class - B.Sc. Part (III)
Subject - Chemistry
Paper - V[th]
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COMPARATIVE CHEMISTRY OF VANADIUM, NIOBIUM AND TANTALUM -

Vanadium is commercially important as the alloy ferrovanadium which is used to make alloy steel. V_2O_5 is well known compound and it a good catalyst also. Vanadium metal is also used as a catalyst. Niobium and tantalum are used in small quantities. However, there is great theoritical interest in the cluster chemistry

POSITION IN PERIODIC TABLE -

Vanadium - V_{23} - $[Ar]\ 3d^3 4s^2$
Niobium - Nb_{41} - $[Kr]\ 4d^3 5s^2$ or $[Kr]\ 4d^4 5s^1$
Tantalum - Ta_{73} - $[Xe]\ 4f^{14} 5d^3 6s^2$

Vanadium, Niobium and tantalum are the member of V B or (5) gronp and 4^{th}, 5^{th} and

and 5th period respectively. The electronic configuration of these elements are $(n-1)d^3 ns^2$. In case of niobium one electron from 5s orbital get shifted to 4d orbital and hence the valence shell configuration of Nb becomes $4d^4 5s^1$ instead of expected configuration $4d^3 5s^2$. The irregularity of electronic configuration of Nb can be explained on basis of the fact that energy differences of ns and (n-1)d subshell is very small. Hence the incoming electron may enter into ns or (n-1)d subshell. The abnormality is due to nucleus-electron and electron-electron forces.

The valence shell configuration show that the last electron goes to (n-1)d orbital, hence these three elements are the member of d-block element.

OXIDATION STATES —

The valence shell of all three elements have five electrons, so the maximum

for this group is (+V). All three electrons have the full range of oxidation states from (-I) to (+V). For vanadium the (+II) and (+III) states are reducing, (+IV) is stable, and (+V) state is slightly oxidising. For niobium and tantalum the (+V) state is the stable and although lower oxidation states are known. The (+V) oxidation state stability increasing from V to Ta, and the lower oxidation states stability is decrease

Compounds with (+V) oxidation state —

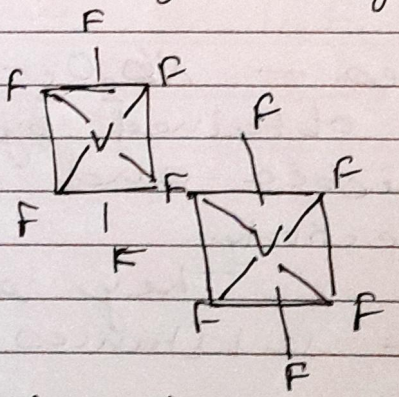
vanadium forms a limited number of compounds in which it shows +5 oxidation state. Some important compounds are given below —

(1) vanadium pentaoxide - V_2O_5 -
This compound is also known as vanadic anhydride because is is the anhydride of ortho - vanadic acid H_3VO_4.
It is a yellowish poisonous

powder having melting point 670°c. It is slightly soluble in water. and with haematite ore (Fe_2O_3) V_2O_5 after reduction by carbon it gives ferro-vanadium alloy. Ferro-vanadium alloy is used as a scavenger in steel industry. V_2O_5 is a good catalyst and used in a number of reactions. V_2O_5 is also used in the preparation of glass.

(iii) Vanadium pentafluoride, VF_5 —

It is only pentahalide of vanadium. It is obtained by heating vanadium and fluorine. It is a powerful oxidising agent. In the gaseous state it is monomeric having trigonal bipyramidal structure. In the solid and liquid state have polymeric structure of octahedral unit joint together by V-F-V bridges.



Polymeric structure of VF_5

(iii) Vanadium oxohalide - VOX_3 - Vanadium oxochloride $VOCl_3$ and Vanadium oxobromide $VOBr_3$ are known and they are prepared by the halogenation of V_2O_3.

(iv) Vanadic acid and their salts — Acids —

HVO_3 Metavanadic acid

$H_4V_2O_7$ Pyrovanadic acid

H_3VO_4 Orthovanadic acid.

Their Salts —

NH_4VO_3 — Ammonium metavanadate

$Na_4V_2O_7$ — Sodium pyrovanadate

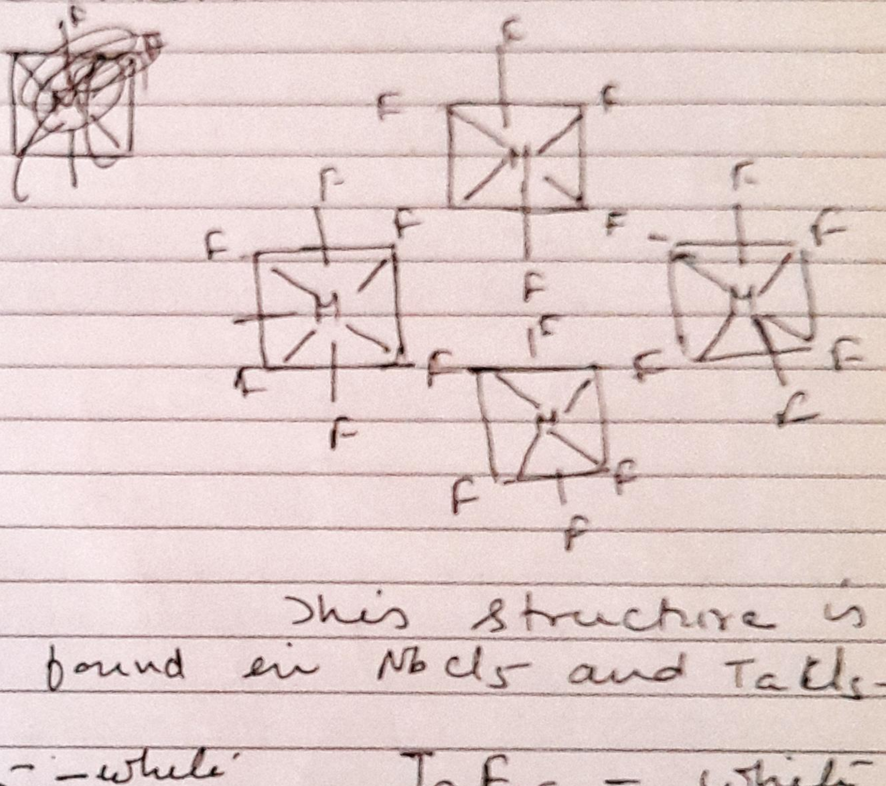
$Na_3VO_4 \cdot 12H_2O$ — Sodium orthovanadate.

Nb and Ta have very stable (+V) oxidation state. Both of them have following compounds in (+V) oxidation state.

(1) Oxides — Nb_2O_5 and Ta_2O_5 - They obtained by dehydration of niobic and tantalic acid respectively.

They are relatively inert substances.

(2) Halides — Niobium and tantalum form the full range of halides. These may be formed by direct reaction of the element. ~~or by the reactions~~ NbF_5 and TaF_5 form cyclic tetramer with four octahedron joined in a cyclic manner.



This structure is also found in $NbCl_5$ and $TaCl_5$.

NbF_5 — white TaF_5 — white
$NbCl_5$ — yellow $TaCl_5$ — white
$NbBr_5$ — orange $TaBr_5$ — yellow
NI_5 — brass TaI_5 — black

(3) Oxohalides — Some known oxohalides of the two metals are $NbOCl_3$, $NbOBr_3$, $NbOI_2$, $NbOI_3$, $TaOCl_3$ and $TaOBr_3$.