

B.Sc. III (Hons), Paper-6 (Inorganic Chem.), Group-B (By Dr. Birendra Kumar)
 Unit-2, (a) General/Comparative Chemistry of Group-5 elements (V, Nb & Ta)

* Position in periodic table (PT): Vanadium

Electronic Configurations: (V₂₃): [Ar₁₈]3d³4s²

Niobium (Nb₄₁): [Kr₃₆]4d³5s²

Tantalum (Ta₇₃): [Xe₅₄]4f¹⁴5d³6s²

Outer electronic configuration of these elements is (n-1)d³ns². Valence electrons in them is 5 and last electron occupy in penultimate (i.e. n-1) d orbital. So, Block-d, Group-5, Periods = 4 (for V), 5 (for Nb) & 6 (for Ta).

Thus, V, Nb & Ta occupy position in Group-5 under d-block of modern periodic table, but different periods (4, 5, 6). Their position in same group-5 is due to resemblance in properties.

* Oxidation states: Group-5 elements (V, Nb & Ta) exhibit variable oxidation states, shown below:

Element	Outer ele. conf.	Oxidation states
Vanadium (V)	3d ³ 4s ²	(-1), (0), (+1), +2, +3, +4, +5
Niobium (Nb)	4d ³ 5s ²	(-1), +2, +3, +4, +5
Tantalum (Ta)	5d ³ 6s ²	(-1), +2, +3, +4, +5

The maximum oxidation state for Gr. 5 (Vanadium group) is +5. Vanadium has a very wide range of oxidation states from -1 to +5, of which the oxidation state +2, +3, +4 & +5 are important and exist both as solids and in solution. The oxidation states +2 & +3 are reducing, 0 state +4 is stable and 0 state +5 is slightly oxidising. For niobium (Nb) & tantalum (Ta), the oxidation state +5 is by far the most stable and the best known, although lower oxidation states are known. 0 states enclosed () are very less stable. Zn/HCl (dilute) reduces V⁵⁺ to V²⁺ & Nb⁵⁺ to Nb³⁺, but not Ta⁵⁺. This shows the increasing stability of the 0 state +5, in group-5, stability of lower oxidation states decreases from V to Ta while higher oxidation states stability increases from V to Ta.

* Complex formation: Vanadium (V) forms complexes in its all oxidation states (-1 to +5) and different coordination numbers (4 to 8). Some important complexes of V in different oxidation states are given below:

O. State	Co. No.	Geometry	Examples
-1	6	Octahedral	[V(CO) ₆] ⁻ , Li[V(dipy) ₃]·4C ₄ H ₈ O, K ₅ [V(CN) ₅ NO]
0	6	do	[V(CO) ₆], [V(dipy) ₃].
+1	6	do	[V(CO) ₄ arene] ⁺ , [V(dipy) ₃] ⁺
+2	6	do	[V(H ₂ O) ₆] ²⁺ , [V(CN) ₆] ⁴⁻
+3	4	Tetrahedral	[VCl ₄] ⁻
	5	Trigonal bipyramidal	Trans [VCl ₂ (SMe ₂) ₂]
	6 (M. Imp)	Octahedral	[V(MH ₂) ₆] ³⁺ , [V(SO ₄) ₃] ³⁻ , [VF ₆] ³⁻
+4	4	Tetrahedral	[VCl ₄]
	5	Trigonal bipyramidal	[VO(acac) ₃]
	6 (M. Imp)	Octahedral	K ₂ [VO ₂], [VO(acac) ₂ ·4H ₂ O]
	8	Dodecahedral	[VCl ₄ (diars) ₂]
+5	4	Tetrahedral	[VOCl ₃]
	5	Trigonal bipyramidal	[VF ₅], K[VOF ₄]
	6 (M. Imp)	Octahedral	Na ₂ [VOF ₅].

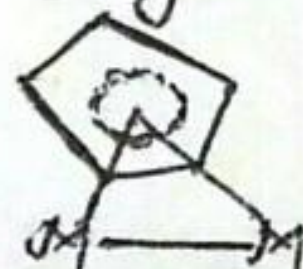
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A considerable number of octahedral complexes are known such as $[V(H_2O)_6]^{3+}$, $[VF_6]^{3-}$, $[V(NCS)_6]^{3-}$, $[V(CN)_6]^{3-}$ and $[V(oxalato)_3]^{3-}$. In these complexes, O. state of V is +3 and C.No. is 6. Complexes of Vanadium in oxidation states +4 & +5, and C.No. 6 are most important.

Nb & Ta form complexes in oxidation states -1, +4 & +5 and C.No. 6 or 8. Some important complexes are as follows:

O. States	Coordination No.	Geometry	Examples
-1	6	Octahedral	$[M(CO)_6]^-$ (M = Nb, Ta)
+4	6	Octahedral	$[MCl_4(Py)_2]$
	8	Dodecahedral	$[NbX_4(diars)_2]$
+5	6	Octahedral	$Nb[MO_3]$, $[TaF_6]^-$
	8	Square antiprism	$Nb_9[TaF_8]$

* Organometallic compounds: Group-5 elements form organometallic compounds (M-C bond) with CO (Carbonyl), alkyl (R), aryl (Aryl), Cyclopentadienyl groups etc in lower oxidation states -1, 0. Metal carbonyls of these metals in O. state -1 & 0 are of type $[M(CO)_6]^-$ & $[M(CO)_6]$ respectively. $[V(CO)_6]$ is monomeric although other transition metal carbonyls are dimeric. The dipyrityl complex in O. state +1 is $[V(dipyridyl)_3]^+$. These metals (Gr. 5 elements) form organometallic compounds with alkyl or aryl groups in lower O. states, e.g. $[V^0(CH_2Si(CH_3)_3)_3]$, $[Nb(CH_3)_5]$, $[Ta(CH_3)_5]$, $[NbCl_3(CH_3)_2]$ etc. These complexes are square pyramidal geometry (C.No. 5). Gr. 5 metals also form organometallic compounds with cyclopentadienyl group of type C_p^+M (where C_p = Cyclopentadienyl, bridging ligand, M = V, Nb or Ta), and structure:



* Reactivity:

Vanadium is not affected by air, water, alkalis or non-oxidising acids other than HF. It dissolves in hot conc. H_2SO_4 , HNO_3 and aqua regia. Niobium & Tantalum are also very unreactive and resistant to acids except HF, but dissolve in fused alkali. At high temperature, the elements react with many non-metals (N, C, H etc.). They form interstitial nitrides of type MN & two series of carbides of type MC & MC_2 . The former are interstitial, refractory and very hard, and the latter are ionic & react with water liberating acetylene (C_2H_2) gas. These elements form non-stoichiometric hydrides, and the amount of hydrogen absorbed depends on the temperature and pressure.

Vanadium forms many different positive ions, but Nb & Ta form virtually none. Thus, though Nb & Ta are metals, their compounds in the O. state +5 are mostly covalent, volatile and readily hydrolysed properties associated with non-metals. The tendency to form simple ionic compounds decreases with increasing oxidation state. Thus, V^{2+} & V^{3+} both exist as hexahydrates. The oxidation state +4 may be covalent as in VCl_4 , but there are a wide range of compounds containing the hydrated vanadyl VO^{2+} ion. The oxidation state +5 may be covalent as in VF_5 or form VO_2^+ or VO_3^- or VO_4^{3-} hydrated ions. In lower oxidation states, Nb & Ta form a large number of cluster compounds in which groups of metal atoms are bonded together.