The Group Ib Elements (Cu, Ag, Au) and Their Principle Ions

Copper. Copper is reddish coloured metal, takes on a bright metallic luster, and is soft, malleable, ductile, and a good conductor of heat and electricity (second only to silver in electrical conductivity). It melts at 1083 °C. It is only superficially oxidised in air, sometimes acquiring a green coating of hydroxo carbonate and hydroxo sulphate.

Silver. Pure silver has a brilliant white metallic luster. It is a little harder than gold and is very ductile and malleable, being exceeded only by gold and perhaps palladium. Pure silver has the highest electrical and thermal conductivity of all metals. It melts at 962 °C. It is stable in pure air and water, but tarnishes when exposed to ozone, hydrogen sulphide, or air containing sulphur.

Gold. Gold is a heavy metal with its characteristic yellow colour when in a mass. In powderous form it is usually reddish-brown, but when finely divided it may be black, ruby, or purple. It melts at 1064 °C. Gold is the most malleable and ductile metal, it is soft and a good conductor of heat and electricity, and is unaffected by air and most reagents.

Solubility in acids and alkalis

Because of their positive standard electrode potential copper, silver, and gold are insoluble in hydrochloric acid and in dilute sulphuric acid.

Hot, concentrated sulphuric acid dissolves copper and silver, but gold is resistant against it.

\[
\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} + \text{SO}_2 \uparrow + 2\text{H}_2\text{O}
\]

\[
2\text{Ag} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{Ag}^+ + \text{SO}_4^{2-} + \text{SO}_2 \uparrow + 2\text{H}_2\text{O}
\]

Medium-concentrated (8M) nitric acid also dissolves copper and silver, but gold is resistant.

\[
3\text{Cu} + 8\text{HNO}_3 \rightarrow 3\text{Cu}^{2+} + 6\text{NO}_3^- + 2\text{NO} \uparrow + 4\text{H}_2\text{O}
\]

\[
6\text{Ag} + 8\text{HNO}_3 \rightarrow 6\text{Ag}^+ + 6\text{NO}_3^- + 2\text{NO} \uparrow + 4\text{H}_2\text{O}
\]

Aqua regia dissolves copper and gold:

\[
3\text{Cu} + 6\text{HCl} + 2\text{HNO}_3 \rightarrow 3\text{Cu}^{2+} + 6\text{Cl}^- + 2\text{NO} \uparrow + 4\text{H}_2\text{O}
\]

\[
\text{Au} + 4\text{HCl} + \text{HNO}_3 \rightarrow \text{H[AuCl}_4] + \text{NO} \uparrow + 2\text{H}_2\text{O}
\]
Silver and gold are resistant against alkalis.
Copper is hardly soluble in strong alkalis in the presence of oxygen, but it is soluble in concentrated ammonia solution in the presence of oxygen:

$$4 \text{Cu} + 8 \text{NH}_3 + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 4 \left[\text{Cu(NH}_3\right]_2^+ + 4 \text{OH}^-$$

Copper, silver, and gold is soluble in alkali cyanide solutions in the presence of oxygen:

$$4 \text{Cu} + 8 \text{KCN} + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 8 \text{K}^+ + 4 \left[\text{Cu(CN)}_2\right]^- + 4 \text{OH}^-$$

$$4 \text{Ag} + 8 \text{KCN} + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 8 \text{K}^+ + 4 \left[\text{Ag(CN)}_2\right]^- + 4 \text{OH}^-$$

$$4 \text{Au} + 8 \text{KCN} + 2 \text{H}_2\text{O} + \text{O}_2 \rightarrow 8 \text{K}^+ + 4 \left[\text{Au(CN)}_2\right]^- + 4 \text{OH}^-$$

<table>
<thead>
<tr>
<th>Compare the standard redox potentials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-Au$^{+}$ = +1.69 V</td>
</tr>
<tr>
<td>Au-Au$^{3+}$ = +1.50 V</td>
</tr>
<tr>
<td>NO-NO$^{3-}$ = +0.96 V</td>
</tr>
<tr>
<td>Au-[AuCl$_4$]$^- = +1.00$ V</td>
</tr>
<tr>
<td>Ag-Ag$^+$ = +0.80 V</td>
</tr>
<tr>
<td>Cu-Cu$^+$ = +0.52 V</td>
</tr>
<tr>
<td>OH$^-$-O$_2$ = +0.40 V</td>
</tr>
<tr>
<td>Cu-Cu$^{2+}$ = +0.34 V</td>
</tr>
<tr>
<td>H$_2$-H$^+$ = 0.0 V</td>
</tr>
<tr>
<td>Cu-[Cu(NH$_3$)$_2$]$^+$ = -0.12 V</td>
</tr>
<tr>
<td>Ag-[Ag(CN)$_2$]$^- = -0.31$ V</td>
</tr>
<tr>
<td>Cu-[Cu(CN)$_2$]$^- = -0.43$ V</td>
</tr>
<tr>
<td>Au-[Au(CN)$_2$]$^- = -0.60$ V</td>
</tr>
</tbody>
</table>

Summarise the solubility of selected elements in cold concentrated nitric acid:

<table>
<thead>
<tr>
<th></th>
<th>Au</th>
<th>Be</th>
<th>Al</th>
<th>C</th>
<th>Si</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>cc HNO$_3$</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Principal cations of copper, silver, and gold

<table>
<thead>
<tr>
<th></th>
<th>(Cu(^{+})) *</th>
<th>Ag(^{+})</th>
<th>(Au(^{+})) **</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td></td>
<td></td>
<td>Au(^{3+})</td>
</tr>
</tbody>
</table>

* Copper(I) ions are unstable in aqueous solution. Copper(I) compounds are colourless and most of them are insoluble in water.

** Au\(^{+}\) ions are exceedingly unstable with respect to the disproportionation to Au and Au\(^{3+}\).

*** The ion is unstable to water (reduced by water into Ag\(^{+}\)).

Oxides of copper, silver and gold

<table>
<thead>
<tr>
<th>oxide</th>
<th>Cu(_2)O</th>
<th>CuO</th>
<th>Ag(_2)O</th>
<th>AgO</th>
<th>Au(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>colour</td>
<td>red</td>
<td>black</td>
<td>brown</td>
<td>black</td>
<td>brown</td>
</tr>
</tbody>
</table>

Copper oxides are insoluble in water. CuO is soluble in acids, in NH\(_4\)Cl or KCN solutions. Cu\(_2\)O is soluble in hydrochloric acid, in ammonia, and in NH\(_4\)Cl solutions, slightly soluble in dilute nitric acid.

Silver oxides are soluble in nitric acid, in sulphuric acid, and also in ammonia solution. Ag\(_2\)O is slightly soluble in water (solubility at 20 °C is 0.0013 g/100 ml water) and its aqueous suspensions are alkaline. It is more soluble in strongly alkaline solutions than in water, and AgOH and Ag(OH)\(_2\)\(^{-}\) are formed. AgO is of little importance, it is actually Ag\(^{+}\)Ag\(^{III}\)O\(_2\).

Gold(III) oxide is of little importance. It is obtained in hydrated form as an amorphous brown precipitate on addition of base to AuCl\(_4\)\(^{-}\) solutions. It is weakly acidic and dissolves in excess strong base, probably as Au(OH)\(_4\)\(^{-}\). It is soluble in hydrochloric acid, in concentrated nitric acid, and in alkali cyanide solutions.

Reactions of copper(II) ions, Cu\(^{2+}\)

Solubility of the most common copper(II) compounds

Copper(II) chloride, chlorate, nitrate, and sulphate are soluble in water. Copper(II) acetate and fluoride are slightly soluble in water, and all the other compounds are practically insoluble.

E.g. at 20 °C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (g / 100 ml H(_2)O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl(_2)</td>
<td>170.6 (0 °C-on)</td>
</tr>
<tr>
<td>CuF(_2)</td>
<td>4.7</td>
</tr>
<tr>
<td>CuS</td>
<td>0.000033</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of copper(II) sulphate.
1. **Hydrogen sulphide gas:** black precipitate of copper(II) sulphide. Solubility product: $K_{sp}(\text{CuS}, 25^\circ\text{C}) = 1.27 \times 10^{-36}$.

\[
\text{Cu}^{2+} + \text{H}_2\text{S} \rightarrow \text{CuS} \downarrow + 2 \text{H}^+ 
\]

The solution must be acidic in order to obtain a crystalline, well-filterable precipitate.

The precipitate is insoluble in hydrochloric acid, in boiling dilute sulphuric acid, in sodium hydroxide, in ammonium sulphide, in sodium sulphide, and only very slightly soluble in polysulphides.

Hot, concentrated nitric acid dissolves the copper(II) sulphide, leaving behind sulphur as a white precipitate:

\[
3 \text{CuS} \downarrow + 8 \text{HNO}_3 \rightarrow 3 \text{Cu}^{2+} + 6 \text{NO}_3^- + 3 \text{S} \downarrow + 2 \text{NO} \uparrow + 4 \text{H}_2\text{O}
\]

When boiled for longer, sulphur is oxidised to sulphuric acid and a clear, blue solution is obtained:

\[
\text{S} \downarrow + 2 \text{HNO}_3 \rightarrow 2 \text{H}^+ + \text{SO}_4^{2-} + 2 \text{NO} \uparrow
\]

Potassium cyanide dissolves the precipitate, when colourless tetracyanocuprate(I) ions and disulphide ions are formed (copper is reduced, sulphur is oxidised):

\[
2 \text{CuS} \downarrow + 8 \text{CN}^- \rightarrow 2 [\text{Cu(CN)}_4]^{3-} + \text{S}_2^{2-}
\]

2. **Ammonia solution:** when added sparingly, a blue precipitate of basic copper sulphate is obtained:

\[
2 \text{Cu}^{2+} + \text{SO}_4^{2-} + 2 \text{NH}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Cu(OH)}_2\cdot\text{CuSO}_4 \downarrow + 2 \text{NH}_4^+
\]

the precipitate is soluble in excess reagent, when a deep blue coloration is obtained owing to the formation of tetraamminocuprate(II) complex ions:

\[
\text{Cu(OH)}_2\cdot\text{CuSO}_4 \downarrow + 8 \text{NH}_3 \rightarrow 2 [\text{Cu(NH}_3)_4]^{2+} + \text{SO}_4^{2-} + 2 \text{OH}^- 
\]

If the solution contains ammonium salts, precipitation does not occur at all, but the blue colour is formed right away. (The reaction is characteristic for copper(II) ions in the absence of nickel.)

3. **Sodium hydroxide in cold solution:** blue precipitate of copper(II) hydroxide:

\[
\text{Cu}^{2+} + 2 \text{OH}^- \rightarrow \text{Cu(OH)}_2 \downarrow
\]

The precipitate is insoluble in excess reagent, but soluble in ammonia solution when a deep blue coloration is obtained:

\[
\text{Cu(OH)}_2 \downarrow + 4 \text{NH}_3 \rightarrow [\text{Cu(NH}_3)_4]^{2+} + 2 \text{OH}^-
\]
When heated, the precipitate is converted to black copper(II) oxide by dehydration:

\[ \text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{O} \]

4. **Potassium iodide solution:** precipitates white copper(I) iodide (solubility product: \( K_{sp}(\text{CuI}, \ 25 \ ^\circ\text{C}) = 1.27 \times 10^{-12} \)), but the solution is intensely brown because of the formation of tri-iodide ions (iodine):

\[ 2 \text{Cu}^{2+} + 5 \text{I}^- \rightarrow 2 \text{CuI} \downarrow + \text{I}_3^- \]

Adding an excess of sodium thiosulphate to the solution, tri-iodide ions are reduced to colourless iodide ions and the white colour of the precipitate becomes visible:

\[ \text{I}_3^- + 2 \text{S}_2\text{O}_3^{2-} \rightarrow 3 \text{I}^- + \text{S}_4\text{O}_6^{2-} \]

5. **Potassium cyanide:** when added sparingly forms first a yellow precipitate of copper(II) cyanide:

\[ \text{Cu}^{2+} + 2 \text{CN}^- \rightarrow \text{Cu(CN)}_2 \downarrow \]

The precipitate quickly decomposes into white copper(I) cyanide and cyanogen (highly poisonous gas):

\[ 2 \text{Cu(CN)}_2 \rightarrow 2 \text{CuCN} + (\text{CN})_2 \]

The precipitate dissolves in excess reagent, when colourless tetracyanocuprate(I) complex is formed:

\[ \text{CuCN} + 3 \text{CN}^- \rightarrow [\text{Cu(CN)}_4]^{3-} \]

The complex is so stable (i.e. the concentration of copper(I) ions is so low) that hydrogen sulphide cannot precipitate copper(I) sulphide from this solution. (Solubility product: \( K_{sp}(\text{Cu}_2\text{S}, \ 25 \ ^\circ\text{C}) = 2.26 \times 10^{-48} \)).

6. **Potassium thiocyanate:** black precipitate of copper(II) thiocyanate.

\[ \text{Cu}^{2+} + 2 \text{SCN}^- \rightarrow \text{Cu(SCN)}_2 \downarrow \]

The precipitate decomposes slowly to form white copper(I) thiocyanate (Solubility product: \( K_{sp}(\text{CuSCN}, \ 25 \ ^\circ\text{C}) = 1.77 \times 10^{-13} \)):

\[ 2 \text{Cu(SCN)}_2 \rightarrow 2 \text{CuSCN} + (\text{SCN})_2 \]

Copper(II) thiocyanate can be transformed to copper(I) thiocyanate immediately by adding a suitable reducing agent; e.g. a saturated solution of sulphur dioxide:

\[ 2 \text{Cu(SCN)}_2 + \text{SO}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{CuSCN} + 2 \text{SCN}^- + \text{SO}_4^{2-} + 4 \text{H}^+ \]
8. **Iron:** if a clean iron nail is immersed in a solution of a copper salt, a red deposit of copper is obtained and equivalent amount of iron dissolves:

\[
\text{Cu}^{2+} + \text{Fe} \rightarrow \text{Cu} + \text{Fe}^{2+}
\]

The electrode potential of the copper-copper(II) system is more positive than that of the iron-iron(II) system.

9. **Flame test:** green colour is imparted to the Bunsen flame.

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**Compare the characteristic reactions of copper(II) and bismuth(III):**

<table>
<thead>
<tr>
<th></th>
<th>H₂S</th>
<th>NH₃ soln. in excess</th>
<th>NaOH</th>
<th>KI</th>
<th>Fe</th>
<th>flame test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu²⁺</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi³⁺</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

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**Reactions of silver(I) ions, Ag⁺**

*Solubility of the most common silver(I) compounds*

Silver nitrate, fluoride, chlorate, and perchlorate are readily soluble in water, silver acetate, nitrite, and sulphate are slightly soluble, while all the other silver compounds are practically insoluble.

E.g. at 0 °C:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (g / 100 ml H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgNO₃</td>
<td>122</td>
</tr>
<tr>
<td>Ag₂SO₄</td>
<td>0,57</td>
</tr>
<tr>
<td>AgI</td>
<td>0,0000002</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of silver(I) nitrate.

1. **Dilute hydrochloric acid (or soluble chlorides):** white precipitate of silver chloride. Solubility product: \(K_{sp}(\text{AgCl}, 25 \degree C) = 1.77 \times 10^{-10}\).

\[
\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl} \downarrow
\]

With concentrated hydrochloric acid precipitation does not occur. Decanting the liquid from over the precipitate, it dissolves in concentrated hydrochloric acid, when a dichloroargentate complex is formed:

\[
\text{AgCl} \downarrow + \text{Cl}^- \leftrightarrow [\text{AgCl}_2]^-
\]
By diluting with water, the equilibrium shifts back to the left and the precipitate reappears.

Dilute ammonia solution dissolves the precipitate when diamminargentate complex ion is formed:

\[
\text{AgCl} \downarrow + 2 \text{NH}_3 \leftrightarrow [\text{Ag(NH}_3)_2]^+ + \text{Cl}^-
\]

Dilute nitric acid or hydrochloric acid neutralises the excess ammonia, and the precipitate reappears because of the equilibrium is shifted back towards the left.

Potassium cyanide or sodium thiosulphate dissolves the AgCl precipitate:

\[
\text{AgCl} \downarrow + 2 \text{CN}^- \rightarrow [\text{Ag(CN)}_2]^- + \text{Cl}^-
\]
\[
\text{AgCl} \downarrow + 2 \text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag(S}_2\text{O}_3)_2]^{3-} + \text{Cl}^-
\]

2. **Hydrogen sulphide gas:** in neutral or acidic medium, black precipitate of silver sulphide. Solubility product: \(K_{sp}(\text{Ag}_2\text{S}, 25 \, ^\circ\text{C}) = 6.69 \times 10^{-50}\).

\[
2 \text{Ag}^+ + \text{H}_2\text{S} \rightarrow \text{Ag}_2\text{S} \downarrow + 2 \text{H}^+
\]

The precipitate is insoluble in ammonium sulphide, ammonium polysulphide, ammonia, potassium cyanide, or sodium thiosulphate. (Silver sulphide can be precipitated from solutions containing dicyanato- or dithiosulphato-argentate complexes with hydrogen sulphide.)

Hot, concentrated nitric acid decomposes the silver sulphide, and sulphur remains in the form of a white precipitate:

\[
3 \text{Ag}_2\text{S} \downarrow + 8 \text{HNO}_3 \rightarrow 6 \text{Ag}^+ + 6 \text{NO}_3^- + \text{S} \downarrow + 2 \text{NO} \uparrow + 4 \text{H}_2\text{O}
\]

If the mixture is heated with concentrated nitric acid for a considerable time, sulphur is oxidised to sulphate and the precipitate disappears:

\[
\text{S} \downarrow + 2 \text{HNO}_3 \rightarrow 2 \text{H}^+ + \text{SO}_4^{2-} + 2 \text{NO} \uparrow
\]

3. **Ammonia solution:** brown precipitate of silver oxide:

\[
2 \text{Ag}^+ + 2 \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O} \downarrow + 2 \text{NH}_4^+
\]

The reaction reaches an equilibrium and therefore precipitation is incomplete at any stage. The precipitate dissolves in diluted nitric acid and also in excess of the reagent:

\[
\text{Ag}_2\text{O} \downarrow + 2 \text{HNO}_3 \rightarrow 2 \text{Ag}^+ + 2 \text{NO}_3^- + \text{H}_2\text{O}
\]
\[
\text{Ag}_2\text{O} \downarrow + 4 \text{NH}_3 + \text{H}_2\text{O} \rightarrow 2 [\text{Ag(NH}_3)_2]^+ + 2 \text{OH}^-
\]
4. **Sodium hydroxide:** brown precipitate of silver oxide:

\[
2 \text{Ag}^+ + \text{OH}^- \rightarrow \text{Ag}_2\text{O} \downarrow + \text{H}_2\text{O}
\]

The precipitate is insoluble in excess reagent. The precipitate dissolves in ammonia solution or in nitric acid:

\[
\text{Ag}_2\text{O} \downarrow + 4 \text{NH}_3 + \text{H}_2\text{O} \rightarrow 2 [\text{Ag(NH}_3)_2]^+ + 2 \text{OH}^-
\]

\[
\text{Ag}_2\text{O} \downarrow + 2 \text{HNO}_3 \rightarrow 2 \text{Ag}^+ + 2 \text{NO}_3^- + \text{H}_2\text{O}
\]

A well-washed suspension of the precipitate shows a slight alkaline reaction owing to the hydrolysis equilibrium:

\[
\text{Ag}_2\text{O} \downarrow + \text{H}_2\text{O} \leftrightarrow 2 \text{AgOH} \downarrow \leftrightarrow 2 \text{Ag}^+ + 2 \text{OH}^-
\]

5. **Potassium iodide:** yellow precipitate of silver iodide. Solubility product: \(K_{sp}(\text{AgI}, 25 \, ^\circ\text{C})= 8.51 \times 10^{-17}\).

\[
\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI} \downarrow
\]

The precipitate is insoluble in dilute or concentrated ammonia, but dissolves readily in potassium cyanide or in sodium thiosulphate solution:

\[
\text{AgI} \downarrow + 2 \text{CN}^- \rightarrow [\text{Ag(CN)}_2]^- + \text{I}^-
\]

\[
\text{AgI} \downarrow + 2 \text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag(S}_2\text{O}_3)_2]^{3-} + \text{I}^-
\]

6. **Potassium chromate in neutral solution:** brownish-red precipitate of silver chromate. Solubility product: \(K_{sp}(\text{Ag}_2\text{CrO}_4, 25 \, ^\circ\text{C})= 1.12 \times 10^{-12}\).

\[
2 \text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4 \downarrow
\]

The precipitate is soluble in ammonia solution and in dilute nitric acid:

\[
\text{Ag}_2\text{CrO}_4 \downarrow + 4 \text{NH}_3 \rightarrow 2 [\text{Ag(NH}_3)_2]^+ + \text{CrO}_4^{2-}
\]

\[
2 \text{Ag}_2\text{CrO}_4 \downarrow + 2 \text{H}^+ \leftrightarrow 4 \text{Ag}^+ + \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}
\]

7. **Potassium cyanide solution:** when added dropwise to a neutral solution of silver nitrate, white precipitate of silver cyanide is formed. Solubility product: \(K_{sp}(\text{AgCN}, 25 \, ^\circ\text{C})= 5.97 \times 10^{-17}\).

\[
\text{Ag}^+ + \text{CN}^- \rightarrow \text{AgCN} \downarrow
\]

When potassium cyanide is added in excess, the precipitate disappears owing to the formation of dicyanoargentate ions:

\[
\text{AgCN} \downarrow + \text{CN}^- \rightarrow [\text{Ag(CN)}_2]^-
\]
8. **Sodium carbonate solution:** yellowish-white precipitate of silver carbonate. Solubility product: $K_{sp}(Ag_2CO_3, 25^{\circ}C) = 8.45 \times 10^{-12}$.

$$2 \text{Ag}^+ + 2 \text{CO}_3^{2-} \rightarrow \text{Ag}_2\text{CO}_3 \downarrow$$

Nitric acid and ammonia solution dissolve the precipitate:

$$\text{Ag}_2\text{CO}_3 \downarrow + 2 \text{HNO}_3 \rightarrow 2 \text{Ag}^+ + 2 \text{NO}_3^- + \text{CO}_2 \uparrow + \text{H}_2\text{O}$$

$$\text{Ag}_2\text{CO}_3 \downarrow + 4 \text{NH}_3 \rightarrow 2 [\text{Ag(NH}_3)_2]^+ + \text{CO}_3^{2-}$$

When heating, the silver carbonate precipitate decomposes and brown silver oxide precipitate is formed:

$$\text{Ag}_2\text{CO}_3 \downarrow \rightarrow \text{Ag}_2\text{O} \downarrow + \text{CO}_2 \uparrow$$

9. **Disodium hydrogen phosphate in neutral solution:** yellow precipitate of silver phosphate. $K_{sp}(Ag_3PO_4, 25^{\circ}C) = 8.88 \times 10^{-17}$.

$$3 \text{Ag}^+ + \text{HPO}_4^{2-} \rightarrow \text{Ag}_3\text{PO}_4 \downarrow + \text{H}^+$$

Nitric acid and ammonia solution dissolve the precipitate:

$$\text{Ag}_3\text{PO}_4 \downarrow + 3 \text{HNO}_3 \rightarrow 3 \text{Ag}^+ + 3 \text{NO}_3^- + \text{H}_3\text{PO}_4$$

$$\text{Ag}_3\text{PO}_4 \downarrow + 6 \text{NH}_3 \rightarrow 3 [\text{Ag(NH}_3)_2]^+ + \text{PO}_4^{3-}$$

**Fill in the following table:**

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Zn</th>
<th>Sn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag$^+$</td>
<td></td>
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</tr>
</tbody>
</table>

Standard redox potentials: Fe-Fe$^{2+}$ = -0.44 V; Zn-Zn$^{2+}$ = -0.76 V; Sn-Sn$^{2+}$ = -0.14 V; Cu-Cu$^{2+}$ = +0.34 V; Ag-Ag$^+$ = +0.80 V.
The Group IIb Elements (Zn, Cd, Hg) and Their Principle Ions

Zinc is a bluish-white, lustrous metal. It is brittle at ordinary temperatures, but malleable and ductile at 100 to 150 °C. It melts at 420 °C. It is a fair conductor of electricity, and burns in air at high red heat with evolution of white clouds of the oxide. Zinc is stable in air at ordinary conditions, because a protective zinc oxide and/or basic zinc carbonate layer forms on the surface.

Cadmium is a soft, malleable, ductile, and bluish-white metal which is easily cut with a knife. It melts at 321 °C. It is stable in air at ordinary conditions and it is similar in many respects to zinc.

Mercury is a heavy, silvery-white, liquid metal; it is the only common metal liquid at ordinary temperatures. It melts at −39 °C. It easily forms alloys with many metals, such as gold, silver, and tin, which are called amalgams. The chemistries of Zn and Cd are very similar, but that of Hg differs considerably and cannot be regarded as homologous.

Solubility in acids and alkalis

The very pure zinc metal dissolves very slowly in acids and in alkalis; the presence of impurities or contact with e.g. platinum or copper accelerates the reaction. This explains the good solubility of commercial zinc.

Zinc, owing to its negative standard electrode potential of −0.76 V, dissolves readily in dilute hydrochloric acid and in dilute sulphuric acid with the evolution of hydrogen:

$$\text{Zn} + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \uparrow$$

With hot, concentrated sulphuric acid, sulphur dioxide is evolved:

$$\text{Zn} + 2 \text{H}_2\text{SO}_4 \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} + \text{SO}_2 \uparrow + 2 \text{H}_2\text{O}$$

Zinc dissolves in very dilute nitric acid, when no gas is evolved:

$$4 \text{Zn} + 10 \text{H}^+ + \text{NO}_3^- \rightarrow 4 \text{Zn}^{2+} + \text{NH}_4^+ + 3 \text{H}_2\text{O}$$

With increasing concentration of nitric acid, dinitrogen oxide (N$_2$O) and nitric oxide (NO) are formed:

$$4 \text{Zn} + 10 \text{H}^+ + 2 \text{NO}_3^- \rightarrow 4 \text{Zn}^{2+} + \text{N}_2\text{O} \uparrow + 5 \text{H}_2\text{O}$$

$$3 \text{Zn} + 8 \text{HNO}_3 \rightarrow 3 \text{Zn}^{2+} + 2 \text{NO} \uparrow + 6 \text{NO}_3^{2-} + 4 \text{H}_2\text{O}$$

Concentrated nitric acid has little effect on zinc because of the low solubility of zinc nitrate in such a medium.
Cadmium dissolves slowly in dilute acids with the evolution of hydrogen, owing to its negative standard electrode potential of −0.40 V:

\[
\text{Cd} + 2 \text{H}^+ \rightarrow \text{Cd}^{2+} + \text{H}_2 \uparrow
\]

It dissolves in hot, concentrated sulphuric acid with the evolution of sulphur dioxide, and in medium concentrated nitric acid with the evolution of nitrogen monoxide.

Mercury, owing to its positive standard potential (Hg/Hg\(_{2+}\) = +0.85 V; Hg/Hg\(_{2+}\) = +0.80 V), is unaffected when treated with hydrochloric acid or dilute (2M) sulphuric acid.

Hot, concentrated sulphuric acid dissolves mercury. The product is mercury(I) ion if mercury is in excess, while if the acid is in excess, mercury(II) ions are formed:

\[
\begin{align*}
\text{Hg in excess:} & \quad 2 \text{Hg} + 2 \text{H}_2\text{SO}_4 \rightarrow \text{Hg}_2^{2+} + \text{SO}_4^{2-} + \text{SO}_2 \uparrow + 2 \text{H}_2\text{O} \\
\text{acid in excess:} & \quad \text{Hg} + 2 \text{H}_2\text{SO}_4 \rightarrow \text{Hg}^{2+} + \text{SO}_4^{2-} + \text{SO}_2 \uparrow + 2 \text{H}_2\text{O}
\end{align*}
\]

It reacts readily with nitric acid. Cold, medium concentrated (8M) nitric acid with an excess of mercury yields mercury(I) ions, and with an excess of hot concentrated nitric acid mercury(II) ions are formed:

\[
\begin{align*}
\text{Hg in excess:} & \quad 6 \text{Hg} + 8 \text{HNO}_3 \rightarrow 3 \text{Hg}_2^{2+} + 2 \text{NO} \uparrow + 6 \text{NO}_3^- + 4 \text{H}_2\text{O} \\
\text{acid in excess:} & \quad 3 \text{Hg} + 8 \text{HNO}_3 \rightarrow 3 \text{Hg}^{2+} + 2 \text{NO} \uparrow + 6 \text{NO}_3^- + 4 \text{H}_2\text{O}
\end{align*}
\]

Zinc dissolves in alkali hydroxides, when tetrahydroxozincate(II) is formed:

\[
\text{Zn} + 2 \text{OH}^- + 2 \text{H}_2\text{O} \rightarrow [\text{Zn(OH)}_4]^2- + \text{H}_2 \uparrow
\]

Cadmium and mercury is insoluble in alkalies.

### Summarise the solubility of selected metals in nitric acid.

<table>
<thead>
<tr>
<th>Ag</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>cold, concentrated HNO(_3)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>medium conc. (8M) HNO(_3)</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Oxides of zinc, cadmium, and mercury:

<table>
<thead>
<tr>
<th>ZnO</th>
<th>CdO</th>
<th>Hg₂O</th>
<th>HgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>white</td>
<td>brown</td>
<td>black</td>
<td>yellow or red</td>
</tr>
</tbody>
</table>

The oxides are practically insoluble in water; ZnO and HgO are a very little soluble, and the solubility at 25 °C is 0.00016 g and 0.0053 g/100 ml of water, respectively. CdO and Hg₂O are insoluble. They all are soluble in acids (Hg₂O only in nitric acid).

Principal cations of zinc, cadmium, and mercury

| Zn²⁺ | Cd²⁺ | Hg₂⁺ |

Reactions of zinc(II) ions, Zn²⁺

Solubility of the most common zinc compounds

Zinc(II) chloride, bromide, iodide, chlorate, nitrate, sulphate, and acetate are soluble in water. Zinc(II) fluoride is very little soluble in water, and all the other compounds (e.g. sulphide, carbonate, phosphate) are practically insoluble.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (g / 100 ml H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnBr₂</td>
<td>447</td>
</tr>
<tr>
<td>Zn(NO₃)₂.6H₂O</td>
<td>184.3</td>
</tr>
<tr>
<td>ZnF₂</td>
<td>1.62</td>
</tr>
<tr>
<td>ZnS (β)</td>
<td>0.000065</td>
</tr>
<tr>
<td>Zn(CN)₂</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of zinc(II) sulphate.

1. Hydrogen sulphide gas: no precipitation occurs in acidic solution (pH about 0–6), only partial precipitation of zinc sulphide in neutral solutions. In alkaline solution, e.g. adding alkali acetate, the precipitation of white zinc(II) sulphide (solubility product: K_{sp}(ZnS, 25 °C)= 2.93x10^{-25}) is almost complete.

   \[ \text{Zn}^{2+} + \text{H}_2\text{S} \rightarrow \text{ZnS} \downarrow + 2 \text{H}^+ \]

Zinc sulphide is also precipitated from alkaline solutions of tetrahydroxozincate:

   \[ [\text{Zn(OH)}_4]^{2-} + \text{H}_2\text{S} \rightarrow \text{ZnS} \downarrow + 2 \text{OH}^- + 2 \text{H}_2\text{O} \]

2. Ammonium sulphide: white precipitate of zinc sulphide from neutral or alkaline solutions:

   \[ \text{Zn}^{2+} + \text{S}^{2-} \rightarrow \text{ZnS} \downarrow \]
The precipitate is insoluble in excess reagent, in acetic acid, and in solutions of caustic alkalis, but dissolves in dilute mineral acids.

The precipitate obtained is partially colloidal; it is difficult to wash and tends to run through the filter paper, particularly on washing. To obtain the zinc sulphide in a form which can be ready filtered, the precipitation is carried out in boiling solution.

3. **Ammonia solution:** white precipitate of zinc hydroxide (solubility product: $K_{sp}(Zn(OH)_{2})$, 25 °C$= 6.86\times10^{-17}$), readily soluble in excess reagent and in solutions of ammonium salts owing to the formation of tetramminezincate(II):

$$Zn^{2+} + 2 NH_3 + 2 H_2O \leftrightarrow Zn(OH)_2 \downarrow + 2 NH_4^+$$

$$Zn(OH)_2 \downarrow + 4 NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+} + 2 OH^-$$

4. **Sodium hydroxide:** white gelatinous precipitate of zinc(II) hydroxide:

$$Zn^{2+} + 2 OH^- \leftrightarrow Zn(OH)_2 \downarrow$$

The precipitate is soluble in acids and also in the excess of the reagent:

$$Zn(OH)_2 \downarrow + 2 H^+ \leftrightarrow Zn^{2+} + 2 H_2O$$

$$Zn(OH)_2 \downarrow + 2 OH^- \leftrightarrow [Zn(OH)_4]^{2-}$$

5. **Disodium hydrogen phosphate solution:** white precipitate of zinc phosphate:

$$3 Zn^{2+} + 2 HPO_4^{2-} \leftrightarrow Zn_3(PO_4)_2 \downarrow + 2 H^+$$

In the presence of ammonium ions zinc ammonium phosphate is formed:

$$Zn^{2+} + NH_4^+ + HPO_4^{2-} \leftrightarrow Zn(NH_4)PO_4 \downarrow + H^+$$

Both precipitates are soluble in dilute acids, when the reaction is reversed. Also, both precipitates are soluble in ammonia:

$$Zn_3(PO_4)_2 \downarrow + 12 NH_3 \rightarrow 3 [Zn(NH_3)_4]^{2+} + 2 PO_4^{3-}$$

$$Zn(NH_4)PO_4 \downarrow + 3 NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + HPO_4^{2-}$$

6. **Potassium hexacyanoferrate(II) solution:** white precipitate of variable composition; if the reagent is added in some excess the composition of the precipitate is $K_2Zn_3[Fe(CN)_6]_2$:

$$3 Zn^{2+} + 2 K^+ + 2 [Fe(CN)_6]^{4-} \rightarrow K_2Zn_3[Fe(CN)_6]_2 \downarrow$$

The precipitate is insoluble in dilute acids, but dissolves readily in sodium hydroxide. This reaction can be used to distinguish zinc from aluminium.
7. **Dithizone test.** Dithizone (diphenyl thiocarbazone) forms complexes with a number of metal ions, which can be extracted with carbon tetrachloride. The zinc complex, formed in neutral, alkaline, or acetic acid solutions, is red:

\[
2 \text{S} = \text{C} \quad \text{NH} \quad \text{NH} \quad + \quad \text{Zn}^{2+} \quad \rightarrow \quad \text{S} = \text{C} \quad \text{NH} \quad \text{NN} \quad \text{Zn}^{2+} \quad \text{N} \quad \text{S} \quad \text{N} + 2 \text{H}^+ \]

Acidify the test solution with acetic acid, and add a few drops of the reagent (dithizone dissolved in carbon tetrachloride). The organic phase turns red in the presence of zinc. (Cu\(^{2+}\), Hg\(^{2+}\), Hg\(^{2+}\), and Ag\(^+\) ions interfere.)

**Summarise the reactions of selected metal ions with various anions.**

<table>
<thead>
<tr>
<th></th>
<th>F(^-)</th>
<th>Cl(^-)</th>
<th>Br(^-)</th>
<th>S(^2-)</th>
<th>SO(_4^{2-})</th>
<th>CrO(_4^{2-})</th>
<th>CO(_3^{2-})</th>
<th>OH(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(^{2+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al(^{3+})</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Ca(^{2+})</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reactions of cadmium(II) ions, Cd\(^{2+}\)**

**Solubility of the most common cadmium compounds**

Cadmium acetate, sulphate, nitrate, iodide, bromide, chloride, and chlorate are readily soluble in water, cadmium fluoride is little soluble, while all the other cadmium compounds (e.g. sulphide, carbonate, phosphate) are practically insoluble.
E.g.: 

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility ( g / 100 ml H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 20 °C:</td>
<td></td>
</tr>
<tr>
<td>CdCl₂</td>
<td>140</td>
</tr>
<tr>
<td>Cd(NO₃)₂</td>
<td>109</td>
</tr>
<tr>
<td>25 °C:</td>
<td></td>
</tr>
<tr>
<td>CdF₂</td>
<td>4.35</td>
</tr>
<tr>
<td>26 °C:</td>
<td></td>
</tr>
<tr>
<td>Cd(OH)₂</td>
<td>0.00026</td>
</tr>
<tr>
<td>Cd₃(PO₄)₂</td>
<td>----</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of cadmium(II) sulphate.

1. **Hydrogen sulphide gas:** in acidic medium, characteristic yellow precipitate of cadmium sulphide. Solubility product: \( K_{sp}(\text{CdS, 25 °C}) = 1.40 \times 10^{-29} \).

\[
\text{Cd}^{2+} + \text{H}_2\text{S} \rightarrow \text{CdS} \downarrow + 2 \text{H}^+ 
\]

The reaction is reversible; if the concentration of a strong acid in the solution is above 0.5M, precipitation is incomplete. Concentrated acids dissolve the precipitate for the same reason.

The precipitate is insoluble in potassium cyanide (difference from copper ions).

2. **Ammonia solution when added dropwise:** white precipitate of cadmium(II) hydroxide (Solubility product: \( K_{sp}(\text{Cd(OH)₂, 25 °C}) = 5.27 \times 10^{-15} \)):

\[
\text{Cd}^{2+} + 2 \text{NH}_3 + 2 \text{H}_2\text{O} \leftrightarrow \text{Cd(OH)₂} \downarrow + 2 \text{NH}_4^+ 
\]

The precipitate dissolves in acid when the equilibrium shifts towards the left.

An excess of the reagent dissolves the precipitate, when colourless tetramminecadminate(II) complex ions are formed:

\[
\text{Cd(OH)₂} \downarrow + 4 \text{NH}_3 \rightarrow [\text{Cd(NH}_3)_4]^{2+} + 2 \text{OH}^- 
\]

3. **Sodium hydroxide solution:** white precipitate of cadmium(II) hydroxide:

\[
\text{Cd}^{2+} + 2 \text{OH}^- \rightarrow \text{Cd(OH)₂} \downarrow 
\]

The precipitate is insoluble in excess reagent.

Dilute acids dissolve the precipitate.

4. **Potassium cyanide solution:** white precipitate of cadmium cyanide, when added slowly to the solution:

\[
\text{Cd}^{2+} + 2 \text{CN}^- \rightarrow \text{Cd(CN)₂} \downarrow 
\]

An excess of the reagent dissolves the precipitate, when tetracyanocadminate(II) ions are formed:

\[
\text{Cd(CN)₂} \downarrow + 2 \text{CN}^- \rightarrow [\text{Cd(CN)_4}]^{2-} 
\]

The colourless compound is not too stable; when hydrogen sulphide gas is introduced, cadmium sulphide is precipitated:
The marked difference in the stabilities of the copper and cadmium tetracyano complexes serves as the basis for the separation of copper and cadmium ions, and also for the identification of cadmium in the presence of copper.

5. **Potassium iodide**: forms no precipitate (difference from copper).

### Summarise the reactions of Cu\(^{2+}\), Cd\(^{2+}\), and Bi\(^{3+}\) ions

<table>
<thead>
<tr>
<th></th>
<th>Cu(^{2+})</th>
<th>Cd(^{2+})</th>
<th>Bi(^{3+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)S in acidic solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH(_3) in excess</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe nail</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Reactions of mercury(I) ions, Hg\(_2\)\(^{2+}\)

**Solubility of the most common mercury(I) compounds:**
Mercury(I) nitrate is soluble in water and tends to decompose. Other common inorganic salts are very slightly soluble or insoluble.

<table>
<thead>
<tr>
<th>E.g. at 25 °C:</th>
<th>Compound</th>
<th>Solubility (g / 100 ml H(_2)O)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hg(_2)SO(_4)</td>
<td>0,06</td>
</tr>
<tr>
<td></td>
<td>Hg(_2)CO(_3)</td>
<td>0,0000045</td>
</tr>
<tr>
<td></td>
<td>Hg(_2)Br(_2)</td>
<td>0,000004</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of mercury(I) nitrate.

1. **Dilute hydrochloric acid or soluble chlorides**: white precipitate of mercury(I) chloride (calomel). Solubility product: \(K_{sp}(\text{Hg}_2\text{Cl}_2, 25 \, ^\circ\text{C}) = 1.45 \times 10^{-18}\).
\[
\text{Hg}^{2+} + 2 \text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 \downarrow
\]

The precipitate is insoluble in dilute acids.

Ammonia solution converts the precipitate into a mixture of mercury(II) amidochloride and mercury metal, both insoluble precipitates; the mercury(II) amidochloride is a white precipitate, but the finely divided mercury makes it shiny black (disproportionation takes place; mercury(I) is converted partly to mercury(II) and partly to mercury metal):

\[
\text{Hg}_2\text{Cl}_2 \downarrow + 2 \text{NH}_3 \rightarrow \text{Hg} \downarrow + \text{Hg(NH}_2\text{)Cl} \downarrow + \text{NH}_4^+ + \text{Cl}^-
\]

This reaction can be used to differentiate mercury(I) ions from lead(II) and silver(I).

Mercury(II) chloride dissolves in aqua regia, forming undissociated but soluble mercury(II) chloride:

\[
3 \text{Hg}_2\text{Cl}_2 \downarrow + 2 \text{HNO}_3 + 6 \text{HCl} \rightarrow 6 \text{HgCl}_2 + 2 \text{NO} \uparrow + 4 \text{H}_2\text{O}
\]

2. **Hydrogen sulphide in neutral or dilute acid medium:** black precipitate, which is a mixture of mercury(II) sulphide and mercury metal:

\[
\text{Hg}^{2+} + \text{H}_2\text{S} \rightarrow \text{Hg} \downarrow + \text{HgS} \downarrow + 2 \text{H}^+
\]

Owing to the extremely low solubility product of mercury(II) sulphide \(6.44 \times 10^{-53}\) the reaction is very sensitive.

Aqua regia dissolves the precipitate, yielding undissociated mercury(II) chloride and sulphur:

\[
3 \text{Hg} \downarrow + 3 \text{HgS} \downarrow + 12 \text{HCl} + 4 \text{HNO}_3 \rightarrow 6 \text{HgCl}_2 + 3 \text{S} \downarrow + 4 \text{NO} \uparrow + 8 \text{H}_2\text{O}
\]

When heated with aqua regia, sulphur is oxidised to sulphuric acid and the solution becomes clear:

\[
\text{S} \downarrow + 6 \text{HCl} + 2 \text{HNO}_3 \rightarrow \text{SO}_4^{2-} + 6 \text{Cl}^- + 8 \text{H}^+ + 2 \text{NO} \uparrow
\]

3. **Ammonia solution:** black precipitate which is a mixture of mercury metal and basic mercury(II) amidonitrate, which itself is a white precipitate:

\[
2 \text{Hg}^{2+} + \text{NO}_3^- + 4 \text{NH}_3 + \text{H}_2\text{O} \rightarrow 2 \text{Hg} \downarrow + \text{HgO.Hg(NH}_2\text{)NO}_3 \downarrow + 3 \text{NH}_4^+
\]

This reaction can be used to differentiate between mercury(I) and mercury(II) ions.

4. **Sodium hydroxide:** black precipitate of mercury(I) oxide.

\[
\text{Hg}^{2+} + 2 \text{OH}^- \rightarrow \text{Hg}_2\text{O} \downarrow + \text{H}_2\text{O}
\]

The precipitate is insoluble in excess reagent, but dissolves readily in dilute nitric acid.

When boiling, the colour of the precipitate turns to grey, owing to disproportionation, when mercury(II) oxide and mercury metal are formed:

\[
\text{Hg}_2\text{O} \downarrow \rightarrow \text{HgO} \downarrow + \text{Hg} \downarrow
\]
5. **Potassium chromate in hot solution**: red crystalline precipitate of mercury(I) chromate:

\[
\text{Hg}_2^{2+} + \text{CrO}_4^{2-} \rightarrow \text{Hg}_2\text{CrO}_4 \downarrow
\]

If the test is carried out in cold, a brown amorphous precipitate is formed with an undefined composition. When heated the precipitate turns to red, crystalline mercury(I) chromate.

Sodium hydroxide turns the precipitate into black mercury(I) oxide:

\[
\text{Hg}_2\text{CrO}_4 \downarrow + 2 \text{OH}^- \rightarrow \text{Hg}_2\text{O} \downarrow + \text{CrO}_4^{2-} + \text{H}_2\text{O}
\]

6. **Potassium iodide, added slowly in cold solution**: green precipitate of mercury(I) iodide:

\[
\text{Hg}_2^{2+} + 2 \text{I}^- \rightarrow \text{Hg}_2\text{I}_2 \downarrow
\]

If excess reagent is added, a disproportionation reaction takes place, soluble tetraiodomercurate(II) ions and a black precipitate of finely divided mercury being formed:

\[
\text{Hg}_2\text{I}_2 \downarrow + 2 \text{I}^- \rightarrow [\text{HgI}_4]^{2-} + \text{Hg} \downarrow
\]

When boiling the mercury(I) iodide precipitate with water, disproportionation takes place again, and a mixture of red mercury(II) iodide precipitate and finely distributed black mercury is formed:

\[
\text{Hg}_2\text{I}_2 \downarrow \rightarrow \text{HgI}_2 \downarrow + \text{Hg} \downarrow
\]

7. **Sodium carbonate in cold solution**: yellow precipitate of mercury(I) carbonate (solubility product: \(K_{sp}(\text{Hg}_2\text{CO}_3, 25 \degree \text{C}) = 3.67 \times 10^{-17}\)):

\[
\text{Hg}_2^{2+} + \text{CO}_3^{2-} \rightarrow \text{Hg}_2\text{CO}_3 \downarrow
\]

The precipitate turns slowly to blackish grey, when mercury(II) oxide and mercury are formed:

\[
\text{Hg}_2\text{CO}_3 \downarrow \rightarrow \text{HgO} \downarrow + \text{Hg} \downarrow + \text{CO}_2 \uparrow
\]

The decomposition can be speeded up by heating the mixture.

8. **Disodium hydrogen phosphate**: white precipitate of mercury(I) hydrogen phosphate:

\[
\text{Hg}_2^{2+} + \text{HPO}_4^{2-} \rightarrow \text{Hg}_2\text{HPO}_4 \downarrow
\]

9. **Potassium cyanide solution**: produces mercury(II) cyanide solution and mercury precipitate:

\[
\text{Hg}_2^{2+} + 2 \text{CN}^- \rightarrow \text{Hg} \downarrow + \text{Hg(CN)}_2
\]

Mercury(II) cyanide, though soluble, is practically undissociated.
10. **Tin(II) chloride solution:** reduces mercury(I) ions to mercury metal, which appears in the form of a greyish-black precipitate:

\[
\text{Hg}_2^{2+} + \text{Sn}^{2+} \rightarrow 2 \text{Hg} \downarrow + \text{Sn}^{4+}
\]

11. **Copper sheet or copper coin:** deposit of mercury metal is formed on the copper surface.

\[
\text{Hg}_2^{2+} + \text{Cu} \rightarrow 2 \text{Hg} \downarrow + \text{Cu}^{2+}
\]

**Compare the reactions of mercury(I), silver(I), and lead(II) ions.**

<table>
<thead>
<tr>
<th></th>
<th>Hg$_2^{2+}$</th>
<th>Ag$^+$</th>
<th>Pb$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H$_2$S</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in excess</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td></td>
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<td></td>
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<tr>
<td>KI</td>
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<tr>
<td>in excess</td>
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<tr>
<td>NaOH</td>
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<td></td>
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<tr>
<td>Na$_2$CO$_3$</td>
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</tr>
<tr>
<td>K$_2$CrO$_4$</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cu</td>
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</tbody>
</table>
Reactions of mercury(II) ions, \( \text{Hg}^{2+} \)

**Solubility of the most common mercury(II) compounds:**

Mercury(II) nitrate is readily soluble in water; chloride, chlorate, cyanide, and acetate are also soluble, but their solubility is much less than that of nitrate. All the other mercury(II) compounds (e.g., sulphide, carbonate, iodide) are practically insoluble.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (g/100 ml H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>at 20 °C:</td>
<td></td>
</tr>
<tr>
<td>Hg(ClO₃)₂</td>
<td>25</td>
</tr>
<tr>
<td>10 °C:</td>
<td></td>
</tr>
<tr>
<td>Hg(Ac)₂</td>
<td>25</td>
</tr>
<tr>
<td>25 °C:</td>
<td></td>
</tr>
<tr>
<td>HgI₂ (α)</td>
<td>0,01</td>
</tr>
<tr>
<td>18 °C:</td>
<td></td>
</tr>
<tr>
<td>HgS (α)</td>
<td>0,000001</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of mercury(II) nitrate.

1. **Hydrogen sulphide gas:** black precipitate of mercury(II) sulphide. Solubility product constant: \( K_{\text{sp}}(\text{HgS}, 25 \, ^\circ \text{C}) = 6.44 \times 10^{-53} \).

   \[
   \text{Hg}^{2+} + \text{H}_2\text{S} \rightarrow \text{HgS} \downarrow + 2 \text{H}^+ \]

   In the presence of dilute hydrochloric acid, initially a white precipitate of mercury(II) chlorosulphide (\( \text{Hg}_3\text{S}_2\text{Cl}_2 \downarrow \)), which decomposes when further amounts of hydrogen sulphide are added and finally a black precipitate of mercury(II) sulphide is formed:

   \[
   3 \text{Hg}^{2+} + 2 \text{Cl}^- + 2 \text{H}_2\text{S} \rightarrow \text{Hg}_3\text{S}_2\text{Cl}_2 \downarrow + 4 \text{H}^+ \\
   \text{Hg}_3\text{S}_2\text{Cl}_2 \downarrow + \text{H}_2\text{S} \rightarrow 3 \text{HgS} \downarrow + 2 \text{H}^+ + 2 \text{Cl}^- 
   \]

   The HgS precipitate is insoluble in water, hot dilute nitric acid, alkali hydroxides, or ammonium sulphide.

   Aqua regia dissolves the precipitate:

   \[
   3 \text{HgS} \downarrow + 6 \text{HCl} + 2 \text{HNO}_3 \rightarrow 3 \text{HgCl}_2 + 3 \text{S} \downarrow + 2 \text{NO} \uparrow + 4 \text{H}_2\text{O} 
   \]

   Sulphur remains as a white precipitate, which however dissolves readily if the solution is heated, to form sulphuric acid.

   Sodium sulphide (2M) dissolves the HgS precipitate when the disulphomercurate(II) complex ion is formed:

   \[
   \text{HgS} \downarrow + \text{S}^{2-} \rightarrow [\text{HgS}_2]^{2-} 
   \]

   Adding ammonium chloride to the solution, mercury(II) sulphide precipitates again.

2. **Ammonia solution:** white precipitate with a mixed composition; essentially it consists of mercury(II) oxide and mercury(II) amidonitrate:

   \[
   2 \text{Hg}^{2+} + \text{NO}_3^- + 4 \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{HgO.Hg(NH}_3\text{)NO}_3 \downarrow + 3 \text{NH}_4^+ 
   \]
3. Sodium hydroxide (added in small amounts): brownish-red precipitate with varying composition; if added in stoichiometric amounts the precipitate turns to yellow when mercury(II) oxide is formed:

\[
\text{Hg}^{2+} + 2 \text{OH}^- \rightarrow \text{HgO} \downarrow + \text{H}_2\text{O}
\]

The precipitate is insoluble in excess sodium hydroxide. Acids dissolve the precipitate readily.

4. Potassium iodide (added slowly to the solution): red precipitate of mercury(II) iodide, \( K_{sp}(\text{HgI}_2, 25 \, ^\circ\text{C}) = 2.82 \times 10^{-29} \):

\[
\text{Hg}^{2+} + 2 \text{I}^- \rightarrow \text{HgI}_2 \downarrow
\]

The precipitate dissolves in excess reagent, when colourless tetraiodomercurate(II) ions are formed:

\[
\text{HgI}_2 \downarrow + 2 \text{I}^- \rightarrow [\text{HgI}_4]^{-}
\]

5. Tin(II) chloride: when added in moderate amounts, white, silky precipitate of mercury(I) chloride (calomel), \( K_{sp}(\text{Hg}_2\text{Cl}_2, 25 \, ^\circ\text{C}) = 1.45 \times 10^{-18} \), is formed:

\[
2 \text{Hg}^{2+} + \text{Sn}^{2+} + 2 \text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 \downarrow + \text{Sn}^{4+}
\]

If more reagent is added, mercury(I) chloride is further reduced and black precipitate of mercury is formed:

\[
\text{Hg}_2\text{Cl}_2 \downarrow + \text{Sn}^{2+} \rightarrow 2 \text{Hg} \downarrow + \text{Sn}^{4+} + 2 \text{Cl}^-
\]

6. Copper sheet or coin: reduces mercury(II) ions to the metal:

\[
\text{Cu} + \text{Hg}^{2+} \rightarrow \text{Hg} \downarrow + \text{Cu}^{2+}
\]

(Standard reduction potentials: \( \text{Cu}/\text{Cu}^{2+} = +0.3419 \, \text{V}; \text{Sn}^{2+}/\text{Sn}^{4+} = +0.151 \, \text{V}; \text{Hg}_2^{2+}/\text{Hg}^{2+} = +0.920 \, \text{V}; \text{Hg}/\text{Hg}^{2+} = +0.851 \, \text{V}; \text{Hg}/\text{Hg}_2^{2+} = +0.7973 \, \text{V} \))

<table>
<thead>
<tr>
<th>Reaction</th>
<th>HCl</th>
<th>H₂S</th>
<th>NH₃</th>
<th>NaOH</th>
<th>KI</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Hg}_2^{2+} )</td>
<td></td>
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<tr>
<td>( \text{Hg}^{2+} )</td>
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</tbody>
</table>
Compare the characteristic reactions of arsenic(III)(arsenite), antimony(III), tin(II), tin(IV), copper(II), cadmium(II), bismuth(III), and mercury(II) ions.

<table>
<thead>
<tr>
<th></th>
<th>As$^{3+}$</th>
<th>Sb$^{3+}$</th>
<th>Sn$^{2+}$</th>
<th>Sn$^{4+}$</th>
<th>Cu$^{2+}$</th>
<th>Cd$^{2+}$</th>
<th>Bi$^{3+}$</th>
<th>Hg$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
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<tr>
<td>H$_2$S</td>
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<tr>
<td>NaOH</td>
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<td>KI</td>
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<tr>
<td>NH$_3$</td>
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<tr>
<td>SnCl$_2$</td>
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<tr>
<td>Fe</td>
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</tr>
</tbody>
</table>
Titanium (Group IVb) and Its Common Ions

Titanium, when pure, is a lustrous, white metal. It has a low density, good strength, is easily fabricated, and has excellent corrosion resistance (melting point: 1660 °C). The metal is not attacked by mineral acids at room temperature or even by hot aqueous alkali.

**Solubility in acids**

The titanium metal is not soluble in mineral acids at room temperature, but soluble in hot, concentrated hydrochloric acid and sulphuric acid, and in hydrogen fluoride:

\[
2 \text{Ti} + 6 \text{HCl} \rightarrow 2 \text{Ti}^{3+} + 6 \text{Cl}^- + 3 \text{H}_2 \uparrow
\]

\[
\text{Ti} + 4 \text{H}_2\text{SO}_4 \rightarrow \text{Ti}^{4+} + 2 \text{SO}_4^{2-} + 2 \text{SO}_2 \uparrow + 4 \text{H}_2\text{O}
\]

The best solvents of the metal are HF and acids to which fluoride ions have been added; such media dissolve titanium and hold it in solution as fluoro complexes.

Titanium is insoluble in hot, concentrated nitric acid, like tin, because of the formation of titanic acid (TiO_2.xH_2O) on the surface of the metal, which protects the rest of the metal from the acid.

**Common cations of titanium** in aqueous solution

<table>
<thead>
<tr>
<th>Ti^{3+}</th>
<th>Ti^{4+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>violet</td>
<td>colourless</td>
</tr>
</tbody>
</table>

* Titanium(II) ions are not stable in aqueous solution; they liberate hydrogen gas from water (Ti^{3+/Ti^{4+}} = −0.369 V; Ti^{2+/Ti(OH)_2}^{2+} = −0.135 V).
** Titanium(III) ions are rather unstable and are readily oxidised to titanium(IV) in aqueous solutions, e.g. by air oxygen if exposed to air (Ti^{3+/Ti(OH)_2}^{2+} = +0.099 V).

The white titanium(IV) oxide, TiO_2, is used as a pigment and is far the most important titanium oxide, which occurs also in the nature. The solubility of TiO_2 depends considerably on its chemical and thermal history; strongly roasted specimens are chemically inert.

Titanium(IV) ions exist only in strongly acid solutions; they tend to hydrolyse. In strong acid the Ti^{4+} (aquated) ions are in equilibrium with Ti(OH)_2^{2+}, Ti(OH)_3^{+} and TiO^{2-} ions (aquated); the main species is Ti(OH)_2^{2+} and if the acidity of the solution is lowered titanium(IV) hydroxide is precipitated.
**Reactions of titanium(IV) ions. Ti⁴⁺**

To study these reactions use a 0.1 M solution of titanium(IV) sulphate, which is prepared by dissolving Ti(SO₄)₂ in 5 per cent sulphuric acid.

1. **Solutions of sodium hydroxide, ammonia or ammonium sulphide solution:** white gelatinous precipitate of titanium(IV) hydroxide, Ti(OH)₄ (or orthotitanic acid, H₄TiO₄), in the cold; this is almost insoluble in excess reagent, but soluble in mineral acids:

   \[\text{Ti(OH)}_2^{2+} + 2 \text{OH}^- \rightarrow \text{Ti(OH)}_4\downarrow\]
   \[\text{Ti(OH)}_4\downarrow + \text{H}_2\text{SO}_4 \rightarrow \text{Ti(OH)}_2^{2+} + 2 \text{H}_2\text{O} + \text{SO}_4^{2-}\]
   \[\text{Ti(OH)}_4\downarrow + 3 \text{HCl} \rightarrow \text{Ti(OH)}\text{Cl}^{2+} + 3 \text{H}_2\text{O} + 2 \text{Cl}^-\]

   If precipitation takes place from hot solution, white TiO(OH)₂ (or metatitanic acid, H₂TiO₃) is formed, which is sparingly soluble in dilute acids.

   \[\text{Ti(OH)}_2^{2+} + 2 \text{OH}^- \rightarrow \text{TiO(OH)}_2\downarrow + \text{H}_2\text{O}\]

2. **Water:** a white precipitate of metatitanic acid is obtained on boiling a solution of a titanic salt with excess water:

   \[\text{Ti(OH)}_2^{2+} + 2 \text{OH}^- \rightarrow \text{TiO(OH)}_2\downarrow + \text{H}_2\text{O}\]

3. **Sodium phosphate solution:** white precipitate of titanium(IV) phosphate in dilute sulphuric acid solution:

   \[\text{Ti(OH)}_2^{2+} + 2 \text{H}_2\text{PO}_4^- \rightarrow \text{Ti(HPO}_4)_2\downarrow + 2 \text{H}_2\text{O}\]

4. **Zinc or tin metal:** when any of these metals is added to an acid solution of a titanium(IV) salt, a violet coloration is produced, due to reduction to titanium(III) ions:

   \[2 \text{Ti}^{4+} + \text{Zn} \rightarrow 2 \text{Ti}^{3+} + \text{Zn}^{2+}\]

5. **Hydrogen peroxide.** An intense orange coloration is produced (yellow with very dilute solution), due to formation of stable peroxo complexes:

   \[\text{Ti(OH)}_2^{2+} + \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{Ti(O}_2\text{OH}^+ + 2 \text{H}_2\text{O}\]
Vanadium (Group Vb) and Its Common Ions

Vanadium is a bright, white metal, and is soft and ductile (melting point: 1890 °C). It has good corrosion resistance to alkalis, sulphuric and hydrochloric acid, and salt waters. The metal has good structural strength.

Solubility in acids

The vanadium metal is not soluble in hydrochloric, nitric, or sulphuric acids or in alkalis at room temperature due to passivation (thin protective oxide layer forms).

It dissolves readily in aqua regia, in hot nitric acid, hot and concentrated sulphuric acid, or in a mixture of concentrated nitric acid and hydrogen fluoride:

$$3 \text{V} + 4 \text{HNO}_3 + 6 \text{HCl} \rightarrow 3 \text{VO}^{2+} + 6 \text{Cl}^- + 4 \text{NO}_2 + 5 \text{H}_2\text{O}$$
$$3 \text{V} + 10 \text{HNO}_3 \rightarrow 3 \text{VO}^{2+} + 6 \text{NO}_3^- + 4 \text{NO}_2 + 5 \text{H}_2\text{O}$$
$$\text{V} + 3 \text{H}_2\text{SO}_4 \rightarrow \text{VO}^{2+} + \text{SO}_4^{2-} + 2 \text{SO}_2 + 3 \text{H}_2\text{O}$$

Common ions of vanadium in aqueous solutions

<table>
<thead>
<tr>
<th>oxidation state</th>
<th>cations</th>
<th>anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td>V$^{2+}$</td>
<td>VO$_4^{3-}$ vanadate</td>
</tr>
<tr>
<td>+3</td>
<td>V$^{3+}$</td>
<td>HVO$_4^{2-}$ monovanadate</td>
</tr>
<tr>
<td>+4</td>
<td>VO$^{2+}$</td>
<td>HV$_2$O$_7^{3-}$ divanadate</td>
</tr>
<tr>
<td>+5</td>
<td>VO$_2^+$</td>
<td>VO$_3^-$ metavanadate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V$<em>{10}$O$</em>{28}^-$ decavanadate</td>
</tr>
</tbody>
</table>

* The orange decavanadate ion can exist in several protonated form, and with increasing acidity of the solution rapidly gives the dioxygenvanadium(V) ion, VO$_2^+$. 

Vanadium(II) and vanadium(III) ions are stable in aqueous solution, and easily oxidised to vanadium(IV), due to their small standard reduction potentials:

$$[\text{VO}_2(\text{H}_2\text{O})_4]^+ \rightarrow [\text{VO}(\text{H}_2\text{O})_3]^{2+} \rightarrow [\text{V}(\text{H}_2\text{O})_6]^{3+} \rightarrow [\text{V}(\text{H}_2\text{O})_6]^{2+} \rightarrow \text{V}$$

$$\text{V}^{2+} \rightarrow \text{V}^{3+} \rightarrow \text{V}^{4+}$$

$$\text{V}^{2+} \rightarrow \text{V}^{3+} \rightarrow \text{V}^{4+}$$

$$\text{V}^{2+} \rightarrow \text{V}^{3+} \rightarrow \text{V}^{4+}$$

$$\text{V}^{2+} \rightarrow \text{V}^{3+} \rightarrow \text{V}^{4+}$$

$$\text{V}^{2+} \rightarrow \text{V}^{3+} \rightarrow \text{V}^{4+}$$

$$\text{V}^{2+} \rightarrow \text{V}^{3+} \rightarrow \text{V}^{4+}$$
Vanadium(V) oxide, $\text{V}_2\text{O}_5$, is the most stable and is far the most important vanadium oxide. It is an orange (or brick red) powder, which is insoluble in water, but soluble in both mineral acids and alkalis. Vanadium(V) is moderately strong oxidising agent, thus if the oxide is dissolved in hydrochloric acid chlorine gas is evolved and vanadium(IV) is produced. The oxide is also reduced by warm sulphuric acid. Vanadium pentoxide dissolves in sodium hydroxide to give colourless solutions and in the highly alkaline region, pH$\geq$13, the main ion is $\text{VO}_4^{3-}$. As the basicity is reduced, a series of complicated reactions occurs with the formation of various vanadates (mono, di, meta, deca, etc.).

Metavanadates, $\text{VO}_3^-$

To study these reactions use a 0.1 M solution of ammonium metavanadate, $\text{NH}_4\text{VO}_3$, or sodium metavanadate, $\text{NaVO}_3$. The addition of some sulphuric acid keeps these solutions stable.

1. **Hydrogen sulphide.** No precipitate is produced in acidic solution, but a blue solution (due to the production of vanadium(IV) ions) is formed and sulphur separates:

$$2 \text{VO}_3^- + \text{H}_2\text{S} + 6 \text{H}^+ \rightarrow 2 \text{VO}^{2+} + \text{S} \downarrow + 8 \text{H}_2\text{O}$$

2. **Zinc or aluminium acid solution.**

Zn and Al carry the reduction still further than $\text{H}_2\text{S}$. The solution turns at first blue ($\text{VO}_2^{2+}$ ions), then green ($\text{V}^{3+}$ ions) and finally violet ($\text{V}^{2+}$ ions). The redox potentials are:

$$\text{VO}_2^+/\text{VO}^{2+} = +0.999 \text{ V}$$
$$\text{V}^{3+}/\text{VO}_2^+ = +0.359 \text{ V}$$
$$\text{V}^{2+}/\text{V}^{3+} = -0.256 \text{ V}$$
$$\text{Zn}/\text{Zn}^{2+} = -0.762 \text{ V}$$

3. **Ammonium sulphide solution:** the solution is coloured claret-red, due to the formation of thiovanadates ($\text{VS}_4^{3-}$).

$$\text{VO}_3^- + 4 \text{S}^{2-} + 3 \text{H}_2\text{O} \rightarrow \text{VS}_4^{3-} + 6 \text{OH}^-$$

Upon acidification of the solution, brown vanadium sulphide, $\text{V}_2\text{S}_5$, is precipitated, and the filtrate usually has a blue colour:

$$2 \text{VS}_4^{3-} + 6 \text{H}^+ \rightarrow \text{V}_2\text{S}_5 \downarrow + 3 \text{H}_2\text{S} \uparrow$$

The precipitate is soluble in solutions of alkalis, alkali carbonates, and sulphides.
4. **Hydrogen peroxide:** A red coloration is produced when a few drops of hydrogen peroxide solution are added dropwise to an acid (15-20 per cent sulphuric acid) solution of a vanadate; excess hydrogen peroxide should be avoided. The red colour is due to the formation of the mono- and diperoxovanadium(V) ions, $\text{VO(O}_2\text{)}^+$ and $\text{VO(O}_2\text{)}_2^−$:

$$\begin{align*}
\text{VO}_3^- + 2 \text{H}^+ + \text{H}_2\text{O}_2 & \rightarrow \text{VO(O}_2\text{)}^+ + 2 \text{H}_2\text{O} \\
\text{VO}_3^- + 2 \text{H}_2\text{O}_2 & \rightarrow \text{VO(O}_2\text{)}_2^− + 2 \text{H}_2\text{O}
\end{align*}$$

If the solution is made alkaline and more hydrogen peroxide is added, the colour changes to yellow, due to the formation of diperoxoorthovanadate(V) ions:

$$\begin{align*}
\text{VO(O}_2\text{)}^+ + \text{H}_2\text{O}_2 + 4 \text{OH}^- & \rightarrow \text{VO}_2(\text{O}_2)\text{)}_2^3^- + 3 \text{H}_2\text{O} \\
\text{VO(O}_2\text{)}_2^− + 2 \text{OH}^- & \leftrightarrow \text{VO}_2(\text{O}_2)\text{)}_2^3^- + \text{H}_2\text{O}
\end{align*}$$

The reaction is reversible; on acidification the solution again turns red.

5. **Lead acetate solution:** yellow precipitate of lead vanadate, turning white or pale yellow on standing; the precipitate is insoluble in dilute acetic acid but soluble in dilute nitric acid.

6. **Barium chloride solution:** yellow precipitate of barium vanadate; soluble in dilute hydrochloric acid.

7. **Copper sulphate solution:** green precipitate with metavanadates.

8. **Iron(III) chloride:**

$$\text{VO}_3^- + 4 \text{H}^+ + \text{Fe}^{2+} \leftrightarrow \text{VO}^{2+} + \text{Fe}^{3+} + 2 \text{H}_2\text{O}$$

The reaction proceeds from left to right in acid solution and in the reverse direction in alkaline solution. ($\varepsilon(\text{Fe}^{2+}/\text{Fe}^{3+})= +0.771 \text{ V}$)
Chromium (Group VIb) and Its Common Ions

Chromium is a silver-white, lustrous, hard, and brittle metal that takes a high polish (melting point: 1857 °C). Chromium is extremely resistant to ordinary corrosive agents, which accounts for its extensive use as an electroplated protective coating.

Solubility in acids

The metal, if it is passivated (probably due to a thin protective oxide layer), is not soluble in mineral acids, but the metal is rather active when not passivated.

Redox potentials: $\varepsilon^\circ(Cr/Cr^{2+}) = -0.913 \, V$; $\varepsilon^\circ(Cr/Cr^{3+}) = -0.744 \, V$.

The chromium metal is soluble in dilute or concentrated hydrochloric acid. If air is excluded, chromium(II) ions are formed:

$$Cr + 2 \, HCl \rightarrow Cr^{2+} + 2 \, Cl^- + H_2$$

In the presence of atmospheric oxygen chromous(II) gets wholly oxidised to the tervalent state:

$$4 \, Cr^{2+} + O_2 + 4 \, H^+ \rightarrow 4 \, Cr^{3+} + 2 \, H_2O$$

Even if the solution is protected from air, chromium(II) ions decompose at rates varying with acidity, by reducing water with liberation of hydrogen ($\varepsilon^\circ(Cr^{2+}/Cr^{3+}) = -0.407 \, V$).

Chromium(II) ions are stable only in neutral and pure solutions at the exclusion of air.

Dilute sulphuric acid attacks chromous slowly, with the formation of hydrogen.

In hot, concentrated sulphuric acid chromium dissolves readily, when chromium(III) ions and sulphur dioxide are formed:

$$2 \, Cr + 6 \, H_2SO_4 \rightarrow 2 \, Cr^{3+} + 3 \, SO_4^{2-} + 3 \, SO_2 + 6 \, H_2O$$

Both dilute and concentrated nitric acid render chromium passive, as does cold, concentrated sulphuric acid and aqua regia.

<table>
<thead>
<tr>
<th>Principal cations and anions of chromium in aqueous solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cr$^{2+}$ chromous)*</td>
</tr>
<tr>
<td>Cr$^{3+}$ chromic</td>
</tr>
</tbody>
</table>

* chromium(II) ions are rather unstable, as they are strong reducing agents. Atmospheric oxygen oxidises them readily to chromium(III) ions.
The green chromium(III) oxide, \( \text{Cr}_2\text{O}_3 \), and its hydrous form, \( \text{Cr}_2\text{O}_3\cdot\text{nH}_2\text{O} \), are amphoteric, dissolving readily in acids and in concentrated alkali, but if ignited too strongly \( \text{Cr}_2\text{O}_3 \) becomes inert toward both acid and base.

**Chromate \( (\text{CrO}_4^{2-}) \) and dichromate \( (\text{Cr}_2\text{O}_7^{2-}) \) ions**

In basic solutions above pH 7, the yellow chromate ion \( \text{CrO}_4^{2-} \) is the main species; between pH 1 and 6, \( \text{HCrO}_4^- \) and the orange-red dichromate ion \( \text{Cr}_2\text{O}_7^{2-} \) are in equilibrium; and at pH<0 the main species are \( \text{H}_2\text{CrO}_4 \) and \( \text{HCr}_2\text{O}_7^- \).

The equilibria are the following:

\[
\begin{align*}
\text{H}_2\text{CrO}_4 & \rightleftharpoons \text{HCrO}_4^- + \text{H}^+ \\
\text{HCrO}_4^- & \rightleftharpoons \text{CrO}_4^{2-} + \text{H}^+ \\
2 \text{HCrO}_4^- & \rightleftharpoons \text{H}_2\text{O} + \text{Cr}_2\text{O}_7^{2-}
\end{align*}
\]

The chromates of the alkali metals and of magnesium and calcium are soluble in water. Strontium chromate is sparingly soluble in water, and most other metallic chromates are insoluble.

Sodium, potassium, and ammonium dichromates are well known and they are soluble in water.

**Reactions of chromium(III) ions, \( \text{Cr}^{3+} \)**

Chromium(III) sulphide, \( \text{Cr}_2\text{S}_3 \), like aluminium sulphide, can be prepared only in dry, because it hydrolyses readily with water to form chromium(III) hydroxide and hydrogen sulphide.
Hydrated chromium(III) sulphate, nitrate, chloride, bromide, iodide, and acetate are soluble in water. Chromium oxide, hydroxide, phosphate, and anhydrous halogenides (fluoride, chloride, bromide, iodide) are hardly soluble or not soluble in water.

E.g.:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (g / 100 ml H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂(SO₄)₃·18H₂O</td>
<td>120</td>
</tr>
<tr>
<td>CrCl₃·6H₂O</td>
<td>58.5</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>----</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of chromium(III) chloride CrCl₃ or chromium(III) sulphate Cr₂(SO₄)₃.

1. **Ammonia solution:** grey-green to grey-blue gelatinous precipitate of chromium(III) hydroxide, slightly soluble in excess of the reagent in the cold forming a violet or pink solution containing complex hexammine-chromate(III) ion; upon boiling the solution, chromium(III) hydroxide is precipitated. Hence for complete precipitation of chromium as the hydroxide, it is essential that the solution be boiling and excess aqueous ammonia solution be avoided.

\[
\text{Cr}^{3+} + 3 \text{NH}_3 + 3 \text{H}_2\text{O} \rightarrow \text{Cr(OH)}_3 + 3 \text{NH}_4^+ \\
\text{Cr(OH)}_3 + 6 \text{NH}_3 \rightarrow [\text{Cr(NH}_3)_6]^{3+} + 3 \text{OH}^- 
\]

2. **Sodium hydroxide solution:** precipitate of chromium(III) hydroxide:

\[
\text{Cr}^{3+} + 3 \text{OH}^- \rightarrow \text{Cr(OH)}_3 \\
\text{Cr(OH)}_3 + \text{OH}^- \leftrightarrow [\text{Cr(OH)}_4]^- 
\]

The solution is green. On adding hydrogen peroxide to the alkaline solution, a yellow solution is obtained, owing to the oxidation of chromium(III) to chromate:

\[
2 [\text{Cr(OH)}_4]^- + 3 \text{H}_2\text{O}_2 + 2 \text{OH}^- \rightarrow 2 \text{CrO}_4^{2-} + 8 \text{H}_2\text{O} 
\]

After decomposing the excess of hydrogen peroxide by boiling, chromate ions may be identified in the solution by one of their characteristic reactions.

3. **Sodium carbonate solution:** precipitate of chromium(III) hydroxide:

\[
2 \text{Cr}^{3+} + 3 \text{CO}_3^{2-} + 3 \text{H}_2\text{O} \rightarrow 2 \text{Cr(OH)}_3 + 3 \text{CO}_2 
\]

4. **Ammonium sulphide solution:** precipitate of chromium(III) hydroxide:

\[
2 \text{Cr}^{3+} + 3 \text{S}^{2-} + 6 \text{H}_2\text{O} \rightarrow 2 \text{Cr(OH)}_3 + 3 \text{H}_2\text{S} 
\]
5. **Chromate test.**
Chromium(III) ions can be oxidised to chromate, and than chromate ions can be identified on the basis of their characteristic reactions.

**Oxidation of chromium(III):** adding an excess of sodium hydroxide to a solution of chromium(III) salt followed by a few ml of hydrogen peroxide.

\[
2 \,[\text{Cr(OH)}_4]^- \, + \, 3 \, \text{H}_2\text{O}_2 \, + \, 2 \, \text{OH}^- \, \rightarrow \, 2 \, \text{CrO}_4^{2-} \, + \, 8 \, \text{H}_2\text{O}
\]

The excess of H\textsubscript{2}O\textsubscript{2} can be removed by boiling the mixture for a few minutes.

**Identification of chromium after oxidation to chromate:**

a. **Barium chloride test.**

After acidifying the solution with acetic acid and adding barium chloride solution, a yellow precipitate of barium chromate is formed:

\[
\text{Ba}^{2+} \, + \, \text{CrO}_4^{2-} \, \rightarrow \, \text{BaCrO}_4 \, \downarrow
\]

b. **Chromium pentoxide test.**

Acidifying the solution with dilute sulphuric acid, adding 2-3 ml of ether or amyl alcohol to the mixture and finally adding some hydrogen peroxide, a blue coloration is formed, which can be extracted into the organic phase by gently shaking. Chromium pentoxide is formed during the reaction:

\[
\text{CrO}_4^{2-} \, + \, 2 \, \text{H}^+ \, + \, 2 \, \text{H}_2\text{O}_2 \, \rightarrow \, \text{CrO}_5 \, + \, 3 \, \text{H}_2\text{O}
\]

In aqueous solution the blue colour fades rapidly, because chromium pentoxide decomposes to chromium(III) and oxygen.

**Reactions of chromate (\text{CrO}_4^{2-}) and dichromate (\text{Cr}_2\text{O}_7^{2-}) ions**

The chromates of metal ions are usually coloured solids, yielding yellow solutions when dissolved in water. In the presence of dilute mineral acids chromates are partially converted into dichromates; the latter yield orange-red aqueous solutions.

\[
2 \, \text{CrO}_4^{2-} \, + \, 2 \, \text{H}^+ \, \leftrightarrow \, \text{Cr}_2\text{O}_7^{2-} \, + \, \text{H}_2\text{O}
\]

To study the reactions of chromates and dichromates use a 0.1 M solution of potassium chromate and dichromate, respectively.

1. **Barium chloride solution:** pale-yellow precipitate of barium chromate, solubility product constant \(K_{sp}(\text{BaCrO}_4) = 1.17\times10^{-10} \):

\[
\text{CrO}_4^{2-} \, + \, \text{Ba}^{2+} \, \rightarrow \, \text{BaCrO}_4 \, \downarrow
\]

The precipitate is insoluble in water, sodium hydroxide, and acetic acid, but soluble in mineral acids.
Dichromate ions produce the same precipitate, but as strong acid is formed, precipitation is only partial:

\[ \text{Cr}_2\text{O}_7^{2-} + 2 \text{Ba}^{2+} + \text{H}_2\text{O} \leftrightarrow 2 \text{BaCrO}_4 \downarrow + 2 \text{H}^+ \]

2. **Silver nitrate solution:** brownish-red precipitate of silver chromate with a solution of a chromate, \( K_{sp}(\text{Ag}_2\text{CrO}_4) = 1.12 \times 10^{-12} \):

\[ \text{CrO}_4^{2-} + 2 \text{Ag}^+ \rightarrow \text{Ag}_2\text{CrO}_4 \downarrow \]

The precipitate is soluble in dilute nitric acid and in ammonia solution, but is insoluble in acetic acid. Hydrochloric acid converts the precipitate into silver chloride, \( K_{sp}(\text{AgCl}) = 1.77 \times 10^{-10} \):

\[
\begin{align*}
2 \text{Ag}_2\text{CrO}_4 \downarrow & + 2 \text{H}^+ \rightarrow 4 \text{Ag}^+ + \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \\
\text{Ag}_2\text{CrO}_4 \downarrow & + 4 \text{NH}_3 \rightarrow 2 [\text{Ag(NH}_3)_2]^+ + \text{CrO}_4^{2-} \\
\text{Ag}_2\text{CrO}_4 \downarrow & + 2 \text{Cl}^- \rightarrow 2 \text{AgCl} \downarrow + \text{CrO}_4^{2-}
\end{align*}
\]

A reddish-brown precipitate of silver dichromate is formed with a concentrated solution of a dichromate; this passes into the less soluble silver chromate on boiling with water:

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-} + 2 \text{Ag}^+ & \rightarrow \text{Ag}_2\text{Cr}_2\text{O}_7 \downarrow \\
\text{Ag}_2\text{Cr}_2\text{O}_7 \downarrow & + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{CrO}_4 \downarrow + \text{CrO}_4^{2-} + 2 \text{H}^+
\end{align*}
\]

3. **Lead acetate solution:** yellow precipitate of lead chromate, \( K_{sp}(\text{PbCrO}_4) = 1.77 \times 10^{-14} \):

\[ \text{CrO}_4^{2-} + \text{Pb}^{2+} \rightarrow \text{PbCrO}_4 \downarrow \]

The precipitate is insoluble in acetic acid, but soluble in dilute nitric acid and sodium hydroxide solution:

\[
\begin{align*}
2 \text{PbCrO}_4 \downarrow & + 2 \text{H}^+ \leftrightarrow 2 \text{Pb}^{2+} + \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \\
\text{PbCrO}_4 \downarrow & + 4 \text{OH}^- \leftrightarrow [\text{Pb(OH)}_4]^{2-} + \text{CrO}_4^{2-}
\end{align*}
\]

4. **Hydrogen peroxide.** (chromium pentoxide test; see above)

5. **Hydrogen sulphide:** an acid solution of a chromate is reduced by this reagent to a green solution of chromium(III) ions:

\[ 2 \text{CrO}_4^{2-} + 3 \text{H}_2\text{S} + 10 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 3 \text{S} \downarrow + 8 \text{H}_2\text{O} \]

6. **Potassium iodide solution:** chromate is reduced into chromium(III) in the presence of dilute mineral acids. Iodine formed in the reaction can be extracted with e.g. CCl₄, yielding a violet organic phase.

\[ 2 \text{CrO}_4^{2-} + 6 \text{I}^- + 16 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 3 \text{I}_2 + 8 \text{H}_2\text{O} \]
7. **Iron(II) sulphate**: reduces chromates or dichromates in the presence of mineral acid smoothly:

\[ \text{CrO}_4^{2-} + 3 \text{Fe}^{2+} + 8 \text{H}^+ \rightarrow \text{Cr}^{3+} + 3 \text{Fe}^{3+} + 4 \text{H}_2\text{O} \]

8. **Concentrated hydrochloric acid**: on heating a solid chromate or dichromate with concentrated hydrochloric acid, chlorine is evolved, and a solution containing chromium(III) ions is produced:

\[
\begin{align*}
2 \text{K}_2\text{CrO}_4 &+ 16 \text{HCl} \rightarrow 2 \text{Cr}^{3+} + 3 \text{Cl}_2 \uparrow + 4 \text{K}^+ + 10 \text{Cl}^- + 8 \text{H}_2\text{O} \\
\text{K}_2\text{Cr}_2\text{O}_7 &+ 14 \text{HCl} \rightarrow 2 \text{Cr}^{3+} + 3 \text{Cl}_2 \uparrow + 2 \text{K}^+ + 8 \text{Cl}^- + 7 \text{H}_2\text{O}
\end{align*}
\]

9. **Concentrated sulphuric acid and a chloride**: (see chromyl chloride test)

\[
\begin{align*}
\text{O} & \text{O} \\
\text{Cr} & \text{OH} + \text{HCl} \\
\text{O} & \text{O} \\
\text{OH} & \text{OH} + \text{HCl} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \text{O} \\
\text{Cr} & \text{Cl} + \text{HOH} \\
\text{O} & \text{O} \\
\text{Cl} & \text{Cl} + \text{HOH}
\end{align*}
\]

**Summarise the reactions of chromates.**

<table>
<thead>
<tr>
<th></th>
<th>(\text{Ag}^+)</th>
<th>(\text{Ba}^{2+})</th>
<th>(\text{Pb}^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CrO}_4^{2-}) solubility in acetic acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{HNO}_3) soln.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{NaOH}) soln.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{NH}_3) soln.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Manganese (Group VIIb) and Its Common Ions

Manganese is grey-white, resembling iron, but is harder and very brittle (melting point: 1244 °C). Manganese is roughly similar to Fe in its physical and chemical properties, the chief difference being that it is harder and more brittle. The metal is reactive, and slowly reacts even with cold water.

**Solubility in water and acids**

Due to its highly negative electrode potential \((\varepsilon^o(Mn/Mn(OH)_2)= -1.56 \text{ V})\), manganese reacts with water (the reaction is slow in the cold, but fast if the water is warm) forming manganese(II) hydroxide and hydrogen (there is no protective oxide layer, like in the case of chromium):

\[
\text{Mn} + 2 \text{H}_2\text{O} \rightarrow \text{Mn(OH)}_2 \downarrow + \text{H}_2 \uparrow
\]

Dilute mineral acids and also acetic acid dissolve the metal with the production of manganese(II) salts and hydrogen (\(\varepsilon^o(Mn/Mn^{2+})= -1.185 \text{ V})\):

\[
\text{Mn} + 2 \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2 \uparrow
\]

With hot, concentrated sulphuric acid, sulphur dioxide is evolved:

\[
\text{Mn} + \text{H}_2\text{SO}_4 \rightarrow \text{Mn}^{2+} + \text{SO}_4^{2-} + \text{SO}_2 \uparrow + 2 \text{H}_2\text{O}
\]

**Principal ions of manganese in aqueous solutions**

<table>
<thead>
<tr>
<th>oxidation state</th>
<th>cations</th>
<th>anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>+2</td>
<td>Mn(^{2+})</td>
<td>(MnO(^4-) or MnO(^3-))*</td>
</tr>
<tr>
<td>+3</td>
<td>(Mn(^{3+})*</td>
<td>(MnO(^4-) or MnO(^3-))*</td>
</tr>
<tr>
<td>+4</td>
<td>(Mn(^{4+})*</td>
<td>(MnO(^4-) or MnO(^3-))*</td>
</tr>
<tr>
<td>+5</td>
<td></td>
<td>(MnO(^4-) or MnO(^3-))*</td>
</tr>
<tr>
<td>+6</td>
<td></td>
<td>(MnO(^4-) or MnO(^3-))*</td>
</tr>
<tr>
<td>+7</td>
<td></td>
<td>MnO(^4-)***</td>
</tr>
</tbody>
</table>

* manganese(III) and manganese(IV) cations, and manganate(IV) anion are unstable in aqueous solutions, they are easily reduced to manganese(II).  
** unstable in aqueous solution, disproportionates to Mn(VII) and Mn(IV).  
*** stable in alkaline solutions, but upon neutralisation a disproportionation reaction takes place:

\[
3 \text{MnO}_4^{2-} + 2 \text{H}_2\text{O} \rightarrow \text{MnO}_2 \downarrow + 2 \text{MnO}_4^- + 4 \text{OH}^-
\]
Permanganate ions, $\text{MnO}_4^-$, can be reduced step by step, e.g. with perborate solution, to study the colour of the different oxidation state of manganese:

$$\begin{align*}
\text{MnO}_4^- & \quad \text{MnO}_4^{2-} \quad \text{MnO}_4^{3-} \quad \text{MnO}_4^{4-} \\
+0.564 \text{ V} & \quad +0.27 \text{ V}
\end{align*}$$

**Alkali permanganates**, $\text{MeMnO}_4$ ($\text{Me}=\text{metal ion}$), are stable compounds, producing violet coloured solutions. They are all strong oxidising agents, and are soluble in water.

**Manganese(II)** forms an extensive series of salts with all common anions. Most are soluble in water, although the phosphate and carbonate are only slightly so.

Five oxides of manganese are known so far:

<table>
<thead>
<tr>
<th>MnO</th>
<th>Mn$_2$O$_3$</th>
<th>MnO$_2$</th>
<th>Mn$_2$O$_7$</th>
<th>Mn$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>green</td>
<td>brown</td>
<td>black</td>
<td>reddish oil</td>
<td>reddish-brown</td>
</tr>
</tbody>
</table>

**MnO** is a grey-green to dark green powder, insoluble in water, but soluble in mineral acids.

**Mn$_2$O$_3$** is insoluble in water; it produces Mn(II) ions if treated with mineral acids. If hydrochloric acid or sulphuric acid is used, chlorine and oxygen are evolved, respectively:

$$\begin{align*}
\text{Mn}_2\text{O}_3 \downarrow + 6 \text{ HCl} & \rightarrow 2 \text{ Mn}^{2+} + \text{ Cl}_2 \uparrow + 4 \text{ Cl}^- + 3 \text{ H}_2\text{O} \\
2 \text{ Mn}_2\text{O}_3 \downarrow + 4 \text{ H}_2\text{SO}_4 & \rightarrow 4 \text{ Mn}^{2+} + \text{ O}_2 \uparrow + 4 \text{ SO}_4^{2-} + 4 \text{ H}_2\text{O}
\end{align*}$$

**MnO$_2$** is inert to most acids except when heated, but it does not dissolve to give Mn(IV) in solution; instead it functions as an oxidising agent, the exact manner of this depending on the acid. With concentrated hydrochloric or sulphuric acid, chlorine and oxygen gas are evolved, respectively, and manganese(II) ions are produced:

$$\begin{align*}
\text{MnO}_2 \downarrow + 4 \text{ HCl} & \rightarrow \text{ Mn}^{2+} + \text{ Cl}_2 \uparrow + 2 \text{ Cl}^- + 2 \text{ H}_2\text{O} \\
2 \text{ MnO}_2 \downarrow + 2 \text{ H}_2\text{SO}_4 & \rightarrow 2 \text{ Mn}^{2+} + \text{ O}_2 \uparrow + 2 \text{ SO}_4^{2-} + 2 \text{ H}_2\text{O}
\end{align*}$$

**Mn$_2$O$_7$** is an explosive oil, which can be extracted into CCl$_4$ in which it is reasonably stable and safe. It solidifies at 5 to 9 °C to red crystals.

**Mn$_3$O$_4$** is a spinel, Mn$^{III}$_Mn$^{II}_3$O$_4$ (MnO$_2$.Mn$_2$O$_3$). It is insoluble in water, but soluble in mineral acids.
Reactions of manganese(II) ions, Mn\(^{2+}\)

Manganese(II) sulphate, nitrate, chloride, bromide, and iodide are soluble in water. Other common inorganic manganese(II) compounds (e.g. phosphate and carbonate) are hardly soluble or insoluble in water.

<table>
<thead>
<tr>
<th>E.g.:</th>
<th>Compound</th>
<th>Solubility (g / 100 ml H(_2)O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 °C:</td>
<td>MnBr(_2)</td>
<td>127.3</td>
</tr>
<tr>
<td>25 °C:</td>
<td>MnCl(_2)</td>
<td>72.3</td>
</tr>
<tr>
<td>40 °C:</td>
<td>MnF(_2)</td>
<td>0.66</td>
</tr>
<tr>
<td>18 °C:</td>
<td>Mn(OH)(_2)</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of manganese(II) chloride or manganese(II) sulphate.

1. Sodium hydroxide solution: an initially white precipitate of manganese(II) hydroxide; solubility product constant, \(K_{sp}(\text{Mn(OH)}_2, 25 \, ^\circ\text{C})= 2.06 \times 10^{-13}\):

\[
\text{Mn}^{2+} + 2 \text{OH}^- \rightarrow \text{Mn(OH)}_2 \downarrow
\]

The precipitate is insoluble in excess reagent, but soluble in dilute acids.

The precipitate rapidly oxidises on exposure to air, becoming brown, when hydrated manganese dioxide, MnO\(_2\).yH\(_2\)O, is formed (\(\varepsilon^\circ(\text{Mn(OH)}_2/\text{MnO}_2)=-0.05 \, \text{V}\)):

\[
2 \text{Mn(OH)}_2 \downarrow + \text{O}_2 \rightarrow 2 \text{MnO}_2 \cdot \text{H}_2\text{O} \downarrow
\]

Hydrogen peroxide converts manganese(II) hydroxide rapidly into hydrated manganese dioxide:

\[
\text{Mn(OH)}_2 \downarrow + \text{H}_2\text{O}_2 \rightarrow \text{MnO}_2 \cdot \text{H}_2\text{O} \downarrow + \text{H}_2\text{O}
\]

2. Ammonia solution: partial precipitation of (initially) white manganese(II) hydroxide:

\[
\text{Mn}^{2+} + 2 \text{NH}_3 + 2 \text{H}_2\text{O} \leftrightarrow \text{Mn(OH)}_2 \downarrow + 2 \text{NH}_4^+
\]

The precipitate is soluble in ammonium salts, when the reaction proceeds towards the left.

3. Ammonium sulphide solution: pink precipitate of manganese(II) sulphide, solubility product constant, \(K_{sp}(\text{MnS}, 25 \, ^\circ\text{C})= 4.65 \times 10^{-14}\):

\[
\text{Mn}^{2+} + \text{S}^{2-} \rightarrow \text{MnS} \downarrow
\]

The precipitate is readily soluble in mineral acids and even in acetic acid.

\[
\text{MnS} \downarrow + 2 \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2\text{S} \uparrow
\]
4. **Disodium hydrogen phosphate solution:** in the presence of ammonia (or ammonium ions), pink precipitate of manganese ammonium phosphate:

\[
\text{Mn}^{2+} + \text{NH}_3 + \text{HPO}_4^{2-} \rightarrow \text{Mn(NH}_4\text{)}\text{PO}_4\downarrow
\]

If ammonium salts are absent, manganese(II) phosphate is formed:

\[
3 \text{Mn}^{2+} + 2 \text{HPO}_4^{2-} \rightarrow \text{Mn}_3(\text{PO}_4)_2\downarrow + 2 \text{H}^+
\]

The precipitates are soluble in acids.

5. **Sodium carbonate solution:** rose precipitate of manganese(II) carbonate, solubility product constant, \(K_{sp}(\text{MnCO}_3, 25 \degree C)= 2.24\times10^{-11}:\)

\[
\text{Mn}^{2+} + \text{CO}_3^{2-} \rightarrow \text{MnCO}_3\downarrow
\]

The precipitate is soluble in dilute mineral acids and even in acetic acid.

6. **Lead dioxide and concentrated nitric acid.** On boiling a dilute solution of manganese(II) ions, free from hydrochloric acid and chlorides, with lead dioxide and a little concentrated nitric acid, and then diluting somewhat and allowing the suspended solid containing unattacked lead dioxide to settle, the liquid acquires a violet-red (or purple) colour due to permanganic acid formed.

\[
5 \text{PbO}_2 + 2 \text{Mn}^{2+} + 4 \text{H}^+ \rightarrow 2 \text{MnO}_4^- + 5 \text{Pb}^{2+} + 2 \text{H}_2\text{O}
\]

**Permanganates, MnO_4^-**

To study these reactions use a 0.01 M solution of potassium permanganate, KMnO_4.

1. **Hydrogen peroxide.** The addition of this reagent to a solution of potassium permanganate, acidified with dilute sulphuric acid, results in decolourisation and the formation of pure but moist oxygen:

\[\varepsilon^\circ(\text{Mn}^{2+}/\text{MnO}_4^-)= +1.507 \text{ V} \]
\[\varepsilon^\circ(\text{H}_2\text{O}_2/\text{O}_2)= +0.695 \text{ V} \]

\[
2 \text{MnO}_4^- + 5 \text{H}_2\text{O}_2 + 6 \text{H}^+ \rightarrow 5 \text{O}_2 \uparrow + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}
\]

2. **Concentrated hydrochloric acid.** All permanganates on boiling with concentrated hydrochloric acid evolve chlorine.

\[\varepsilon^\circ(\text{Cl}^-/\text{Cl}_2)= +1.358 \text{ V} \]

\[
2 \text{MnO}_4^- + 16 \text{HCl} \rightarrow 5 \text{Cl}_2 \uparrow + 2 \text{Mn}^{2+} + 6 \text{Cl}^- + 8 \text{H}_2\text{O}
\]
3. **Hydrogen sulphide:** in the presence of dilute sulphuric acid the solution decolourizes and sulphur is precipitated: $\varepsilon^o(H_2S/S)= +0.142$ V

$$2 \text{MnO}_4^- + 5 \text{H}_2\text{S} + 6 \text{H}^+ \rightarrow 5 \text{S} \downarrow + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}$$

4. **Iron(II) sulphate solution:** in the presence of sulphuric acid permanganate is reduced to manganese(II). $\varepsilon^o(\text{Fe}^{2+}/\text{Fe}^{3+})= +0.771$ V

$$\text{MnO}_4^- + 5 \text{Fe}^{2+} + 8 \text{H}^+ \rightarrow 5 \text{Fe}^{3+} + \text{Mn}^{2+} + 4 \text{H}_2\text{O}$$

The solution becomes yellow because of the formation of iron(III) ions. The yellow colour disappears if potassium fluoride is added; it forms colourless complex with iron(III).

5. **Potassium iodide solution:** reduces permanganate with the formation of iodine, in the presence of sulphuric acid.

$$2 \text{MnO}_4^- + 10 \Gamma^- + 16 \text{H}^+ \rightarrow 5 \text{I}_2 + 2 \text{Mn}^{2+} + 8 \text{H}_2\text{O}$$

In alkaline solution the permanganate is decolourized, but manganese dioxide is precipitated. In the presence of sodium hydroxide solution, potassium iodide is converted into potassium iodate.

$$2 \text{MnO}_4^- + \Gamma^- + \text{H}_2\text{O} \rightarrow 2 \text{MnO}_2 \downarrow + \text{IO}_3^- + 2 \text{OH}^-$$

6. **Sodium hydroxide solution.** Upon warming a concentrated solution of potassium permanganate with concentrated sodium hydroxide solution, a green solution of potassium manganate is produced and oxygen is evolved. $\varepsilon^o(\text{MnO}_4^{2-}/\text{MnO}_4^-)= +0.564$ V $\varepsilon^o(\text{OH}^-/\text{O}_2)= +0.401$ V

$$4 \text{MnO}_4^- + 4 \text{OH}^- \rightarrow 4 \text{MnO}_4^{2-} + \text{O}_2 \uparrow + 2 \text{H}_2\text{O}$$

When the manganate solution is poured into a large volume of water or is acidified with dilute sulphuric acid, the purple colour of the potassium permanganate is restored, and manganese dioxide is precipitated. $\varepsilon^o(\text{MnO}_4^{2-}/\text{MnO}_2)= +0.60$ V

$$3 \text{MnO}_4^{2-} + 2 \text{H}_2\text{O} \rightarrow 2 \text{MnO}_4^- + \text{MnO}_2 \downarrow + 4 \text{OH}^-$$
Summarise the reactions of $\text{CrO}_4^{2-}$, $\text{Cr}_2\text{O}_7^{2-}$, and $\text{MnO}_4^-$ ions.

<table>
<thead>
<tr>
<th></th>
<th>$\text{CrO}_4^{2-}$</th>
<th>$\text{Cr}_2\text{O}_7^{2-}$</th>
<th>$\text{MnO}_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>colour</strong> (alkali metal salt)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>$\text{H}_2\text{S}$</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>acid solution</td>
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<tr>
<td><strong>$\text{H}_2\text{O}_2$</strong></td>
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<tr>
<td>acid solution</td>
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</tr>
<tr>
<td><strong>$\text{KI}$</strong></td>
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<td>acid solution</td>
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<tr>
<td><strong>$\text{FeSO}_4$</strong></td>
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<td>acid solution</td>
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</tr>
<tr>
<td><strong>cc $\text{HCl}$</strong></td>
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</tr>
</tbody>
</table>
The Group VIIIb Elements (Fe, Co, Ni) and Their Principle Ions

Iron is a relatively abundant element in the universe. Its nuclei are very stable. The metal is the fourth most abundant element on earth, by weight, making up the crust of the earth. The use of iron is prehistoric. Iron is a vital constituent of plant and animal life, and appears in haemoglobin.

The chemically pure iron is a silver-white, tenacious, and ductile metal. It melts at 1535 °C. The pure metal is very reactive chemically, and rapidly corrodes, especially in moist air or at elevated temperatures. Iron can be magnetised. It has four allotropic forms, from which only the α-form is magnetic.

The commercial iron is rarely pure and usually contains small quantities of carbide, silicide, phosphide, and sulphide of iron, and some graphite. These contaminants play an important role in the strength of iron structures. Other additives such as nickel, chromium, vanadium, etc. are also used to produce alloy steels. Iron is the cheapest and most abundant, useful, and important of all metals.

Cobalt is a steel-grey, slightly magnetic, brittle, and hard metal, closely resembling iron and nickel in appearance. Melting point is 1495 °C.

Nickel is silvery white and takes on a high polish. It is hard, malleable, ductile, very tenacious, somewhat ferromagnetic, and a fair conductor of heat and electricity. It melts at 1453 °C. It is quite resistant to attack by air or water at ordinary temperatures when compact.

Solubility in acids

Dilute or concentrated hydrochloric acid and dilute sulphuric acid dissolve iron, cobalt, and nickel, when iron(II), cobalt(II), and nickel(II) salts and hydrogen gas are produced.

\[
\begin{align*}
\text{Fe} + 2\text{H}^+ & \rightarrow \text{Fe}^{2+} + \text{H}_2 \uparrow & \varepsilon^{\circ}(\text{Fe}/\text{Fe}^{2+}) &= -0.447 \text{ V} \\
\text{Co} + 2\text{H}^+ & \rightarrow \text{Co}^{2+} + \text{H}_2 \uparrow & \varepsilon^{\circ}(\text{Co}/\text{Co}^{2+}) &= -0.28 \text{ V} \\
\text{Ni} + 2\text{H}^+ & \rightarrow \text{Ni}^{2+} + \text{H}_2 \uparrow & \varepsilon^{\circ}(\text{Ni}/\text{Ni}^{2+}) &= -0.257 \text{ V}
\end{align*}
\]

Hot, concentrated sulphuric acid yields iron(III), cobalt(II), and nickel(II) ions and sulphur dioxide:

\[
\begin{align*}
2\text{Fe} + 3\text{H}_2\text{SO}_4 + 6\text{H}^+ & \rightarrow 2\text{Fe}^{3+} + 3\text{SO}_2 \uparrow + 6\text{H}_2\text{O} \\
\text{Co} + \text{H}_2\text{SO}_4 + 2\text{H}^+ & \rightarrow \text{Co}^{2+} + \text{SO}_2 \uparrow + 2\text{H}_2\text{O} \\
\text{Ni} + \text{H}_2\text{SO}_4 + 2\text{H}^+ & \rightarrow \text{Ni}^{2+} + \text{SO}_2 \uparrow + 2\text{H}_2\text{O}
\end{align*}
\]

Cold, concentrated nitric acid and sulphuric acid renders iron passive.
Cold, dilute nitric acid, yields iron(II) and ammonium ions:

\[ 4 \text{Fe} + 10 \text{H}^+ + \text{NO}_3^- \rightarrow 4 \text{Fe}^{2+} + \text{NH}_4^+ + 3 \text{H}_2\text{O} \]

Medium concentrated nitric acid, or hot, concentrated nitric acid dissolves iron with the formation of nitrogen oxide gas and iron(III) ions:

\[ \text{Fe} + \text{HNO}_3 + 3 \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{NO} \uparrow + 2 \text{H}_2\text{O} \]

Dilute nitric acid dissolve cobalt and nickel readily in cold:

\[ 3 \text{Co} + 2 \text{HNO}_3 + 6 \text{H}^+ \rightarrow 3 \text{Co}^{2+} + 2 \text{NO} \uparrow + 4 \text{H}_2\text{O} \]
\[ 3 \text{Ni} + 2 \text{HNO}_3 + 6 \text{H}^+ \rightarrow 3 \text{Ni}^{2+} + 2 \text{NO} \uparrow + 4 \text{H}_2\text{O} \]

Like iron, cobalt and nickel does not dissolve in concentrated nitric acid because it is rendered passive by this reagent.

### Principal cations of iron, cobalt, and nickel

<table>
<thead>
<tr>
<th></th>
<th>Fe$^{2+}$</th>
<th>Fe$^{3+}$</th>
<th>Co$^{2+}$</th>
<th>Ni$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Co$^{3+}$)*</td>
<td></td>
</tr>
</tbody>
</table>

* Cobalt(III) ions are unstable in water, but their complexes are stable both in solution and in dry form.

### Oxides of iron, cobalt, and nickel

<table>
<thead>
<tr>
<th></th>
<th>FeO* black</th>
<th>CoO olive-green</th>
<th>NiO green</th>
<th>Fe$_2$O$_3$ red</th>
<th>Co$_2$O$_3$ brown-black</th>
<th>Ni$_2$O$_3$ **</th>
<th>Fe$_3$O$_4$ red-brown</th>
<th>Co$_3$O$_4$ black</th>
<th>Ni$_3$O$_4$ ***</th>
</tr>
</thead>
</table>

* FeO is not stable under 560 °C; disproportionates to Fe and Fe$_3$O$_4$. It is also easily oxidised by air oxygen.  
** There is no good evidence for Ni$_2$O$_3$. The black NiO(OH), however, is well known.  
*** Ni$_3$O$_4$ is not known, only a Ni$^{II}$Ni$^{III}$ hydroxide of stoichiometry Ni$_3$O$_2$(OH)$_4$.

**Iron(III) oxide**, Fe$_2$O$_3$, is soluble in dilute acids at room temperature, but if heated too strongly it is almost insoluble even in hot concentrated hydrochloric acid.  
**Iron(II,III) oxide**, Fe$_3$O$_4$=Fe$^{II}$Fe$_2^{III}$O$_4$, is very resistant to attack by acids and alkalis.

**Cobalt(II) oxide**, CoO, and **cobalt(III) oxide**, Co$_2$O$_3$, are soluble in mineral acids.  
**Cobalt(II,III) oxide**, Co$_3$O$_4$=Co$^{II}$Co$_2^{III}$O$_4$, is very slightly soluble in mineral acids.

Reactions of iron(II) ions, Fe$^{2+}$

Solubility of the most common iron(II) compounds

The chloride, bromide, iodide, chlorate, perchlorate, nitrate, sulphate, and acetate are soluble in water. The fluoride is very slightly soluble, and oxide, carbonate, sulphide, and phosphate are practically insoluble.

E.g.: Compound | Solubility (g / 100 ml H$_2$O)
--- | ---
FeCl$_2$ | 64.4
FeBr$_2$ | 109
Fe(OH)$_2$ | 0.00015
FeCO$_3$ | 0.0067

To study these reactions use a 0.1 M solution of iron(II) sulphate or iron(II) ammonium sulphate (Mohr’s salt).

1. Sodium hydroxide solution: white precipitate of iron(II) hydroxide in the complete absence of air, solubility product constant $K_{sp}$(Fe(OH)$_2$, 25°C)$= 4.87 \times 10^{-17}$, insoluble in excess of the reagent, but soluble in acids. Upon exposure to air, iron(II) hydroxide is rapidly oxidised, yielding ultimately reddish-brown iron(III) hydroxide, $K_{sp}$(Fe(OH)$_3$, 25°C)$= 2.64 \times 10^{-39}$.

Under ordinary conditions it appears as a dirty-green precipitate; the addition of hydrogen peroxide immediately oxidises it to iron(III) hydroxide.

$$Fe^{2+} + 2 OH^- \rightarrow Fe(OH)_2 \downarrow$$
$$4 Fe(OH)_2 \downarrow + 2 H_2O + O_2 \rightarrow 4 Fe(OH)_3 \downarrow$$
$$2 Fe(OH)_2 \downarrow + H_2O_2 \rightarrow 2 Fe(OH)_3 \downarrow$$


$$Fe^{2+} + 2 NH_3 + 2 H_2O \rightarrow Fe(OH)_2 \downarrow + 2 NH_4^+$$

If, however, larger amounts of ammonium ions are present, precipitation does not occur.

3. Hydrogen sulphide: no precipitation takes place in acid solution since the sulphide ion concentration is insufficient to exceed the solubility product of iron(II) sulphide.

4. Ammonium sulphide solution: black precipitate of iron(II) sulphide FeS, $K_{sp}$(FeS, 25°C)$= 1.59 \times 10^{-19}$:

$$Fe^{2+} + S^{2-} \rightarrow FeS \downarrow$$

FeS is readily soluble in acids with evolution of hydrogen sulphide.

The moist precipitate becomes brown upon exposure to air, due to its oxidation to basic iron(III) sulphate Fe$_2$O(SO$_4$)$_2$. 

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\[ \text{FeS} \downarrow + 2 \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{S} \uparrow \]
\[4 \text{FeS} \downarrow + 9 \text{O}_2 \rightarrow 2 \text{Fe}_2\text{O(SO}_4)_2 \downarrow\]

5. **Potassium hexacyanoferrate(II) solution:** in the complete absence of air a white precipitate of potassium iron(II) hexacyanoferrate(II) is formed:

\[\text{Fe}^{2+} + 2 \text{K}^+ + [\text{Fe(CN)}_6]^{4-} \rightarrow \text{K}_2\text{Fe[Fe(CN)}_6 \downarrow\]

under ordinary atmospheric conditions a pale-blue precipitate is obtained.

6. **Potassium hexacyanoferrate(III) solution:** a dark-blue precipitate is obtained. First hexacyanoferrate(II) and iron(III) is formed from hexacyanoferrate(III) and iron(II) ions according to the following equilibrium,

\[\text{Fe}^{2+} + [\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} \leftrightarrow \text{Fe}^{3+} + [\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}\]

and than these ions combine to a precipitate called Turnbull’s blue:

\[4 \text{Fe}^{3+} + 3 [\text{Fe(CN)}_6]^{4-} \rightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 \downarrow\]

The structure of Turnbull’s blue is based on a three-dimensional cubic framework with Fe\text{II} and Fe\text{III} atoms at the corners of a cube and with Fe\text{II}–N-C-Fe\text{III} links.

Note, that the composition of this precipitate is identical to that of Prussian blue (see below at the reaction of iron(III) ions).

7. **Ammonium thiocyanate solution:** no coloration is obtained with pure iron(II) salts (distinction from iron(III) ions).

8. **Dimethylglyoxime reagent:** soluble red iron(II) dimethylglyoxime in ammoniacal solution. Iron(III) salts give no coloration, but nickel, cobalt, and large quantities of copper salts interfere and must be absent.
Reactions of iron(III) ions, Fe$^{3+}$

Solubility of the most common iron(III) compounds

The chloride, bromide, iodide, chlorate, perchlorate, nitrate and sulphate are soluble in water.
The fluoride is very slightly soluble, and oxide, carbonate, sulphide, and phosphate are practically insoluble.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (g / 100 ml H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeCl$_3$</td>
<td>74.4</td>
</tr>
<tr>
<td>Fe(NO$_3$)$_3$.6H$_2$O</td>
<td>150</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>-----</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of iron(III) chloride FeCl$_3$.

1. Sodium hydroxide solution: reddish-brown, gelatinous precipitate of iron(III) hydroxide, $K_{sp}$(Fe(OH)$_3$, 25°C)$= 2.64\times10^{-39}$, insoluble in excess of the reagent, but soluble in acids.

$$Fe^{3+} + 3 OH^- \rightarrow Fe(OH)_3 \downarrow$$

Iron(III) hydroxide can be converted on strong heating to iron(III) oxide; the heated oxide is soluble with difficulty in dilute acids, but dissolves on vigorous boiling with concentrated hydrochloric acid.

$$2 Fe(OH)_3 \downarrow \rightarrow Fe_2O_3 + 3 H_2O$$

$$Fe_2O_3 + 6 H^+ \rightarrow 2 Fe^{3+} + 3 H_2O$$

2. Ammonia solution: reddish-brown, gelatinous precipitate of iron(III) hydroxide, insoluble in excess of the reagent, but soluble in acids.

$$Fe^{3+} + 3 NH_3 + 3 H_2O \rightarrow Fe(OH)_3 \downarrow + 3 NH_4^+$$

The solubility product of iron(III) hydroxide is so small ($2.64\times10^{-39}$) that complete precipitation takes place even in the presence of ammonium salts.

3. Hydrogen sulphide: in acidic solution reduces iron(III) ions to iron(II) and sulphur is formed as a milky-white precipitate:

$$\varepsilon^{\circ}(Fe^{2+}/Fe^{3+})= +0.771 \text{ V}$$

$$\varepsilon^{\circ}(H_2S/ S)= +0.142 \text{ V}$$

$$2 Fe^{3+} + H_2S \rightarrow 2 Fe^{2+} + 2 H^+ + S \downarrow$$

The finely distributed sulphur cannot be readily filtered with ordinary filter papers.

By boiling the solution with a few torn pieces of filter paper the precipitate coagulates and can be filtered.

4. Ammonium sulphide solution: black precipitate, consisting of iron(II) sulphide and sulphur is formed:

$$2 Fe^{3+} + 3 S^{2-} \rightarrow 2 FeS \downarrow + S \downarrow$$
The black iron(II) sulphide precipitate dissolves in hydrochloric acid and the white colour of sulphur becomes visible:

\[
\text{FeS} \downarrow + 2 \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{S} \uparrow
\]

From alkaline solutions black iron(III) sulphide is obtained:

\[
2 \text{Fe}^{3+} + 3 \text{S}^{2-} \rightarrow \text{Fe}_2\text{S}_3 \downarrow
\]

On acidification with hydrochloric acid iron(III) ions are reduced to iron(II) and sulphur is formed:

\[
\text{Fe}_2\text{S}_3 \downarrow + 4 \text{H}^+ \rightarrow 2 \text{Fe}^{2+} + 2 \text{H}_2\text{S} \uparrow + \text{S} \downarrow
\]

6. **Potassium hexacyanoferrate(II) solution:** intense blue precipitate of iron(III) hexacyanoferrate(II) (Prussian blue):

\[
4 \text{Fe}^{3+} + 3 [\text{Fe(CN)}_6]^{4-} \rightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3
\]

The precipitate is insoluble in dilute acids, but decomposes with concentrated hydrochloric acid. A large excess of the reagent dissolves it partly or entirely, when an intense blue solution is obtained.

7. **Potassium hexacyanoferrate(III) solution:** a brown coloration is produced, due to the formation of an undissociated complex, iron(III) hexacyanoferrate(III):

\[
\text{Fe}^{3+} + [\text{Fe(CN)}_6]^{3-} \rightarrow \text{Fe}[\text{Fe(CN)}_6]
\]

Upon adding some tin(II) chloride solution, the hexacyanoferrate(III) part of the compound is reduced and Prussian blue is precipitated.

8. **Ammonium thiocyanate solution:** in slightly acidic solution a deep-red colouration is produced (difference from iron(II) ions), due to the formation of a non-dissociated iron(III) thiocyanate:

\[
\text{Fe}^{3+} + 3 \text{SCN}^- \rightarrow \text{Fe(SCN)}_3
\]

This molecule can be extracted by ether or amyl alcohol. Fluorides and phosphates bleach the colour because of the formation of the more stable hexafluoro and triphosphato complexes:

\[
\text{Fe(SCN)}_3 + 6 \text{F}^- \rightarrow [\text{FeF}_6]^{3-} + 3 \text{SCN}^-
\]

\[
\text{Fe(SCN)}_3 + 3 \text{PO}_4^{3-} \rightarrow [\text{Fe(PO}_4)_3]^{6-} + 3 \text{SCN}^-
\]

Upon addition of SnCl\(_2\) solution in excess, the red colour disappears due to the reduction of iron(III) to iron(II):

\[
2 \text{Fe(SCN)}_3 + \text{Sn}^{2+} \rightarrow 2 \text{Fe}^{2+} + \text{Sn}^{4+} + 3 \text{SCN}^-
\]
9. *Disodium hydrogen phosphate solution:* a yellowish-white precipitate of iron(III) phosphate is formed, $K_{sp}(\text{FePO}_4\cdot2\text{H}_2\text{O}, 25^\circ\text{C})= 9.92\times10^{-29}$:

$$\text{Fe}^{3+} + \text{HPO}_4^{2-} \rightarrow \text{FePO}_4 \downarrow + \text{H}^+$$

**Summarise the reactions of iron cations with hexacyanoferrates.**

<table>
<thead>
<tr>
<th></th>
<th>$[\text{Fe(CN)}_6]^{4-}$</th>
<th>$[\text{Fe(CN)}_6]^{3-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Fe}^{3+}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Reactions of cobalt(II) ions, $\text{Co}^{2+}$**

*Solubility of the most common cobalt(II) compounds*

The chloride, bromide, iodide, chlorate, perchlorate, nitrate, sulphate, and acetate are soluble in water.
The fluoride is very slightly soluble, and oxide, hidroxide, carbonate, sulhide, and phosphate are practically insoluble.

E.g.:  

<table>
<thead>
<tr>
<th></th>
<th>Compound</th>
<th>Solubility ( g / 100 ml H$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 °C:</td>
<td>$\text{CoCl}_2$</td>
<td>45</td>
</tr>
<tr>
<td>20 °C:</td>
<td>$\text{CoSO}_4$</td>
<td>36,2</td>
</tr>
<tr>
<td>25 °C:</td>
<td>$\text{CoF}_2$</td>
<td>1,5</td>
</tr>
<tr>
<td></td>
<td>$\text{Co(OH)}_2$</td>
<td>0,00032</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of cobalt(II) chloride or cobalt(II) nitrate.

1. *Sodium hydroxyde solution:* in cold a blue basic salt is precipitated:

$$\text{Co}^{2+} + \text{OH}^- + \text{NO}_3^- \rightarrow \text{Co(OH)NO}_3 \downarrow$$

Upon warming with excess alkali (or sometimes merely upon addition of excess reagent) the basic salt is converted into pink cobalt(II) hydroxide precipitate $K_{sp}(\text{Co(OH)}_2, 25^\circ\text{C})= 1.09\times10^{-15}$.
The hydroxide is slowly transformed into the brownish black cobalt(III) hydroxide on exposure to the air:

\[
4 \text{Co(OH)}_2 \downarrow + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{Co(OH)}_3 \downarrow
\]

Cobalt(II) hydroxide precipitate is readily soluble in ammonia or concentrated solutions of ammonium salts.

2. **Ammonia solution:** in the absence of ammonium salts small amounts of ammonia precipitate the basic salt:

\[
\text{Co}^{2+} + \text{NH}_3 + \text{H}_2\text{O} + \text{NO}_3^- \rightarrow \text{Co(OH)}\text{NO}_3 \downarrow + \text{NH}_4^+
\]

The excess of the reagent dissolves the precipitate, when hexamminocobaltate(II) ions are formed:

\[
\text{Co(OH)}\text{NO}_3 \downarrow + 6 \text{NH}_3 \rightarrow [\text{Co(NH}_3)_6]^{2+} + \text{NO}_3^- + \text{OH}^-
\]

The precipitation of the basic salt does not take place at all if larger amounts of ammonium ions are present, but the complex is formed in one step.

3. **Ammonium sulphide solution:** black precipitate of cobalt(II) sulphide from neutral or alkaline solution:

\[
\text{Co}^{2+} + \text{S}^{2-} \rightarrow \text{CoS} \downarrow
\]

The precipitate is insoluble in hydrochloric or acetic acids. Hot, concentrated nitric acid or aqua regia dissolve the precipitate, when white sulphur remains:

\[
3 \text{CoS} \downarrow + 2 \text{HNO}_3 + 6 \text{H}^+ \rightarrow 3 \text{Co}^{2+} + 3 \text{S} \downarrow + 2 \text{NO} \uparrow + 4 \text{H}_2\text{O}
\]

\[
\text{CoS} \downarrow + \text{HNO}_3 + 3 \text{HCl} \rightarrow \text{Co}^{2+} + \text{S} \downarrow + \text{NOCl} \uparrow + 2 \text{Cl}^- + 2 \text{H}_2\text{O}
\]

On longer heating the mixture becomes clear because sulphur gets oxidised to sulphate.

The CoS precipitate dissolves also in the 1+1 mixture of concentrated acetic acid and 30% hydrogen peroxide:

\[
\text{CoS} \downarrow + 4 \text{H}_2\text{O}_2 \rightarrow \text{Co}^{2+} + \text{SO}_4^{2-} + 4 \text{H}_2\text{O}
\]

4. **Potassium nitrite solution:** yellow precipitate of potassium hexanitrito-cobaltate(III), K₃[Co(NO₂)₆].3H₂O:

\[
\text{Co}^{2+} + 7 \text{NO}_2^- + 2 \text{H}^+ + 3 \text{K}^+ \rightarrow K_3[\text{Co(NO}_2)_6] \downarrow + \text{NO} \uparrow + \text{H}_2\text{O}
\]
The test can be carried out most conveniently as follows: to a neutral solution of cobalt(II) add acetic acid, than a freshly prepared saturated solution of potassium nitrite.

5. **Ammonium thiocyanate test:** adding a few crystals of ammonium thiocyanate to a neutral or acidic solution of cobalt(II) a blue colour appears owing to the formation of tetrathiocyanatocobaltate(II) ions:

\[
Co^{2+} + 4 SCN^{-} \rightarrow [Co(SCN)_{4}]^{2-}
\]

If amyl alcohol or ether is added the free acid H₂[Co(SCN)₄] is formed and dissolved by the organic solvent.

\[
2 H^{+} + [Co(SCN)_{4}]^{2-} \leftrightarrow H_{2}[Co(SCN)_{4}]
\]

The test is rendered more sensitive if the solution is acidified with concentrated hydrochloric acid, when the equilibrium shifts towards the formation of the free acid.

**Reactions of nickel(II) ions, Ni²⁺**

*Solubility of the most common nickel compounds*

The chloride, bromide, iodide, chlorate, perchlorate, nitrate, sulphate, and acetate are soluble in water.

The fluoride is very slightly soluble, and oxide, carbonate, sulphide, and phosphate are practically insoluble.

<table>
<thead>
<tr>
<th>E.g.:</th>
<th>Compound</th>
<th>Solubility (g / 100 ml H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 °C:</td>
<td>NiCl₂</td>
<td>64,2</td>
</tr>
<tr>
<td>0 °C:</td>
<td>NiI₂</td>
<td>124,2</td>
</tr>
<tr>
<td>25 °C:</td>
<td>NiF₂</td>
<td>4</td>
</tr>
<tr>
<td>25 °C:</td>
<td>NiCO₃</td>
<td>0,0093</td>
</tr>
</tbody>
</table>

To study these reactions use a 0.1 M solution of nickel(II) sulphate or nickel(II) chloride.

1. **Sodium hydroxyde solution:** green precipitate of nickel(II) hydroxide, solubility product constant, Kₚₛ[Ni(OH)₂, 25 °C]= 5.47x10⁻¹⁶:

\[
Ni^{2+} + 2 OH^- \rightarrow Ni(OH)_{2} \downarrow
\]

The precipitate is insoluble in excess reagent. Ammonia solution dissolves the precipitate; in the presence of excess alkali hydroxide ammonium salts also dissolve the precipitate:
$\text{Ni(OH)}_2 \downarrow + 6 \text{NH}_3 \rightarrow [\text{Ni(NH}_3)_6]^{2+} + 2 \text{OH}^-$

$\text{Ni(OH)}_2 \downarrow + 6 \text{NH}_4^+ + 4 \text{OH}^- \rightarrow [\text{Ni(NH}_3)_6]^{2+} + 6 \text{H}_2\text{O}$

The green nickel(II) hydroxide precipitate can be oxidised to black nickel(III) hydroxide with sodium hypochlorite solution:

$$2 \text{Ni(OH)}_2 \downarrow + \text{ClO}^- + \text{H}_2\text{O} \rightarrow 2 \text{Ni(OH)}_3 \downarrow + \text{Cl}^-$$

Hydrogen peroxide solution, however, does not oxidise nickel(II) hydroxide, but the precipitate catalyses the decomposition of hydrogen peroxide to oxygen and water without any other visible change.

2. **Ammonia solution:** green precipitate of nickel(II) hydroxide:

$$\text{Ni}^{2+} + 2 \text{NH}_3 + 2 \text{H}_2\text{O} \rightarrow \text{Ni(OH)}_2 \downarrow + 2 \text{NH}_4^+$$

which dissolves in excess reagent:

$$\text{Ni(OH)}_2 \downarrow + 6 \text{NH}_3 \rightarrow [\text{Ni(NH}_3)_6]^{2+} + 2 \text{OH}^-$$

the solution turns deep blue. If ammonium salts are present, no precipitation occurs, but the complex is formed immediately.

3. **Ammonium sulphide solution:** black precipitate of nickel sulphide, from neutral or slightly alkaline solutions, $K_{sp}$(NiS, 25 °C)= 1.07x10$^{-21}$:

$$\text{Ni}^{2+} + \text{S}^{2-} \rightarrow \text{NiS} \downarrow$$

If the reagent is added in excess, a dark-brown colloidal solution is formed which runs through the filter paper. If the colloidal solution is boiled, the colloidal solution (hydrosol) is coagulated and can than be filtered.

The precipitate is insoluble in hydrochloric or acetic acids.

Hot, concentrated nitric acid or aqua regia dissolve the precipitate with the separation of white sulphur:

$$3 \text{NiS} \downarrow + 2 \text{HNO}_3 + 6 \text{H}^+ \rightarrow 3 \text{Ni}^{2+} + 3 \text{S} \downarrow + 2 \text{NO} \uparrow + 4 \text{H}_2\text{O}$$

$$\text{NiS} \downarrow + \text{HNO}_3 + 3 \text{HCl} \rightarrow \text{Ni}^{2+} + \text{S} \downarrow + \text{NOCl} \uparrow + 2 \text{Cl}^- + 2 \text{H}_2\text{O}$$

On longer heating the mixture becomes clear because sulphur gets oxidised to sulphate.

$$\text{S} \downarrow + 2 \text{HNO}_3 \rightarrow \text{SO}_4^{2-} + 2 \text{H}^+ + 2 \text{NO} \uparrow$$

$$\text{S} \downarrow + 3 \text{HNO}_3 + 9 \text{HCl} \rightarrow \text{SO}_4^{2-} + 6 \text{Cl}^- + 3 \text{NOCl} \uparrow + 8 \text{H}^+ + 2 \text{H}_2\text{O}$$

The NiS precipitate dissolves also in the 1+1 mixture of concentrated acetic acid and 30% hydrogen peroxide:

$$\text{NiS} \downarrow + 4 \text{H}_2\text{O}_2 \rightarrow \text{Ni}^{2+} + \text{SO}_4^{2-} + 4 \text{H}_2\text{O}$$
4. **Potassium nitrite solution:** no precipitate is produced in the presence of acetic acid (difference from cobalt).

5. **Potassium cyanide solution:** green precipitate of nickel(II) cyanide:

   \[ \text{Ni}^{2+} + 2 \text{CN}^- \rightarrow \text{Ni(CN)}_2 \downarrow \]

   The precipitate is readily soluble in excess reagent, when a yellow solution appears owing to the formation of tetracyanonickelate(II) complex ions:

   \[ \text{Ni(CN)}_2 \downarrow + 2 \text{CN}^- \rightarrow [\text{Ni(CN)}_4]^{2-} \]

6. **Dimethylglyoxime reagent:** red precipitate of nickel dimethylglyoxime from solutions just alkaline with ammonia or acid solutions buffered with sodium acetate:

   \[ \text{Ni}^{2+} + 2 \text{CH}_3\text{C}═\text{N}═\text{OH} \rightarrow [\text{Ni} \text{dimethylglyoxime}]^{2+} + 2 \text{H}^+ \]

   Iron(II) (red colouration), bismuth (yellow precipitate), and larger amount of cobalt (brown colouration) interfere in ammoniakal solution.

---

**Compare the characteristic reactions of copper(II) and nickel(II):**

<table>
<thead>
<tr>
<th></th>
<th>NH$_3$ soln. in excess</th>
<th>H$_2$S</th>
<th>KCN</th>
<th>NaOH</th>
<th>flame test</th>
<th>dimethylglyoxime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td></td>
<td></td>
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</table>
Summarise the solubility of sulphides:

<table>
<thead>
<tr>
<th></th>
<th>MnS</th>
<th>FeS</th>
<th>CoS</th>
<th>NiS</th>
</tr>
</thead>
<tbody>
<tr>
<td>colour</td>
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</tr>
<tr>
<td>HCl</td>
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<tr>
<td>hot, cc. HNO₃</td>
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<tr>
<td>aqua regia</td>
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<tr>
<td>acetic acid +  H₂O₂</td>
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</table>

Summarise the reactions of various metal ions with NaOH and NH₃ solutions.

<table>
<thead>
<tr>
<th></th>
<th>Mn²⁺</th>
<th>Fe²⁺</th>
<th>Fe³⁺</th>
<th>Co²⁺</th>
<th>Ni²⁺</th>
<th>Al³⁺</th>
<th>Cr³⁺</th>
<th>Zn²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td></td>
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<tr>
<td>NaOH in excess</td>
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<td>NH₃</td>
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<tr>
<td>NH₃ in excess</td>
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</tbody>
</table>

Summarise the solubility of selected metals in cold concentrated and 1+1 diluted nitric acid:

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>diluted HNO₃</td>
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<tr>
<td>cc HNO₃</td>
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</tbody>
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