

Trends in stability of Higher oxidation states in halides and oxides

3d series elements shows highest oxidation states when it is combined with more electro negative elements like halogens (x = F, Cl, Br, I) and oxygen.

Stability of higher oxidation states in halides

- i) The highest oxidation numbers are observed in TiX_4 (tetra halides), VF_6 and CrF_6 . Mn to simple halides does not exhibit +7 oxidation states. But Mn in MnO_3F (manganese oxy fluoride) forms shows +7 oxidation states.
- ii) Beyond Mn (except Fe and Co forms trihalide like FeX_3 and CoF_2), more of the metal shows trihalide form.
- iii) Fluorides of metal in higher oxidation states are stable

Reason: The ability of fluorine to stabilise the highest oxidation state is due to either , a) Higher lattice energy, for example: CoF_3

b) Higher bond enthalpy terms for the higher covalent compounds, For Ex: VF_5 and CrF_3

iv) Penta halides of Vanadium are stable and show only with F as VF_5 .

Penta halide of other metals are unstable, due to hydrolysis to give oxo halides (VOx_3)

v) Au Cu (II) halides are known except cupric iodide (CuI_2)

Reason: Cu^{3+} oxidizes I^- to I_2



Copper (I) compounds are unstable in aqueous solution and undergo disproportionation



The stability of $\text{Cu}^{2+}_{(\text{aq})}$ is more than Cu^+ is due to the more negative hydration enthalpy of Cu^{2+} than Cu^+ which is more than the second ionisation enthalpy of Cu

Disproportionation of Oxidation state

Disproportionation reaction is a reaction in which the same element is simultaneously oxidised and reduced

When a particular oxidation state becomes less stable relative to other oxidation state, one lower, one higher it is said to undergo disproportionation.

Ex: $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^{2-} + \text{MnO}_2 + \text{H}_2\text{O}$

Mn (VI) becomes unstable relative to Mn (VII) and Mn (IV) in acidic solution.

Cu(I) compounds are unstable in aqueous solution than Cu(II) and undergo Disproportionation.

Reason: due to more negative ΔH_{Hyd} of Cu^{2+}

Stability of Higher Oxidation States in Oxides

I. The Highest Oxidation No. in oxides of 3d series of transition elements coincides with a group member up to 7 and observed in $\text{Sc}^{\text{III}}\text{O}_3$, $\text{Ti}^{\text{IV}}\text{O}_2$, $\text{V}_2^{\text{V}}\text{O}_5$ and $\text{Mn}_2^{\text{VII}}\text{O}_7$ (i.e., $\text{Sc}^{\text{III}}\text{O}_3$ to $\text{Mn}_2^{\text{VII}}\text{O}_7$) Beyond Group 7, no higher oxides of Fe above are known.

II) The highest oxidation states of Fe is +3 in Fe_2O_3 , But in ferrates FeO_4^{2-} is +6 which is formed in alkaline media, they readily decompose to give FeO and O_2 .

iii) Oxygen shows better ability to stabilise higher oxidation states than fluorine. because oxygen can form multiple bond with metals, while fluorine can't form multiple bond with metals.

For example: Mn with fluorine gives MnF_4 whereas Mn with oxygen gives Mn_2O_7 ,

iv) In the covalent oxide Mn_2O_7 , each Mn is tetrahedrally surrounded by O's including a Mn-O-Mn bridge. The tetrahedral $[\text{MnO}_4]_n$ ions are known for V^{+5} , Cr^{+4} , Mn^{+5} , Mn^{+6} and Mn^{+7}

v) Besides the oxides, oxocations stabilise V^{+5} as VO_2^+ , V^{+4} as VO^{2+} and Ti^{+4} as TiO^{2+}

Trends in the M^{2+}/M standard electrode potentials

*The electrode potential values are measure of reduction tendency i-e, the measure of the tendency for the metal ion, M^{2+} to get reduce to M .
$$M^{2+} + 2e^-_{(aq)} \rightarrow M_{(s)}$$

* Therefore, the tendency of the metal to go into the solution or to undergo oxidation is higher when the standard electrode potential value is more negative. $M_{(s)} \rightarrow M^{2+} + e^-_{(aq)}$

* Higher the electrode potential, Lesser is the tendency to get converted into ions.

Cu with highest positive E° values, does not liberate H_2 from acids. The high energy to transform Cu_s to $Cu^{2+}_{(g)}$ is not balanced by its hydration enthalpy.

* Less negative E° values across the series is related to the increase in the sum of the first and second ionization enthalpies

*The value of E° for Mn is more negative than expected as the enthalpy of atomization and second ionization enthalpy (Mn^{2+} is with d^5) values are relatively smaller.

* The E° value of Zn is more negative than expected as the enthalpy of atomization and second ionization enthalpy (Mn^{2+} is with d^5) values we relatively smaller

* The E° value of Zn is more negative than expected from the trend and the same can be attributed to the lower enthalpy of atomization (metallic bonding in Zn is weaker) and second ionization enthalpy (Zn^{2+} is with d^{10})

Standard electrode potentials (M^{3+}/M^{2+})

* The low value of Sc reflects the stability of Sc^{3+} which has a noble gas configuration.

*The value of Zn should be very high as Zn^{3+} readily gets converted into Zn^{2+} with stable d^{10} . The 3rd ionization enthalpy of zinc is very high

* The high value for Mn shows that Mn^{2+} (d^5) is particularly stable (more than Mn^{3+}) and the third ionization enthalpy of Mn is very high

* Low value for Fe shows the extra stability of Fe^{3+} (d^5) as compared to Fe^{2+} (d^6) Therefore third ionization enthalpy of Fe is also very high.

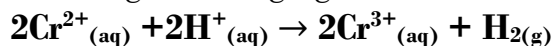
Chemical reactivity of E° values

The metals of the first series with the exception of copper (with positive E° value) are relatively more reactive (with negative E° values) and are dissolved to dilute acids with the liberation of hydrogen.

* Titanium and vanadium are passive to dilute non oxidizing acids because of the formation of passive protective film in on the surface of these metals

* E° values for the redox couple M^{3+}/M^{2+} shows that Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solutions. They have very high E° values and Mn^{3+} and Co^{2+} readily undergo reduction to Mn^{2+} and Co^{2+} respectively.

* The ions Ti^{2+} , Va^{2+} and Cr^{2+} are Strong reducing agent and will liberate hydrogen from a dilute acid.



* E° or M^{3+}/M^{2+} (Ti, V, Cr) are negative indicating that these metals ions have more tendency to undergo oxidation from +2 state to +3 than H to H^+

Oxides and oxoanions of metals

Transition metal combine with oxygen at high temperature and gives metallic oxides

*Except Sc, all the metals upto Mn forms monoxide (MO) which are ionic in nature

Sc_{+3} } it does not form monoxide

Ti	V	Cr	Mn
+2	+2	+2	+2

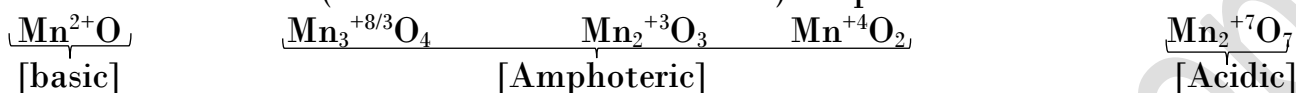


→ There metals combine with O^{2-} MO

*As oxidation numbes increases, covalent native and acidic character increases, while ionic character decreases.

*As oxidation number decreases, covalent character and acidic character decreases

- Metal oxides (lower oxidation state) Basic in nature
- Metal oxides (higher oxidation state) Acidic to nature
- Metal oxides (intermediate oxidation state) Amphoteric in nature



Basic acids: Sc_2O_3 , TiO, Ti_2O_3 , VO, V_2O_3 , MnO, FeO, CuO, CoO, NiO, Cu_2O , CrO

Acidic oxides: Mn_2O_7 , CrO_3 , OsO_4 .

Amphoteric oxides: TiO_2 , ZnO, Cr_2O_3 , Mn_2O_3 , MnO_2 , V_2O_5 , Mn_3O_4 , Fe_3O_4

f-Block elements (The inner transition elements)

The f-block of the periodic table contains the elements of the group 3 in which the 4f and 5f orbitals are progressively filled in the latter two long periods; these elements are formal members of group-3 from which they have been taken out to form a separate f-block of the periodic table, these are also called **inner transition metals**.

