= Group 4 element =

Group 4 is a group of elements in the periodic table . It contains the elements titanium (Ti) , zirconium (Zr) , hafnium (Hf) and rutherfordium (Rf) . This group lies in the d @-@ block of the periodic table . The group itself has not acquired a trivial name ; it belongs to the broader grouping of the transition metals .

The three Group 4 elements that occur naturally are titanium (Ti) , zirconium (Zr) and hafnium (Hf) . The first three members of the group share similar properties ; all three are hard refractory metals under standard conditions . However , the fourth element rutherfordium (Rf) , has been synthesized in the laboratory ; none of its isotopes have been found occurring in nature . All isotopes of rutherfordium are radioactive . So far , no experiments in a supercollider have been conducted to synthesize the next member of the group , unpenthexium (Uph) , and it is unlikely that they will be synthesized in the near future .

= = Characteristics = =

= = = Chemistry = = =

Like other groups , the members of this family show patterns in its electron configuration , especially the outermost shells resulting in trends in chemical behavior :

Most of the chemistry has been observed only for the first three members of the group . The chemistry of rutherfordium is not very established and therefore the rest of the section deals only with titanium , zirconium , and hafnium . All the elements of the group are reactive metals with a high melting point (1668 ° C , 1855 ° C , 2233 ° C , 2100 ° C ?) . The reactivity is not always obvious due to the rapid formation of a stable oxide layer , which prevents further reactions . The oxides TiO_2 , ZrO_2 and HfO_2 are white solids with high melting points and unreactive against most acids .

As tetravalent transition metals , all three elements form various inorganic compounds , generally in the oxidation state of + 4 . For the first three metals , it has been shown that they are resistant to concentrated alkalis , but halogens react with them to form tetrahalides . At higher temperatures , all three metals react with oxygen , nitrogen , carbon , boron , sulfur , and silicon . Because of the lanthanide contraction of the elements in the fifth period , zirconium and hafnium have nearly identical ionic radii . The ionic radius of Zr^{4+} is 79 picometers and that of Hf^{4+} is 78 pm .

This similarity results in nearly identical chemical behavior and in the formation of similar chemical compounds . The chemistry of hafnium is so similar to that of zirconium that a separation on chemical reactions was not possible ; only the physical properties of the compounds differ . The melting points and boiling points of the compounds and the solubility in solvents are the major differences in the chemistry of these twin elements . Titanium is considerably different from the other two owing to the effects of the lanthanide contraction .

= = = Physical = = =

The table below is a summary of the key physical properties of the group 4 elements . The four question @-@ marked values are extrapolated .

= = History = =

= = = Titanium = = =

William Gregor , Franz Joseph Muller and Martin Heinrich Klaproth independently discovered titanium between 1791 and 1795 . Klaproth named it for the Titans of Greek mythology .

= = = Zirconium = = =

Klaproth also discovered zirconium in the mineral zircon in 1789 and named it after the already known Zirkonerde (zirconia) .

= = = Hafnium = = =

Hafnium had been predicted by Dmitri Mendeleev in 1869 and Henry Moseley measured in 1914 the effective nuclear charge by X @-@ ray spectroscopy to be 72 , placing it between the already known elements lutetium and tantalum . Dirk Coster and Georg von Hevesy were the first to search for the new element in zirconium ores . Hafnium was discovered by the two in 1923 in Copenhagen , Denmark , validating the original 1869 prediction of Mendeleev . There has been some controversy surrounding the discovery of hafnium and the extent to which Coster and Hevesy were guided by Bohr 's prediction that hafnium would be a transition metal rather than a rare earth element . While titanium and zirconium , as relatively abundant elements , were discovered in the late 18th century , it took until 1923 for hafnium to be identified . This was only partly due to hafnium 's relative scarcity . The chemical similarity between zirconium and hafnium made a separation difficult and , without knowing what to look for , hafnium was left undiscovered , although all samples of zirconium , and all of its compounds , used by chemists for over two centuries contained significant amounts of hafnium .

= = = Rutherfordium = = =

Rutherfordium was reportedly first detected in 1966 at the Joint Institute of Nuclear Research at Dubna (then in the Soviet Union) . Researchers there bombarded 242Pu with accelerated 22Ne ions and separated the reaction products by gradient thermochromatography after conversion to chlorides by interaction with ZrCl4 .

242
94Pu + 22
10Ne ? 264 ? x
104Rf ? 264 ? x
104RfCl4

= = Production = =

The production of the metals itself is difficult due to their reactivity . The formation of oxides , nitrides and carbides must be avoided to yield workable metals , this is normally achieved by the Kroll process . The oxides (MO2) are reacted with coal and chlorine to form the chlorides (MCl4) .The chlorides of the metals are then reacted with magnesium , yielding magnesium chloride and the metals .

Further purification is done by a chemical transport reaction developed by Anton Eduard van Arkel and Jan Hendrik de Boer . In a closed vessel , the metal reacts with iodine at temperatures of above 500 ° C forming metal (IV) iodide ; at a tungsten filament of nearly 2000 ° C the reverse reaction happens and the iodine and metal are set free . The metal forms a solid coating at the tungsten filament and the iodine can react with additional metal resulting in a steady turn over .

M + 2 I2 (low temp .) ? MI4
MI4 (high temp .) ? M + 2 I2

= = Occurrence = =

If the abundance of elements in Earth 's crust is compared for titanium , zirconium and hafnium , the abundance decreases with increase of atomic mass . Titanium is the seventh most abundant metal in Earth 's crust and has an abundance of 6320 ppm , while zirconium has an abundance of 162

ppm and hafnium has only an abundance of 3 ppm .

All three stable elements occur in heavy mineral sands ore deposits , which are placer deposits formed , most usually in beach environments , by concentration due to the specific gravity of the mineral grains of erosion material from mafic and ultramafic rock . The titanium minerals are mostly anatase and rutile , and zirconium occurs in the mineral zircon . Because of the chemical similarity , up to 5 % of the zirconium in zircon is replaced by hafnium . The largest producers of the group 4 elements are Australia , South Africa and Canada .

= = Applications = =

Titanium metal and its alloys have a wide range of applications , where the corrosion resistance , the heat stability and the low density (light weight) are of benefit . The foremost use of corrosion @-@ resistant hafnium and zirconium has been in nuclear reactors . Zirconium has a very low and hafnium has a high thermal neutron @-@ capture cross @-@ section . Therefore , zirconium (mostly as zircaloy) is used as cladding of fuel rods in nuclear reactors , while hafnium is used as control rod for nuclear reactors , because each hafnium atom can absorb multiple neutrons .

Smaller amounts of hafnium and zirconium are used in super alloys to improve the properties of those alloys .

= = Biological occurrences = =

The group 4 elements are not known to be involved in the biological chemistry of any living systems . They are hard refractory metals with low aqueous solubility and low availability to the biosphere . Titanium is one of the few first row d @-@ block transition metals with no known biological role . Rutherfordium 's radioactivity would make it toxic to living cells .

= = Precautions = =

Titanium is non @-@ toxic even in large doses and does not play any natural role inside the human body . Zirconium powder can cause irritation , but only contact with the eyes requires medical attention . OSHA recommends for zirconium are 5 mg / m3 time weighted average limit and a 10 mg / m3 short @-@ term exposure limit . Only limited data exists on the toxicology of hafnium .