

= Vanadium =

Vanadium is a chemical element with symbol V and atomic number 23 . It is a hard , silvery grey , ductile and malleable transition metal . The elemental metal is rarely found in nature , but once isolated artificially , the formation of an oxide layer ( passivation ) stabilizes the free metal somewhat against further oxidation .

Andrés Manuel del Río discovered compounds of vanadium in 1801 in Mexico by analyzing a new lead @-@ bearing mineral he called " brown lead " , and presumed its qualities were due to the presence of a new element , which he named erythronium ( derived from Greek for " red " ) since , upon heating , most of the salts turned red . Four years later , however , he was ( erroneously ) convinced by other scientists that erythronium was identical to chromium . Chlorides of vanadium were generated in 1830 by Nils Gabriel Sefström who thereby proved that a new element was involved , which he named " vanadium " after the Scandinavian goddess of beauty and fertility , Vanadís ( Freyja ) . Both names were attributed to the wide range of colors found in vanadium compounds . Del Río 's lead mineral was later renamed vanadinite for its vanadium content . In 1867 Henry Enfield Roscoe obtained the pure element .

Vanadium occurs naturally in about 65 different minerals and in fossil fuel deposits . It is produced in China and Russia from steel smelter slag ; other countries produce it either from the flue dust of heavy oil , or as a byproduct of uranium mining . It is mainly used to produce specialty steel alloys such as high @-@ speed tool steels . The most important industrial vanadium compound , vanadium pentoxide , is used as a catalyst for the production of sulfuric acid .

Large amounts of vanadium ions are found in a few organisms , possibly as a toxin . The oxide and some other salts of vanadium have moderate toxicity . Particularly in the ocean , vanadium is used by some life forms as an active center of enzymes , such as the vanadium bromoperoxidase of some ocean algae .

= = History = =

Vanadium was discovered by Andrés Manuel del Río , a Spanish @-@ Mexican mineralogist , in 1801 . Del Río extracted the element from a sample of Mexican " brown lead " ore , later named vanadinite . He found that its salts exhibit a wide variety of colors , and as a result he named the element panchromium ( Greek : ????????? " all colors " ) . Later , Del Río renamed the element erythronium ( Greek : ??????? " red " ) because most of the salts turned red upon heating . In 1805 , the French chemist Hippolyte Victor Collet @-@ Descotils , backed by del Río 's friend Baron Alexander von Humboldt , incorrectly declared that del Río 's new element was only an impure sample of chromium . Del Río accepted Collet @-@ Descotils ' statement and retracted his claim .

In 1831 , the Swedish chemist Nils Gabriel Sefström rediscovered the element in a new oxide he found while working with iron ores . Later that same year , Friedrich Wöhler confirmed del Río 's earlier work . Sefström chose a name beginning with V , which had not been assigned to any element yet . He called the element vanadium after Old Norse Vanadís ( another name for the Norse Vanr goddess Freyja , whose attributes include beauty and fertility ) , because of the many beautifully colored chemical compounds it produces . In 1831 , the geologist George William Featherstonhaugh suggested that vanadium should be renamed " rionium " after del Río , but this suggestion was not followed .

The isolation of vanadium metal proved difficult . In 1831 , Berzelius reported the production of the metal , but Henry Enfield Roscoe showed that Berzelius had in fact produced the nitride , vanadium nitride ( VN ) . Roscoe eventually produced the metal in 1867 by reduction of vanadium ( II ) chloride , VCl<sub>2</sub> , with hydrogen . In 1927 , pure vanadium was produced by reducing vanadium pentoxide with calcium .

The first large @-@ scale industrial use of vanadium was in the steel alloy chassis of the Ford Model T , inspired by French race cars . Vanadium steel allowed for reduced weight while simultaneously increasing tensile strength ( ca . 1905 ) .

German chemist Martin Henze discovered vanadium in the blood cells ( or coelomic cells ) of

Ascidacea ( sea squirts ) in 1911 .

= = Characteristics = =

Vanadium is a medium @-@ hard , ductile , steel @-@ blue metal . Some sources describe vanadium as " soft " , perhaps because it is ductile , malleable and not brittle . Vanadium is harder than most metals and steels ( see Hardnesses of the elements ( data page ) and iron ) . It has good resistance to corrosion and it is stable against alkalis and sulfuric and hydrochloric acids . It is oxidized in air at about 933 K ( 660 ° C , 1220 ° F ) , although an oxide passivation layer forms even at room temperature .

= = Isotopes = =

Naturally occurring vanadium is composed of one stable isotope ,  $^{51}\text{V}$  , and one radioactive isotope ,  $^{50}\text{V}$  . The latter has a half @-@ life of  $1 \times 10^{17}$  years and a natural abundance of 0 @-@ 25 % .  $^{51}\text{V}$  has a nuclear spin of  $7/2$  , which is useful for NMR spectroscopy . Twenty @-@ four artificial radioisotopes have been characterized , ranging in mass number from 40 to 65 . The most stable of these isotopes are  $^{49}\text{V}$  with a half @-@ life of 330 days , and  $^{48}\text{V}$  with a half @-@ life of 16 @-@ 0 days . The remaining radioactive isotopes have half @-@ lives shorter than an hour , most below 10 seconds . At least four isotopes have metastable excited states . Electron capture is the main decay mode for isotopes lighter than  $^{51}\text{V}$  . For the heavier ones , the most common mode is beta decay . The electron capture reactions lead to the formation of element 22 ( titanium ) isotopes , while beta decay leads to element 24 ( chromium ) isotopes .

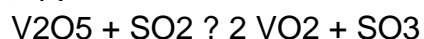
= = Chemistry = =

The chemistry of vanadium is noteworthy for the accessibility of the four adjacent oxidation states 2 @-@ 5 . In aqueous solution , vanadium forms metal aquo complexes of which the colours are lilac [  $\text{V}(\text{H}_2\text{O})_6]^{2+}$  , green [  $\text{V}(\text{H}_2\text{O})_6]^{3+}$  , blue [  $\text{VO}(\text{H}_2\text{O})_5]^{2+}$  , yellow  $\text{VO}_3^-$  . Vanadium ( II ) compounds are reducing agents , and vanadium ( V ) compounds are oxidizing agents . Vanadium ( IV ) compounds often exist as vanadyl derivatives , which contain the  $\text{VO}_2^+$  center .

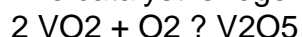
Ammonium vanadate ( V ) (  $\text{NH}_4\text{VO}_3$  ) can be successively reduced with elemental zinc to obtain the different colors of vanadium in these four oxidation states . Lower oxidation states occur in compounds such as  $\text{V}(\text{CO})_6$  , [  $\text{V}(\text{CO})_6$  ] ? and substituted derivatives .

The most commercially important compound is vanadium pentoxide . It is used as a catalyst for the production of sulfuric acid . This compound oxidizes sulfur dioxide (  $\text{SO}_2$  ) to the trioxide (  $\text{SO}_3$  ) .

In this redox reaction , sulfur is oxidized from + 4 to + 6 , and vanadium is reduced from + 5 to + 4 :



The catalyst is regenerated by oxidation with air :



Similar oxidations are used in the production of maleic anhydride , phthalic anhydride , and several other bulk organic compounds .

The vanadium redox battery utilizes all four oxidation states ; one electrode uses the + 5 / + 4 couple and the other uses the + 3 / + 2 couple . Conversion of these oxidation states is illustrated by the reduction of a strongly acidic solution of a vanadium ( V ) compound with zinc dust or amalgam . The initial yellow color characteristic of the pervanadyl ion [  $\text{VO}_2(\text{H}_2\text{O})_4$  ] + is replaced by the blue color of [  $\text{VO}(\text{H}_2\text{O})_5]^{2+}$  , followed by the green color of [  $\text{V}(\text{H}_2\text{O})_6]^{3+}$  and then the violet color of [  $\text{V}(\text{H}_2\text{O})_6]^{2+}$  .

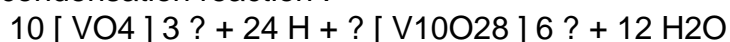
= = Oxyanions = =

In aqueous solution, vanadium (V) forms an extensive family of oxyanions. The interrelationships in this family are described by the predominance diagram, which shows at least 11 species, depending on pH and concentration. The tetrahedral orthovanadate ion,  $\text{VO}_4^{3-}$ ,

is the principal species present at pH 12 @-@ 14. Similar in size and charge to phosphorus (V), vanadium (V) also parallels its chemistry and crystallography. Orthovanadate  $\text{VO}_4^{3-}$

is used in protein crystallography to study the biochemistry of phosphate. The tetrathiovanadate  $[\text{VS}_4]^{3-}$  is analogous to the orthovanadate ion.

At lower pH's, the monomer  $[\text{HVO}_4]^{2-}$  and dimer  $[\text{V}_2\text{O}_7]^{4-}$  are formed, with the monomer predominant at vanadium concentration of less than  $c. 10^{-2} \text{ M}$  ( $pV > 2$ , where  $pV$  is equal to the minus value of the logarithm of the total vanadium concentration / M). The formation of the divanadate ion is analogous to the formation of the dichromate ion. As the pH is reduced, further protonation and condensation to polyvanadates occur: at pH 4 @-@ 6  $[\text{H}_2\text{VO}_4]^-$  is predominant at  $pV$  greater than ca. 4, while at higher concentrations trimers and tetramers are formed. Between pH 2 @-@ 4 decavanadate predominates, its formation from orthovanadate is represented by this condensation reaction:



In decavanadate, each V (V) center is surrounded by six oxide ligands. Vanadic acid,  $\text{H}_3\text{VO}_4$  exists only at very low concentrations because protonation of the tetrahedral species  $[\text{H}_2\text{VO}_4]^-$  results in the preferential formation of the octahedral  $[\text{VO}_2(\text{H}_2\text{O})_4]^+$  species. In strongly acidic solutions,  $\text{pH} < 2$ ,  $[\text{VO}_2(\text{H}_2\text{O})_4]^+$  is the predominant species, while the oxide  $\text{V}_2\text{O}_5$  precipitates from solution at high concentrations. The oxide is formally the inorganic anhydride of vanadic acid. The structures of many vanadate compounds have been determined by X @-@ ray crystallography.

The Pourbaix diagram for vanadium in water, which shows the redox potentials between various vanadium species in different oxidation states, is also complex.

Vanadium (V) forms various peroxo complexes, most notably in the active site of the vanadium @-@ containing bromoperoxidase enzymes. The species  $\text{VO}(\text{O})_2(\text{H}_2\text{O})_4^+$  is stable in acidic solutions. In alkaline solutions, species with 2, 3 and 4 peroxide groups are known; the last forms violet salts with the formula  $\text{M}_3\text{V}(\text{O}_2)_4 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Li}, \text{Na}, \text{etc.}$ ), in which the vanadium has an 8 @-@ coordinate dodecahedral structure.

== Halide derivatives ==