Redox titrations are essential in measuring the chemical composition of a superconductor (\(\text{YBa}_2\text{Cu}_3\text{O}_7 - \frac{2}{3} \text{Cu}^{2+} \text{ and } \frac{1}{3} \text{the unusual } \text{Cu}^{3+}\))
**KMnO\textsubscript{4} Titrations**

\[ 8\text{H}^+ + \text{MnO}_4^- + 5e^- = \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E^0 = +1.51\text{V} \]

permanganate is one of the strongest oxidizing agents available

Fe\textsuperscript{3+} is reduced to Fe\textsuperscript{2+} with Sn\textsuperscript{2+} or a Jones reductor. Titrations are carried out in 1 M H\textsubscript{2}SO\textsubscript{4} or 1 M HCl containing Mn\textsuperscript{2+}, H\textsubscript{3}PO\textsubscript{4}, and H\textsubscript{2}SO\textsubscript{4}. Mn\textsuperscript{2+} inhibits oxidation of Cl\textsuperscript{-} by MnO\textsubscript{4}. H\textsubscript{3}PO\textsubscript{4} complexes Fe\textsuperscript{3+} to prevent formation of yellow Fe\textsuperscript{3+}-chloride complexes.

---

**Preliminary Sample Treatment**


The iron in iron ore is usually both Fe\textsuperscript{2+} and Fe\textsuperscript{3+}, so a reducing agent such as tin(II) chloride is used to convert it entirely to Fe\textsuperscript{2+}.

**Step 1:** Sn\textsuperscript{2+} + 2Fe\textsuperscript{3+} → Sn\textsuperscript{4+} + 2Fe\textsuperscript{2+} where the Sn\textsuperscript{2+} is added in excess

**Step 2:** The excess Sn\textsuperscript{2+} that didn’t react will react with the KMnO\textsubscript{4}, so it is removed by treating with HgCl\textsubscript{2}:

\[ 2\text{HgCl}_2 + \text{Sn}^{2+} \rightarrow \text{Hg}_2\text{Cl}_2(s) + \text{Sn}^{4+} + 2\text{Cl}^- \]

**Step 3:** To prevent the reaction of Cl\textsuperscript{-} with KMnO\textsubscript{4}, the Zimmerman-Reinhardt reagent is added. This reagent contains Mn\textsuperscript{2+} to prevent the oxidation of Cl\textsuperscript{-} and H\textsubscript{3}PO\textsubscript{4} prevents the formation of Fe\textsuperscript{3+}-chloride complexes as the titration proceeds.
**KMnO₄ Standardization Using Na₂C₂O₄**

It takes 38.29 mL of a permanganate solution to titrate 0.2587 g of primary standard NaC₂O₄ (M = 133.999). What is the molarity of the permanganate?

\[ 5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \]

---

**Determination of %Fe in an Ore**

A 0.4857 g iron ore sample was dissolved in concentrated acid and reduced to Fe²⁺ using SnCl₂. 41.21 mL of 0.01963 M MnO₄⁻ was required to titrate the sample. Calculate the %Fe in the ore.

\[ MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \]
Redox System | Standard Potential | Formal Potential | Solution
--- | --- | --- | ---
\( Ce^{4+} + e^- = Ce^{3+} \) | --- | 1.23 | 1 M HCl
 | | 1.44 | 1 M H\(_2\)SO\(_4\)
 | | 1.61 | 1 M HNO\(_3\)
 | | 1.7 | 1 M HClO\(_4\)
\( Fe^{3+} + e^- = Fe^{2+} \) | +0.771 | 0.68 | 1 M H\(_2\)SO\(_4\)
 | | 0.700 | 1 M HCl
 | | 0.767 | 1 M HClO\(_4\)
\( Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O \) | +1.33 | 1.00 | 1 M HCl
 | | 1.05 | 2 M HCl
 | | 1.08 | 3 M HCl
 | | 1.08 | 0.5 M H\(_2\)SO\(_4\)
 | | 1.15 | 4 M H\(_2\)SO\(_4\)
 | | 1.03 | 1 M HClO\(_4\)
\( H_3AsO_4 + 2H^+ + 2e^- = H_3AsO_3 + H_2O \) | +0.559 | 0.557 | 1 M HCl
 | | 0.557 | 1 M HClO\(_4\)
\( Cr^{3+} + e^- = Cr^{2+} \) | -0.42 | -0.38 | 1 M HClO\(_4\)
\( Sn^{4+} + 2e^- = Sn^{2+} \) | +0.15 | 0.14 | 1 M HCl

**Theory of Redox Titrations (Sec 16-1)**

**Titration reaction example** -
\( Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+} \)

titrant analyte

After the titration, most of the ions in solution are Ce\(^{3+}\) and Fe\(^{3+}\), but there will be equilibrium amounts of Ce\(^{4+}\) and Fe\(^{2+}\). All 4 of these ions undergo redox reactions with the electrodes used to follow the titration. These redox reactions are used to calculate the potential developed during the titration.
**Saturated Calomel Reference Electrode half-reaction:**

\[ 2\text{Hg}(l) + 2\text{Cl}^-(aq) = \text{Hg}_2\text{Cl}_2(s) + 2e^- \quad E^o = 0.241 \text{ V} \]

**Pt electrode half-reactions:**

\[ \text{Fe}^{3+} + e^- = \text{Fe}^{2+} \quad E^{o'} = 0.767 \text{ V}^* \]
\[ \text{Ce}^{4+} + e^- = \text{Ce}^{3+} \quad E^{o'} = 1.70 \text{ V}^* \]

The net cell reaction can be described in two equivalent ways:

\[ 2\text{Fe}^{3+} + 2\text{Hg}(l) + 2\text{Cl}^- = 2\text{Fe}^{2+} + \text{Hg}_2\text{Cl}_2(s) \]
\[ 2\text{Ce}^{4+} + 2\text{Hg}(l) + 2\text{Cl}^- = 2\text{Ce}^{3+} + \text{Hg}_2\text{Cl}_2(s) \]

* formal potential in 1.0 M HClO$_4$

---

**1. Before the Equivalence Point**

It's easier to use the Fe half-reaction because we know how much was originally present and how much remains for each aliquot of added titrant (otherwise, using Ce would require a complicated equilibrium to solve for).

\[
E = E_{\text{Fe}^{3+}/\text{Fe}^{2+}} - E_{\text{Sat'd Calomel Electrode}}
\]

\[
= \left[ 0.767 \text{V} - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right] - 0.241 \text{V}^*
\]

Nernst equation for

\[ \text{Fe}^{3+} + e^- = \text{Fe}^{2+} (n=1) \]
\[ E^o = 0.767 \text{V} \]

\[
= 0.526 \text{V} - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \]

E$_{\text{SCE}}$ = Sat'd Calomel Electrode voltage (E$_{\text{SCE}}$)
We're only going to calculate the potential at the half-equivalence point where $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$:

$$E_{1/2} = 0.526V - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$E_{1/2} = 0.526V$ or more generally for the half-equivalence point:

$$E_{1/2} = E_+ - E_- \quad \text{where } E_+ = E^0 (\text{since the log term went to zero)}$$

$$E_{1/2} = E^0 - E_{SCE}$$

\section*{2. At the Equivalence Point}

$\text{Ce}^{3+} + \text{Fe}^{3+} = \text{Ce}^{4+} + \text{Fe}^{2+}$ (reverse of the titration reaction)

titrant analyte

\textit{from the reaction stoichiometry, at the eq. pt. -}

$$[\text{Ce}^{3+}] = [\text{Fe}^{3+}]$$

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

\textit{the two }\frac{1}{2}\text{ reactions are at equilibrium with the Pt electrode -}

$$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$$

$$\text{Ce}^{4+} + e^- = \text{Ce}^{3+}$$

\textit{so the Nernst equations are -}

$$E_+ = E^0_{\text{Fe}} - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$E_- = E^0_{\text{Ce}} - 0.0592 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$
adding the two equations together gives:

\[
2E_+ = E^o_{Fe} + E^o_{Ce} - 0.0592 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.0592 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}
\]

and since \([Ce^{3+}] = [Fe^{3+}]\) and \([Ce^{4+}] = [Fe^{2+}]\)

\[
2E_+ = E^o_{Fe} + E^o_{Ce} - 0.0592 \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.0592 \log \frac{[Ce^{3+}]}{[Ce^{4+}]}
\]

More generally, this is the cathode potential at the eq. pt. for any redox reaction where the number of electrons in each half reaction is equal.

\[
E_{e.p.} = E_+ - E_- = E_+ - E_{SCE} = 1.23 - 0.241 = 0.99V
\]
Equivalence Point Potentials

*Use these equations with Standard Reduction Potentials!*

1. Equal number of electrons

   \[ E_e = \frac{E^0_{\text{titrant}} + E^0_{\text{analyte}}}{2} \]

2. Unequal number of electrons (\( m = \#e's \) cathode \( \frac{1}{2} \) rxn, 
   \( n = \#e's \) anode \( \frac{1}{2} \) rxn)

   \[ E_e = \frac{mE^0_{\text{titrant}} + nE^0_{\text{analyte}}}{m + n} \]
Examples

1. Equal number of electrons

\[ \text{Fe}^{2+} + \text{Ce}^{4+} = \text{Fe}^{3+} + \text{Ce}^{3+} \text{ in 1 M HClO}_4 \text{ titrant} \]

2. Unequal number of electrons

\[ \text{Sn}^{4+} + 2\text{Cr}^{2+} = \text{Sn}^{2+} + 2\text{Cr}^{3+} \text{ in 1 M HCl} \text{ titrant} \]

\[ \text{KMnO}_4 \text{ is its own indicator, and electrodes can be used also, in which case the eq. pt. is obtained by calculating the 2nd derivative. Otherwise, an indicator is chosen that changes color at the eq. pt. potential.} \]

**TABLE 16-1 Redox indicators**

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Color</th>
<th>Reduced</th>
<th>Oxidized</th>
<th>$E^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenosafranine</td>
<td>Colorless</td>
<td>Red</td>
<td></td>
<td>0.28</td>
</tr>
<tr>
<td>Indigo tetrasulfonate</td>
<td>Colorless</td>
<td>Blue</td>
<td></td>
<td>0.36</td>
</tr>
<tr>
<td>Methylene blue</td>
<td>Colorless</td>
<td>Blue</td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td>Diphenylamine</td>
<td>Colorless</td>
<td>Violet</td>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td>4′-Ethoxy-2,4-diaminoazobenzene</td>
<td>Red</td>
<td>Yellow</td>
<td></td>
<td>0.76</td>
</tr>
<tr>
<td>Diphenylamine sulfoic acid</td>
<td>Colorless</td>
<td>Red-violet</td>
<td></td>
<td>0.85</td>
</tr>
<tr>
<td>Diphenylbenzidine sulfoic acid</td>
<td>Colorless</td>
<td>Violet</td>
<td></td>
<td>0.87</td>
</tr>
<tr>
<td>Tris(2,2′-bipyridine)iron</td>
<td>Red</td>
<td>Pale blue</td>
<td></td>
<td>1.120</td>
</tr>
<tr>
<td>Tris(1,10-phenanthroline)iron (ferroin)</td>
<td>Red</td>
<td>Pale blue</td>
<td></td>
<td>1.147</td>
</tr>
<tr>
<td>Tris(5-nitro-1,10-phenanthroline)iron</td>
<td>Red-violet</td>
<td>Pale blue</td>
<td></td>
<td>1.25</td>
</tr>
<tr>
<td>Tris(2,2′-bipyridine) ruthenium</td>
<td>Yellow</td>
<td>Pale blue</td>
<td></td>
<td>1.29</td>
</tr>
</tbody>
</table>
Oxidized ferroin (pale blue)  In(oxidized)

Reduced ferroin (red)  In(reduced)

\[ \text{Fe(III)}^{3+} \rightarrow \text{Fe(II)}^{2+} + e^- \]