▶ Video explanation (YouTube Short)

Stability of Higher Oxidation States: Oxides and Fluorides

The purple of potassium permanganate ($KMnO_4$) is manganese in its highest oxidation state, **+7**. Fluorine is the most electronegative element, yet the highest fluoride of manganese is only MnF_4 (+4). Oxygen takes manganese all the way to +7. This note explains why (NCERT 4.3.7).

1. Where the highest oxidation state is found

A metal shows its highest oxidation state only when it is combined with a small, highly electronegative element: **fluorine or oxygen**. So the highest states appear in fluorides and oxides (and in oxoanions such as MnO_4^-).

2. Counting electrons: why oxygen goes further than fluorine

Mn is $3d^5 4s^2$: 7 valence electrons. In oxidation-state counting, all seven must be assigned to the partner atoms to reach +7.

Partner	Bond to the metal	Electrons counted per atom	Atoms needed for +7	What is actually known
Fluorine	single bond	1	7 (MnF_7)	MnF_7 has never been made; the highest fluoride is **MnF_4 (+4)**
Oxygen	multiple bond	2	only 4 (in MnO_4^-)	**MnO_4^- and Mn_2O_7 (+7)**

In MnO_4^-: 4 oxygens × 2 = 8 electrons = 7 from Mn + 1 extra (from K in $KMnO_4$), which is why the ion carries a 1− charge. Check: x + 4(−2) = −1, so x = +7.

Key point: oxygen does *not* win because it "pulls harder" (fluorine is more electronegative). It wins because of its **ability to form multiple bonds** with the metal.

Remember that an oxidation state is a counting rule. There is no free Mn^{7+} ion in MnO_4^- or Mn_2O_7; the bonds are covalent.

3. Highest oxides of the 3d metals (NCERT Table 4.6)

Group	3	4	5	6	7
Highest oxide	Sc_2O_3	TiO_2	V_2O_5	CrO_3	Mn_2O_7
Oxidation state	+3	+4	+5	+6	+7

- From Sc to Mn, the highest oxidation state in the oxide = **group number**.
- Beyond group 7, no oxide of iron above Fe_2O_3 is known. Ferrates(VI), FeO_4^{2-}, form in alkaline medium but readily decompose to Fe_2O_3 and O_2.
- Oxocations also stabilise high states: V(V) as VO_2^+, V(IV) as VO^{2+}, Ti(IV) as TiO^{2+}.

- Tetrahedral $[MO_4]^{n-}$ ions are known for V(V), Cr(VI), Mn(V), Mn(VI) and Mn(VII).
- **Mn_2O_7** is a covalent oxide: each Mn is tetrahedrally surrounded by O atoms, with one Mn–O–Mn bridge.

4. Highest halides (NCERT Table 4.5)

Ti	V	Cr	Mn	Fe	Co
TiX_4 (+4)	VF_5 (+5)	CrF_6 (+6)	MnF_4 (+4)	FeX_3 (+3)	CoF_3 (+3)

- The highest oxidation numbers are reached in TiX_4 (tetrahalides), VF_5 and CrF_6. *(CrF_6 is listed in NCERT Table 4.5.)*
- Mn does not show +7 in any simple halide, but the oxofluoride **MnO_3F** is known.
- Beyond Mn, no metal has a trihalide except FeX_3 and CoF_3.
- Fluorine stabilises a high state through high **lattice energy** (ionic CoF_3) or high **bond enthalpy** (covalent VF_5, CrF_6).
- V(+5) is represented only by VF_5; the other halides hydrolyse to oxohalides VOX_3.
- Fluorides are unstable in the *low* oxidation states: VX_2 and CuX exist only for X = Cl, Br, I.

5. A state this high is a strong oxidising agent

Mn(+7) readily takes electrons from other substances and goes to a lower state. That is why $KMnO_4$ is a strong oxidising agent, and why Mn_2O_7 reacts explosively with organic matter. Oxidising power increases in the order $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$ (NCERT Example 4.5), because the lower state they are reduced to becomes increasingly stable.

6. Also in NCERT 4.3.7: the low state Cu^+ in water

$Cu^+(aq)$ is unstable and **disproportionates**: $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$.

- $Cu^{2+}(aq)$ is more stable than $Cu^+(aq)$ because its hydration enthalpy is much more negative; this more than compensates for the second ionisation enthalpy of Cu.
- All Cu(II) halides are known except the iodide: $2Cu^{2+} + 4I^- \rightarrow Cu_2I_2(s) + I_2$ (Cu^{2+} oxidises I^- to I_2).

Solved example

Q. $E°(Cu^+/Cu) = +0.52$ V and $E°(Cu^{2+}/Cu^+) = +0.16$ V. Show that $Cu^+(aq)$ disproportionates.
A. Reduction: $Cu^+ + e^- \rightarrow Cu$ ($E° = +0.52$ V). Oxidation: $Cu^+ \rightarrow Cu^{2+} + e^-$ ($E°$ of the couple = +0.16 V). $E°cell = E°(cathode) - E°(anode) = 0.52 - 0.16 =$ **+0.36 V**. $E°cell$ is positive, so $2Cu^+ \rightarrow Cu^{2+} + Cu$ is spontaneous.

Key takeaways

- The highest oxidation state of a metal appears in its oxides and fluorides.
- Oxygen beats fluorine because of multiple bonding: one O counts 2 electrons, one F counts 1. Mn: +4 in MnF_4, +7 in Mn_2O_7 and MnO_4^-.
- Highest oxide: oxidation state = group number, from Sc_2O_3 to Mn_2O_7.
- A very high oxidation state means a strong oxidising agent ($KMnO_4$, Mn_2O_7).

Practice questions

1. (MCQ) The highest fluoride of manganese is: (a) MnF_2 (b) MnF_3 (c) MnF_4 (d) MnF_7
2. (MCQ) Oxygen stabilises higher oxidation states than fluorine because oxygen: (a) is more electronegative (b) forms multiple bonds with metals (c) is larger (d) is a gas
3. (MCQ) The oxide in which the metal's oxidation state equals its group number 7 is: (a) MnO_2 (b) Mn_2O_3 (c) Mn_3O_4 (d) Mn_2O_7
4. (Very short) Write the highest oxides of Sc, Ti, V and Cr.
5. (Very short) Name one oxofluoride in which Mn is in the +7 state.
6. (Short) Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?
7. (Short) Why is Cu^+ not stable in aqueous solution?
8. (Numerical) Find the oxidation state of the metal in (i) MnO_4^- (ii) $Cr_2O_7^{2-}$ (iii) VO_2^+.

Answer key

1. (c) MnF_4.
2. (b) forms multiple bonds with metals.
3. (d) Mn_2O_7.
4. Sc_2O_3, TiO_2, V_2O_5, CrO_3.
5. MnO_3F: $x + 3(-2) + (-1) = 0$, so $x = +7$.
6. Oxygen and fluorine are small and highly electronegative, so they can oxidise the metal to its highest state; oxygen can also form multiple bonds with the metal.
7. $Cu^+(aq)$ disproportionates: $2Cu^+ \rightarrow Cu^{2+} + Cu$. $Cu^{2+}(aq)$ has a much more negative hydration enthalpy, which more than compensates for the second ionisation enthalpy of Cu.
8. (i) $x - 8 = -1$, $x = +7$. (ii) $2x - 14 = -2$, $x = +6$. (iii) $x - 4 = +1$, $x = +5$.

▶ Watch the video explanation