Reactions of transition metals and catalysis

Vanadium oxidation states, chromium chemistry, reactions of aqueous ions with sodium hydroxide and ammonia, ligand exchange, amphoteric behaviour, and heterogeneous and homogeneous catalysis.

Vanadium

Vanadium shows four oxidation states in aqueous solution:

Oxidation state	Ion	Colour
+5	VO_2^+	**Yellow**
+4	VO^{2+}	**Blue**
+3	V^{3+}	**Green**
+2	V^{2+}	**Violet (lilac)**

Zinc in acid reduces VO_2^+ in steps: yellow → **blue** → **green** → **violet**, as each reduction occurs. The $E^\ominus$ values show that Zn ($E^\ominus = -0.76$ V) is a strong enough reducing agent to reduce vanadium all the way to +2, because $E^\ominus_{cell}$ is positive for every step.

> **NOTE**
>
> Each step is a redox reaction with a positive $E^\ominus_{cell}$ for the reduction by zinc. Compare the electrode potentials of VO_2^+/VO^{2+} (+1.00 V), VO^{2+}/V^{3+} (+0.34 V) and V^{3+}/V^{2+} (−0.26 V) with Zn^{2+}/Zn.

Chromium

Ion	Oxidation state	Colour
$Cr_2O_7^{2-}$	+6	**Orange**
CrO_4^{2-}	+6	**Yellow**
Cr^{3+}	+3	**Green** (violet in some forms)
Cr^{2+}	+2	**Blue**

- **Reduction**: zinc in acid reduces $Cr_2O_7^{2-}$ (orange) to Cr^{3+} (green) and then to Cr^{2+} (blue). The Cr^{2+} is oxidised back by air.

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- **Oxidation**: Cr^{3+} is oxidised to chromate(VI) by **hydrogen peroxide in alkaline solution**, then acidified to give dichromate(VI).
- **Chromate–dichromate equilibrium**:

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$$

Adding alkali (removing H^+) moves the position to the right and turns the solution **yellow**. Adding acid moves it to the left and turns it **orange**. There is no change in oxidation number.

Reactions of aqueous ions with NaOH and ammonia

Hexaaqua ions, $[M(H_2O)_6]^{n+}$, are weakly acidic. Adding hydroxide **deprotonates** the water ligands, to form neutral hydroxide precipitates. Ammonia acts first as a base, then as a ligand in excess.

Ion	With a little NaOH(aq)	Excess NaOH	With a little NH_3(aq)	Excess NH_3
Cr^{3+} (green)	Green precipitate, $Cr(OH)_3$	**Dissolves** to a dark green solution, $[Cr(OH)_6]^{3-}$	Green precipitate	Dissolves slowly to a purple solution, $[Cr(NH_3)_6]^{3+}$
Mn^{2+} (pale pink)	Pale brown/buff precipitate (darkens in air)	Insoluble	Same	Insoluble
Fe^{2+} (pale green)	**Green** precipitate, $Fe(OH)_2$ (turns brown in air)	Insoluble	Same	Insoluble
Fe^{3+} (yellow)	**Brown** precipitate, $Fe(OH)_3$	Insoluble	Same	Insoluble
Co^{2+} (pink)	Blue then pink precipitate	Insoluble	Blue/pink precipitate	**Dissolves** to a brown/straw-coloured solution
Ni^{2+} (green)	Green precipitate	Insoluble	Green precipitate	**Dissolves** to a blue/violet solution, $[Ni(NH_3)_6]^{2+}$
Cu^{2+} (blue)	**Pale blue** precipitate, $Cu(OH)_2$	Insoluble	Pale blue precipitate	**Dissolves** to a deep blue solution, $[Cu(NH_3)_4(H_2O)_2]^{2+}$
Zn^{2+} (colourless)	**White** precipitate, $Zn(OH)_2$	**Dissolves**, $[Zn(OH)_4]^{2-}$	White precipitate	**Dissolves**, $[Zn(NH_3)_4]^{2+}$

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Equations

Deprotonation (acting as an acid):

$$[Cu(H_2O)_6]^{2+} + 2OH^- \rightarrow Cu(OH)_2(H_2O)_4 + 2H_2O$$

Amphoteric behaviour (reacting with both acid and base). Chromium(III) hydroxide dissolves in acid and in excess alkali:

$$Cr(OH)_3(H_2O)_3 + 3OH^- \rightarrow [Cr(OH)_6]^{3-} + 3H_2O$$

Ligand exchange (excess ammonia):

$$Cu(OH)_2(H_2O)_4 + 4NH_3 \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+} + 2OH^- + 2H_2O$$

> **Ligand exchanges to know:** $[Cu(NH_3)_4(H_2O)_2]^{2+}$ **from** $[Cu(H_2O)_6]^{2+}$ **via the hydroxide,** $[CuCl_4]^{2-}$ **from** $[Cu(H_2O)_6]^{2+}$ **with concentrated HCl, and** $[CoCl_4]^{2-}$ **from** $[Co(H_2O)_6]^{2+}$**.**

The coordination number of the copper(II) complex goes from 6 to 4 with chloride, but stays at 6 with ammonia (four NH_3 replace four of the water ligands and two water remain).

Catalysis by transition metals

Transition metals and their compounds are good catalysts because they have **variable oxidation states** and can form intermediates, and (for solid catalysts) have **surfaces** with partly filled d orbitals to bond reactants.

Heterogeneous catalysts

A **heterogeneous catalyst** is in a **different phase** from the reactants, with the reaction occurring at the **surface**.

1. Reactant molecules are **adsorbed** on to the surface.
2. Bonds in the reactants are **weakened**, and the reactants are brought close together in the right orientation.
3. Reaction occurs.
4. Product molecules **desorb**.

Vanadium(V) oxide in the **contact process**: V_2O_5 is **reduced** by sulfur dioxide, then **re-oxidised** by oxygen.

$$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4 \; 2V_2O_4 + O_2 \rightarrow 2V_2O_5$$

Vanadium goes from +5 to +4 and back, an example of variable oxidation numbers.

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Catalytic converters use platinum, palladium or rhodium on a ceramic honeycomb. CO and NO are adsorbed, react and the products CO_2 and N_2 are desorbed:

$$2CO + 2NO \rightarrow 2CO_2 + N_2$$

> **NOTE**
>
> A catalyst is **poisoned** when impurities (e.g. sulfur, or lead in leaded petrol) bond to the surface and block the active sites. Using a thin layer of metal on a large surface area reduces the cost.

Homogeneous catalysts

A **homogeneous catalyst** is in the **same phase** as the reactants and works through an **intermediate species**.

- Fe^{2+} **(or** Fe^{3+}**)** catalyses the reaction between iodide and peroxodisulfate ions: $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$. Both reactants are negative ions that repel, so reaction between them has a high activation energy. With the catalyst, each reaction is between oppositely charged ions:
  - $S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2SO_4^{2-} + 2Fe^{3+}$
  - $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$
- Mn^{2+} **autocatalyses** the reaction between MnO_4^- and ethanedioate ions, $C_2O_4^{2-}$. The reaction starts slowly, then speeds up as Mn^{2+} is formed in the reaction, and it is the **autocatalyst**. The rate–time graph shows an initial slow rate, then a sharp increase.

> **TRY IT**
>
> Explain why the reaction between MnO_4^- and $C_2O_4^{2-}$ is slow at first.

Both ions are negatively charged and repel each other, so few collisions have enough energy. As the reaction produces Mn^{2+} ions, they catalyse it (by forming Mn^{3+} as an intermediate), so the rate increases.

Core Practical 14: preparing a transition metal complex

A complex is made, for example **hexaamminenickel(II) chloride** or a **copper(II) complex**, by mixing solutions of the metal salt and ligand, **crystallising**, filtering under reduced pressure, **washing** with a small volume of cold solvent, and drying. The yield and purity are calculated and compared.

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