▶ Video explanation (YouTube Short)

Why $KMnO_4$ Is So Intensely Coloured (It Has No d Electrons)

A pinch of potassium permanganate colours a whole jar of water deep purple. Yet the colour of transition-metal ions is usually explained by d–d transitions, and Mn in MnO_4^- has no d electrons. These notes explain where the colour comes from and why it is so strong.

1. The puzzle: Mn is +7, $3d^0$

- Mn: [Ar] $3d^5 4s^2$. In MnO_4^-, Mn is **+7**, so Mn^{7+} is **$3d^0$**.
- With no d electrons, **no d–d transition** is possible. Other d^0 ions such as Sc^{3+} and Ti^{4+} are colourless in water.

2. The answer: charge transfer

- The oxygen atoms around Mn have filled 2p orbitals; Mn^{7+} has empty 3d orbitals.
- When light is absorbed, an electron moves from **oxygen (ligand) to manganese (metal)**: **ligand-to-metal charge transfer (LMCT)**.
- This happens only while the light is being absorbed; the ion remains MnO_4^-.
- Very high oxidation states (like +7) make the metal's d orbitals low in energy, and O^{2-} gives up an electron easily, so this jump needs the energy of visible light.

Colour seen: the O → Mn jump absorbs **green-yellow** light (maximum near 525 nm). Red and blue light pass, and together they look **purple**.

3. Why the colour is so intense

- d–d transitions are **restricted** ("forbidden" by a symmetry rule, the Laporte rule), so only a small fraction of photons is absorbed: typical molar absorptivity ε ≤ about 100 L mol^{-1} cm^{-1}. These colours are pale (e.g. $Ti^{3+}(aq)$, $Mn^{2+}(aq)$).
- Charge-transfer transitions are **allowed**, so absorption is much stronger: for MnO_4^-, ε ≈ 3×10^3 L mol^{-1} cm^{-1} at 525 nm, typically **tens to hundreds of times** stronger than d–d bands.

Ion	d electrons	Origin of colour	Intensity
$Ti^{3+}(aq)$	$3d^1$	d–d	pale purple
$Mn^{2+}(aq)$	$3d^5$	d–d (very weak)	almost colourless (pale pink)
MnO_4^-	$3d^0$	charge transfer O → Mn	deep purple
CrO_4^{2-}	$3d^0$	charge transfer O → Cr	yellow
$Cr_2O_7^{2-}$	$3d^0$	charge transfer O → Cr	orange

4. Worked examples

Example 1

Q. Why is MnO_4^- coloured though Mn is in the +7 state? **A.** Mn^{7+} is d^0, so the colour is not d–d; it is due to charge transfer of an electron from O to the empty d orbitals of Mn (LMCT).

Example 2

Q. Is $K_2Cr_2O_7$ coloured because of d–d transitions? **A.** No. Cr is +6 (d^0); the orange colour is due to O → Cr charge transfer.

Example 3

Q. Which is more intensely coloured at the same concentration, Ti^{3+}(aq) or MnO_4^-? **A.** MnO_4^-, because charge-transfer absorption is allowed and far stronger than the d–d absorption of Ti^{3+}.

Example 4

Q. MnO_4^- absorbs near 525 nm. What colour does it appear? **A.** Purple (the complementary colour of green-yellow).

5. Common mistakes

- ✗ "Every coloured transition-metal ion has d electrons." ✓ d^0 oxo-anions are coloured by charge transfer.
- ✗ "$KMnO_4$ is purple because it absorbs purple light." ✓ It absorbs green-yellow.
- ✗ "In the solution, Mn changes to +6." ✓ The electron transfer is only in the excited state during absorption.

6. Key takeaways

- MnO_4^- (Mn^{7+}, $3d^0$): colour by charge transfer O → Mn, not d–d.
- It absorbs green-yellow (≈ 525 nm); we see purple.
- Charge transfer is allowed, so the colour is far more intense than d–d colours.
- CrO_4^{2-} (yellow) and $Cr_2O_7^{2-}$ (orange) are d^0 and coloured for the same reason.

Practice questions

1. (MCQ) The electronic configuration of Mn in MnO_4^- is: (a) $3d^5$ (b) $3d^4$ (c) $3d^0$ (d) $3d^2$
2. (MCQ) The colour of $KMnO_4$ is due to: (a) d–d transition (b) charge transfer (c) f–f transition (d) unpaired electrons
3. (MCQ) Which of these is coloured though it is d^0? (a) Sc^{3+} (b) Ti^{4+} (c) CrO_4^{2-} (d) Zn^{2+}
4. (MCQ) $KMnO_4$ absorbs light of colour: (a) purple (b) green-yellow (c) red (d) blue
5. (Very short) What is meant by ligand-to-metal charge transfer?
6. (Very short) Why is Sc^{3+}(aq) colourless?
7. (Short) Explain why $KMnO_4$ is coloured although Mn has no d electrons.
8. (Short) Why are charge-transfer colours more intense than d–d colours?
9. (Short) Name two other ions coloured by charge transfer and state their colours.
10. (HOTS) Mn^{2+} has five d electrons, yet its solution is almost colourless. Explain.

Answer key

1. (c) $3d^0$.
2. (b) charge transfer.
3. (c) CrO_4^{2-}.
4. (b) green-yellow.
5. Absorption of light moves an electron from an orbital on the ligand (e.g. O) to an empty orbital on the metal.
6. Sc^{3+} is $3d^0$: no d–d transition, and no charge transfer in the visible region.
7. Mn^{7+} is $3d^0$; an electron moves from O to the empty d orbitals of Mn on absorbing green-yellow light; the transmitted red + blue appear purple.
8. Charge-transfer transitions are allowed; d–d transitions are restricted (forbidden by symmetry), so far fewer photons are absorbed.
9. CrO_4^{2-} (yellow) and $Cr_2O_7^{2-}$ (orange), both O → Cr(VI).
10. Its only absorption is d–d, which is restricted (and for Mn^{2+}, d^5, especially weak), so very little light is absorbed and the colour is very pale.

▶ Watch the video explanation