Group 4: Ti, Zr, Hf

The discovery of titanium in 1791 is attributed to William Gregor, a Cornish vicar and amateur chemist. He isolated an impure oxide from limenite (FeTiO₃) by treatment with HCl and H₂SO₄.

Named after the "Titans", (the sons of the Earth goddess in Greek mythology)

Ti A silver-white metal, known for its hardness, low density (4.5g cm⁻³) Titanium is the second most abundant transition metal on Earth (6320 ppm) and plays a vital role as a material of construction because of its:

Excellent Corrosion Resistance, High Heat Transfer Efficiency Superior Strength-To-Weight Ratio

When it's alloyed with 6% aluminum and 4% vanadium, titanium has half the weight of steel and up to four times the strength.

Although a biological function in man is not known, it has excellent biocompatibility
--hat is the ability to be ignored by the human body's immune system—and an extreme resistance to corrosion.

Titanium is now the metal of choice for hip and knee replacements. It is used in military aircraft, nuclear submarines, areas where cost is not really a concern.

Other applications include: MAC TiBooks, golf clubs, bicycles.



Isolation of Ti

The most common form of Ti in the terrasphere is ${\rm TiO}_2$. This is a white solid often used in paint as well as as a "sunshield".

Kroll allows isolation of Ti.

Conversion to TiCl₄.....and reduction to Ti with Mg

Reactions of Ti

Reaction of titanium with air

Titanium metal is coated with a passivating oxide layer that usually renders it inactive. (This is similar to Al and Si)

However once titanium starts to burn in air it burns with a spectacular white flame to form titanium dioxide, TiO₂ and titanium nitride, TiN. Titanium metal even burns in pure nitrogen to form titanium nitride.

$$\mathsf{Ti}_{(s)} + \mathsf{O}_{2(g)} \to \mathsf{TiO}_{2(s)}$$

$$2Ti_{(s)} + N_{2(g)} \rightarrow TiN_{(s)}$$

Reaction of titanium with water

Titanium will react with steam and form the dioxide, titanium(IV) oxide, ${\rm TiO_2},$ and hydrogen, ${\rm H_2}.$

$$Ti_{(s)} + 2H_2O_{(q)} \rightarrow TiO_{2(s)} + 2H_{2(q)}$$

Reaction of titanium with the halogens

Titanium does react with halogens upon warming to form titanium(IV) halides. The reaction with fluorine requires heating to 200°C.

$$Ti(s) + 2F_{2(q)} \rightarrow TiF_{4(s)}$$
 [white]

$$Ti(s) + 2Cl_{2(g)} \rightarrow TiCl_{4(l)}$$
 [colourless]

$$Ti(s) + 2Br_{2(g)} \rightarrow TiBr_{4(s)}$$
 [orange]

$$Ti(s) + 2I_{2(g)} \rightarrow TiI_{4(s)}$$
 [dark brown]

Reaction of titanium with acids

Dilute aqueous hydrofluoric acid, HF, reacts with titanium to form the complex anion [TiF $_6$]3-together with hydrogen, H $_2$.

$$2Ti_{(s)} + 12HF_{(aq)} \rightarrow 2[TiF_6]^{3-}_{(aq)} + 3H_{2(q)} + 6H^+_{(aq)}$$

Titanium metal does not react with mineral acids at ambient temperature but does react with hot hydrochloric acid to form titanium(III) complexes.

Reaction of titanium with bases

3

Titanium does not react with bases under normal conditions, even when hot.

A dramatic demonstration of a Ti reaction.

 $\text{Ti}_{(s)} + \text{KCIO}_4 \rightarrow \text{TiO}_{2(s)} + \text{KCI}_{(s)} + \text{energy}$

A few examples of Ti applications.



Hip implants







Golf Clubs



Aircraft





Zirconium

Zirconium is a greyish-white lustrous metal.
Finely divided metal can ignite spontaneously in air, at elevated T.
(The solid metal is much more difficult to ignite.)
The inherent toxicity of zirconium compounds is low.

Ores are mined in a number of countries including Australia, Brazil, India, South Africa and the USA.

Isolation

The Kroll method is also used for zirconium and involves the reaction of chlorine and carbon upon baddeleyite (ZrO_2) .

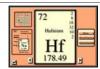
Zirconium tetrachloride, ${\rm ZrCl_4}$, is separated from the iron trichloride, ${\rm FeCl_3}$, by fractional distillation.

Finally ZrCl₄ is reduced to metallic zirconium by reduction with magnesium, Mg. Air is excluded so as to prevent contamination of the product with oxygen or nitrogen.

Excess magnesium and magnesium chloride are removed from the product with water and hydrochloric acid to leave a zirconium "sponge". This can be melted under helium by electrical heating.



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.



7

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.

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 (VCIs) with hydrogen gas to give vanadium metal and HCI.

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 Cara for 1912 Vanadium foil is used as a bonding agent in binding titanium to

The pentoxide $V2O_5$ is used in ceramics and as a chemical catalyst.

Vanadium compounds are used for dyeing and printing fabrics.

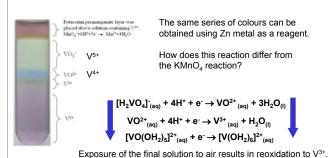
A vanadium-gallium mixture is used in producing superconductive magnets.

Vanadium Chemistry

Redox Chemistry

Readily exists in four different oxidation states d⁰⁻³

Oxidation states of vanadium



Biological role

11

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 .

$$4V_{(s)} + 5O_{2(q)} \rightarrow 2V_2O_{5(s)}$$
 [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.

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

Reaction of vanadium with acids and bases

Vanadium metal is resistant to attack by molten alkali.

Niobium



13

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.

$$\begin{split} &2Nb_{(s)}+5F_{2(g)}\rightarrow NbF_{5(s)} \text{ [white]} \\ &2Nb_{(s)}+5Cl_{2(g)}\rightarrow NbCl_{5(j)} \text{ [yellow]} \\ &2Nb_{(s)}+5Br_{2(g)}\rightarrow NbBr_{5(s)} \text{ [orange]} \\ &2Nb_{(s)}+5l_{2(g)}\rightarrow Nbl_{5(s)} \text{ [brass coloured]} \end{split}$$

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 cross section 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.

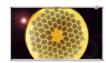
It is used in advanced engineering systems such as those used in the Gemini space program.

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.

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.



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.

$$\begin{split} &2\mathsf{Ta}_{(s)} + \mathsf{5F}_{2(g)} \to \mathsf{TaF}_{5(s)} \text{ [white]} \\ &2\mathsf{Ta}_{(s)} + \mathsf{5CI}_{2(g)} \to \mathsf{TaCI}_{5(l)} \text{ [white]} \\ &2\mathsf{Ta}_{(s)} + \mathsf{5BI}_{2(g)} \to \mathsf{TaBF}_{5(s)} \text{ [pale yellow]} \\ &2\mathsf{Ta}_{(s)} + \mathsf{5I}_{2(s)} \to \mathsf{TaI}_{5(s)} \text{ [black]} \end{split}$$

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 sulphur acid, H, SO_4 , also known as furning sulphuric acid).

Reaction of tantalum with bases

The metal is attacked by molten alkali.

Chromium

Discovered by Louis-Nicholas Vauquelin in France 1797

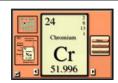
Chromium is steel-gray, lustrous, hard, metallic, and takes a high polish.

Its compounds are toxic.

It is found as chromite ore.

Siberian red lead (crocoite, PrCrO₄) 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, $\mathrm{Al_2O_3}$) as a replacement for some of the $\mathrm{Al^{3+}}$ ions results in another highly coloured gem stone, in this case the red ruby.





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, FeCr₂O₄.

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.

$$\begin{array}{c} \operatorname{Cr_2O_3} + 2\operatorname{AI} \to \ 2\operatorname{Cr} + \operatorname{AI_2O_3} \\ 2\operatorname{Cr_2O_3} + 3\operatorname{Si} & \to & 4\operatorname{Cr} + 3\operatorname{SiO_2} \end{array}$$

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 $[Cr(OH_2)_\delta]^{2^*}$. 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, HNO₃ and in fact is passivated.

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

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 .

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

Under milder conditions, chromium(V) fluoride, CrF₅, is formed.

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

Under still milder conditions, chromium metal reacts with the halogens fluorine, F_2 , chlorine, Cl_2 , bromine, Br_2 , and iodine, L_2 to form the corresponding trihalides chromium(III) fluoride, CrF_3 , chromium(III) chloride, $CrCl_3$, chromium(III) bromide, $CrBl_3$, or chromium(III) iodide, Crl_3 .

$$2Cr(s) + 3F_2(g) \rightarrow 2CrF_3(s)$$
 [green]
 $2Cr(s) + 3Cl_2(g) \rightarrow 2CrCl_3(s)$ [red-violet]
 $2Cr(s) + 3Br_2(g) \rightarrow 2CrBr_3(s)$ [very dark green]

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

Where does Cr come from?

Chromium is not found as the free metal in nature.

The most important ore is chromite (FeCr₂O₄) 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, PbCrO₄, is also a chromium mineral and this is found in Russia, Brazil, USA, and Tasmania.

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)

Industrial prep of dichromate.

We start with a mixed metal oxide: Chromite FeCr₂O₄.

The addition of water results in LEACHING to leave the iron(III) oxide and a solution of sodium chromate.

To obtain sodium dichromate it is necessary to apply Who's Principle?

$$2Na_2CrO_{4 (aq)} + 2CO_{2 (aq)} + H_2O \longrightarrow Na_2Cr_2O_{4 (aq)} + 2NaHCO_{3 (s)}$$
 What does this do?

A little about Cr(VI)

 $Cr(VI)\ compounds\ are\ thermodynamically\ unstable\ BUT$ kinetic factors lead to several $Cr(VI)\ compounds\ exisiting.$

Chromate [CrO₄]²⁻

This ion exists in neutral and basic conditions

Dichromate [Cr₂O₇]²⁻

This ion exists in acidic conditions

The following equilibrium explains why...

$$2[CrO_4]^{2-}_{aq} + 2H^+_{(aq)} \leftrightarrow [Cr_2O_7]^{2-}_{(aq)} + H_2O_{(I)}$$

The chromate ion is the conj. base of hydrogen chromate....hence it exists in basic solution.

$$[CrO_4]^{2-}_{(aq)} + H_2O_{(I)} \leftrightarrow [HCrO_4]^{-}_{(aq)} + OH^{-}_{(aq)}$$

Chromates

Many chromates are insoluble.....

PbCrO₄ has a high refractive index, low solubility in water and it is yellow.

What might it be used for?

How can different colours be obtained from this compound.... they can range from red/orange-yellow.

This should worry you.....how can Cr(VI) be coloured?

What is its electron configuration?

The Mohr Method for Cl-determination

Silver (I) chromate (Ag₂CrO₄) is brick red.

$$Ag^+_{(aq)} + CI^-_{(aq)} \rightarrow AgCI_{(s)}$$

$$2Ag^{+}_{(aq)} + [CrO_4]^{2-}_{(aq)} \rightarrow Ag_2CrO_{4(s)}$$

- 1. Add silver ions to a solution containing CI-.
- When all of the Cl⁻ is consumed it is very difficult to identify the endpoint. Enter Ag₂CrO₄!

At very low concentration of CrO₄²-(~0.01M) the brick red ppt will for indicating the endpoint.



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 K2Cr2O7 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









Molybdenum



Discovered by Carl William Scheele in Sweden 1781.

Isolated from molybdenite.

From the Greek word "molybdos" meaning "lead" Molybdenum metal was prepared in an impure form in 1782 by Peter Jacob Hjelm.

Molybdenum is not found as the free metal. The main ore is molybdenite (molybdenum sulphide, ${\rm MoS_2}$). Molybdenum is recovered as a by-product of copper and tungsten production.



The metal is prepared from the powder made by the hydrogen reduction of purified molybdic trioxide or ammonium molybdate.

Reactions of molybdenum

Δiı

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 formal

$$2Mo_{(s)} + 3O_{2(g)} \rightarrow 2MoO_{3(s)}$$

Water

At room temperature, molybdenum does not react with water.

Halogens

Molybdenum reacts directly with fluorine, F_2 , at room temperature to form molybdenum(VI) fluoride, MoF_8 . The conditions are much milder than those required for chromium (immediately above molybdenum in the periodic table).

$$Mo_{(s)} + 3F_{2(g)} \rightarrow MoF_{6(l)}$$
 [colourless]

Under carefully controlled conditions, molybdenum(V) fluoride, MoF₅, is formed in the reaction between molybdenum metal and chlorine, Cl₂.

$$2Mo_{(s)} + 5Cl_{2(g)} \rightarrow 2MoCl_{5(s)}$$
 [black]



Mo uses

valuable alloying agent (contributes to the hardness and toughness of quenched and tempered steels). Almost all ultra-high strength steels contain molybdenum in amounts from 0.25 to 8%

improves the strength of steel 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



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

an ancient Japanese sword blade made by Masamuné in 1330 was found to contain molybdenum



Tungsten



Discovered by Fausto and Juan Jose de Elhuyar in Spain 1783

From the Swedish words "tung sten" meaning "heavy stone" (the origin of the symbol W is "wolfram", named after the tungsten mineral wolframite)

Tungsten used to be known as wolfram (from wolframite, said to be named from wolf rahm or spumi lupi, because the ore interfered with the smelting of tin and was supposed to devour the tin). The de Elhuyar brothers found an acid in wolframite in 1783 that they succeeded in reducing to the elemental metal with charcoal.

Tungsten is found in:

- wolframite (iron-manganese tungstate, FeWO4/MnWO4)
- scheelite (calcium tungstate, CaWO4) ores.

China produces 75% of the world's tungsten.

Reaction of tungsten with air

At room temperature, tungsten does not react with air or oxygen, O2. At elevated temperatures (red heat), the trioxide tungsten(VI) oxide, WO3, is formed.

Finely divided tungsten metal is pyrophoric.

$$2W(s) + 3O_2(g) \rightarrow 2WO_3(s)$$

Reaction of tungsten with water

At room temperature, tungsten does not react with water.

Reaction of tungsten with the halogens

Tungsten reacts directly with fluorine, F2, at room temperature to form tungsten(VI) fluoride, WF6. The conditions are much milder than those required for chromium.

$$W(s) + 3F_2(g) \rightarrow WF_6(g)$$
 [colourless]

Tungsten reacts directly with chlorine, Cl2, at 250°C or bromine, Br2, to. Under carefully controlled conditions, tungsten(V) chloride, WCl5, is formed in the reaction between tungsten metal and chlorine, Cl2.

Reaction of tungsten with the halogens and the light bulb



A halogen lamp also uses a tungsten filament, but it is encased inside a much smaller quartz envelope.

I₂ vapor combines with tungsten vapor to form WI₂.
WI₂ redeposits on the filament and decomposes to produce
W them on the filament.

This recycling process lets the filament last a lot longer.

Biological role

Tungsten has a limited biological role. A number of enzymes (oxidoreductases) employ tungsten in a way related to molybdenum, (using tungsten.pterin complex). The structure of a tungstoenzyme aldehyde ferredoxin oxidoreductase is known (Protein Data Bank code 1AOR).

37

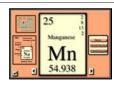






W applications

- glass-to-metal seals since the thermal expansion is about the same as borosilicate glass
- tungsten and its alloys are used extensively for filaments for electric lamps, electron and television tubes, and for metal evaporation work
- electrical contact points for car distributors
- X-ray targets
- windings and heating elements for electrical furnaces
- missile and high-temperature applications
- high-speed tool steels
- the carbide is important to the metal-working, mining, and petroleum industries
- calcium and magnesium tungstates are widely used in fluorescent lighting
- tungsten salts are used in the chemical and tanning industries
- tungsten disulphide is a dry, high-temperature lubricant, stable to 500°C
- -tungsten bronzes and other tungsten compounds are used in paints



Manganese



Discovered by Johann Gahn in Sweden (1774)

From the Latin word "magnes" meaning "magnet", or "magnesia nigri" meaning "black magnesia" (MnO2)

Gahn reduced the dioxide (MnO2, as the mineral pyrolusite) with charcoal (essentially carbon) by heating and the result was a sample of the metal manganese.

Manganese compounds are essential to life. They are essential for the action of some enzymes. Soil deficiencies lead to infertility in mammals and to bone malformation in growing chicks.

Reaction of manganese with air

Manganese is not particularly reactive to air. The surface of manganese lumps oxidize slightly. When finely divided, manganese metal burns in air. It burns in oxygen to form the oxide Mn304 and in nitrogen to form the nitride Mn3N2.

$$3Mn(s) + 2O2(g) \rightarrow Mn3O4(s)$$

 $3Mn(s) + N2(g) \rightarrow Mn3N2(s)$

Reaction of manganese with water

Manganese does not react with water under normal conditions.

Reaction of manganese with the halogens

 $\begin{array}{l} Mn(s) + Cl2(g) \rightarrow MnCl2(s) \\ Mn(s) + Br2(g) \rightarrow MnBr2(s) \\ Mn(s) + I2(g) \rightarrow MnI2(s) \\ Mn(s) + F2(g) \rightarrow MnF2(s) \\ 2Mn(s) + 3F2(g) \rightarrow 2MnF3(s) \end{array}$

Reaction of manganese with acids

Manganese metal dissolves readily in dilute sulphuric acid to form solutions containing the aquated Mn(II) ion together with hydrogen gas, Hz. In practice, the Mn(II) is present as the virtually colourless complex ion [Mn(OH2)6]2+.

$$Mn(s) + H2SO4(aq) \rightarrow Mn^{2+}(aq) + SO4^{2-}(aq) + H2(g)$$



Mn Uses

-used to form many important alloys. In steel, manganese improves the rolling and forging qualities, strength, toughness, stiffness, wear resistance, hardness, and hardenability. With aluminium and antimony, especially with small amounts of copper, it forms highly ferromagnetic alloys. Manganese metal is ferromagnetic only after special treatment

- MNO_2 is used in the preparation of oxygen, chlorine, and in drying black paints
- MNO₂ (pyrolusite) is used as a depolariser in dry cells, and is used to "decolourise" glass that is coloured green by impurities of iron.

Manganese by itself colours glass an amethyst colour, and is responsible for the colour of true amethyst

- important in the utilisation of vitamin B1
- the permanganate is a powerful oxidising agent and is used in quantitative analysis and in medicine

41