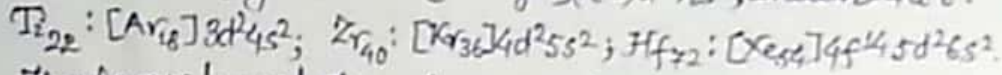


B. Sc. Part-II (Hons), Paper-III B (Inorganic Chemistry)

Group-B, Unit-2 Comparative Chemistry of Group-4 elements (Ti, Zr & Hf)

[By Dr. Birendra Kumar, Maharaja College]

⇒ Position in P.T: The Titanium group/Group-4 of modern periodic table comprises of three elements: Titanium (Ti), Zirconium (Zr) & Hafnium (Hf). They have similar electronic configurations: [Noble gas](n-1)d²ns², where n = 4 to 6.



They have valence electrons 4, so placed in Group-4 under d-block as last electron enters in penultimate (n-1) d-subshell. Their positions in same group due to following similarity properties:

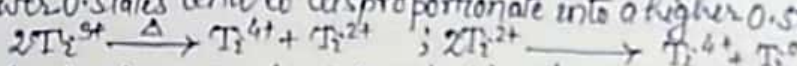
- (i) All are metallic in nature and have high melting & boiling point.
- (ii) They exhibit variable oxidation states +2, +3 & +4, and common/stable state is +4.
- (iii) Their compounds in O. state +4 are colourless and diamagnetic whereas those formed in lower O. state⁽⁺²⁾ are coloured and paramagnetic.
- (iv) They are not reactive at ordinary temperature. However, they react with halogen (X₂), oxygen, N₂ and C to give tetrahalides, dioxides, nitrides & carbides respectively.
- (v) Ti & Zr form all the tetrahalides but Hf forms only tetrachloride & tetrafluoride. All the tetrahalides are hydrolysed. Most of the tetrahalides form complexes.
- (vi) They are quite reactive towards most of the oxidising agents.
- (vii) These metals are not attacked by conc. acids in cold but are attacked by certain acids when heated. Hf dissolves the metal to form hexafluoro complexes.



⇒ Oxidation states: They show variable oxidation states, given below:

Element	Oxidation states
Titanium (Ti)	(-2), (-1), (0), (+2), +3, +4
Zirconium (Zr)	(0), (+2), (+3), +4
Hafnium (Hf)	(+3), +4

The most common and stable oxidation state for all the elements is +4 which has stable noble gas conf. Compds. in this state are generally covalent due to high E values. However, the oxides (MO₂) are regarded as ionic but insoluble in water and M⁴⁺ ion do not exist in solution. The O. state +3 is reducing, and Ti³⁺ ions are more strongly reducing than Sn²⁺. They are reasonably stable, and exist as solids as well as in solution. O. state +2 is very unstable and so strongly reducing nature in aqueous medium. Hence, few compounds known exist only in solid state. The O. states 0, -1, -2 are found in the dipyrrolyl complexes of Ti, e.g. [Ti⁰(dipy)₂], Li[Ti⁰(dipy)₃], Li₂[Ti⁻²(dipy)₃] etc. The lower O. states tend to disproportionate into a higher O. state and a lower O. state.

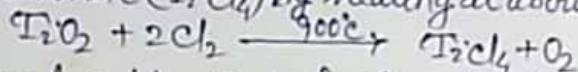


⇒ Atomic/Ionic Size: The atomic (covalent) and ionic radii increase normally from Ti to Zr, but the expected increase in size from Zr to Hf is very small due to lanthanide contraction (filling of the 4f-subshell in Hf, almost identical size to La).

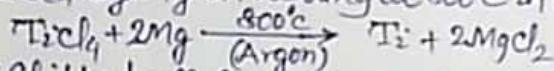
Element	Covalent radius (Å)	Ionic radius (Å), M ⁴⁺
Ti	1.32	0.68
Zr	1.45	0.80
Hf	1.44	0.80

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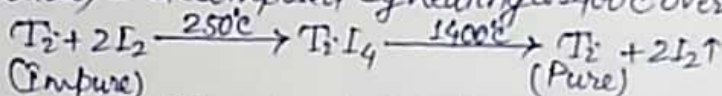
⇒ Extraction of metal: Titanium (Ti) is found in the earth's crust as Rutile (TiO_2) & Ilmenite ($FeTiO_3$). Titanium metal is extracted from Rutile ore (TiO_2) by Kroll process. In this process, rutile ore (TiO_2) is first converted into titanium tetrachloride ($TiCl_4$) by heating at about $900^\circ C$ in a current of Cl_2 gas.



$TiCl_4$ is then reduced by Mg on heating at $800^\circ C$ in an atmosphere of Argon (Ar) gas



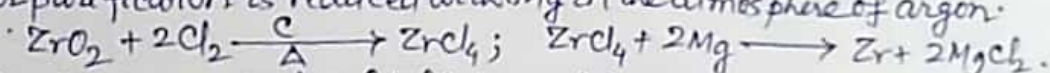
Titanium metal is chipped off from the reactor mechanically. The residual Mg & $MgCl_2$ are removed from metal chips by leaching with dilute HCl. The metal thus obtained is not pure. It is purified by Van Arkel method. In this method, the impure Ti -metal is heated with I_2 (iodine) and the resulting TiI_4 (titanium tetraiodide) is decomposed by heating to $1400^\circ C$ over tungsten filament to get pure Ti .



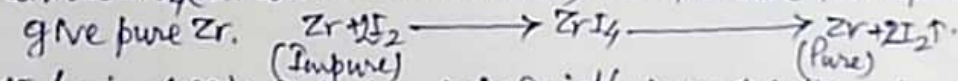
(Impure)

(Pure)

Zirconium (Zr): Zirconium is found in the earth's crust as Zircon ($ZrSiO_4$) & Baddeleyite (ZrO_2). The method employed for the extraction of Zr from its ore is essentially the same as used for the extraction of Ti . The ore is first treated with carbon & Cl_2 at red hot temperature to get crude $ZrCl_4$ (zirconium tetrachloride). This compound ($ZrCl_4$), after purification is reduced with Mg in the atmosphere of argon.



If metal is required in highly pure state, the metal (impure) is heated with I_2 to convert ZrI_4 (zirconium tetraiodide). ZrI_4 is then decomposed by strong heating to give pure Zr.

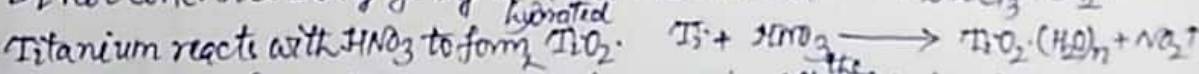


(Impure)

(Pure)

Hafnium (Hf): Hafnium is invariably present in the extracted samples of Zr and it is difficult to separate them chemically because of their close similarity in atomic and ionic radii. These elements are separated by fractional crystallisation of their potassium hexafluoro complexes $K_2[ZrF_6]$ & $K_2[HfF_6]$. These are preferred for this purpose because of greater difference in their solubilities. The best method for separating Hf from Zr is ion-exchange, chromatography method.

⇒ Chemical reactivity: The titanium group metals are unreactive or passive at low temperatures because of the formation of a thin impermeable oxide film. At room temperature, they are unaffected by either acids or alkali. However, Ti dissolves in hot conc. HCl slowly giving Ti^{3+} salt.



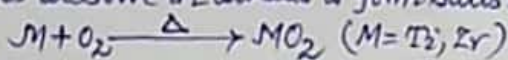
Titanium reacts with HNO_3 to form TiO_2 . $Ti + 4HNO_3 \xrightarrow{H_2O} TiO_2 \cdot (H_2O)_n + 4NO_2 \uparrow$

Zirconium dissolves in hot conc. H_2SO_4 and aqua regia. All metals dissolve in HF due to formation of a complex salt. e.g. $Ti + 6HF \longrightarrow H_2[TiF_6] + 2H_2 \uparrow$

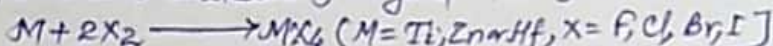
All the metals are very reactive at higher temperatures (above $600^\circ C$). They react with O_2 to

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to form stable non-volatile oxides MO_2 , which are insoluble and are rendered refractory by strong ignition. These oxides are ionic and basic. Ti_2O_3 is more basic and ZrO_2 pure basic in nature. These oxides dissolve in alkalis to form salts but only titanates, TiO_3^{2-} & $Ti_2O_5^{2-}$ are well known.

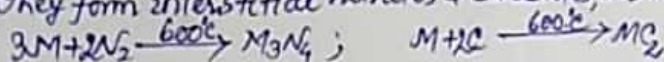


(iii) They form tetrahalides (MX_4) and oxy-halides (MOX_2). $TiCl_4$ is a fuming covalent liquid. Zr & Hf fluorides are covalent solids. All the tetrahalides are hydrolysed. Most of the tetrahalides form complexes, $M_2[Ti_2X_6]$.



(iv) Powdered metals absorb hydrogen gas to form hydrides of limiting composition (MH_2). The amount of H_2 absorbed depends on the temperature and pressure. The hydrides are stable in air and not affected by water.

(v) They form interstitial nitrides & carbides on heating at $600^\circ C$ with N_2 & C respectively.



(vi) They form phosphates which are insoluble in dilute acids. Hence, this ^{reaction} is used to remove PO_4^{3-} (phosphate) as $Zr_3(PO_4)_2$ by adding $Zr(NO_3)_2$. Hf compounds may also be used. Titanium phosphate is relatively more stable in acids.

(vii) Titanium forms a number of alkyls and aryls, e.g. CH_3TiCl_3 , $Ti(CH_3)_4$, $Ti(C_2H_5CH_2)_4$ etc. $Ti(CH_3)_4$ is stable below $-20^\circ C$ while others are stable at ordinary temperature. Alkyl organo-titanium compounds polymerize alkenes. Ziegler-Natta catalyst is an important organometallic compound of titanium, formed by reaction of $TiCl_4$ & $Al(C_2H_5)_3$ used for polymerizing C_3H_6 .

⇒ Colours of ions: The metals in oxidation state +4, i.e. M^{4+} ions have a d^0 conf. and typically white or colourless, e.g. TiO_2 (colourless), $Ti_2(SO_4)_3$ (white), ZrO_2 (white), $ZrCl_4$ (white), $Hf(OH)_4$ (white) etc. M^{3+} ions have a d^1 conf. with only one d-electron, there is only one possible d-d transition hence there is only one band in the visible spectrum and nearly all the compounds are purple and deep coloured, e.g. Ti_2O_3 (black), Ti_2S_3 (black), $[Ti_2(H_2O)_6]^{3+}$ (violet), $ZrCl_3$ (brown) etc. M^{2+} ions have a d^2 conf, there is d-d transition, hence compounds are generally dark coloured, e.g. TiO (yellow), $TiCl_2$ (black), TiS (red), ZrH_2 (grey) etc.

⇒ Uses/Applications: Titanium is used (i) in steel industry to remove adsorbed N_2 & O_2 , and make it hard and tough (ii) as a structural material for jet engines, gears, car wheel high temperature tools and steel rails (iii) for hardening and toughening steel. Its compounds e.g. Titanox is used as white pigment, $TiCl_3$ as an important volumetric reagent etc. Zirconium is used (i) in removing trace of O_2 & N_2 from thermoionic valves (ii) in making bullet proof alloy steels. Its compounds e.g. Zirconia (ZrO_2) is used as a refractory material and Zirconium nitrate as an excellent reagent for the removal of phosphate in qualitative analysis.

Hafnium is used (i) in the construction of radiotubes, incandescent lamps, cathodes for x-ray tubes, rectifiers and tungsten filament (ii) as a radioactivity shields.

HfO_2 is used in special types of glasses.

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