Qualitative Chemical Analysis

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Institute of Chemistry, Eötvös University

2018
Acid-base theories; reduction-oxidation reactions: reducing and oxidizing agents, balancing redox equations; complex equilibria; precipitation reactions, principles of solubility equilibria; factors influencing solubility equilibria

Classification and reactions of ions; group reagents for qualitative analysis of cations and anions; identifications reactions for cations and anions

pH calculations; solubility of precipitates; effect of pH and other complexing agents on the solubility equilibria
Schedule

Major Tests during the semester:

- Test Paper I on 5\textsuperscript{th} of March
- Test Paper II on 16\textsuperscript{th} of April
- Final Test on 7\textsuperscript{th} of May
- Retakes 23\textsuperscript{rd} of April and 14\textsuperscript{th} of May
Analytical chemistry is the study of the separation, identification, and quantification of the chemical components of natural and artificial materials. Qualitative analysis gives an indication of the identity of the chemical species in the sample and quantitative analysis determines the amount of these components.

<table>
<thead>
<tr>
<th>Substance</th>
<th>(mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>6.5</td>
</tr>
<tr>
<td>Potassium</td>
<td>1</td>
</tr>
<tr>
<td>Calcium</td>
<td>80</td>
</tr>
<tr>
<td>Magnesium</td>
<td>26</td>
</tr>
<tr>
<td>Chlorides</td>
<td>6.8</td>
</tr>
<tr>
<td>Nitrates</td>
<td>3.7</td>
</tr>
<tr>
<td>Bicarbonates</td>
<td>360</td>
</tr>
<tr>
<td>Sulfates</td>
<td>12.6</td>
</tr>
<tr>
<td>pH</td>
<td>7.2</td>
</tr>
<tr>
<td>Silica</td>
<td>15</td>
</tr>
<tr>
<td>Fluoride</td>
<td>0.07</td>
</tr>
</tbody>
</table>
Analytical chemistry plays an increasingly important role in the pharmaceutical industry where, aside from quality assurance, it is used in discovery of new drug candidates and in clinical applications where understanding the interactions between the drug and the patient are critical.
Analytical chemistry plays an increasingly important role in the pharmaceutical industry where, aside from quality assurance, it is used in discovery of new drug candidates and in clinical applications where understanding the interactions between the drug and the patient are critical.

"If a pharmaceutical substance may contain residues of metal elements, used as catalyst(s) or reagent(s) in the synthesis, for each of these residual elements an acceptance criterion should be set. . . For the determination of each of the specified elements an appropriate and validated method should be used in relation to the limit to be applied. . . General semi-quantitative heavy metal limit tests based on the precipitation at pH 3.5 of coloured metal sulfides are described in several publications (e.g. Ph. Eur.). “

(Guideline on the specifications limits for residues of metal catalyst- European Medicines Agency)
Introduction

Reactions

Classical qualitative inorganic analysis is a method of analytical chemistry which seeks to find elemental composition of inorganic compounds. It is mainly focused on detecting ions in an aqueous solution. The solution is treated with various reagents to test for reactions characteristic of certain ions:

- reactions which form insoluble products, e.g. precipitates,
- reactions which give a characteristic color, e.g. colored complex ions,
- reactions which liberate gases, e.g. ammonia, carbon-dioxide.
**Specific** reaction are reactions which under certain conditions make it possible to detect some ions in the presence of others by the specific change in color, the formation of characteristic precipitate etc.

A reaction is **selective** if it reacts in a similar way with only few ions.

A reaction is **sensitive** if just a very small amount of ion gives an easily observable change.
Sensitivity of reactions

Limiting concentration:
The smallest amount of ion (usually in $\mu g$) in 1 ml of solution that still gives a positive reaction in a particular test (ppm).

Detection limit:
The smallest amount of the ions ($\mu g$ or ng) that can be detected by the method concerned.
Group reagents

Hydrolysis:
- CH$_3$COONa-NaCl ($pH \sim 7 - 8$, *acid-base reactions, ppt formation*)
- hexametilenetetramine (CH$_2$)$_6$N$_4$ ($pH \sim 5$, *acid-base reactions, ppt formation*)

\[
\text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O} \rightleftharpoons 6\text{HCHO} + 4\text{NH}_3
\]
Group reagents:

- HCl (*acid-base reactions, ppt formation*)
- Alkali hydroxides (OH\(^{-}\)) (*acid-base reactions, ppt formation, complex formation*)
- NH\(_3\) (*acid-base reactions, ppt formation, complex formation*)
- H\(_2\)S (*ppt formation, complex formation, redox reactions*)
- (NH\(_4\))\(_2\)S and (NH\(_4\))\(_2\)S\(_x\) (*ppt formation, complex formation, redox reactions*)
Group reagents:

- KI (*ppt formation, complex formation, redox reactions*)
- H$_2$SO$_4$ (*ppt formation, acid-base reactions*)
- Zn (*redox reactions*)
- KMnO$_4$ (*redox reactions*)
- I$_2$ sol. (I$^-$$_3$) (*redox reactions, ppt formation, complex formation*)
Classification of cations

Karl Remigius FRESENIUS (1818 - 1897)
Classification of cations

Group I

*Cations which can be precipitated as sulfides from acidic solution (pH~2) by \( H_2S \); the precipitates are insoluble in \((NH_4)_2S\) and KOH.*

\[ \text{Cu}^{2+}, \text{Ag}^+, \text{Cd}^{2+}, \text{Hg}_2^{2+}, \text{Hg}^2+, \text{Pb}^{2+}, \text{Bi}^{3+} \]
Group I

*Cations which can be precipitated as sulfides from acidic solution (pH ~ 2) by H₂S; the precipitates are insoluble in (NH₄)₂S and KOH.*

Cu²⁺, Ag⁺, Cd²⁺, Hg₂²⁺, Hg²⁺, Pb²⁺, Bi³⁺

Group II

*Cations which can be precipitated in acidic media with H₂S but the sulfides of are soluble in (NH₄)₂Sₓ and KOH with formation of thiocomplexes.*

As(III), As(V), Sb(III), Sb(V), Sn(II), Sn(IV)
{Se(IV), V(V), Mo(VI), W(VI), Au(I,III), Pt(IV)}
Classification of cations

Group III

*Cations which can be precipitated with (NH$_4$)$_2$S in neutral or slightly alkaline solutions, but cannot be precipitated with H$_2$S in acidic solutions.*

Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Mn$^{2+}$, Zn$^{2+}$, Cr$^{3+}$, Al$^{3+}$

{Be$^{2+}$, TiO$^{2+}$, Tl$^+$, Ce(III,IV), UO$_2^{2+}$}
Classification of cations

**Group IV**

The cations of Group IV cannot be precipitated with $H_2S$ or $(NH_4)_2S$, but they form precipitate with $(NH_4)_2CO_3$ in neutral or slightly alkaline solutions, in the presence of $NH_4Cl$.

$Ca^{2+}$, $Sr^{2+}$, $Ba^{2+}$

**Group V**

The cations of Group V cannot be precipitated with any of above reagents.

$Mg^{2+}$, $Na^+$, $K^+$, $NH_4^+$

{Li$^+$}
Sulfide precipitates

\[ 2 \text{Ag}^+ + \text{S}^2^- \xleftrightarrow{\text{precipitation}} \xrightarrow{\text{dissolution}} \text{Ag}_2\text{S} \]
Sulfide precipitates

\[ 2 \text{Ag}^+ + S^{2-} \xrightleftharpoons{\text{precipitation}} \xleftarrow{\text{dissolution}} \text{Ag}_2S \]

\[ K_{so} = [\text{Ag}^+]^2[S^{2-}] \]
Sulfide precipitates

$$2 \text{Ag}^+ + S^{2-} \xrightleftharpoons{\text{precipitation}} \text{Ag}_2S$$

$$K_{so} = [\text{Ag}^+]^2[S^{2-}]$$

- Common ion effect: more reactants $\rightarrow$ precipitation
Sulfide precipitates

$$2 \text{Ag}^+ + S^{2-} \rightleftharpoons \text{Ag}_2S$$

$$K_{so} = [\text{Ag}^+]^2[S^{2-}]$$

- Common ion effect: more reactants $\rightarrow$ precipitation
- pH effect: decrease of pH $\rightarrow$ dissolution

$$[S^{2-}]_t = [H_2S] + [HS^-] + [S^{2-}]$$

$$([H_2S]_t = 0.1 \text{ mol/dm}^3 \text{ and pH} = 2 \Rightarrow [S^{2-}] \approx 10^{-17} \text{M})$$
Sulfide precipitates

\[ 2 \text{Ag}^+ + S^{2-} \xrightleftharpoons{\text{precipitation}} \xleftleftharpoons{\text{dissolution}} \text{Ag}_2S \]

\[ K_{so} = [\text{Ag}^+]^2[S^{2-}] \]

- Complex formation: increase of ligand conc. $\rightarrow$ dissolution

\[ [\text{Ag}^+]_t = [\text{Ag}^+] + [\text{Ag(NH}_3\text{)}^+] + [\text{Ag(NH}_3\text{)}_2^+] \]
Sulfide precipitates

\[ 2 \text{Ag}^{+} + \text{S}^{2-} \xrightleftharpoons{\text{precipitation}} \xleftarrow{\text{dissolution}} \text{Ag}_2\text{S} \]

\[ K_{so}=\left[\text{Ag}^{+}\right]^{2}\left[\text{S}^{2-}\right] \]

- Complex formation: increase of ligand conc. → dissolution
  \[ [\text{Ag}^{+}]_{t} = [\text{Ag}^{+}] + [\text{Ag(NH}_{3}\text{)}^{+}] + [\text{Ag(NH}_{3}\text{)}_{2}^{+}] \]

- Redox reactions: oxidation of sulfide ions → dissolution
  \[ \text{H}_{2}\text{S} + 2 \text{NO}_{3}^{-} + 2 \text{H}^{+} \rightarrow 3 \text{S} + 2 \text{NO} + 4 \text{H}_{2}\text{O} \]
  (5 M HNO\text{$_{3}$} [S$^{2-}$] $\approx 10^{-45}$ M (! $N_A = 6 \times 10^{23}$))
Group I cations

Cation which can be precipitated as sulfides from acidic solution \((pH \sim 2)\) by \(H_2S\); the precipitates are insoluble in \((NH_4)_2S\) and KOH.

<table>
<thead>
<tr>
<th>Ions</th>
<th>(E_0/V) (Ion/Metal)</th>
<th>Electronic config.</th>
<th>Pearson</th>
<th>Oxidation states</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cu^{2+})</td>
<td>0.34</td>
<td>3d(^9)</td>
<td>borderline</td>
<td>+2, +1, 0</td>
</tr>
<tr>
<td>(Ag^+)</td>
<td>0.80</td>
<td>4d(^{10})</td>
<td>soft acid</td>
<td>+1, 0</td>
</tr>
<tr>
<td>(Cd^{2+})</td>
<td>-0.40</td>
<td>4d(^{10})</td>
<td>soft acid</td>
<td>+2, 0</td>
</tr>
<tr>
<td>(Hg^{2+})</td>
<td>0.91</td>
<td>5d(^{10})</td>
<td>soft acid</td>
<td>+2, +1, 0</td>
</tr>
<tr>
<td>(Hg_2^{2+})</td>
<td>0.80</td>
<td>5d(^{10})6s(^1)</td>
<td>soft acid</td>
<td>+2, +1, 0</td>
</tr>
<tr>
<td>(Pb^{2+})</td>
<td>-0.13</td>
<td>5d(^{10})6s(^2)</td>
<td>borderline</td>
<td>+4, +2, 0</td>
</tr>
<tr>
<td>(Bi^{3+})</td>
<td>0.23</td>
<td>5d(^{10})6s(^2)</td>
<td>borderline</td>
<td>+5, +3, 0</td>
</tr>
</tbody>
</table>
Group I cations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Color</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td></td>
<td>+cc HNO₃</td>
</tr>
<tr>
<td>CuS</td>
<td>brownish black</td>
<td>dissolves (redox reaction)</td>
</tr>
<tr>
<td>Ag₂S</td>
<td>black</td>
<td>dissolves (redox reaction)</td>
</tr>
<tr>
<td>PbS</td>
<td>black</td>
<td>dissolves (redox reaction)</td>
</tr>
<tr>
<td>Bi₂S₃</td>
<td>black</td>
<td>dissolves (redox reaction)</td>
</tr>
</tbody>
</table>

\[
3 \text{ CuS} + 2 \text{ NO}_3^- + 8 \text{ H}^+ = 3 \text{ Cu}^{2+} + 3 \text{ S} + 2 \text{ NO} + 4 \text{ H}_2\text{O}
\]
**Group I cations**

<table>
<thead>
<tr>
<th>H$_2$S</th>
<th>CdS (yellow)</th>
<th>HNO$_3$ +cc</th>
<th>Yellow dissolves, but it dissolves even if the conc. of strong acid &gt;0.5M in acid-base reaction</th>
</tr>
</thead>
</table>

\[
\text{CdS} + 2 \text{H}^+ = \text{Cd}^{2+} + 2 \text{H}_2\text{S}
\]
### Group I cations

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$S</td>
<td></td>
<td>+cc HNO$_3$ does not dissolve, but dissolves in Br$_2$/HCl (redox+complex formation reaction)</td>
</tr>
<tr>
<td>Hg$_2$S (Hg + HgS)</td>
<td>black</td>
<td></td>
</tr>
<tr>
<td>HgS</td>
<td>black</td>
<td>does not dissolve, but Br$_2$/HCl, dissolves in Br$_2$/HCl (redox+complex formation reaction)</td>
</tr>
</tbody>
</table>

\[
\text{HgS} + 4 \text{Br}_2 + 4 \text{H}_2\text{O} = \text{HgBr}_4^{2-} + \text{SO}_4^{2-} + 4 \text{Br}^- + 8 \text{H}^+
\]
Group I cations

Group Ia:

$\text{Ag}^+\,\,\text{Pb}^{2+}\,\,\text{Hg}_2^{2+}$

White ppt with chloride ions (HCl, NaCl...):

$\text{AgCl, PbCl}_2\,\,\text{Hg}_2\text{Cl}_2$
Group I cations

Group Ia:

Ag\(^+\), Pb\(^{2+}\), Hg\(^{2+}\)

White ppt with chloride ions (HCl, NaCl...):

AgCl, PbCl\(_2\), Hg\(_2\)Cl\(_2\)

\[ \text{AgCl} \xrightarrow{\text{NH}_3} \text{Ag(NH}_3\text{)}_2^+ \]

\[ \text{Hg}_2\text{Cl}_2 \xrightarrow{\text{NH}_3} \text{HgNH}_2\text{Cl} + \text{Hg} \]

\[ \text{PbCl}_2 \xrightarrow{\text{NH}_3} \text{no reaction} \]
**Group I cations**

\[
\begin{align*}
\text{KI} & \quad \text{Cu}^{2+} \quad \text{Cul} + \text{I}_2 \quad \text{yellowish white} \quad \text{Cul}_2^- (\text{KI}_s) \\
\end{align*}
\]
<table>
<thead>
<tr>
<th>Group I cations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KI</strong></td>
</tr>
<tr>
<td>Cu(^{2+})</td>
</tr>
<tr>
<td>Ag(^{+})</td>
</tr>
</tbody>
</table>

yellowish white
yellow

\[ +I^- \]

\[ \text{Cul}_2^- (\text{Kl}(s)) \]
\[ \text{AgI}_2^- (\text{Kl}(s)) \]
Group I cations

\[
\begin{array}{cccc}
\text{KI} & \text{Cu}^{2+} & \text{Ag}^+ & \text{Cd}^{2+} \\
\text{Cul} & \text{Agl} & \text{Agl} & \text{CdI}_4^{2-} \\
\text{yellowish white} & \text{yellow} & \text{yellow} & \text{greenish yellow} \\
\text{CuI}_2\ (\text{KI}_s) & \text{AgI}_2\ (\text{KI}_s) & \text{Cdl}_4^{2-} & \\
\end{array}
\]
Group I cations

<table>
<thead>
<tr>
<th>Ion</th>
<th>Reaction</th>
<th>Color Description</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>KI + CuI</td>
<td>yellowish white</td>
<td>CuI$<em>2$ (KI$</em>{(s)}$)</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>KI + AgI</td>
<td>yellow</td>
<td>AgI$<em>2$ (KI$</em>{(s)}$)</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>KI + CdI</td>
<td>greenish yellow</td>
<td>CdI$_4^{2-}$</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>KI + HgI$_2$</td>
<td>greenish yellow</td>
<td>HgI$_4^{2-}$ + Hg</td>
</tr>
<tr>
<td>Cation</td>
<td>Reaction</td>
<td>Precipitate Color</td>
<td>Formula</td>
</tr>
<tr>
<td>----------</td>
<td>-------------------</td>
<td>---------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>CuI + I(_2)</td>
<td>yellowish white</td>
<td>CuI(_2) (KI(_s))</td>
</tr>
<tr>
<td>Ag(^{+})</td>
<td>AgI</td>
<td>yellow</td>
<td>AgI(_2) (KI(_s))</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>CdI(_4)⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(_2)(^{2+})</td>
<td>Hg(_2)I(_2)</td>
<td>greenish yellow</td>
<td>HgI(_4)⁻ + Hg</td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>HgI(_2)</td>
<td>red</td>
<td>HgI(_4)⁻</td>
</tr>
</tbody>
</table>

KI + I\(^-\)
## Group I Cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>Reaction</th>
<th>Color</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>CuI + I(_2)</td>
<td>yellowish white</td>
<td>CuI(^-) (KI(_s))</td>
</tr>
<tr>
<td>Ag(^+)</td>
<td>AgI</td>
<td>yellow</td>
<td>AgI(^-) (KI(_s))</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>CdI(_4^-)</td>
<td>yellow</td>
<td>CdI(_4^-)</td>
</tr>
<tr>
<td>Hg(^2+)</td>
<td>HgI(_2)</td>
<td>greenish yellow</td>
<td>HgI(^2-) + Hg</td>
</tr>
<tr>
<td>Hg(^2+)</td>
<td>HgI(_2)</td>
<td>red</td>
<td>HgI(^2-)</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>PbI(_2)</td>
<td>yellow</td>
<td>PbI(^2-) (KI(_s))</td>
</tr>
</tbody>
</table>

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Group I cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>Iodide Compounds</th>
<th>Color/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>Cul + I$_2$</td>
<td>yellowish white</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>AgI</td>
<td>yellow</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>Hg$_2$I$_2$</td>
<td>greenish yellow</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>Hgl$_2$</td>
<td>red</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>PbI$_2$</td>
<td>yellow</td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>Bi$_3$ (BiOI)</td>
<td>black</td>
</tr>
</tbody>
</table>

KI$^-$ + I$_2$  

<table>
<thead>
<tr>
<th>Cation</th>
<th>Iodide Compounds</th>
<th>Color/Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>CuI$^-$ (KI$_s$)</td>
<td></td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>AgI$^-$ (KI$_s$)</td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>CdI$_4^-$</td>
<td></td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>Hgl$_4^-$ + Hg</td>
<td>yellow</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>Hgl$_4^-$</td>
<td></td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>PbI$_4^-$ (KI$_s$)</td>
<td></td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>BiI$_4^-$</td>
<td>orange</td>
</tr>
</tbody>
</table>
Group I cations

\[
\begin{align*}
\text{NaOH} & \quad \text{Cu}^{2+} \quad \text{Cu(OH)}_2 \quad \text{light blue} \quad \text{+OH}^- \\
\end{align*}
\]
### Group I Cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>Reaction</th>
<th>Product</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>NaOH + OH$^-$</td>
<td>Cu(OH)$_2$</td>
<td>light blue</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>Ag$^+$ + O$_2$</td>
<td>Ag$_2$O</td>
<td>brown</td>
</tr>
</tbody>
</table>

$István Szalai (Institute of Chemistry, Eötvös)$

Qualitative Chemical Analysis

$2018$
<table>
<thead>
<tr>
<th>Cation</th>
<th>Reaction</th>
<th>Color</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Cu(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>light blue</td>
<td>-</td>
</tr>
<tr>
<td>Ag&lt;sup&gt;+&lt;/sup&gt;</td>
<td>Ag&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>brown</td>
<td>-</td>
</tr>
<tr>
<td>Cd&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Cd(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>white</td>
<td>-</td>
</tr>
</tbody>
</table>
### Group I cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>Reaction</th>
<th>Color</th>
<th>Precipitate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>$\text{Cu(OH)}_2$</td>
<td>light blue</td>
<td>$\text{Cu(OH)}_2$</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>$\text{Ag}_2\text{O}$</td>
<td>brown</td>
<td>$\text{Ag}_2\text{O}$</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>$\text{Cd(OH)}_2$</td>
<td>white</td>
<td>$\text{Cd(OH)}_2$</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>$\text{Hg}_2\text{O}$ (Hg, HgO)</td>
<td>black</td>
<td>$\text{Hg}_2\text{O}$ (Hg, HgO)</td>
</tr>
<tr>
<td>Ion</td>
<td>Reaction</td>
<td>Color</td>
<td>Product</td>
</tr>
<tr>
<td>--------</td>
<td>--------------</td>
<td>-----------</td>
<td>---------</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>$\text{Cu}^{2+} + \text{OH}^- \rightarrow \text{Cu(OH)}_2$</td>
<td>light blue</td>
<td>−</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>$\text{Ag}^+ + \text{OH}^- \rightarrow \text{Ag}_2\text{O}$</td>
<td>brown</td>
<td>−</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>$\text{Cd}^{2+} + \text{OH}^- \rightarrow \text{Cd(OH)}_2$</td>
<td>white</td>
<td>−</td>
</tr>
<tr>
<td>Hg$_2^{2+}$</td>
<td>$\text{Hg}_2\text{O} (\text{Hg, HgO})$</td>
<td>black</td>
<td>−</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>$\text{Hg}^{2+} + \text{OH}^- \rightarrow \text{HgO}$</td>
<td>yellow</td>
<td>−</td>
</tr>
</tbody>
</table>
### Group I Cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>Reaction</th>
<th>Color</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>Cu(OH)$_2$</td>
<td>light blue</td>
<td>-</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>Ag$_2$O</td>
<td>brown</td>
<td>-</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>Cd(OH)$_2$</td>
<td>white</td>
<td>-</td>
</tr>
<tr>
<td>Hg$_2^{2+}$</td>
<td>Hg$_2$O (Hg, HgO)</td>
<td>black</td>
<td>-</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>HgO</td>
<td>yellow</td>
<td>-</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>Pb(OH)$_2$</td>
<td>white</td>
<td>Pb(OH)$_4^{2-}$</td>
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</tbody>
</table>
### Group I cations

<table>
<thead>
<tr>
<th>Cation</th>
<th>Reaction</th>
<th>Colour</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}^{2+} )</td>
<td>( \text{Cu(OH)}_2 )</td>
<td>light blue</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Ag}^+ )</td>
<td>( \text{Ag}_2\text{O} )</td>
<td>brown</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Cd}^{2+} )</td>
<td>( \text{Cd(OH)}_2 )</td>
<td>white</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Hg}_2^{2+} )</td>
<td>( \text{Hg}_2\text{O} ) (Hg, HgO)</td>
<td>black</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Hg}^{2+} )</td>
<td>( \text{HgO} )</td>
<td>yellow</td>
<td>–</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} )</td>
<td>( \text{Pb(OH)}_2 )</td>
<td>white</td>
<td>( \text{Pb(OH)}_4^{2-} )</td>
</tr>
<tr>
<td>( \text{Bi}^{3+} )</td>
<td>( \text{Bi(OH)}_3 )</td>
<td>white</td>
<td>–</td>
</tr>
</tbody>
</table>
Group I cations

\[
\begin{align*}
\text{NH}_3 & \quad + \text{NH}_3 \\
\text{Cu}^{2+} & \quad \text{Cu(OH)}_2 \\
\text{Cu(NH}_3)_2^{2+} & \quad \text{Cu(NH}_3)_4^{2+}
\end{align*}
\]
Group I cations

\[
\begin{array}{cc}
\text{NH}_3 & \text{+NH}_3 \\
\hline
\text{Cu}^{2+} & \text{Cu(OH)}_2 & \text{Cu(NH}_3)_4^{2+} \\
\text{Ag}^+ & \text{Ag}_2\text{O} & \text{Ag(NH}_3)_2^+ \\
\end{array}
\]
Group I cations

\[ \begin{array}{ccc}
\text{NH}_3 & + \text{NH}_3 \\
\text{Cu}^{2+} & \text{Cu(OH)}_2 & \text{Cu(NH}_3)_2^{2+} \\
\text{Ag}^+ & \text{Ag}_2\text{O} & \text{Ag(NH}_3)_2^{+} \\
\text{Cd}^{2+} & \text{Cd(OH)}_2 & \text{Cd(NH}_3)_2^{2+}
\end{array} \]
Group I cations

\[
\begin{array}{ccc}
\text{NH}_3 & + \text{NH}_3 \\
\text{Cu}^{2+} & \text{Cu(OH)}_2 \\
\text{Ag}^+ & \text{Ag}_2\text{O} \\
\text{Cd}^{2+} & \text{Cd(OH)}_2 \\
\text{Hg}_2^{2+} & \text{Hg(NH}_2\text{)Cl} + \text{Hg} \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{Cu(NH}_3)_2^{2+} \\
\text{Cu(NH}_3)_4^{2+} \\
\text{Ag(NH}_3)_{2}^{+} \\
\text{Cd(NH}_3)_4^{2+} \\
- \\
\end{array}
\]
Group I cations

\[
\begin{align*}
\text{NH}_3 & \quad + \text{NH}_3 \\
\text{Cu}^{2+} & \quad \underline{\text{Cu(OH)}_2} \\
\text{Ag}^+ & \quad \underline{\text{Ag}_2\text{O}} \\
\text{Cd}^{2+} & \quad \underline{\text{Cd(OH)}_2} \\
\text{Hg}_2^{2+} & \quad \underline{\text{Hg(NH}_2\text{)Cl}} + \underline{\text{Hg}} \\
\text{Hg}^{2+} & \quad \underline{\text{Hg(NH}_2\text{)Cl}} \\
& \quad \underline{\text{HgO} \cdot \text{Hg(NH}_2\text{)NO}_3}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Cation</th>
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<th>Product</th>
<th>Product</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>NH$_3$</td>
<td>Cu$^{2+}$Cu(OH)$_2$</td>
<td>Cu(NH$_3$)$_2^{2+}$</td>
<td>Cu(NH$_3$)$_2^{2+}$</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>Ag$_2$O</td>
<td>Ag(NH$_3$)$_2^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>Cd(OH)$_2$</td>
<td>Cd(NH$_3$)$_2^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg$_2$$^{2+}$</td>
<td>Hg(NH$_2$)Cl $+$ Hg</td>
<td>Hg$^{2+}$Hg(NH$_2$)Cl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>Hg(NH$_2$)Cl</td>
<td>HgO$\cdot$Hg(NH$_2$)NO$_3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>Pb(OH)$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Group I Cations

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<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>+NH$_3$</td>
<td>Cu(OH)$_2$</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td></td>
<td>Ag$_2$O</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td></td>
<td>Cd(OH)$_2$</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>Hg(NH$_2$)Cl + Hg</td>
<td>-</td>
</tr>
<tr>
<td>Hg$_2^{2+}$</td>
<td>Hg(NH$_2$)Cl</td>
<td>-</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td></td>
<td>HgO·Hg(NH$_2$)NO$_3$</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>Pb(OH)$_2$</td>
<td>-</td>
</tr>
<tr>
<td>Bi$^{3+}$</td>
<td>Bi(OH)$_3$</td>
<td>-</td>
</tr>
</tbody>
</table>
## Group I cations

### Redox reactions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>$-$</td>
<td>$\text{Cu}^2+$ $\overset{\text{Fe,Zn}}{\rightarrow}$ $\text{Cu}$, $\text{Cu}^2+$ $\overset{\text{l}^-}{\rightarrow}$ $\text{CuI}$ + $\text{l}_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Cu}^2+$ $\overset{\text{CN}^-}{\rightarrow}$ $\text{CuCN}$ + (CN)$_2$</td>
</tr>
</tbody>
</table>
### Group I cations

**Redox reactions**

<table>
<thead>
<tr>
<th>Ion</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>–</td>
<td>Cu$^{2+}$ $\xrightarrow{Fe,Zn}$ Cu, Cu$^{2+}$ $\xrightarrow{l^-}$ CuI $+$ I$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu$^{2+}$ $\xrightarrow{CN^-}$ CuCN $+$ (CN)$_2$</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>–</td>
<td>Ag$^+$ $\xrightarrow{Cu}$ Ag, Ag(NH$_3$)$_2^+$ $\xrightarrow{formaldehyde}$ Ag</td>
</tr>
</tbody>
</table>
## Group I cations

### Redox reactions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>–</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt; $\xrightarrow{Fe,Zn}$ Cu, Cu&lt;sup&gt;2+&lt;/sup&gt; $\xrightarrow{I^-}$ CuI + I&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\quad$</td>
</tr>
<tr>
<td>Ag&lt;sup&gt;+&lt;/sup&gt;</td>
<td>–</td>
<td>Ag&lt;sup&gt;+&lt;/sup&gt; $\xrightarrow{Cu}$ Ag, Ag(NH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt; $\xrightarrow{\text{formaldehyde}}$ Ag</td>
</tr>
<tr>
<td>Cd&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>–</td>
<td>Cd&lt;sup&gt;2+&lt;/sup&gt; $\xrightarrow{Zn}$ Cd</td>
</tr>
</tbody>
</table>

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## Group I cations

### Redox reactions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>–</td>
<td>Cu$^{2+}$ (\xrightarrow{\text{Fe, Zn}}) Cu, Cu$^{2+}$ (\xrightarrow{l^-}) Cul + I$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu$^{2+}$ (\xrightarrow{CN^-}) CuCN + (CN)$_2$</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>–</td>
<td>Ag$^+$ (\xrightarrow{Cu}) Ag, Ag(NH$_3$)$_2^+$ (\xrightarrow{\text{formaldehyde}}) Ag</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>–</td>
<td>Cd$^{2+}$ (\xrightarrow{Zn}) Cd</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>–</td>
<td>Hg$^{2+}$ (\xrightarrow{Cu}) Hg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HgCl$_2$ (\xrightarrow{SnCl_4^{2-}}) Hg$_2$Cl$_2$ (\xrightarrow{SnCl_4^{2-}}) Hg</td>
</tr>
</tbody>
</table>
Redox reactions

<table>
<thead>
<tr>
<th>Ion</th>
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</tr>
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<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>–</td>
<td>Cu$^{2+} \xrightarrow{Fe, Zn} Cu$, Cu$^{2+} \xrightarrow{l^-} CuI + I_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu$^{2+} \xrightarrow{CN^-} CuCN + (CN)_2$</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>–</td>
<td>Ag$^+$ $\xrightarrow{Cu}$ Ag, Ag(NH$_3$)$_2^+ \xrightarrow{formaldehyde} Ag$</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>–</td>
<td>Cd$^{2+} \xrightarrow{Zn} Cd$</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>–</td>
<td>Hg$^{2+} \xrightarrow{Cu} Hg$</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td></td>
<td>HgCl$_2 \xrightarrow{SnCl_4^{2-}} Hg_2Cl_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hg$^{2+} \xrightarrow{MnO_4^-} Hg^{2+}$</td>
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</tbody>
</table>
### Redox reactions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td>Pb(OH)(_2) OCl(^{-}) → PbO(_2)</td>
<td>Pb(^{2+}) Zn → Pb</td>
</tr>
</tbody>
</table>

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Group I cations

Redox reactions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>Pb(OH)$_2$</td>
<td>PbO$_2$</td>
</tr>
</tbody>
</table>
# Group I cations, analysis

<table>
<thead>
<tr>
<th>Group reagents</th>
<th>Observation</th>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>blue</td>
<td>Cu^{2+} and all the colourless ions</td>
</tr>
</tbody>
</table>
## Group I cations, analysis

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</tr>
<tr>
<td></td>
<td>colorless</td>
<td>no Cu$^{2+}$</td>
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<tr>
<td></td>
<td>colorless</td>
<td>no Cu$^{2+}$</td>
</tr>
<tr>
<td>HCl</td>
<td>precipitate</td>
<td>Ag$^+$, Pb$^{2+}$, Hg$_2^{2+}$</td>
</tr>
</tbody>
</table>

Hydrolysis: no ppt no Bi$^{3+}$
### Group I cations, analysis

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<td>blue</td>
<td>Cu(^{2+}) and all the colourless ions</td>
</tr>
<tr>
<td></td>
<td>colorless</td>
<td>no Cu(^{2+})</td>
</tr>
<tr>
<td>HCl + heating</td>
<td>precipitate</td>
<td>Ag(^{+}), Pb(^{2+}) Hg(^{2+})</td>
</tr>
<tr>
<td></td>
<td>no ppt</td>
<td>no Ag(^{+}) and Hg(^{2+}) only Pb(^{2+})</td>
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</tbody>
</table>
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<td>Color</td>
<td>blue</td>
<td>(\text{Cu}^{2+}) and all the colourless ions</td>
</tr>
<tr>
<td></td>
<td>colorless</td>
<td>no (\text{Cu}^{2+})</td>
</tr>
<tr>
<td>HCl + heating</td>
<td>precipitate</td>
<td>(\text{Ag}^+), (\text{Pb}^{2+}), (\text{Hg}_2^{2+})</td>
</tr>
<tr>
<td></td>
<td>no ppt</td>
<td>no (\text{Ag}^+) and (\text{Hg}_2^{2+}) only (\text{Pb}^{2+})</td>
</tr>
<tr>
<td></td>
<td>ppt does not dissolve</td>
<td>(\text{Ag}^+) and (\text{Hg}_2^{2+})</td>
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<td>no Cu(^{2+})</td>
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<tr>
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<tr>
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<tr>
<td>Hydrolysis</td>
<td>ppt</td>
<td>Ag(^{+}) and Hg(^{2+})</td>
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<tr>
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<td>ppt does not dissolve</td>
<td>Bi(^{3+})</td>
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<tr>
<td>Group reagents</td>
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<td>---------------------</td>
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<td>Color</td>
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<td>$\text{Cu}^{2+}$ and all the colourless ions no $\text{Cu}^{2+}$</td>
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<tr>
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<td>colorless</td>
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</tr>
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<td>HCl + heating</td>
<td>precipitate no ppt</td>
<td>$\text{Ag}^+\text{, }\text{Pb}^{2+}\text{, }\text{Hg}_2^{2+}$ no $\text{Ag}^+$ and $\text{Hg}_2^{2+}$ only $\text{Pb}^{2+}$</td>
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<td>Hydrolysis</td>
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<td></td>
<td>no ppt</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>no Bi$^{3+}$, Pb$^{2+}$, Hg$^{2+}$</td>
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<td></td>
<td></td>
<td>only Cu$^{2+}$, Ag$^+$, Cd$^{2+}$</td>
</tr>
<tr>
<td>NaOH</td>
<td>ppt</td>
<td>can be Cu$^{2+}$, Bi$^{3+}$, Cd$^{2+}$, Hg$^{2+}$, Ag$^+$</td>
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<tr>
<td></td>
<td>no ppt</td>
<td>only Pb²⁺</td>
</tr>
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</table>
### Group I cations, analysis

<table>
<thead>
<tr>
<th>Group reagents</th>
<th>Observation</th>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>KI</td>
<td>colored ppt</td>
<td>Bil₃ black, Hgl₂ red</td>
</tr>
<tr>
<td></td>
<td>complexes</td>
<td></td>
</tr>
<tr>
<td></td>
<td>no ppt</td>
<td>Pbl₂ yellow, Bil⁻₄ orange</td>
</tr>
<tr>
<td></td>
<td></td>
<td>only Cd²⁺</td>
</tr>
</tbody>
</table>
### Group I cations, analysis

<table>
<thead>
<tr>
<th>Reagent, observation</th>
<th>products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>Cu(NH$_3$)$_4^{2+}$</td>
</tr>
<tr>
<td>NH$_3$, blue</td>
<td></td>
</tr>
</tbody>
</table>
## Group I cations, analysis

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<thead>
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<th>Reagent, observation</th>
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</tr>
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<tbody>
<tr>
<td>Cu$^{2+}$ NH$_3$, blue</td>
<td>Cu(NH$_3$)$_4^{2+}$</td>
</tr>
<tr>
<td>Ag$^+$ HCl white ppt</td>
<td>AgCl$^{NH_3}_2$Ag(NH$_3$)$_2^+$</td>
</tr>
<tr>
<td>can be dissolved in NH$_3$</td>
<td></td>
</tr>
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</table>
### Group I cations, analysis

<table>
<thead>
<tr>
<th>Cation</th>
<th>Reagent, observation</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+})</td>
<td>NH(_3), blue</td>
<td>Cu(NH(_3))(_4^{2+})</td>
</tr>
<tr>
<td>Ag(^{+})</td>
<td>HCl white ppt, can be dissolved in NH(_3)</td>
<td>AgCl + NH(_3) → Ag(NH(_3))(_2^{+})</td>
</tr>
<tr>
<td>Hg(_2^{2+})</td>
<td>HCl white ppt, +NH(_3) ppt become black</td>
<td>Hg(_2)Cl(_2) + NH(_3) → HgNH(_2)Cl + + Hg</td>
</tr>
</tbody>
</table>
Group I cations, analysis

<table>
<thead>
<tr>
<th>Cation</th>
<th>Reagent, observation</th>
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<tr>
<td>Cu$^{2+}$</td>
<td>NH$_3$, blue</td>
<td>Cu(NH$_3$)$_4^{2+}$</td>
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<tr>
<td>Ag$^+$</td>
<td>HCl white ppt, can be dissolved in NH$_3$</td>
<td>AgCl$\xrightarrow{\text{NH}_3}$ Ag(NH$_3$)$_2^+$</td>
</tr>
<tr>
<td>Hg$_2^{2+}$</td>
<td>HCl white ppt, +NH$_3$ ppt become black</td>
<td>Hg$_2$Cl$_2$ $\xrightarrow{\text{NH}_3}$ HgNH$_2$Cl + + Hg</td>
</tr>
<tr>
<td>Hg$^{2+}$</td>
<td>SnCl$_4^{2-}$ white ppt, in excess gray</td>
<td>Hg$_2$Cl$_2$ $\xrightarrow{\text{SnCl}_4^{2-}}$ Hg</td>
</tr>
<tr>
<td></td>
<td>KI red ppt, that dissolves in excess</td>
<td>HgI$_2$ $\xrightarrow{I^-}$ HgI$_4^{2-}$</td>
</tr>
</tbody>
</table>

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### Group I cations, analysis

<table>
<thead>
<tr>
<th>Reagent, observation</th>
<th>products</th>
</tr>
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<tbody>
<tr>
<td>Pb$^{2+}$</td>
<td>PbSO$_4$</td>
</tr>
<tr>
<td>H$_2$SO$_4$ white ppt</td>
<td></td>
</tr>
<tr>
<td>KI yellow ppt.</td>
<td>PbI$_2$</td>
</tr>
</tbody>
</table>

- Bi$^{3+}$: KI black ppt., in excess BiI$_4$ orange solution
- Sn(OH)$_2$$^{-}_4$ black ppt Bi(OH)$_3$$^{-}_4$

- Cd$^{2+}$: (a) heating with Fe powder CdS filtrate +HCl+H$_2$S yellow ppt  
(b) NH$_3$, filtration + CN$^-$(NH$_4$)$_2$S yellow ppt
## Group I cations, analysis

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<th>Reagent, observation</th>
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<tr>
<td><strong>Pb$^{2+}$</strong></td>
<td><strong>PbSO$_4$</strong></td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$ white ppt</td>
<td>PbI$_2$</td>
</tr>
<tr>
<td>KI yellow ppt.</td>
<td></td>
</tr>
<tr>
<td><strong>Bi$^{3+}$</strong></td>
<td>Bi$_3$ $\xrightarrow{I^-}$ Bi$_4$</td>
</tr>
<tr>
<td>KI black ppt., in excess orange solution</td>
<td>Bi(OH)$_3$ $\xrightarrow{Sn(OH)_4^{2-}}$ Bi</td>
</tr>
<tr>
<td>Sn(OH)$_4^{2-}$ black ppt</td>
<td>BiOCl</td>
</tr>
</tbody>
</table>
## Group I Cations, Analysis

<table>
<thead>
<tr>
<th>Reagent, Observation</th>
<th>Products</th>
</tr>
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<tbody>
<tr>
<td><strong>Pb(^{2+})</strong></td>
<td>H(_2)SO(_4) white ppt</td>
</tr>
<tr>
<td></td>
<td>KI yellow ppt.</td>
</tr>
<tr>
<td><strong>Bi(^{3+})</strong></td>
<td>KI black ppt., in excess orange solution</td>
</tr>
<tr>
<td></td>
<td>Sn(OH)(_4^−) black ppt</td>
</tr>
<tr>
<td></td>
<td>hidrolysis, white ppt</td>
</tr>
<tr>
<td><strong>Cd(^{2+})</strong></td>
<td>(a) heating with Fe powder filtrate + HCl + H(_2)S yellow ppt</td>
</tr>
<tr>
<td></td>
<td>(b) NH(_3), filtration + CN(^−) + (NH(_4))(_2)S yellow ppt</td>
</tr>
</tbody>
</table>
Group I cations, analysis

Cd$^{2+}$ and Cu$^{2+}$ in presence of each other

1. $\text{NH}_3 \Rightarrow [\text{Cu(NH}_3)_4]^{2+}$ and $[\text{Cd(NH}_3)_4]^{2+}$
2. $\text{KCN} \Rightarrow [\text{Cu(CN}_4]^{3-}$ and $[\text{Cd(CN}_4]^{2-}$
3. $(\text{NH}_4)_2\text{S} \Rightarrow \text{CdS}$
Cd$^{2+}$ and Cu$^{2+}$ in presence of each other

1. NH$_3$ $\Rightarrow$ [Cu(NH$_3$)$_4$]$^{2+}$ and [Cd(NH$_3$)$_4$]$^{2+}$
2. KCN $\Rightarrow$ [Cu(CN)$_4$]$^{3-}$ and [Cd(CN)$_4$]$^{2-}$
3. (NH$_4$)$_2$S $\Rightarrow$ CdS

1. iron powder $\Rightarrow$ Cu and Cd$^{2+}$
2. H$_2$S $\Rightarrow$ CdS
Group I cations, analysis

Hg$^{2+}$ and Bi$^{3+}$ in presence of each other

1. CH$_3$COONa-NaCl or hexametilenetetramine $\Rightarrow$ Hg$^{2+}$, BiOCl
2. filtration
3. ppt + HOCl $\Rightarrow$ BiO$_2$(OH)
4. solution + SnCl$_4^{2-}$ $\Rightarrow$ Hg$_2$Cl$_2$ + SnCl$_4^{2-}$ $\Rightarrow$ Hg
The cations of Group II can be precipitated in acidic media with $H_2S$ but the sulfides of are soluble in $(NH_4)_2S_x$ and KOH with formation of thiocomplexes.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Elektronic config.</th>
<th>Pearson</th>
<th>Oxidation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>$3d^{10}4s^2$</td>
<td>hard acid</td>
<td>$+5, +3, 0, (-3)$</td>
</tr>
<tr>
<td>$H_3AsO_3$, $AsO_3^{3-}$</td>
<td></td>
<td></td>
<td></td>
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The cations of Group II can be precipitated in acidic media with $H_2S$ but the sulfides of are soluble in $(NH_4)_2S_x$ and KOH with formation of thiocomplexes.

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<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As(V)</td>
<td>3d$^{10}$</td>
<td>hard acid</td>
<td></td>
</tr>
<tr>
<td>$H_3AsO_4$, $AsO_4^{3-}$</td>
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### Group II cations

<table>
<thead>
<tr>
<th>Ion</th>
<th>Elektronic config.</th>
<th>Pearson</th>
<th>Oxidation number</th>
</tr>
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<tbody>
<tr>
<td>Sb(III)</td>
<td>4d^{10}4s^{2}</td>
<td>borderline</td>
<td>+5, +3, 0, (-3)</td>
</tr>
<tr>
<td>SbCl&lt;sub&gt;4&lt;/sub&gt;^-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn(II)</td>
<td>4d^{10}4s^{2}</td>
<td>borderline</td>
<td>+4, +2, 0, (-4)</td>
</tr>
<tr>
<td>SnCl&lt;sub&gt;2&lt;/sub&gt;^-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion</td>
<td>Electronic config.</td>
<td>Pearson</td>
<td>Oxidation number</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------</td>
<td>------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>4d(^{10})4s(^{2})</td>
<td>borderline</td>
<td>+5, +3, 0, (-3)</td>
</tr>
<tr>
<td>SbCl(_4^-)</td>
<td></td>
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<tr>
<td>Sb(V)</td>
<td>4d(^{10})</td>
<td>hard acid</td>
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<tr>
<td>SbCl(_6^-)</td>
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### Group II cations

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<tr>
<td>SbCl$_4^-$</td>
<td>$4d^{10}$</td>
<td>hard acid</td>
<td></td>
</tr>
<tr>
<td>Sb(V)</td>
<td>$4d^{10}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SbCl$_6^-$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn(II)</td>
<td>$4d^{10}4s^2$</td>
<td>borderline</td>
<td>$+4, +2, 0, (-4)$</td>
</tr>
<tr>
<td>SnCl$_4^{2-}$</td>
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<td>Sb(V)</td>
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<tr>
<td>Sn(II)</td>
<td>$4d^{10} 4s^2$</td>
<td>borderline</td>
<td>$+4, +2, 0, (-4)$</td>
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<tr>
<td>SnCl$_4^{2-}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>$4d^{10}$</td>
<td>hard acid</td>
<td></td>
</tr>
<tr>
<td>SnCl$_6^{2-}$</td>
<td></td>
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</tbody>
</table>
**Group II cations**

Sulfide precipitates

<table>
<thead>
<tr>
<th></th>
<th>(NH$_4$)$_2$S</th>
<th>(NH$_4$)$_2$S$_x$</th>
<th>KOH</th>
<th>cc HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td>As$_2$S$_3$ + S</td>
<td>AsS$_3^{3-}$</td>
<td>AsO$_3^{3-}$ + AsS$_3^{3-}$</td>
<td>-</td>
</tr>
<tr>
<td>(As$_2$S$_5$)</td>
<td></td>
<td>AsS$_4^{3-}$</td>
<td></td>
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</tbody>
</table>
### Group II cations

#### Sulfide precipitates

<table>
<thead>
<tr>
<th>Cation</th>
<th>Sulfide Precipitate</th>
<th>(NH$_4$)$_2$S $\rightarrow$ AsS$_3^-$</th>
<th>(NH$_4$)$_2$S$_x$ $\rightarrow$ AsS$_4^-$</th>
<th>KOH $\rightarrow$ AsO$_3^-$ + AsS$_3^-$</th>
<th>cc HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td>$\frac{As_2S_3 + S}{(As_2S_5)}$</td>
<td>AsS$_3^-$</td>
<td>AsS$_4^-$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>As(III)</td>
<td>$\frac{As_2S_3}{As_2S_3}$</td>
<td>AsS$_3^-$</td>
<td>AsS$_4^-$</td>
<td>AsO$_3^-$ + AsS$_3^-$</td>
<td>-</td>
</tr>
</tbody>
</table>
### Group II cations

Sulfide precipitates

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<thead>
<tr>
<th></th>
<th>$(\text{NH}_4)_2\text{S}$</th>
<th>$(\text{NH}_4)_2\text{S}_x$</th>
<th>KOH</th>
<th>cc HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td>$\text{As}_2\text{S}_3 + S$</td>
<td>$\text{AsS}_3^-$</td>
<td>$\text{AsO}_3^- + \text{AsS}_3^-$</td>
<td>$-$</td>
</tr>
<tr>
<td></td>
<td>$(\text{As}_2\text{S}_5)$</td>
<td>$\text{AsS}_4^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As(III)</td>
<td>$\text{As}_2\text{S}_3$</td>
<td>$\text{AsS}_3^-$</td>
<td>$\text{AsO}_3^- + \text{AsS}_3^-$</td>
<td>$-$</td>
</tr>
<tr>
<td>Sb(V)</td>
<td>$\text{Sb}_2\text{S}_3 + S$</td>
<td>$\text{SbS}_3^-$</td>
<td>$\text{Sb(OH)}_4^- + \text{SbS}_3^-$</td>
<td>$\text{Sb(}\text{Cl})_4^-$</td>
</tr>
<tr>
<td></td>
<td>$\text{Sb}_2\text{S}_5$</td>
<td>$\text{SbS}_4^-$</td>
<td>$\text{Sb(OH)}_6^-$</td>
<td>$\text{Sb(}\text{Cl})_6^-$</td>
</tr>
</tbody>
</table>
### Group II cations

#### Sulfide precipitates

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
<th>(NH₄)₂S</th>
<th>(NH₄)₂Sₓ</th>
<th>KOH</th>
<th>cc HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(V)</td>
<td>As₂S₃ + S</td>
<td>AsS₃⁻</td>
<td>AsS₄⁻</td>
<td>AsO₃⁻ + AsS₃⁻</td>
<td>--</td>
</tr>
<tr>
<td>As(III)</td>
<td>As₂S₃</td>
<td>AsS₃⁻</td>
<td>AsS₄⁻</td>
<td>AsO₃⁻ + AsS₃⁻</td>
<td>--</td>
</tr>
<tr>
<td>Sb(V)</td>
<td>Sb₂S₃ + S</td>
<td>SbS₃⁻</td>
<td>SbS₄⁻</td>
<td>Sb(OH)₄⁻ + SbS₃⁻</td>
<td>Sb(Cl)₄⁻</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>Sb₂S₃</td>
<td>SbS₃⁻</td>
<td>SbS₄⁻</td>
<td>Sb(OH)₆⁻</td>
<td>Sb(Cl)₆⁻</td>
</tr>
</tbody>
</table>
# Group II Cations

## Sulfide Precipitates

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<th></th>
<th>(NH$_4$)$_2$S</th>
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<th>cc HCl</th>
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<td>As$_2$S$_3$ + S</td>
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<td>AsS$_4^-$</td>
<td>AsO$_3^-$ + AsS$_3^-$</td>
</tr>
<tr>
<td></td>
<td>$(\text{As}_2\text{S}_5)$</td>
<td></td>
<td></td>
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<tr>
<td>As(III)</td>
<td>As$_2$S$_3$</td>
<td>AsS$_3^-$</td>
<td>AsS$_4^-$</td>
<td>AsO$_3^-$ + AsS$_3^-$</td>
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<tr>
<td>Sb(V)</td>
<td>Sb$_2$S$_3$ + S</td>
<td>SbS$_3^-$</td>
<td>SbS$_4^-$</td>
<td>Sb(OH)$_4^-$ + SbS$_3^-$</td>
</tr>
<tr>
<td></td>
<td>$(\text{Sb}_2\text{S}_5)$</td>
<td></td>
<td></td>
<td>Sb(OH)$_6^-$</td>
</tr>
<tr>
<td>Sb(III)</td>
<td>Sb$_2$S$_3$</td>
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<td>SbS$_4^-$</td>
<td>Sb(OH)$_4^-$ + SbS$_3^-$</td>
</tr>
<tr>
<td>Sn(IV)</td>
<td>SnS$_2$</td>
<td>SnS$_3^-$</td>
<td>SnS$_3^-$</td>
<td>Sn(OH)$_6^{2-}$ + S$_2^-$</td>
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### Group II cations

**Sulfide precipitates**

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<td>Sb(OH)$_6^-$</td>
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<td>SnS$_3^-$</td>
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</tr>
<tr>
<td>Sn(II)</td>
<td>SnS</td>
<td>–</td>
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