

Variable Oxidation state

N Goalby
Chemrevise.org

Variable Oxidation States of Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+4	+5	+6	+7	+6	+5	+4	+3	+2
	+3	+4	+5	+6	+5	+4	+3	+2	
	+2	+3	+4	+5	+4	+3	+2	+1	
	+1	+2	+3	+4	+3	+2	+1		
		+1	+2	+3	+2	+1			
			+1	+2	+1				
				+1					

Stability of Oxidation states

General trends

- Relative stability of +2 state with respect to +3 state increases across the series
- Compounds with high oxidation states tend to be oxidising agents e.g MnO_4^-
- Compounds with low oxidation states are often reducing agents e.g V^{2+} & Fe^{2+}

Vanadium

Vanadium has four main oxidation states

VO_2^+ O.N. 5 yellow solution

VO^{2+} O.N. 4 blue solution

V^{3+} O.N. 3 green solution

V^{2+} O.N. 2 mauve solution



The ion with the V at O.N. 5 exists as a solid compound in the form of a VO_3^- ion, usually as NH_4VO_3 (ammonium vanadate (V)).

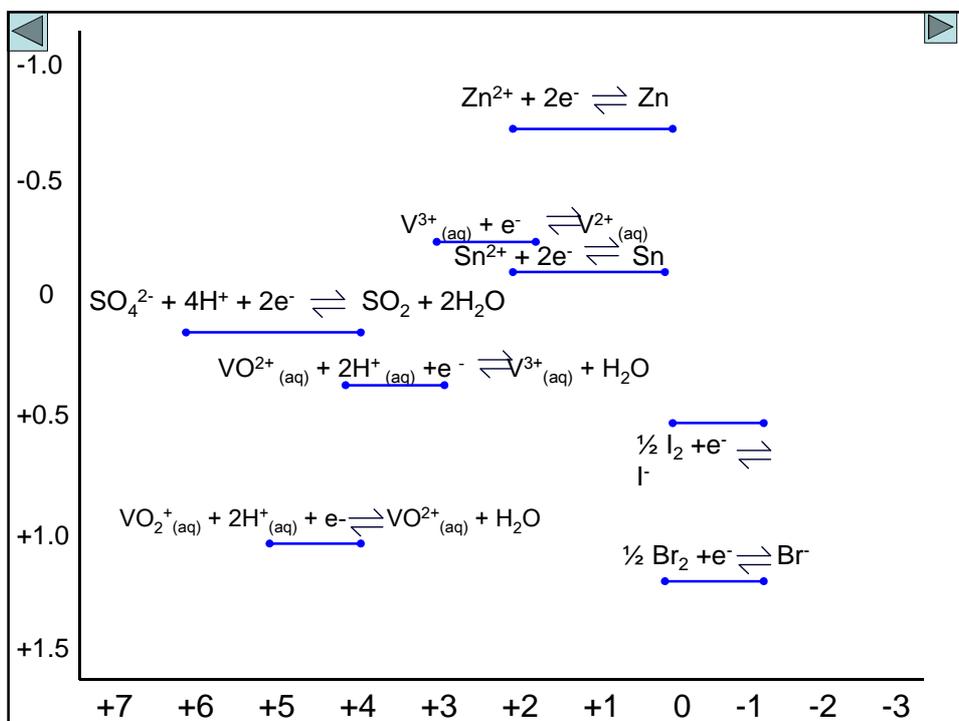
It is a reasonably strong oxidising agent. Addition of acid to the solid will turn into the yellow solution containing the VO_2^+ ion.

Addition of **zinc** to the vanadium (V) will reduce the vanadium down through each successive oxidation state

Oxidation State	Ion	Colour	Redox Equation	E° Values
+5	VO ₃ ⁻ or VO ₂ ⁺	YELLOW	VO ₂ ⁺ (aq) + 2H ⁺ (aq) + e ⁻ → VO ²⁺ (aq) + H ₂ O	+1.00 V
+4	VO ²⁺	BLUE	VO ²⁺ (aq) + 2H ⁺ (aq) + e ⁻ → V ³⁺ (aq) + H ₂ O	+0.34 V
+3	V ³⁺	GREEN	V ³⁺ (aq) + e ⁻ → V ²⁺ (aq)	-0.26 V
+2	V ²⁺	VIOLET		

The most stable ion is the V³⁺.

The V²⁺ is relatively unstable and will oxidise in air to V³⁺ (similar to iron)

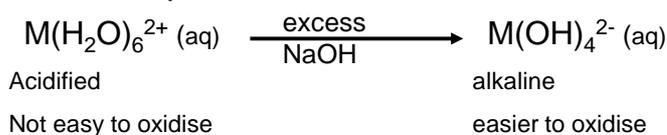


Using the data on the previous slide answer the following questions.

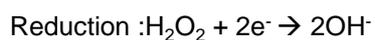
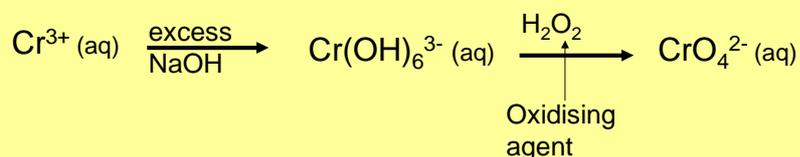
- 1 If Sn is added to VO_2^+ what oxidation state will the V reduce to?
- 2 If KI is added to VO_2^+ what oxidation state will the V reduce to?
- 3 What would oxidise V^{2+} to VO_2^+ ?
- 4 What would oxidise V^{2+} to only V^{3+} ?

Oxidation in alkaline solution

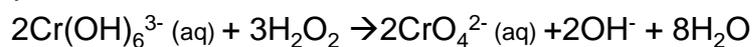
When transition metals in low oxidation states are in alkaline solution they are more easily oxidised than when in acidic solution

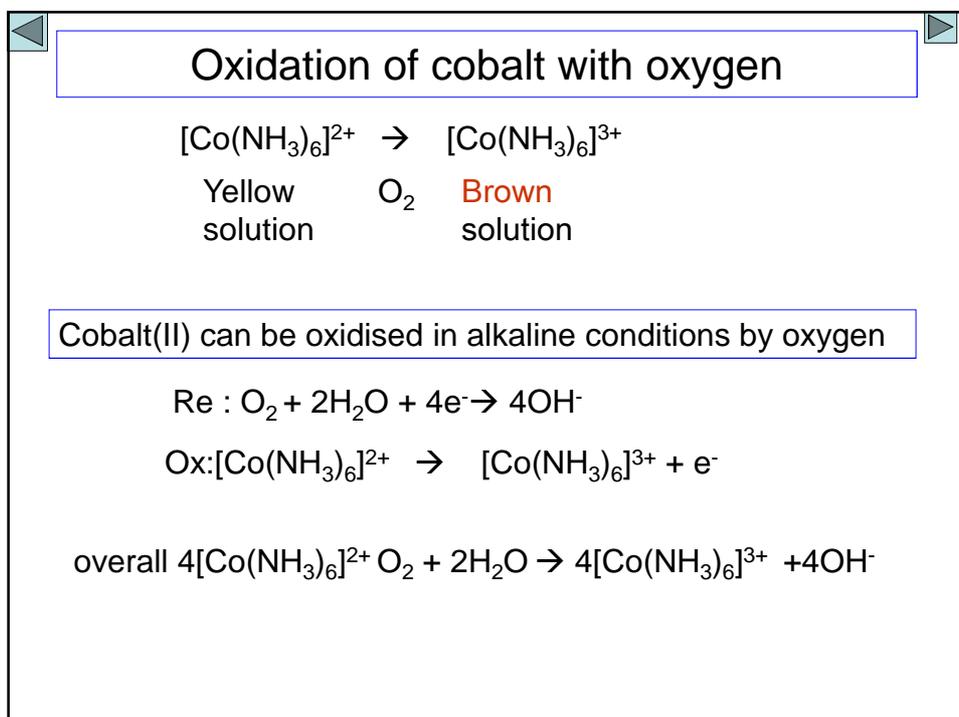
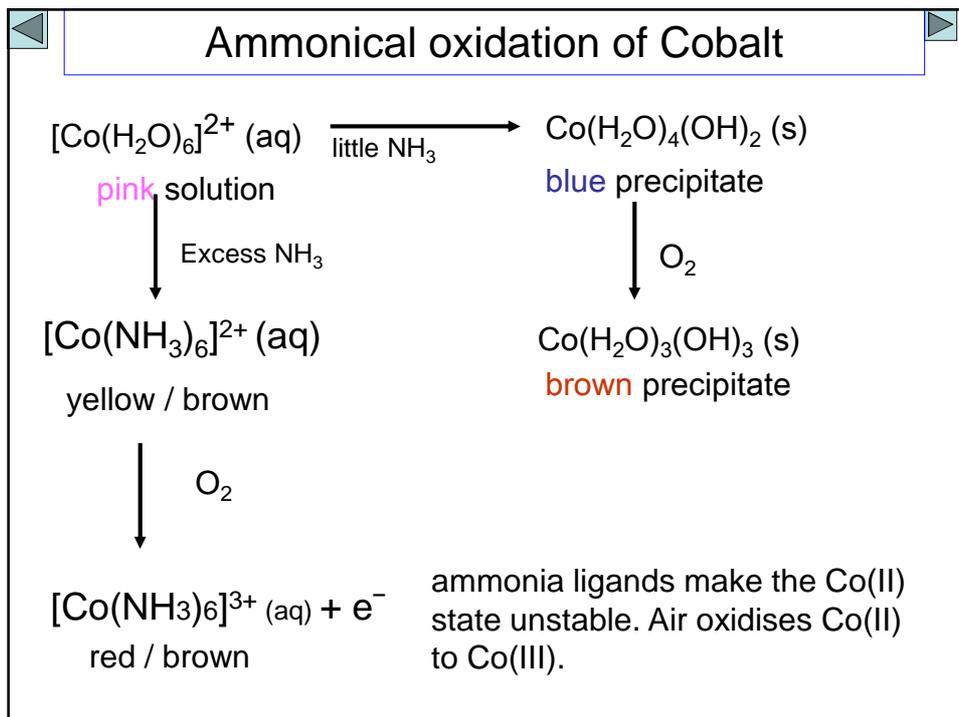


It is easier to remove an electron from a -vely charged ion

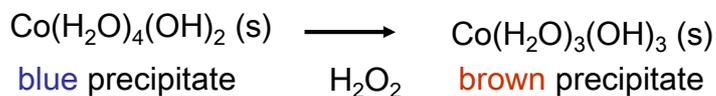


Equation for oxidation

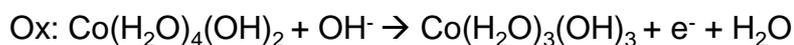
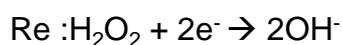




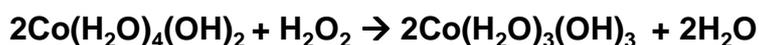
Oxidation of cobalt with hydrogen peroxide



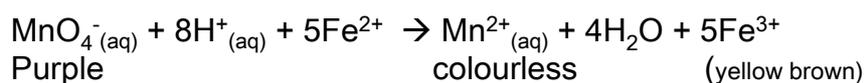
Cobalt(II) can also be oxidised in alkaline conditions by hydrogen peroxide



overall



Potassium manganate titrations



Generally put KMnO_4 in burette. You do not need an indicator. The end point will be the first permanent purple colour in the conical flask.

Two potential starting points

1. Have a substance with an unknown amount of Fe^{2+} . Given the mass of the impure substance and one calculates the % iron
2. Have a metal alloy which contains Iron. Given the mass of the alloy and one calculates the % iron. (First need to react the alloy with acid to produce the Fe^{2+} ions. Assume 1mole Fe gives 1 mole Fe^{2+})

Choosing the right acid

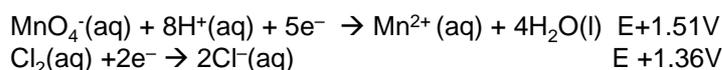
The acid is needed to supply the 8H^+ ions. Some acids are not suitable as they set up alternative redox reactions and hence make the titration readings inaccurate.

- The acid must be strong because a high concentration of H^+ ions are needed (the 8H^+).
- The acid must not be an oxidising agent because it would react with the reducing agent.
- The acid must not be a reducing agent as it would react with the manganate

The usual acid to use is excess dilute H_2SO_4

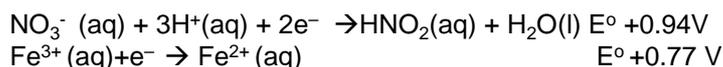
Which acid to use?

It cannot be **conc HCl** as the Cl^- ions would be oxidised to Cl_2 by MnO_4^- as the $E^\circ \text{MnO}_4^-/\text{Mn}^{2+} > E^\circ \text{Cl}_2/\text{Cl}^-$



This would lead to a greater volume of manganate being used and poisonous Cl_2 being produced

It cannot be **nitric acid** as it is an oxidising agent. It oxidises Fe^{2+} to Fe^{3+} as $E^\circ \text{NO}_3^-/\text{HNO}_2 > E^\circ \text{Fe}^{3+}/\text{Fe}^{2+}$

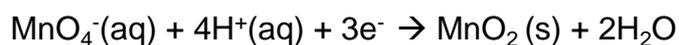


This would lead to a smaller volume of manganate being used

It cannot be conc H_2SO_4 as this is an oxidising agent.

Which acid to use?

Insufficient volumes of sulphuric acid will mean the solution is not acidic enough and MnO_2 will be produced instead of Mn^{2+}



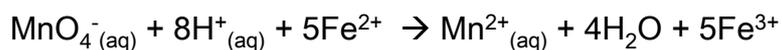
The brown MnO_2 will mask the colour change and lead to a greater (inaccurate) volume of Manganate being used in the titration

Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed (8H^+)

Question

A 2.41g nail made from an alloy containing iron is dissolved in 100cm^3 acid. The solution formed contains $\text{Fe}(\text{II})$ ions. 10cm^3 portions of this solution are titrated with potassium manganate (VII) solution of 0.02M. 9.80cm^3 of KMnO_4 were needed to react with the solution containing the iron.

What is the percentage of Iron by mass in the nail?



Step 1 : find moles of KMnO_4
 moles = conc x vol
 $0.02 \times 9.8/1000$
 $= 1.96 \times 10^{-4} \text{ mol}$

Step 2 : find moles Fe^{2+} in 10cm^3
 $= \text{moles of } \text{KMnO}_4 \times 5$
 $= 9.8 \times 10^{-4} \text{ mol}$

Step 3 : find moles Fe^{2+} in 100cm^3
 $= 9.8 \times 10^{-4} \text{ mol} \times 10$
 $= 9.8 \times 10^{-3} \text{ mol}$

Step 4 : find mass of Fe in $9.8 \times 10^{-3} \text{ mol}$
 mass = moles x RAM = $9.8 \times 10^{-3} \times 55.8 = 0.547\text{g}$

Step 5 ; find % mass
 $\% \text{mass} = 0.547/2.41 \times 100$
 $= 22.6\%$

Other useful manganate titrations

With hydrogen peroxide

Ox $\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
 Red $\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O}$

Overall $2\text{MnO}_4^- (\text{aq}) + 6\text{H}^+ (\text{aq}) + 5\text{H}_2\text{O}_2 \rightarrow 5\text{O}_2 + 2\text{Mn}^{2+} (\text{aq}) + 8\text{H}_2\text{O}$

With ethanedioate

Ox $\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{e}^-$
 Red $\text{MnO}_4^- (\text{aq}) + 8\text{H}^+ (\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4\text{H}_2\text{O}$

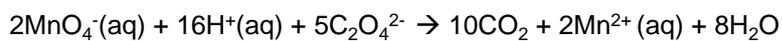
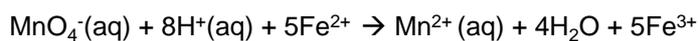
Overall
 $2\text{MnO}_4^- (\text{aq}) + 16\text{H}^+ (\text{aq}) + 5\text{C}_2\text{O}_4^{2-} (\text{aq}) \rightarrow 10\text{CO}_2 (\text{g}) + 2\text{Mn}^{2+} (\text{aq}) + 8\text{H}_2\text{O} (\text{l})$

The reaction between MnO_4^- and $\text{C}_2\text{O}_4^{2-}$ is slow to begin with (as the reaction is between two negative ions) To do as a titration the conical flask can be heated to 60°C to speed up the initial reaction.

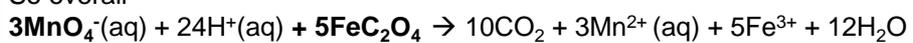
Iron ethanedioate

With Iron (II) ethanedioate both the Fe^{2+} and the $\text{C}_2\text{O}_4^{2-}$ react with the MnO_4^-

1MnO_4^- reacts with 5Fe^{2+} and 2MnO_4^- reacts with $5\text{C}_2\text{O}_4^{2-}$



So overall



So overall the ratio is **3** MnO_4^- to **5** FeC_2O_4