PREPARATION AND THE PROPERTIES OF THE COMPOUNDS OF d-BLOCK ELEMENTS

Potassium Permanganate ($KMnO_4$)

Preparation

The production of potassium permanganate involves the utilization of mineral pyrolusite (MnO_2) and includes the following steps.

(a) Conversion of pyrolusite ore to potassium manganate

The Pyrolusite (MnO_2) is melted with either caustic potash (KOH) or potassium carbonate in the presence of air or oxidizing agents like KNO_3 or $KClO_3$. This process results in the formation of a green mass, attributed to the creation of potassium manganate (K_2MnO_4).

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$$

(b) Oxidation of potassium manganate to potassium permanganate

The green mass is dissolved in water, yielding a green solution of potassium manganate. This solution is subsequently subjected to a current of Cl_2, ozone, or CO_2 to oxidize K_2MnO_4 to $KMnO_4$. Following concentration, dark purple crystals of KMnO4 precipitate from the solution.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KCl + 2KMnO_4$$

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2K_2CO_3 + MnO_2\downarrow + 2KMnO_4$$

Alternatively, alkaline potassium manganate is electrolytically oxidised.

Electrolytic method

The electrolytic cell, housing an iron cathode and nickel anode, is filled with the potassium manganate solution. Upon passing a current, the manganate ions are oxidized to permanganate ions at the anode, and concurrently, hydrogen is liberated at the cathode.

	K_2MnO_4	$\longrightarrow$	$2K^+ + MnO_4^{2-}$
At anode:	MnO_4^{-2}	$\longrightarrow$	$MnO_4^- + e^-$
	Green		Purple
At cathode:	$2H^+ + 2e^-$	$\longrightarrow$	$2H$
	$2H$	$\longrightarrow$	H_2

Properties

(a) Colour and M.P.: - Dark violet crystalline solid, M.P. 523 K

(b) Solubility: - Moderately soluble is room temperature, but fairly soluble in hot water giving purple solution.

(c) Heating: - When heated strongly it decomposes at 746 K to give K_2MnO_4 and O_2.

$$2KMnO_4 \xrightarrow{746\text{ k}} K_2MnO_4 + MnO_2 + O_2$$

Solid $KMnO_4$ gives KOH, MnO and water vapours, when heated in current of hydrogen.

$$2KmnO_4 + 5H_2 \xrightarrow{\Delta} 2KOH + 2MnO + 4H_2O$$

(d) Action of alkali: On heating with alkali, potassium permanganate changes into potassium manganate and oxygen gas are evolved.

$$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$$

(e) Action of con. H_2SO_4: With cold H_2SO_4, it gives Mn_2O_7 which on heating decomposes into MnO_2.

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$

$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

(f) Oxidising character: - $KMnO_4$ acts as powerful oxidising agent in neutral, alkaline or acidic solution because it liberates nascent oxygen as: -

Acidic solution: - Mn^{+2} ions are formed

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

or $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O \ [\text{ equal wt. } = \tfrac{M}{5}]$$

Neutral solution :- MnO_2 is formed

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

or $$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^- \ [\text{ equal wt. } = \tfrac{M}{3}]$$

In the course of the reaction, the alkali produced induces the formation of an alkaline medium, even when commencing from a neutral medium.

Alkaline medium: - Manganate ions are formed.

$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + [O]$$

Reactions in Acidic Medium: In acidic medium $KMnO_4$ oxidizes –

(a) Ferrous salts to ferric salts

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O$$

$$Fe^{+2} \longrightarrow Fe^{+3} + e^-] \times 5$$

$$MnO_4^- + 5Fe^{+2} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{+3} + 4H_2O$$

(b) Oxalates to CO_2:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 5$$

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

(c) Iodides to Iodine

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$$

$$2I^- \longrightarrow I_2 + 2e^-] \times 5$$

$$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{+2} + 5I_2 + 8H_2O$$

(d) Sulphites to sulphates

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$$

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$$

$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{+2} + 5SO_4^{2-} + 3H_2O$$

(e) It oxidizes H_2S to S

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{+2} + 4H_2O] \times 2$$

$$S^{2-} \longrightarrow S + 2e^-] \times 5$$

$$2MnO_4^- + 16H^+ + 5S^{-2} \longrightarrow 2Mn^{+2} + 5S + 8H_2O$$

(f) It oxidizes SO_2 to sulphuric acid

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$SO_2 + H_2O + [O] \longrightarrow H_2SO_4] \times 5$$
$$2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

(g) It oxidizes Nitrites to nitrates

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$KNO_2 + O \longrightarrow KNO_3] \times 5$$
$$2KMnO_4 + 5KNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O$$

Reactions in Neutral Medium

(a) It oxidizes H_2S to sulphur:

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3\,[O]$$
$$H_2S + O \longrightarrow H_2O + S] \times 3$$
$$2KMnO_4 + 3H_2S \longrightarrow 2KOH + 2MnO_2 + 2H_2O + 3S$$

(b) It oxidizes Manganese sulphate ($MnSO_4$ to MnO_2) manganese dioxide:

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3\,[O]$$
$$MnSO_4 + H_2O + O \longrightarrow MnO_2 + H_2SO_4] \times 3$$
$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$
$$2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

(c) It oxidizes Sodium thiosulphate to sulphate and sulphur:

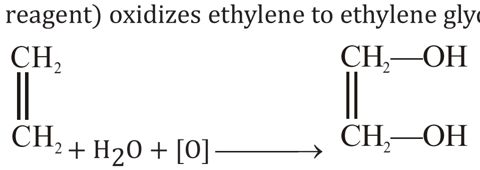
$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3\,[O]$$
$$Na_2S_2O_3 + O \longrightarrow Na_2SO_4 + S] \times 3$$
$$2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2MnO_2 + 3Na_2SO_4 + 2KOH + 3S$$

Reactions in Alkaline Medium

(a) It oxidizes Iodides to Iodates in alkaline medium:

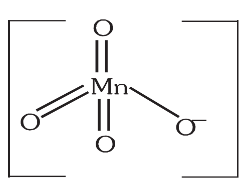
$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3\,[O]$$
$$KI + 3O \longrightarrow KIO_3$$
$$2KMnO_4 + KI + H_2O \longrightarrow 2MnO_2 + 2KOH + KIO_3$$

(b) Alkaline $KMnO_4$ (Baeyer's reagent) oxidizes ethylene to ethylene glycol.



Structure

MnO_4^-



Uses

(a) Employed in volumetric analysis to estimate ferrous salts, oxalates, and other reducing agents, though it is not utilized as a primary standard due to challenges in obtaining it in a pure state.
(b) Functions as a potent oxidizing agent in both laboratory and industrial settings.
(c) Used as a disinfectant and germicide.
(d) Found in dry cells.
(e) Utilized for washing wounds in the form of a highly diluted $KMnO_4$ solution.

Ex. Potassium permanganate acts as an oxidant in neutral, alkaline as well as acidic media. The final products obtained from it in three conditions are respectively:

(A) MnO_4^{2-}, Mn^{3+} and Mn^{2+}
(B) MnO_2, MnO_2 and Mn^{2+}
(C) MnO_2, MnO_2^+ and Mn^{3+}
(D) MnO, MnO_2^+ and Mn^{2+}

Sol.

$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^- \text{ (neutral medium)}$$

$$e^- + MnO_4^- \longrightarrow MnO_4^{-2} \text{ (dilute alkaline medium)}$$

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \text{ (acidic medium)}$$

Therefore, (B) option is correct.

Potassium Dichromate ($K_2Cr_2O_7$)

Preparation

The chromite ore is roasted with sodium carbonate in presence of air in a reverberatory furnace.

$$4FeO.\,Cr_2O_3 \text{ (chromite ore)} + 8Na_2CO_3 + 7O_2 \xrightarrow[\text{in air}]{\text{Roasting}} 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

The roasted mass is extracted with water when Na_2CrO_4 goes into the solution leaving behind insoluble Fe_2O_3. The solution is then treated with calculated amount of H_2SO_4.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The solution is concentrated when less soluble Na_2SO_4 crystallizes out. The solution is further concentrated when crystals of $Na_2Cr_2O_7$ are obtained. Hot saturated solution of $Na_2Cr_2O_7$ is then treated with KCl when orange red crystals of $K_2Cr_2O_7$ are obtained on crystallization.

$$Na_2Cr_2O_7 + 2KCI \rightarrow K_2Cr_2O_7 + 2\,NaCl$$

Note: $K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a primary standard in volumetric estimation because $Na_2Cr_2O_7$ is hygroscopic in nature but $K_2Cr_2O_7$ is not.

Properties

(a) Physical

This crystalline compound exhibits an orange-red color and displays moderate solubility in cold water, becoming freely soluble in hot water. Its melting point is 398°C.

(b) Chemical

(i) Effect of heating:

On heating strongly, it decomposes liberating oxygen.

$$2K_2Cr_2O_7 \rightarrow 2K_2CrO_4 + Cr_2O_3 + O_2$$

Upon exposure to alkalies, it undergoes conversion to chromate, resulting in a color change from orange to yellow. Upon acidification, the yellow color reverts to orange.

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$$

$$Cr_2O + 2OH^- \rightarrow 2CrO + H_2O$$

Orange Yellow

$$2CrO + 2H^+ \rightarrow Cr_2O + H_2O$$

Yellow Orange

Thus CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium and are interconvertible by altering the pH of solution.

$$2CrO + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O + H_2O$$

Chromate ions are present in alkaline solutions, whereas dichromate ions are present in acidic solutions.

(ii) $K_2Cr_2O_7 + 2H_2SO_4$ (conc. & cold) $\rightarrow 2CrO_3\downarrow$ (bright orange/red) $+ 2KHSO_4 + H_2O$

$2K_2Cr_2O_7 + 8H_2SO_4$ (conc. & Hot) $\rightarrow 2K_2SO_4 + 8H_2O + 2Cr_2(SO_4)_3 + 3O_2$

(iii) Acidified $K_2Cr_2O_7$ solution reacts with H_2O_2 to give a deep blue solution due to the formation of CrO_5.

$$Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \rightarrow 2CrO_5 + 5H_2O$$

The gradual fading of the blue color in an aqueous solution is attributed to the decomposition of CrO_5 into Cr^{3+} ions and oxygen. In a less acidic solution, the combination of $K_2Cr_2O_7$ and H_2O_2 produces a violet-colored and diamagnetic salt due to the formation of $[CrO(O_2)(OH)]^-$. In an alkaline medium with 30% H_2O_2, a red-brown K_3CrO_8 (diperoxo) is formed, representing a tetra-peroxy species $[Cr(O_2)_4]^{3-}$, and thus, chromium is in the +V oxidation state. In an ammoniacal solution, a dark red-brown compound, $(NH_3)_3CrO_4$, which is a diperoxo compound with Cr(IV), is generated.

(iv) Potassium dichromate reacts with hydrochloric acid and evolves chlorine gas.

$$K_2Cr_2O_7 + 14HCl \rightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

(v) It acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4)

$$Cr_2O + 14H^+ + 6e^- \rightarrow 2Cr^{+3} + 7H_2O.\ (E^o = 1.33\ V)$$

The oxidation state of Cr changes from + 6 to +3.

(a) Iodine is liberated from potassium iodide:

$$Cr_2O + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$2I^- \rightarrow I_2 + 2e^- \times [3]$$

$$\overline{Cr_2O + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O}$$

(b) Ferrous salts are oxidised to ferric salts:

$$6Fe^{2+} + Cr_2O + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

(c) Sulphites are oxidised to sulphates:

$$Cr_2O + 3SO + 8H^+ \rightarrow 3SO + 2Cr^{3+} + 4H_2O$$

(d) H_2S is oxidised to sulphur:

$$Cr_2O + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3S$$

(e) SO_2 is oxidised to H_2SO_4:

$$Cr_2O_7^{2-} + 3SO_2 + 2H^+ \rightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O\ ;$$

Chrome alum is obtained when acidified $K_2Cr_2O_7$ solution is saturated with SO_2.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 + 23H_2O \xrightarrow{T < 70^\circ C} K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$$

(f) It oxidises ethyl alcohol to acetaldehyde and acetaldehyde to acetic acid

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} \xrightarrow{[O]} \underset{\text{acetaldehyde}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{acetic acid}}{CH_3COOH}$$

(g) It also oxidises nitrites to nitrates, arsenates to arsenates, HBr to Br_2. HI to I_2, etc.

(h) $K_2Cr_2O_7 + 2C \text{ (charcoal)} \xrightarrow{\Delta} Cr_2O_3 + K_2CO_3 + CO\uparrow$

(vi) Chromyl chloride test: $4Cl^- + Cr_2O_7^{2-} + 6H^+ \rightarrow 2CrO_2Cl_2\uparrow \text{ (deep red)} + 3H_2O$

$$CrO_2Cl_2 + 4OH^- \rightarrow CrO_4^{2-} \text{ (yellow)} + 2Cl^- + 2H_2O$$

$$CrO_4^{2-} \text{ (yellow)} + Pb^{2+} \rightarrow PbCrO_4\downarrow \text{ (yellow)}$$

(vii) $Cr_2O_7^{2-} \text{ (concentrated solution)} + 2Ag^+ \rightarrow Ag_2Cr_2O_7\downarrow \text{ (reddish brown)}$

$$Ag_2Cr_2O_7 + H_2O \rightarrow Ag_2CrO_4 + CrO_4^{2-} + 2H^+.$$

(viii) $Cr_2O_7^{2-} + Ba^{2+} + H_2O \rightleftharpoons 2BaCrO_4\downarrow + 2H^+$

As strong acid is produced, the precipitation is only partial. But if NaOH or CH_3COONa is added, precipitate becomes quantitative.

Uses

It is used:

(i) Employed as a volumetric reagent for estimating reducing agents like oxalic acid, ferrous ions, iodide ions, etc., and serves as a primary standard.

(ii) Utilized in the synthesis of various chromium compounds such as chrome alum, chrome yellow, chrome red, zinc yellow, etc.

(iii) Applied in various industries including dyeing, chrome tanning, calico printing, photography, etc.

(iv) Functions as a cleansing agent for glassware in the form of chromic acid.

Ex. An inorganic compound (A) has garnet red prismatic crystals. (A) is moderately soluble in water and dissolves in cold concentrated H_2SO_4 to yield red crystals (B). In presence of dilute H_2SO_4 it converts a pungent gas(C) into a yellow turbidity (D) and converts a suffocating gas (E) into a green solution (F). The gas (C)and (E) also combine to produce the yellow turbidity (D). With KI and starch in presence of dilute. H_2SO_4 (A) yields blue colour. (A) and concentrated H_2SO_4 mixture is used as a cleansing agent for glassware in the laboratory. Identify (A)and explain the reactions.

Sol. As compound (A) has garnet red prismatic crystals which with cold conc. H_2SO_4 gives red crystals and a suffocating gas (SO_2) turns its solution in water in to green coloured solution, therefore compound (A) may be $K_2Cr_2O_7$.

$$\underset{(A)}{K_2Cr_2O_7} + 4H_2SO_4 + 3H_2S \rightarrow KHSO_4 + \underset{(B)}{2\,CrO_3 \text{ (red crystals)}} + H_2O$$

$$K_2Cr_2O_7 + 4H_2SO_4 + \underset{(C)}{3H_2S} \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + \underset{(D)}{3S\downarrow \text{ (Yellow)}}$$

$$K_2Cr_2O_7 + H_2SO_4 + \underset{(E)}{3SO_2} \rightarrow \underset{(F)}{Cr_2(SO_4)_3 \text{ (Green solution)}} + K_2SO_4 + H_2O$$

$$K_2Cr_2O_7 + 7H_2SO_4 + 6KI \rightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2 \quad I_2 + \text{Starch Blue colour}$$

Silver Nitrate (Lunar Caustic), $AgNO_3$

Silver nitrate stands out as the prevalent and pivotal salt within the realm of silver compounds.

Preparation

It is derived through the process of heating diluted nitric acid with silver. Upon concentration and subsequent cooling of the solution, silver nitrate crystals precipitate out.

$$3Ag + 4HNO_3 \xrightarrow{\text{Heat}} 3AgNO_3 + NO + 2H_2O$$

Properties

1. This compound manifests as colorless crystalline structures, possessing solubility in both water and alcohol mediums. Its melting point registers at 212°C.
2. When encountering organic materials, it undergoes decomposition, resulting in the formation of metallic silver, thus imparting a blackened appearance.
3. Subjected to temperatures surpassing its melting point, it initiates decomposition, yielding silver nitrite and oxygen as the resultant products.

$$2AgNO_3 \rightarrow 2AgNO_2 + O_2$$

$$2AgNO_2 \xrightarrow{\text{Red heat}} 2Ag + 2NO_2$$

Precipitation reaction

(a) Chlorides, bromides, and iodides produce a precipitate that exhibits insolubility when exposed to dilute nitric acid (HNO_3).

$$NaCl + AgNO_3 \rightarrow \underset{\text{white ppt}}{AgCl} + NaNO_3$$

$$KBr + AgNO_3 \rightarrow \underset{\text{Pale yellow ppt}}{AgBr} + KNO$$

$$Nal + AgNO_3 \rightarrow \underset{\text{Pale yellow ppt}}{Agl} + NaNO_3$$

(b) Phosphates and arsenites produce a yellow precipitate that dissolves in both dilute nitric acid and ammonia.

$$3AgNO_3 + Na_3PO_4 \rightarrow Ag_3PO_4 + 3NaNO_3$$

$$Na_3AsO_3 + 3AgNO_3 \rightarrow Ag_3AsO_3 + 3NaNO_3$$

(c) Chromates and arsinates yield a precipitate that is red in color.

$$K_2CrO_4 + 2AgNO_3 \rightarrow Ag_2CrO_4 + 2KNO_3$$

(d) Sulphides produce a precipitate that is black in color.

$$Na_2S + 2AgNO_3 \rightarrow Ag_2S + 2NaNO_3$$

(e) Oxalates and borates yield a precipitate that is white in color.

$$Na_2C_2O_4 + 2AgNO_3 \rightarrow Ag_2C_2O_4 + 2NaNO_3$$

$$Na_3BO_3 + 3AgNO_3 \rightarrow \underset{\text{silver borate}}{Ag_3BO_3} + 3NaNO_3$$

(f) Thiosulfates produce a white precipitate composed of $Ag_2S_2O_3$, which progressively darkens to black as a result of hydrolysis over time.

$$Na_2S_2O_3 + 2AgNO_3 \rightarrow Ag_2S_2O_3 + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O \rightarrow Ag_2S + H_2SO_4$$

(g) Upon treatment with a sodium hydroxide (NaOH) solution, it results in the formation of a precipitate consisting of silver oxide.

$$2AgNO_3 + 2NaOH \rightarrow Ag_2O + 2NaNO_3 + H_2O$$

(h) Upon the addition of potassium cyanide (KCN) to silver nitrate, a white precipitate of silver cyanide emerges, which dissolves in an excess of KCN, giving rise to a complex salt known as potassium argent cyanide.

$$AgNO_3 + KCN \rightarrow AgCN + KNO_3$$
$$AgCN + KCN \rightarrow K[Ag(CN)_2]$$

(i) Upon the introduction of sodium thiosulfate to silver nitrate, a white precipitate of silver thiosulfate becomes evident. Nonetheless, this precipitate dissolves in an excess of sodium thiosulfate, resulting in the formation of a complex salt.

$$2AgNO_3 + Na_2S_2O_3 \rightarrow Ag_2S_2O_3 + 2NaNO_3$$
$$Ag_2S_2O_3 + 3Na_2S_2O_3 \rightarrow 2Na_3\,[Ag(S_2O_3)_2]$$

sodium argent thiosulphate