Reactions of silver complexes

N Goalby
Chemrevise.org

Silver complex ions

Various bits of silver chemistry are found across the syllabus. Sometimes questions will go across the module boundaries

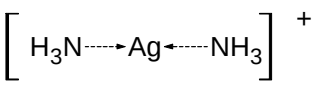
The most common silver complex ions are:

$[Ag(NH_3)_2]^+$

$[Ag(CN)_2]^-$

$[Ag(S_2O_3)_2]^{3-}$

They are all linear complex ions



They are all colourless solutions which suggests that silver must have a complete d sub shell

Silver – transition metal?

Silver behaves like the transition metals in that it can form complexes and can show catalytic behaviour (although it adsorbs too weakly for many examples)

Silver is unlike the transition metals in that it does not form coloured compounds and does not have variable oxidation states

Silver complexes all have a +1 oxidation state with a full 4d subshell ($4d^{10}$). As it is $4d^{10}$ in both its atom and ion, it does not have a partially filled d subshell and so is not a transition metal by definition. It is not therefore able to do electron transitions between d orbitals that enable coloured compounds to occur.

The reactions of halide ions with silver nitrate.

Method

The test solution is made acidic with **nitric acid,** and then **Silver nitrate solution** is added dropwise:

The role of nitric acid is to react with any carbonates present to prevent formation of the precipitate Ag_2CO_3. This would mask the desired observations

e.g. $2\ HNO_3 + Na_2CO_3 \rightarrow 2\ NaNO_3 + H_2O + CO_2$

Observations

Fluorides produce no precipitate

Chlorides produce a white precipitate

Bromides produce a cream precipitate

Iodides produce a pale yellow precipitate

AgCl AgBr AgI

key

Equations for the reactions of halide ions with silver nitrate.

Full equation for reactions

$AgNO_3$ (aq) + NaCl (aq) → AgCl (s) + $NaNO_3$ (aq)

$AgNO_3$ (aq) + NaBr (aq) → AgBr (s) + $NaNO_3$ (aq)

$AgNO_3$ (aq) + NaI (aq) → AgI (s) + $NaNO_3$ (aq)

Normally we write ionic equations for these reactions

ionic equation for reactions

$Ag^+(aq) + Cl^-(aq)$ → AgCl(s) (White precipitate)

$Ag^+(aq) + Br^-(aq)$ → AgBr(s) (Cream precipitate)

$Ag^+(aq) + I^-(aq)$ → AgI(s) (Yellow precipitate)

key

Addition of Ammonia to Silver Halides

The precipitates can be reacted with ammonia solution (to help differentiate between them if the colours look similar):

	AgCl	AgBr	AgI
Addition of aqueous ammonia	Dissolves	Does not dissolve	Does not dissolve
Addition of concentrated ammonia	Dissolves	Dissolves	Does not dissolve

The solubility of the silver halides in ammonia decreases in the order: AgF > AgCl > AgBr > AgI

key

Equations for reactions with ammonia

Silver chloride dissolves in **dilute ammonia (**to form a complex ion)

$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

Colourless solution

Silver bromide only dissolves in **concentrated ammonia** to form a complex ion

$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Br^-(aq)$

Colourless solution

Silver iodide does not react with ammonia – it is too insoluble.

Effect Of Light on Silver Halides

The silver halide precipitates darken in light decomposing to form silver. This reaction is used in photography to form the dark bits on photographic film.

The image is fixed by the addition of sodium thiosulphate. The thiosulphate ions ($S_2O_3^{2-}$) form a linear complex ion $[Ag(S_2O_3)_2]^{3-}$ with the Silver halide that have not been decomposed by light and so removing the light sensitive reactant (AgBr).

$[Ag(S_2O_3)_2]^{3-}$ is a colourless solution

Test for presence of aldehyde :
Tollen's Reagent

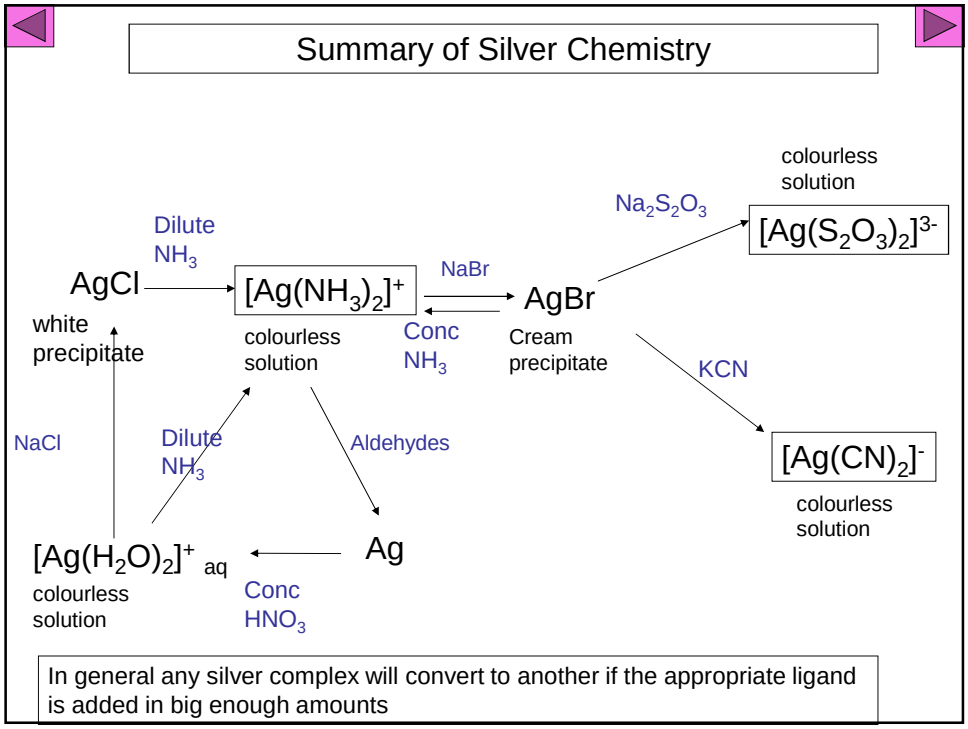
- **Reagent:** Tollen's Reagent formed by mixing aqueous ammonia and silver nitrate. The active substance is the complex ion of $[Ag(NH_3)_2]^+$.
- **Conditions:** heat gently
- **Reaction: aldehydes only** are oxidised by Tollen's reagent into a carboxylic acid and the silver(I) ions are reduced to silver atoms coating the inside of the test tube .

The silver coating the test tube is called a silver mirror .
(**ketones do not react**)

$CH_3CHO + 2Ag^+ + H_2O \rightarrow CH_3COOH + 2Ag + 2H^+$

Use of $[Ag(CN)_2]^-$ ion

- The $[Ag(CN)_2]^-$ complex is used in electroplating silver on to the surface of other metals.
- The object that is to electroplated is made the cathode and is dipped in a solution containing $[Ag(CN)_2]^-$ complex ion
- The Ag^+ ions are then reduced to form silver


Summary of Silver Chemistry
AgCl
white precipitate
Dilute NH_3
$[Ag(NH_3)_2]^+$
colourless solution
NaBr
Conc NH_3
AgBr
Cream precipitate
$Na_2S_2O_3$
colourless solution
$[Ag(S_2O_3)_2]^{3-}$
KCN
$[Ag(CN)_2]^-$
colourless solution
NaCl
Dilute NH_3
Aldehydes
$[Ag(H_2O)_2]^+$ aq
colourless solution
Conc HNO_3
Ag
In general any silver complex will convert to another if the appropriate ligand is added in big enough amounts