in the molybdenum.

In 1894, grey molybdenum oxide was produced in an electric furnace. The oxide contained 9% carbon, which made the compound hard enough to scratch glass. This inspired French chemist Henri Moissan to do his own electric furnace experiments. He succeeded in producing molybdenum which was 99.98% pure. He then set about determining the atomic weight and other properties of molybdenum.

Due to a variety of economic conditions and the difficulty in reliably producing pure molybdenum, very little commercial use was seen until World War I when molybdenum was widely used as an additive to toughen armor plating. Even after that, molybdenum did not enjoy immediate success. Speculation on whether or not there would ever be a market for molybdenum gained it the moniker "the metallurgical mystery".

The use of molybdenum has increased steadily, and today it is in demand both in pure form and as a steel additive. Today most molybdenum is mined in The United States, Chile, and Canada - in that order. Strangely enough, an ancient Japanese sword blade made by Masamuné in 1330 was found to contain molybdenum.

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Reaction of molybdenum with air

At room temperature, molybdenum does not react with air or oxygen, $O_2$. At elevated temperatures (red heat), the trioxide molybdenum(VI) oxide, $MoO_3$, is formd.

$2Mo(s) + 3O_2(g) \quad 2MoO_3(s)$

Reaction of molybdenum with water

At room temperature, molybdenum does not react with water.

Reaction of molybdenum with the halogens

Molybdenum reacts directly with fluorine, $F_2$, at room temperature to form molybdenum(VI) fluoride, $MoF_6$. The conditions are much milder than those required for chromium (immediately above molybdenum in the periodic table).

$Mo(s) + 3F_2(g) \quad MoF_6(l)$ [colourless]

Under carefully controlled conditions, molybdenum(V) fluoride, $MoF_5$, is formed in the reaction between molybdenum metal and chlorine, $Cl_2$.

$2Mo(s) + 5Cl_2(g) \quad 2MoCl_5(s)$ [black]

# Mo uses

va ontributes to the hardenability and toughness of quenched and tempered steels). strength steels contain molybdenum in amounts from 0.25 to 8%

in teel at high temperatures

electrodes for electrically heated glass furnaces

nuclear energy applications

missile and aircraft parts

valuable catalyst in petroleum refining

filament material in electrical applications

essential trace element in plant nutrition. Some soils are barren for lack of this element in the soil

molybdenum disulphide is a good lubricant, especially at high temperatures where normal oils decompose

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Molybdenum is a necessary element, apparently for all species. Only very small amounts are required. Molybdenum plays a role in nitrogen fixation, (a process by which the normally unreactive nitrogen gas is turned into other compounds) enzymes, and nitrate reduction enzymes