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= halide ; L = other ligand ) .
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Many vanadium oxyhalides (formula VOmXn) are known. The oxytrichloride and oxytrifluoride (VOCl3 and VOF3) are the most widely studied. Akin to POCl3, they are volatile, adopt tetrahedral structures in the gas phase, and are Lewis acidic.

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= = = Coordination compounds = = =
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Complexes of vanadium ( II ) and ( III ) are relatively exchange inert and reducing . Those of V ( IV ) and V ( V ) are oxidants . Vanadium ion is rather large and some complexes achieve coordination numbers greater than 6 , as is the case in [ V ( CN ) 7 ] 4 ? . Oxovanadium ( V ) also forms 7 coordinate coordination complexes with tetradentate ligands and peroxides and these complexes are used for oxidative brominations and thioether oxidations . The coordination chemistry of V4 + is dominated by the vanadyl center , VO2 + , which binds four other ligands strongly and one weakly ( the one trans to the vanadyl center ) . An example is vanadyl acetylacetonate ( V ( O ) ( O2C5H7 ) 2 ) . In this complex , the vanadium is 5 @-@ coordinate , square pyramidal , meaning that a sixth ligand , such as pyridine , may be attached , though the association constant of this process is small . Many 5 @-@ coordinate vanadyl complexes have a trigonal bypyramidal geometry , such as VOCI2 ( NMe3 ) 2 . The coordination chemistry of V5 + is dominated by the relatively stable dioxovanadium coordination complexes which are often formed by aerial oxidation of the vanadium ( IV ) precursors indicating the stability of the + 5 oxidation state and ease of interconversion between the + 4 and + 5 states .

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= = = Organometallic compounds = = =
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Organometallic chemistry of vanadium is well developed , although they are mainly only academic significance . Vanadocene dichloride is a versatile starting reagent and even finds some applications in organic chemistry . Vanadium carbonyl , V ( CO ) 6 , is a rare example of a paramagnetic metal carbonyl . Reduction yields V ( CO ) ?

6 ( isoelectronic with Cr (CO) 6), which may be further reduced with sodium in liquid ammonia to yield V (CO) 3?

5 (isoelectronic with Fe (CO)5).

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= = Occurrence = =
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= = = Universe = = =
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The cosmic abundance of vanadium in the universe is  $0\ @. @. @. 0001\ \%$ , making the element nearly as common as copper or zinc. Vanadium is detected spectroscopically in light from the Sun and sometimes in the light from other stars.

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= = = Earth 's crust = = =
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Vanadium is the 22nd most abundant element in the earth 's crust ; metallic vanadium is rare in nature ( known as the mineral vanadium , native vanadium ) , but vanadium compounds occur naturally in about 65 different minerals . Economically significant examples include patronite ( VS4 ) , vanadinite ( Pb5 ( VO4 ) 3Cl ) , and carnotite ( K2 ( UO2 ) 2 ( VO4 )  $2 \cdot 3$ H2O ) . Much of the world 's vanadium production is sourced from vanadium @-@ bearing magnetite found in ultramafic gabbro bodies . Vanadium is mined mostly in South Africa , north @-@ western China , and eastern Russia . In 2013 these three countries mined more than 97 % of the 79 @,@ 000 tonnes of produced vanadium .

Vanadium is also present in bauxite and in deposits of crude oil, coal, oil shale and tar sands. In

crude oil, concentrations up to 1200 ppm have been reported. When such oil products are burned, traces of vanadium may cause corrosion in engines and boilers. An estimated 110 @,@ 000 tonnes of vanadium per year are released into the atmosphere by burning fossil fuels.

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= = = Water = =
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The vanadyl ion is abundant in seawater , having an average concentration is 30 nM . Some mineral water springs also contain the ion in high concentrations . For example , springs near Mount Fuji contain as much as 54 ?g per liter .

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= = Production = =
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Most vanadium is used as a steel alloy called ferrovanadium . Ferrovanadium is produced directly by reducing a mixture of vanadium oxide , iron oxides and iron in an electric furnace . The vanadium ends up in pig iron produced from vanadium @-@ bearing magnetite . Depending on the ore used , the slag contains up to 25 % of vanadium .

Vanadium metal is obtained by a multistep process that begins with the roasting of crushed ore with NaCl or Na2CO3 at about 850 ° C to give sodium metavanadate ( NaVO3 ) . An aqueous extract of this solid is acidified to give " red cake " , a polyvanadate salt , which is reduced with calcium metal . As an alternative for small @-@ scale production , vanadium pentoxide is reduced with hydrogen or magnesium . Many other methods are also in use , in all of which vanadium is produced as a byproduct of other processes . Purification of vanadium is possible by the crystal bar process developed by Anton Eduard van Arkel and Jan Hendrik de Boer in 1925 . It involves the formation of the metal iodide , in this example vanadium ( III ) iodide , and the subsequent decomposition to yield pure metal .

2 V + 3 I2 ? 2 VI3

= = Applications = =

= = = Alloys = = =

Approximately 85 % of vanadium produced is used as ferrovanadium or as a steel additive . The considerable increase of strength in steel containing small amounts of vanadium was discovered in the early 20th century . Vanadium forms stable nitrides and carbides , resulting in a significant increase in the strength of steel . From that time on , vanadium steel was used for applications in axles , bicycle frames , crankshafts , gears , and other critical components . There are two groups of vanadium steel alloys . Vanadium high @-@ carbon steel alloys contain 0 @.@ 15 % to 0 @.@ 25 % vanadium , and high @-@ speed tool steels ( HSS ) have a vanadium content of 1 % to 5 % . For high @-@ speed tool steels , a hardness above HRC 60 can be achieved . HSS steel is used in surgical instruments and tools . Powder @-@ metallurgic alloys contain up to 18 % percent vanadium . The high content of vanadium carbides in those alloys increases wear resistance significantly . One application for those alloys is tools and knives .

Vanadium stabilizes the beta form of titanium and increases the strength and temperature stability of titanium . Mixed with aluminium in titanium alloys , it is used in jet engines , high @-@ speed airframes and dental implants . One of the common alloys is Titanium 6AL @-@ 4V , a titanium alloy with 6 % aluminium and 4 % vanadium .

Several vanadium alloys show superconducting behavior . The first A15 phase superconductor was a vanadium compound , V3Si , which was discovered in 1952 . Vanadium @-@ gallium tape is used in superconducting magnets ( 17 @.@ 5 teslas or 175 @,@ 000 gauss ) . The structure of the superconducting A15 phase of V3Ga is similar to that of the more common Nb3Sn and Nb3Ti .

It has been proposed that a small amount, 40 to 270 ppm, of vanadium in Wootz steel and Damascus steel significantly improved the strength of the product, though the source of the

vanadium is unclear.

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= = = Other uses = = =
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Vanadium foil is used in cladding titanium to steel because it is compatible with both iron and titanium. The moderate thermal neutron @-@ capture cross @-@ section and the short half @-@ life of the isotopes produced by neutron capture makes vanadium a suitable material for the inner structure of a fusion reactor .

The most common oxide of vanadium , vanadium pentoxide V2O5 , is used as a catalyst in manufacturing sulfuric acid by the contact process and as an oxidizer in maleic anhydride production . Vanadium pentoxide is used in ceramics . Vanadium is an important component of mixed metal oxide catalysts used in the oxidation of propane and propylene to acrolein , acrylic acid or the ammoxidation of propylene to acrylonitrile . In service , the oxidation state of vanadium changes dynamically and reversibly with the oxygen and the steam content of the reacting feed mixture . Another oxide of vanadium , vanadium dioxide VO2 , is used in the production of glass coatings , which blocks infrared radiation ( and not visible light ) at a specific temperature . Vanadium oxide can be used to induce color centers in corundum to create simulated alexandrite jewelry , although alexandrite in nature is a chrysoberyl .

The Vanadium redox battery , a type of flow battery , is an electrochemical cell consisting of aqueous vanadium ions in different oxidation states . Batteries of the type were first proposed in the 1930s and developed commercially from the 1980s onwards . Cells use + 5 and + 2 formal oxidization state ions , and ( as of 2016 ) are used commercially for small scale ( c . 0 @ .@ 1 - 10 MW , 0 @ .@ 1 - 100 GJ ) grid energy storage .

Vanadate can be used for protecting steel against rust and corrosion by conversion coating.

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= = = = Proposed = = =
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Lithium vanadium oxide has been proposed for use as a high energy density anode for lithium ion batteries , at 745~Wh / L when paired with a lithium cobalt oxide cathode . Vanadium phosphates have been proposed as the cathode in the Lithium Vanadium Phosphate Battery , another type of lithium ion battery .

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= = Biological role = =
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Vanadium plays a limited role in human biology. It is more important in marine environments than terrestrial.

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= = = Vanadoenzymes = = =
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A number of species of marine algae produce vanadium bromoperoxidase as well as the closely related chloroperoxidase ( which may use a heme or vanadium cofactor ) and iodoperoxidases . The bromoperoxidase produces an estimated 1 ? 2 million tons of bromoform and 56 @,@ 000 tons of bromomethane annually . Most naturally occurring organobromine compounds are produced by this enzyme , catalyzing the following reaction ( R @-@ H is hydrocarbon substrate ) :

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R @-@ H + Br ? + H2O2 ? R @-@ Br + H2O + OH ?
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A vanadium nitrogenase is used by some nitrogen @-@ fixing micro @-@ organisms, such as Azotobacter. In this role, vanadium replaces more common molybdenum or iron, and gives the nitrogenase slightly different properties.

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= = = Vanadium accumulation in tunicates and ascidians = = =
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Vanadium is essential to ascidians and tunicates, where it is stored in the highly acidified vacuoles of certain blood cell types, designated "vanadocytes". Vanabins (vanadium binding proteins)

have been identified in the cytoplasm of such cells . The concentration of vanadium in the blood of ascidians is as much as ten million times higher than the surrounding seawater , which normally contains 1 to 2  $\mu g$  / I . The function of this vanadium concentration system and these vanadium @-@ bearing proteins is still unknown , but the vanadocytes are later deposited just under the outer surface of the tunic where they may deter predation .

$$=$$
  $=$   $=$  Fungi  $=$   $=$   $=$ 

Amanita muscaria and related species of macrofungi accumulate vanadium ( up to 500 mg / kg in dry weight ) . Vanadium is present in the coordination complex amavadin in fungal fruit @-@ bodies . The biological importance of the accumulation is unknown . Toxic or peroxidase enzyme functions have been suggested .

## = = = Mammals and birds = = =

Deficiencies in vanadium result in reduced growth and impaired reproduction in rats and chickens . Vanadium is a relatively controversial dietary supplement , used primarily for increasing insulin sensitivity and body @-@ building . Whether it works for the latter purpose has not been proven; some evidence suggests that athletes who take it are merely experiencing a placebo effect . Vanadyl sulfate may improve glucose control in people with type 2 diabetes . Decavanadate and oxovanadates appear to play a role in a variety of biochemical processes , such as those relating to oxidative stress .

## = = Safety = =

All vanadium compounds should be considered toxic . Tetravalent VOSO4 has been reported to be more than 5 times as toxic than trivalent V2O3 . The Occupational Safety and Health Administration ( OSHA ) has set an exposure limit of 0 @.@ 05 mg / m3 for vanadium pentoxide dust and 0 @.@ 1 mg / m3 for vanadium pentoxide fumes in workplace air for an 8 @-@ hour workday , 40 @-@ hour work week . The National Institute for Occupational Safety and Health ( NIOSH ) has recommended that 35 mg / m3 of vanadium be considered immediately dangerous to life and health , that is , likely to cause permanent health problems or death .

Vanadium compounds are poorly absorbed through the gastrointestinal system. Inhalation of vanadium and vanadium compounds results primarily in adverse effects on the respiratory system. Quantitative data are, however, insufficient to derive a subchronic or chronic inhalation reference dose. Other effects have been reported after oral or inhalation exposures on blood parameters, liver, neurological development, and other organs in rats.

There is little evidence that vanadium or vanadium compounds are reproductive toxins or teratogens. Vanadium pentoxide was reported to be carcinogenic in male rats and in male and female mice by inhalation in an NTP study, although the interpretation of the results has recently been disputed. The carcinogenicity of vanadium has not been determined by the United States Environmental Protection Agency.

Vanadium traces in diesel fuels are the main fuel component in high temperature corrosion . During combustion , vanadium oxidizes and reacts with sodium and sulfur , yielding vanadate compounds with melting points as low as 530  $^{\circ}$  C , which attack the passivation layer on steel and render it susceptible to corrosion . The solid vanadium compounds also abrade engine components .