Both oxidation and reduction occur during a titration. The equivalence point is based on the concentration of the oxidized and reduced form of all species involved.

\[ A_{ox} + B_{red} = A_{red} + B_{ox} \]

\[ Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+} \]

For a REDOX titration, the equivalence point is the point where \( E_{\text{forward}} = E_{\text{reverse}} \).

\[ E_{\text{cell}} = 0 \]

Since the \( E \) values are concentration dependent, we must rely on the Nernst equation

\[ E = E^0 - \frac{0.0592}{n} \log \frac{[A_{\text{red}}]}{[A_{ox}]} \]

At the equivalence point:

\[ E_{\text{eq}} = \frac{n_A E^0_A + n_B E^0_B}{n_A + n_B} \]

Determine the \( E_{eq} \) for the following reaction:

\[ Fe^{2+} + Ce^{4+} = Fe^{3+} + Ce^{3+} \]

\( E^0_{Fe^{3+}/Fe^{2+}} = +0.771 \text{V} \)

\( E^0_{Ce^{3+}/Ce^{4+}} = +1.70 \text{V} \)

\( n_{Fe} = 1, n_{Ce} = 1 \)

\[ E_{eq} = \frac{1.70V + 0.771V}{2} = 1.24 \text{ V} \]
Determining $E_{eq}$ becomes much more complicated for more complex systems.

The inclusion of one additional species, like $H^+$ is relatively common.

Let's look at another example.

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ = 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

First, obtain both half reactions:

$$E_{eq} = E_{Fe}^{o} \frac{0.0592}{1} \log \left[ \frac{Fe^{2+}}{Fe^{3+}} \right]$$

$$E_{eq} = E_{Cr}^{o} \frac{0.0592}{6} \log \left[ \frac{Cr^{3+}}{Cr_2O_7^{2-}} \right] \left[ H^+ \right]^{14}$$

At the equivalence point:

$$[Fe^{2+}] = 6[Cr_2O_7^{2-}]$$

$$[Fe^{3+}] = 3[Cr^{3+}]$$

So for this reaction, the equivalence point is dependent on both $[Cr^{3+}]$ and $[H^+]$.

This explains why we commonly work in 1M acid and with dilute solutions.

If the reaction was conducted under these conditions then:

$$E_{eq} = 1.25V - 8.46 \times 10^{-3} \log \left[ \frac{2[Cr^{3+}]}{[H^+]^{14}} \right]$$

$E_{eq}$ shows only a small dependence on $Cr^{3+}$.

As with acid/base titrations, we can get either to the following types of curves.

Based on the type of reaction.
Unlike acid/base titrations, we really can’t do much with this region.

While some Fe^{3+} must be present, we can only guess what the concentration is.

No Ce^{4+} or Ce^{3+} are present, so we don’t have a complete reaction.

Between 0% and 100% titration, we can use the Nernst equation for Fe^{2+}/Fe^{3+}.

\[
E_{Fe} = 0.771 - 0.0592 \log \left[ \frac{[Fe^{2+}]}{[Fe^{3+}]} \right]
\]

There is no significant level of Ce^{4+} to work with anyway.

We can simplify our calculations by using the % titration.

\[
E_{Fe} = 0.771 - 0.0592 \log \frac{\%Fe^{2+}}{\%Fe^{3+}}
\]
1.70V + 0.771V
2
0.6
0.7
0.8
0.9
1
1.1
1.2
1.3
0 20 40 60 80 100 120
Note the large jump in E at the equivalence point.

At greater than 100% titration, the predominate change is that Ce^{4+} is being added and diluted into a solution of Ce^{3+}.

All Fe^{2+} has been converted to Fe^{3+} and no longer figures into the calculations.

We just need to keep track of the amounts of Ce^{3+} and Ce^{4+} as well as the total volume of the system.

So far, we've not needed to worry about the actual concentrations. However, to know the volumes involved, we now need them.

Let's assume that we started with 100ml of a Fe^{2+} solution and our titrant was 0.1M Ce^{4+}.

Now we can determine the E for overtitration.

At the equivalence point:
Solution volume = 200 ml
[Ce^{3+}] = 0.05M

At 10% overtitration, we've added an additional 10ml of our Ce^{4+} solution so:

[Ce^{3+}] = 0.0476 M
[Ce^{4+}] = 0.00476 M

In this case, however, we'll use the values for Ce^{3+} and Ce^{4+}.

E = 1.40 - 0.0592 log \frac{0.0476}{0.00476}
= 1.34

At 20% overtitration, E would be 1.36.
**Redox indicators**

**General**

Rely on a color change with $\text{Ind}_{\text{ox}}$ and $\text{Ind}_{\text{red}}$ being different colors.

\[
\text{Ind}_{\text{ox}} + n\text{e} = \text{Ind}_{\text{red}}
\]

\[
E = E_{\text{ind}}^o - \frac{0.0592}{n} \log \left[ \frac{[\text{Ind}_{\text{red}}]}{[\text{Ind}_{\text{ox}}]} \right]
\]

**Specific**

React with a specific chemical species involved in the titration.

**Examples**

1,10 phenanthroline - Fe salt

\[
\text{(Phen)}_3\text{Fe}^{3+} + e = \text{(Phen)}_3\text{Fe}^{2+}
\]

N-Fe pale blue \quad red

$E^o = 1.06V$

$n = 1 \quad \Delta E = 0.118 \ V$

$n = 2 \quad \Delta E = 0.0592 \ V$

$n = 3 \quad \Delta E = 0.0395 \ V$

**General**

In order to see a color change, you typically need approximately a 10% conversion from one form to another.

\[
\frac{[\text{Ind}_{\text{red}}]}{[\text{Ind}_{\text{ox}}]} \leq \frac{1}{10} \quad \text{or} \quad \geq 10
\]

So our region of color change is at

\[
E = E_{\text{ind}}^o \pm \frac{0.0592}{n}
\]
If the goal is to reduce your analyte to a single oxidation state, you can use either a Jones or Walden Reductor.

Both are columns containing a metal.

You slowly wash your sample through the column with water.
If the goal is to oxidize your analyte to a single form, no material is available that can be used as a column.

You must have a method to remove any excess oxidizing reagents prior to titration.

Often, the results in the preparation step being more complicated than the rest of the method.

**Jones Reductor**

\[ \text{Zn(Hg)} + \text{Zn}^{2+} + \text{Hg} + 2e \]

An amalgam is used to prevent

\[ \text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2(g) \]

**Walden Reductor**

\[ \text{Ag} + \text{HCl} \rightarrow \text{AgCl(s)} + e \]

Cl\(^-\) is needed to prevent Ag\(^+\) from entering the solution - typically use HCl

Jones Reductor is stronger than Walden.

**Oxidizing**

**Sodium bismuthate - NaBiO\(_3\)**

Very powerful, will even convert Mn\(^{2+}\) to MnO\(_4^-\)

Not very soluble so excess reagent can be removed by filtration.

You typically make a suspension with your sample and then boil it.

**Oxidizing**

**Ammonium peroxodisulfate - (NH\(_4\))\(_2\)S\(_2\)O\(_8\)**

In acid, we can covert

\[ \text{Cr}^{3+} \rightarrow \text{Cr}_2\text{O}_7^{2-}, \text{Mn}^{2+}, \text{MnO}_4^-, \text{Ce}^{3+}, \text{Ce}^{4+} \]

Excess is removed by adding a trace of Ag\(^+\) and boiling. This decomposes the reagent

\[ 2\text{S}_2\text{O}_8^{2-} + 2\text{H}_2\text{O} \rightarrow \text{Ag}^+ + 4\text{SO}_4^{2-} + \text{O}_2(g) + 4\text{H}^+ \]

**Oxidizing**

**Peroxide**

Not as strong as the other examples

Must be used in acidic solution

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e = 2\text{H}_2\text{O} \]

Excess can be removed by boiling.

**Oxidizing titrants**

**Cr\(_2\)O\(_7^{2-}\)**

Primary standard material

Need an indicator such as diphenylamine sulfonic acid.

Very stable solutions. If air is kept out, it can last for years.

\[ E = 1.44 \text{ V} \]
**Common titrants**

**Oxidizing titrants**

**MnO₄⁻**  \[ E^\circ = 1.51 \text{ V} \]

Solutions must be standardized - typically use Na₂C₂O₄ (a primary standard material.)

Reagent slowly degrades and MnO₂ must be removed

No indicator is needed - excess reagent produces a pink solution.

**Reducing titrants**

**Fe²⁺**

Used in the form of as

\[ \text{Fe(NH}_4\text{)}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} \text{ in 1.0 N H}_2\text{SO}_4 \]

Solution must be standardized each day.

---

**Common titrants**

**Reducing titrants**

**Iodide - indirect method**

\[ 2\text{I}^- = \text{I}_2 + 2\text{e}^- \]

It can’t be used directly due to its intense color and reaction with air.

It's more common to add excess iodide and use starch as an indicator.

Any iodine that is produced can be determined by titration with Na₂S₂O₃.

**Reducing titrants**

**Iodide - indirect method**

What happens is that

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

It looks like it would just be easier to reduce our analyte with S₂O₃²⁻ directly.

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**Common titrants**

**Iodide - indirect method**

S₂O₃²⁻ can’t be used directly with most material. It results in a mixture of S₂O₆²⁻ and SO₄²⁻ which can’t be predicted

Reaction with I₂ is unique in that only S₂O₆²⁻ is formed.

**Reducing titrants**

- S₂O₃²⁻ is not a primary standard material.
- It must be standardized using KIO₃.
  \[ IO₃^- + 5 I^- + 6 H^+ = 3 I_3^- + 3 H_2O \]
- KI is added to form I₃⁻, which is water soluble.
- Although S₂O₃²⁻ solutions are resistant to air oxidation, the trend to decompose:
  \[ S₂O₃^{2-} + H^+ \rightarrow HSO₃^- + S_{(s)} \]
Methanol is added to remove the reactive $\text{C}_5\text{H}_5\text{N}.\text{SO}_3$ complex.

$$\text{C}_5\text{H}_5\text{N}.\text{SO}_3 + \text{CH}_3\text{OH} \rightarrow \text{C}_5\text{H}_5\text{N}(\text{H})\text{SO}_4\text{CH}_3$$

This is done because the SO₃ complex can react with water as well as many other species.

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**Another example**

The reagent is proprietary so it must be purchased.

Fortunately, it is relatively stable.

It is most commonly used with a special auto titrator system.

**Endpoint detection.**

Intense color produced by $I_2$ complex.