▶ Video explanation (YouTube Short)

# Potassium Permanganate: Preparation and Oxidising Action

More than 350 years ago the chemist J. R. Glauber melted a black mineral (pyrolusite, $MnO_2$) with alkali and dropped the product in water: the green solution slowly turned purple. He called it the "mineral chameleon". (Carbon dioxide from the air was acidifying the solution.) That colour change is the preparation of potassium permanganate, $KMnO_4$ (NCERT 4.4.1).

## 1. Preparation

### Step 1: alkaline oxidative fusion (Mn +4 → +6)

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

$MnO_2$ is fused with an alkali metal hydroxide and an oxidising agent such as $KNO_3$ (or air). The product, **potassium manganate $K_2MnO_4$**, is **dark green**.

### Step 2: manganate → permanganate (Mn +6 → +7)

- **Disproportionation** in neutral or acidic solution:
  $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$
  Two Mn go up (+6 → +7, purple $MnO_4^-$) and one comes down (+6 → +4, brown $MnO_2$).
- **Commercially:** electrolytic oxidation of manganate in alkaline solution (at the anode): $MnO_4^{2-} \rightarrow MnO_4^- + e^-$.
- **In the laboratory:** a manganese(II) salt is oxidised by peroxodisulphate: $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$.

## 2. Properties

- Dark purple (almost black) crystals, isostructural with $KClO_4$; moderately soluble in water at room temperature.
- On heating at 513 K: $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$.
- Both manganate and permanganate are **tetrahedral**. Manganate (green, $Mn^{6+}$, $d^1$) is **paramagnetic**; permanganate (purple, $Mn^{7+}$, $d^0$) is **diamagnetic**.

## 3. Oxidising action

| Medium | Half-reaction | $e^-$ | Product |
|---|---|---|---|
| acidic | $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ ($E^\circ = 1.52$ V) | 5 | $Mn^{2+}$, almost colourless |
| neutral / faintly alkaline | $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$ ($E^\circ = 0.59$ V) | 3 | $MnO_2$, brown |

### In acid it oxidises

- $Fe^{2+} \rightarrow Fe^{3+}$: $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$
- $I^- \rightarrow I_2$: $10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$
- oxalate $\rightarrow CO_2$ (at 333 K): $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$
- $H_2S \rightarrow S$; $SO_3^{2-} \rightarrow SO_4^{2-}$; $NO_2^- \rightarrow NO_3^-$.

### In neutral / faintly alkaline solution

- $I^- \rightarrow IO_3^-$; $S_2O_3^{2-} \rightarrow SO_4^{2-}$; $Mn^{2+} \rightarrow MnO_2$ (in the presence of $ZnSO_4$ or ZnO).

**Self-indicator:** in a titration in acid, each purple drop is decolourised while $Fe^{2+}$ (or oxalate) is left. The first extra drop gives a permanent **pale pink** colour: that is the end point, so no separate indicator is needed. ($KMnO_4$ is not a primary standard; its solutions are standardised, e.g. against oxalic acid.)

**Uses:** analytical reagent; bleaching wool, cotton and silk; decolourising oils; water treatment (oxidising iron, manganese and odours). Dilute solutions are used as an antiseptic. Handle with care: it is a strong oxidiser and stains skin.

## 4. Worked examples

### Example 1

**Q.** Show that $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$ is a disproportionation. **A.** Mn +6 in all three reactants; two end at +7 (oxidised, 2 × $1e^-$ lost) and one at +4 (reduced, $2e^-$ gained): the same element is both oxidised and reduced.

### Example 2

**Q.** How many moles of $Fe^{2+}$ does 0.02 mol $MnO_4^-$ oxidise in acid? **A.** 1 : 5, so 0.10 mol.

### Example 3

**Q.** Why does $KMnO_4$ give a brown precipitate in a neutral solution of a reducing agent? **A.** In neutral medium it takes only $3e^-$ and forms $MnO_2$ (brown, insoluble).

### Example 4

**Q.** Why is manganate paramagnetic but permanganate diamagnetic? **A.** Mn(VI) is $3d^1$ (one unpaired electron); Mn(VII) is $3d^0$.

## 5. Common mistakes

- ✗ "Permanganate always gives $Mn^{2+}$." ✓ Only in acid; in neutral / weakly alkaline medium it gives $MnO_2$.
- ✗ "$Mn^{2+}$ is purple." ✓ $Mn^{2+}$ is almost colourless (very pale pink); purple is $MnO_4^-$.
- ✗ "Manganate and permanganate have the same colour." ✓ Manganate is green, permanganate purple.

## 6. Key takeaways

- $MnO_2$ + KOH + oxidiser, fused → green $K_2MnO_4$ (Mn +6).
- Manganate → purple permanganate (Mn +7): disproportionation in acid/neutral water, or electrolysis.

- Acid: $5e^- \rightarrow Mn^{2+}$ (self-indicator); neutral: $3e^- \rightarrow MnO_2$.

## Practice questions

1. (MCQ) The colour of potassium manganate is: (a) purple (b) green (c) brown (d) colourless
2. (MCQ) In acid, $MnO_4^-$ is reduced to: (a) $MnO_2$ (b) $MnO_4^{2-}$ (c) $Mn^{2+}$ (d) Mn
3. (MCQ) In neutral medium, one $MnO_4^-$ accepts: (a) $1e^-$ (b) $3e^-$ (c) $5e^-$ (d) $7e^-$
4. (MCQ) Which is diamagnetic? (a) $MnO_4^{2-}$ (b) $MnO_4^-$ (c) $Mn^{2+}$ (d) $MnO_2$
5. (Very short) Write the equation for the disproportionation of manganate in acid.
6. (Very short) Name the ore of manganese used to make $KMnO_4$.
7. (Short) Why is no indicator needed in $KMnO_4$ titrations?
8. (Short) Write the ionic equation for $KMnO_4$ with $Fe^{2+}$ in acid.
9. (Short) Describe the commercial preparation of $KMnO_4$.
10. (HOTS) A purple solution gives a brown precipitate with a reducing agent but becomes almost colourless with the same agent after adding dilute $H_2SO_4$. Explain.

## Answer key

1. (b) green.
2. (c) $Mn^{2+}$.
3. (b) $3e^-$.
4. (b) $MnO_4^-$ ($d^0$).
5. $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$.
6. Pyrolusite, $MnO_2$.
7. Purple $MnO_4^-$ is decolourised as long as the reductant remains; the first excess drop gives a permanent pale pink.
8. $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$.
9. $MnO_2$ fused with KOH and air/$KNO_3$ → $K_2MnO_4$; manganate oxidised electrolytically in alkaline solution: $MnO_4^{2-} \rightarrow MnO_4^- + e^-$.
10. In neutral medium $MnO_4^-$ takes $3e^-$ → brown $MnO_2$; in acid it takes $5e^-$ → almost colourless $Mn^{2+}$.

▶ Watch the video explanation