

= Ruthenium =

Ruthenium is a chemical element with symbol Ru and atomic number 44 . It is a rare transition metal belonging to the platinum group of the periodic table . Like the other metals of the platinum group , ruthenium is inert to most other chemicals . The Baltic German scientist Karl Ernst Claus discovered the element in 1844 and named it after his homeland , the Russian Empire (one of Russia 's Latin names is Ruthenia) . Ruthenium is usually found as a minor component of platinum ores ; the annual production is about 20 tonnes . Most ruthenium produced is used in wear @-@ resistant electrical contacts and thick @-@ film resistors . A minor application for ruthenium is in platinum alloys and as a chemistry catalyst .

= = Characteristics = =

= = = Physical properties = = =

A polyvalent hard white metal , ruthenium is a member of the platinum group and is in group 8 of the periodic table :

Whereas all other group 8 elements have 2 electrons in the outermost shell , in ruthenium , the outermost shell has only one electron (the final electron is in a lower shell) . This anomaly is observed in the neighboring metals , niobium (41) , rhodium (45) , and palladium (46) .

Ruthenium has four crystal modifications and does not tarnish unless subject to high temperatures . Ruthenium dissolves in fused alkalis to give ruthenates (RuO_2 ?

4) , is not attacked by acids (even aqua regia) but is attacked by halogens at high temperatures . Indeed , ruthenium is most readily attacked by oxidizing agents . Small amounts of ruthenium can increase the hardness of platinum and palladium . The corrosion resistance of titanium is increased markedly by the addition of a small amount of ruthenium . The metal can be plated by electroplating and by thermal decomposition . A ruthenium @-@ molybdenum alloy is known to be superconductive at temperatures below 10 @. @ 6 K. Ruthenium is the last of the 4d transition metals that can assume the group oxidation state + 8 , and even then is less stable there than the heavier congener osmium : this is the first group from the left of the table where the second and third @-@ row transition metals display notable differences in chemical behavior . Like iron but unlike osmium , ruthenium can form aqueous cations in its lower oxidation states of + 2 and + 3 .

Ruthenium is the first in a downward trend in the melting and boiling points and atomization enthalpy in the 4d transition metals after the maximum seen at molybdenum , because the 4d subshell is more than half full and the electrons are contributing less to metallic bonding . (Technetium , the previous element , has an exceptionally low value that is off the trend due to its half @-@ filled [Kr] $4d^5 5s^2$ configuration , though the small amount of energy needed to excite it to a [Kr] $4d^6 5s^1$ configuration indicates that it is not as far off the trend in the 4d series as manganese in the 3d transition series .) Unlike the lighter congener iron , ruthenium is paramagnetic at room temperature , as iron also is above its Curie point .

The reduction potentials in acidic aqueous solution for some common ruthenium ions are shown below :

= = = Isotopes = = =

Naturally occurring ruthenium is composed of seven stable isotopes . Additionally , 34 radioactive isotopes have been discovered . Of these radioisotopes , the most stable are ^{106}Ru with a half @-@ life of 373 @. @ 59 days , ^{103}Ru with a half @-@ life of 39 @. @ 26 days and ^{97}Ru with a half @-@ life of 2 @. @ 9 days .

Fifteen other radioisotopes have been characterized with atomic weights ranging from 89 @. @ 93 u (^{90}Ru) to 114 @. @ 928 u (^{115}Ru) . Most of these have half @-@ lives that are less than five minutes except ^{95}Ru (half @-@ life : 1 @. @ 643 hours) and ^{105}Ru (half @-@ life : 4 @. @ 44

hours) .

The primary decay mode before the most abundant isotope , ^{102}Ru , is electron capture and the primary mode after is beta emission . The primary decay product before ^{102}Ru is technetium and the primary decay product after is rhodium .

== Occurrence ==

As the 74th most abundant element in Earth 's crust , ruthenium is relatively rare , found in about 100 parts per trillion . This element is generally found in ores with the other platinum group metals in the Ural Mountains and in North and South America . Small but commercially important quantities are also found in pentlandite extracted from Sudbury , Ontario , Canada , and in pyroxenite deposits in South Africa . The native form of ruthenium is a very rare mineral (Ir replaces part of Ru in its structure) .

== Production ==

== Mining ==

Roughly 12 tonnes of ruthenium are mined each year with world reserves estimated as 5 @, @ 000 tonnes . The composition of the mined platinum group metal (PGM) mixtures varies widely , depending on the geochemical formation . For example , the PGMs mined in South Africa contain on average 11 % ruthenium while the PGMs mined in the former USSR contain only 2 % (1992) . Ruthenium , osmium , and iridium are considered the minor platinum group metals .

Ruthenium , like the other platinum group metals , is obtained commercially as a by @-@ product from nickel , and copper , and platinum metals ore processing . During electrorefining of copper and nickel , noble metals such as silver , gold , and the platinum group metals precipitate as anode mud , the feedstock for the extraction . The metals are converted to ionized solutes by any of several methods , depending on the composition of the feedstock . One representative method is fusion with sodium peroxide followed by dissolution in aqua regia , and solution in a mixture of chlorine with hydrochloric acid . Osmium , ruthenium , rhodium , and iridium are insoluble in aqua regia and readily precipitate , leaving the other metals in solution . Rhodium is separated from the residue by treatment with molten sodium bisulfate . The insoluble residue , containing Ru , Os , and Ir is treated with sodium oxide , in which Ir is insoluble , producing dissolved Ru and Os salts . After oxidation to the volatile oxides , RuO_4

4 is separated from OsO_4

4 by precipitation of (NH_4) 3RuCl_6 with ammonium chloride or by distillation or extraction with organic solvents of the volatile osmium tetroxide . Hydrogen is used to reduce ammonium ruthenium chloride yielding a powder . The first method to precipitate the ruthenium with ammonium chloride is similar to the procedure that Smithson Tennant and William Hyde Wollaston used .

Several methods are suitable for industrial scale production . In either case , the product is reduced using hydrogen , yielding the metal as a powder or sponge metal that can be treated with powder metallurgy techniques or argon @-@ arc welding .

== From used nuclear fuels ==

Fission products of uranium @-@ ^{235}U contain significant amounts of ruthenium and the lighter platinum group metals , and spent nuclear fuel is a potential source of ruthenium . The extraction and refinement is expensive and the radioactive isotopes of ruthenium require the spent fuel to be stored for multiple half @-@ lives of those isotopes . Those factors have so far discouraged large @-@ scale extraction , and none has been started .

== Chemical compounds ==

The oxidation states of ruthenium range from 0 to + 8 , and ? 2 . The properties of ruthenium and osmium compounds are often similar . The + 2 , + 3 , and + 4 states are the most common . The most prevalent precursor is ruthenium trichloride , a red solid that is poorly defined chemically but versatile synthetically .

== Oxides and chalcogenides ==

Ruthenium can be oxidized to ruthenium (IV) oxide (RuO_2 , oxidation state + 4) which can in turn be oxidized by sodium metaperiodate to the volatile yellow tetrahedral ruthenium tetroxide , RuO_4 , an aggressive , strong oxidizing agent with structure and properties analogous to osmium tetroxide . Like osmium tetroxide , ruthenium tetroxide is a potent fixative and stain for electron microscopy of organic materials , and is mostly used to reveal the structure of polymer samples . Dipotassium ruthenate (K_2RuO_4 , + 6) , and potassium perruthenate (KRuO_4 , + 7) are also known . Unlike osmium tetroxide , ruthenium tetroxide is less stable and is strong enough as an oxidising agent to oxidise dilute hydrochloric acid and organic solvents like ethanol at room temperature , and is easily reduced to ruthenate (RuO_2 ?

4) in aqueous alkaline solutions ; it decomposes to form the dioxide above 100 ° C. Unlike iron but like osmium , ruthenium does not form oxides in its lower + 2 and + 3 oxidation states . Ruthenium forms dichalcogenides only when reacted directly with the chalcogens , which are diamagnetic semiconductors crystallizing in the pyrite structure and thus must contain ruthenium (II) .

Like iron , ruthenium does not readily form oxoanions , and prefers to achieve high coordination numbers with hydroxide ions instead . Ruthenium tetroxide is reduced by cold dilute potassium hydroxide to form black potassium perruthenate , KRuO_4 , with ruthenium in the + 7 oxidation state . Potassium perruthenate can also be produced by oxidising potassium ruthenate , K_2RuO_4 , with chlorine gas . The perruthenate ion is unstable and is reduced by water to form the orange ruthenate . Potassium ruthenate may be synthesized by reacting ruthenium metal with potassium hydroxide and potassium nitrate .

Some mixed oxides are also known , such as MIIIRuIVO_3 , Na_3RuVO_4 , Na

2RuV

2O

7 , and MII

2LnIIIRuVO

6 .

== Halides and oxyhalides ==

The highest known ruthenium halide is the hexafluoride , a dark brown solid that melts at 54 ° C. It hydrolyzes violently upon contact with water and easily disproportionates to form a mixture of lower ruthenium fluorides , releasing fluorine gas . Ruthenium pentafluoride is a tetrameric dark green solid that is also readily hydrolyzed , melting at 86 @. 5 ° C. The yellow ruthenium tetrafluoride is probably also polymeric and can be formed by reducing the pentafluoride with iodine . Among the binary compounds of ruthenium , these high oxidation states are known only in the oxides and fluorides .

Ruthenium trichloride is a well @-@ known compound , existing in a black ? @-@ form and a dark brown ? @-@ form : the trihydrate is red . Of the known trihalides , trifluoride is dark brown and decomposes above 650 ° C , tetrabromide is dark @-@ brown and decomposes above 400 ° C , and triiodide is black . Of the dihalides , difluoride is not known , dichloride is brown , dibromide is black , and diiodide is blue . The only known oxyhalide is the pale green ruthenium (VI) oxyfluoride , RuOF_4 .

== Coordination and organometallic complexes ==

Ruthenium forms a variety of coordination complexes . Examples are the many pentammine derivatives $[\text{Ru}(\text{NH}_3)_5\text{L}]^{n+}$ that often exist for both $\text{Ru}(\text{II})$ and $\text{Ru}(\text{III})$. Derivatives of bipyridine and terpyridine are numerous , best known being the luminescent tris (bipyridine) ruthenium (II) chloride .

Ruthenium forms a wide range compounds with carbon @-@ ruthenium bonds . Grubbs ' catalyst is used for alkene metathesis . Ruthenocene is analogous to ferrocene structurally , but exhibits distinctive redox properties . The colorless liquid ruthenium pentacarbonyl converts in the absence of CO pressure to the dark red solid triruthenium dodecacarbonyl . Ruthenium trichloride reacts with carbon monoxide to give many derivatives including $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and $\text{Ru}(\text{CO})_2(\text{PPh}_3)_3$ (Roper 's complex) . Heating solutions of ruthenium trichloride in alcohols with triphenylphosphine gives tris (triphenylphosphine) ruthenium dichloride ($\text{RuCl}_2(\text{PPh}_3)_3$) , which converts to the hydride complex chlorohydridotris (triphenylphosphine) ruthenium (II) ($\text{RuHCl}(\text{PPh}_3)_3$) .

= = History = =

Though naturally occurring platinum alloys containing all six platinum @-@ group metals were used for a long time by pre @-@ Columbian Americans and known as a material to European chemists from the mid @-@ 16th century , not until the mid @-@ 18th century was platinum identified as a pure element . That natural platinum contained palladium , rhodium , osmium and iridium was discovered in the first decade of the 19th century . Platinum in alluvial sands of Russian rivers gave access to raw material for use in plates and medals and for the minting of ruble coins , starting in 1828 . Residues from platinum production for coinage were available in the Russian Empire , and therefore most of the research on them was done in Eastern Europe .

It is possible that the Polish chemist J?drzej ?niadecki isolated element 44 (which he called " vestium " after the asteroid Vesta discovered shortly before) from South American platinum ores in 1807 . He published an announcement of his discovery in 1808 . His work was never confirmed , however , and he later withdrew his claim of discovery .

J?ns Berzelius and Gottfried Osann nearly discovered ruthenium in 1827 . They examined residues that were left after dissolving crude platinum from the Ural Mountains in aqua regia . Berzelius did not find any unusual metals , but Osann thought he found three new metals , which he called pluranium , ruthenium , and polinium . This discrepancy led to a long @-@ standing controversy between Berzelius and Osann about the composition of the residues . As Osann was not able to repeat his isolation of ruthenium , he eventually relinquished his claims . The name " ruthenium " was chosen by Osann because the analysed samples stemmed from the Ural Mountains in Russia . The name itself derives from Ruthenia , the Latin word for Rus ' , a historical area that included present @-@ day western Russia , Ukraine , Belarus , and parts of Slovakia and Poland .

In 1844 , Karl Ernst Claus , a Russian scientist of Baltic German descent , showed that the compounds prepared by Gottfried Osann contained small amounts of ruthenium , which Claus had discovered the same year . Claus isolated ruthenium from the platinum residues of rouble production while he was working in Kazan University , Kazan , the same way its heavier congener osmium had been discovered four decades earlier . Claus showed that ruthenium oxide contained a new metal and obtained 6 grams of ruthenium from the part of crude platinum that is insoluble in aqua regia . Choosing the name for the new element , Claus stated : " I named the new body , in honour of my Motherland , ruthenium . I had every right to call it by this name because Mr. Osann relinquished his ruthenium and the word does not yet exist in chemistry . "

= = Applications = =

Because it hardens platinum and palladium alloys , ruthenium is used in electrical contacts , where a thin film is sufficient to achieve the desired durability . With similar properties and lower cost than rhodium , electric contacts are a major use of ruthenium . The plate is applied to the base by electroplating or sputtering .

Ruthenium dioxide with lead and bismuth ruthenates are used in thick @-@ film chip resistors . These two electronic applications account for 50 % of the ruthenium consumption .

Ruthenium is seldom alloyed with metals outside the platinum group , where small quantities improve some properties . The added corrosion resistance in titanium alloys led to the development of a special alloy with 0 @. @ 1 % ruthenium . Ruthenium is also used in some advanced high @-@ temperature single @-@ crystal superalloys , with applications that include the turbines in jet engines . Several nickel based superalloy compositions are described , such as EPM @-@ 102 (with 3 % Ru) , TMS @-@ 162 (with 6 % Ru) , TMS @-@ 138 , and TMS @-@ 174 , the latter two containing 6 % rhenium . Fountain pen nibs are frequently tipped with ruthenium alloy . From 1944 onward , the famous Parker 51 fountain pen was fitted with the " RU " nib , a 14K gold nib tipped with 96 @. @ 2 % ruthenium and 3 @. @ 8 % iridium .

Ruthenium is a component of mixed @-@ metal oxide (MMO) anodes used for cathodic protection of underground and submerged structures , and for electrolytic cells for such processes as generating chlorine from salt water . The fluorescence of some ruthenium complexes is quenched by oxygen , finding use in optode sensors for oxygen . Ruthenium red , [(NH₃)₅Ru @-@ O @-@ Ru (NH₃)₄ @-@ O @-@ Ru (NH₃)₅]⁶⁺ , is a biological stain used to stain polyanionic molecules such as pectin and nucleic acids for light microscopy and electron microscopy . The beta @-@ decaying isotope 106 of ruthenium is used in radiotherapy of eye tumors , mainly malignant melanomas of the uvea . Ruthenium @-@ centered complexes are being researched for possible anticancer properties . Compared with platinum complexes , those of ruthenium show greater resistance to hydrolysis and more selective action on tumors . NAMI @-@ A and KP1019 are two drugs undergoing clinical evaluation for treatment of metastatic tumors and colon cancers .

Ruthenium tetroxide exposes latent fingerprints by reacting on contact with fatty oils or fats with sebaceous contaminants and producing brown / black ruthenium dioxide pigment .

== = Catalysis == =

Ruthenium is a versatile catalyst . With an aqueous suspension of CdS particles loaded with ruthenium dioxide , the energy of visible light can split Hydrogen sulfide . This process may be one day be used to remove H₂S in oil refineries and other industrial processing facilities . Organometallic ruthenium carbene and alkylidene complexes have been found to be highly efficient catalysts for olefin metathesis , a process with important applications in organic and pharmaceutical chemistry . Ruthenium @-@ promoted cobalt catalysts are used in Fischer @-@ Tropsch synthesis .

== = Solar energy conversion == =

Some ruthenium complexes absorb light throughout the visible spectrum and are being actively researched for solar energy technologies . For example , Ruthenium @-@ based compounds have been used for light absorption in dye @-@ sensitized solar cells , a promising new low @-@ cost solar cell system .

== = Data storage == =

Chemical vapor deposition of ruthenium is used to produce thin films of pure ruthenium on substrates . These films show promise for use in microchips and for the giant magnetoresistive read element for hard disk drives . Ruthenium is also suggested for microelectronics because it is compatible with semiconductor processing techniques .

== = Exotic materials == =

Many ruthenium @-@ based oxides show very unusual properties , such as a quantum critical point behavior , exotic superconductivity , and high @-@ temperature ferromagnetism .