CONCEPT: OXIDIZING AGENTS – PERMANGANATE ION

The most commonly used oxidizing agent titrants include _____, _____, _____ and _____.

- An analyte that is a weak reducing agent requires one of these strong oxidizing agents during titrations.

Permanganate ion is difficult to isolate because it can easily oxidize its aqueous solvent to form MnO_2 precipitate.

- In order to isolate the oxidizing agent we must catalyze it with _____, _____, _____ or _____.

$$MnO_4^- (aq) + 8\,H^+ (aq) + 5\,e^- \rightleftharpoons Mn^{2+} (aq) + 4\,H_2O (l)$$

Standardization

Boiling it for an hour followed by filtration to MnO_2 can produce a stable permanganate solution.

- Pairing it with a reducing agent such as Fe^{2+} or $H_2C_2O_4$ can accomplish this standardization.

$$MnO_4^- (aq) + 5\,Fe^{2+} (aq) + 8\,H^+ (aq) \rightarrow Mn^{2+} (aq) + 5\,Fe^{3+} (aq) + 4\,H_2O (l)$$

$$2\,MnO_4^- (aq) + 5\,H_2C_2O_4 (aq) + 6\,H^+ (aq) \rightarrow 2\,Mn^{2+} (aq) + 10\,CO_2 (g) + 8\,H_2O (l)$$

- Near the endpoint a slight _____ color will appear to represent excess MnO_4^-.

Oxidation Reactions

In highly basic solutions with pH ≥ 12, permanganate is reduced to the _____ manganate ion:

$$MnO_4^- (aq) + e^- \rightleftharpoons MnO_4^{2-} (aq)$$

In highly acidic solutions with pH ≤ 1, permanganate is reduced to the _____ manganese (II) ion:

$$MnO_4^- (aq) + 8\,H^+ (aq) + 5\,e^- \rightleftharpoons Mn^{2+} (aq) + 4\,H_2O (l)$$

In neutral and basic solutions, permanganate is reduced to a _____ manganese (IV) oxide precipitate:

$$MnO_4^- (aq) + 4\,H^+ (aq) + 3\,e^- \rightleftharpoons MnO_2 (s) + 2\,H_2O (l)$$

CONCEPT: OXIDIZING AGENTS – CERIUM (IV) ION

Like other strong oxidizing agents the cerium (IV) ion must first be prepared before it can take part in a redox titration.

- It is less commonly used because of the cost in preparation, storage and utilization.

$$Ce^{4+}(aq) + e^{-} \rightleftharpoons Ce^{3+}(aq)$$

- The cerium (III) ion is more stable oxidative state of the two ions.

Standardization

There are different ways to prepare a cerium (IV) ion solution:

- From a primary standard of cerium (IV) ammonium nitrate, $Ce(NO_3)_4 \cdot 2\,NH_4NO_3$ dissolved in 1.0 M H_2SO_4 solution.
- From $Ce(OH)_4$ being standardized against primary reducing agents such as Fe^{2+} or $H_2C_2O_4$ as using a ferroin indicator.

$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

$$2\,Ce^{4+}(aq) + H_2C_2O_4(aq) \rightarrow 2\,Ce^{3+}(aq) + 2\,CO_2(aq) + 2\,H^{+}(aq)$$

Oxidation Reactions

A common reaction involves the reaction of ferrous ammonium sulfate hexahydrate, $(NH_4)_2Fe(SO_4)_2 \cdot 6\,H_2O$, cerium (IV) ammonium nitrate, $Ce(NO_3)_4 \cdot 2\,NH_4NO_3$.

- The net-ionic equation can be seen as:

$$Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

Another reaction involves the oxidation of malonic acid.

- The overall reaction can be seen as:

$$HC_3H_3O_4(aq) + 6\,Ce^{4+}(aq) \rightarrow HCO_2H + 2\,CO_2(g) + 6\,Ce^{3+}(aq) + 6\,H^{+}(aq)$$

CONCEPT: OXIDIZING AGENTS – DICHROMATE ION

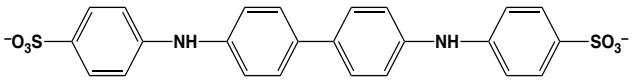
The dichromate ion is not as strong of an oxidizing agent as Ce^{4+} or MnO_4^-, but is more readily available and stable.

- Its reduction half-cell reaction within an acidic solution can be seen as:

$$Cr_2O_7^{2-}\,(aq) + 14\,H^+\,(aq) + 6\,e^- \rightleftharpoons 2\,Cr^{3+}\,(aq) + 7\,H_2O\,(l)$$

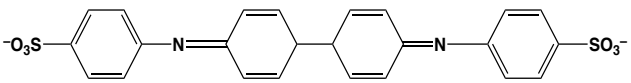
- Diphenylamine sulfonic acid or diphenylbenzidine sulfonic acid are the preferred indicators to discover the end point, while the overall reaction is monitored the calomel and Pt electrodes.

Diphenylamine sulfonic acid



Reduced form (_____)

Diphenylbenzidine sulfonic acid



$+ 2\,H^+ + 2\,e^-$ *Oxidized form (_____)*

- Once placed into a basic solution dichromate is converted to chromate ion:

$$CrO_4^{2-}\,(aq) + 4\,H_2O\,(l) + 3\,e^- \rightleftharpoons Cr(OH)_3\,(s) + 5\,OH^-\,(aq)$$

Oxidation Reactions

The dichromate ion is predominantly used as an oxidizing agent in organic reactions.

- 1º Alcohols can be oxidized into aldehydes and, under more stringent conditions into carboxylic acids.

- 2º Alcohols can be oxidized into ketones, while 3º Alcohols cannot be oxidized.

CONCEPT: OXIDIZING AGENTS – TRIIODIDE ION

Triiodide ion represents the weakest of the 4 strong oxidizing agents.

- It is only useful when the analyte is a stronger reducing agent.

It's half-cell reduction reaction can be seen as:

$$I_2\,(aq) + 2\,e^- \rightleftharpoons 2\,I^-\,(aq)$$

Molecular iodine is slightly soluble in an aqueous solution and so iodide ion is added to form the more soluble triiodide ion.

$$I_2\,(aq) + I^-\,(aq) \rightleftharpoons I_3^-\,(aq)$$

This creates the new reduction reaction as:

$$I_3^-\,(aq) + 2\,e^-\,(aq) \rightleftharpoons 3\,I^-\,(aq)$$

Standardization

A solution of triiodide ion is normalized by using $Na_2S_2O_3$ while using starch as an indicator for the triiodide ion.

$$I_3^-\,(aq) + 2\,S_2O_3^{2-}\,(aq) \rightleftharpoons 3\,I^-\,(aq) + 2\,S_4O_6^{2-}\,(aq)$$

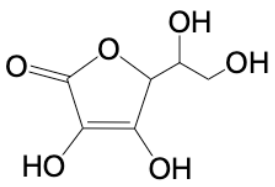
Newly created iodide solution is colorless, but with exposure to air the iodide ion will undergo oxidation to the yellow triiodide ion.

Oxidation Reactions

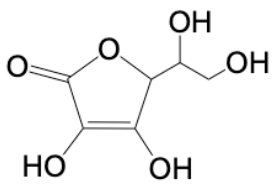
Ascorbic acid, also known as Vitamin C, is often called the "biological anti-oxidant" because of its role as a reducing agent.

- Iodine can quickly oxidize ascorbic acid, $C_6H_8O_6$, to generate dehydroascorbic acid, $C_6H_6O_6$:

$$C_6H_8O_6\,(aq) + I_2\,(aq) \rightleftharpoons C_6H_6O_6\,(aq) + 2\,I^-\,(aq) + 2\,H^+\,(aq)$$



Ascorbic Acid
$C_6H_8O_6$



Dehydroascorbic Acid
$C_6H_6O_6$