Potentiometric Titration

**Goal:** Quantify $[\text{Fe}^{2+}]$ using RedOx titration with $\text{Ce}^{4+}$ as the oxidizing agent

**Usefulness:** Determination of Fe content in certain minerals, ores, blood, etc.

<table>
<thead>
<tr>
<th>Half-reactions</th>
<th>Standard potential ($E^0$)*</th>
<th>Formal potential ($E^0'$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$</td>
<td>0.771 V</td>
<td>0.68 V in 1M $\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>$\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}$</td>
<td>-</td>
<td>1.44 V in 1M $\text{H}_2\text{SO}_4$</td>
</tr>
</tbody>
</table>

* Relative to Standard Hydrogen Electrode (SHE). See chapter 18 for the discussion of the formal potentials

**Full reaction:** $\text{Fe}^{2+} + \text{Ce}^{4+} \leftrightarrow \text{Fe}^{3+} + \text{Ce}^{3+}$

This reaction equilibrium sets in very rapidly, implying that the effective electrode potentials for both half-reactions are equal throughout the titration process:

$$E'_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E^0'_{\text{Fe}^{3+}/\text{Fe}^{2+}} - (0.0592 \text{ V}) \times \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right)$$

$$E'_{\text{Ce}^{4+}/\text{Ce}^{3+}} = E^0'_{\text{Ce}^{4+}/\text{Ce}^{3+}} - (0.0592 \text{ V}) \times \log \left( \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right)$$

$$E_{\text{cell}} = E'_{\text{Fe}^{3+}/\text{Fe}^{2+}} = E'_{\text{Ce}^{4+}/\text{Ce}^{3+}}$$

We can use either one half-reaction or the other for calculating the potential of the system when it reaches an equilibrium. Note that the potentials given here are relative to SHE, not relative to AgCl electrode:

<table>
<thead>
<tr>
<th>Reference electrode</th>
<th>Standard potential ($E^0$)*</th>
<th>Formal potential ($E^0'$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^-$</td>
<td>0.222 V</td>
<td>0.222 V in 1M $\text{H}_2\text{SO}_4$</td>
</tr>
</tbody>
</table>
1. Making the Reference Electrode

In this lab, the potential associated with the oxidation of Fe$^{2+}$ by Ce$^{4+}$ is measured relative to a home made Ag/AgCl reference electrode. The electrode is prepared by electrolysis of NaCl solution on a Ag wire:

**Silver wire:**
- for oxidation of Cl$^-$ on Ag anode
- \( \text{Ag} + \text{Cl}^- \rightarrow \text{AgCl} + e^- \)
- **Result:** a black layer of AgCl deposited on the Ag wire

**1.5 V battery**

**Platinum wire:**
- for reduction of H$_2$O on Pt cathode
- \( \text{H}_3\text{O}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2 + \text{H}_2\text{O} \)
- \( \text{H}_2\text{O} + e^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^- \) (depending on the acidity)
- **Result:** evolution of H$_2$ bubbles from the electrode

NaCl filling solution
Tips for Lab 5

- Do the calculations for the solutions (NaCl & HCl) BEFORE coming to lab.
- Make sure the ground glass cap stays on the electrode for the entire experiment (otherwise, you will have to start over).
- Make sure the entire end of the electrode, including the ground glass cap, is in the solution (otherwise, the salt bridge won’t work).
- Be extra careful working with Ce⁴⁺ (strong oxidizer) and the strong acids. You’ll be pouring water into acid—BE VERY CAREFUL & PATIENT!!
2. Performing the Actual Measurement

a. Standardization of the $\text{Ce}^{4+}$ solution relative to a $\text{Fe}^{2+}$ standard

b. Measurements on your unknown $\text{Fe}^{2+}$ solution

Reference $\text{Ag}/\text{AgCl}$ electrode prepared during the previous step – filled with NaCl solution and capped at the bottom.

pH meter configured to measure the potential difference between the electrodes.

1.22 V

$\text{Fe}^{2+}$ in 1 M HCl

$\text{NaCl}$
Titration Curve Calculations

Titrator volume \( V_{Fe} \) containing \( Fe^{2+} \) with the initial concentration \([Fe^{2+}]_0\) using \( Ce^{4+} \) solution with initial concentration \([Ce^{4+}]_0\) (both solutions are in 1M H\(_2\)SO\(_4\) )

The total volume during the titration:

\[
V_{total} = V_{Fe}^0 + V_{Ce}^{added}
\]

Effective starting concentration of \( Fe^{2+} \):
(accounting for the dilution)

\[
[Fe^{2+}]_{0 \text{diluted}} = [Fe^{2+}]_0 \times \frac{V_{Fe}^0}{V_{total}}
\]

And for \([Ce^{4+}]\):

\[
[Ce^{4+}]_{0 \text{diluted}} = [Ce^{4+}]_0 \times \frac{V_{added}}{V_{total}}
\]

**Starting solution** the potential is not well defined (because \([Fe^{3+}]\) is poorly defined)

**Some \( Ce^{4+} \) added** (before the equiv. point)
(assume that most of added \( Ce^{4+} \) reacted)

\[
[Fe^{2+}] \approx [Fe^{2+}]_{0 \text{diluted}} - [Ce^{4+}]_{0 \text{diluted}}
\]

\[
[Fe^{3+}] \approx [Ce^{4+}]_{0 \text{diluted}}
\]

**Equivalence point**

\[
[Fe^{2+}] \approx [Ce^{4+}]
\]

\[
[Fe^{3+}] \approx [Ce^{3+}]
\]

**Excess \( Ce^{4+} \) added** (after the equiv. point)
(assume that almost no \( Fe^{2+} \) is left)

\[
[Ce^{4+}] \approx [Ce^{4+}]_{0 \text{diluted}} - [Fe^{2+}]_{0 \text{diluted}}
\]

\[
[Ce^{3+}] \approx [Fe^{2+}]_{0 \text{diluted}}
\]
In this part of the curve:

\[
[\text{Fe}^{2+}] \approx [\text{Ce}^{4+}]_0 - [\text{Fe}^{2+}]_0 \\
[\text{Fe}^{3+}] \approx [\text{Ce}^{4+}]_0
\]

(after accounting for the dilution)

\[
E'_\text{cell} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - (0.0592 \ V) \times \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} 
\]

In this part of the curve,

\[
[\text{Ce}^{4+}] \approx [\text{Ce}^{4+}]_0 - [\text{Fe}^{2+}]_0 \\
[\text{Ce}^{3+}] \approx [\text{Fe}^{2+}]_0
\]

(after accounting for the dilution)

\[
E'_\text{cell} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 - (0.0592 \ V) \times \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} 
\]

We must correct for the fact that our reference is AgCl/Cl\(^-\) electrode, not SHE:

\[
E'_{\text{measured}} = E'_\text{cell} - E_{\text{AgCl}/\text{Cl}^-} = E'_\text{cell} - 0.222V
\]
**Expected Potential at the Equivalence Point**

Right at the equivalence point, we have:

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

Both of these equations apply:

\[
E'_{\text{cell}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0'} - (0.0592 \ V) \times \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}
\]

\[
E'_{\text{cell}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{0'} - (0.0592 \ V) \times \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}
\]

We are going to use a trick - add these equations up:

\[
E'_{\text{cell}} + E'_{\text{cell}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0'} + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{0'} - (0.0592 \ V) \times \log \left( \frac{[\text{Fe}^{2+}] [\text{Ce}^{3+}]}{[\text{Fe}^{3+}] [\text{Ce}^{4+}]} \right) - (0.0592 \ V) \times \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}
\]

\[
2E'_{\text{cell}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0'} + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{0'} - (0.0592 \ V) \times \log \left( \frac{[\text{Fe}^{2+}] [\text{Ce}^{3+}]}{[\text{Fe}^{3+}] [\text{Ce}^{4+}]} \right) = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0'} + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{0'}
\]

\[
E'_{\text{cell}} = \frac{E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{0'} + E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{0'}}{2} = \frac{0.68V + 1.44V}{2} = 1.06V
\]

It follows that the potential is always the same (= 1.06 V relative to SHE) at the equivalence point. Since we do our measurements relative to the AgCl/Cl\(^{-}\) electrode, the actual measured potential should be 1.06V – 0.222V = 0.84V.
Analysis of Results

Step 1. Concentration of the Ce\(^{4+}\) solution from standardization

- Weigh exactly several FeSO\(_4\)\(\cdot\)(H\(_2\)O)\(_7\) samples (mass\(_{FeSO_4\cdot(H_2O)_7}\) should be \(\sim0.5\) g)
- Dissolve each under acidic conditions as described in the procedure
- The number of moles of Fe\(^{2+}\) in each of your solutions is (MW = 278.05 g/mol):

\[
n_{Fe^{2+}} = \frac{mass_{FeSO_4\cdot(H_2O)_7}}{MW_{FeSO_4\cdot(H_2O)_7}}
\]

- Titrate each solution with your Ce\(^{4+}\) solution and determine \([Ce^{4+}]\)

\[
C_{Ce^{4+}} = \frac{n_{Fe^{2+}}}{V_{Ce\text{ end-point}}} = \frac{mass_{FeSO_4\cdot(H_2O)_7}}{MW_{FeSO_4\cdot(H_2O)_7} \times V_{Ce\text{ end-point}}}
\]

- You will have 2-4 values of \(V_{Ce\text{ end-point}}\); use them to calculate the uncertainty \(\Delta V_{Ce\text{ end-point}}\) (either standard deviation or confidence interval)
- Neglect the error in weighing. This will lead to a simple result for the uncertainty in the concentration:

\[
\Delta C_{Ce^{4+}} = C_{Ce^{4+}} \times \frac{\Delta V_{Ce\text{ end-point}}}{V_{Ce\text{ end-point}}}
\]
Step 2. Mass fraction of Fe in your unknown

- Weigh your unknown exactly \( \text{mass}_{\text{unknown}} \)
- Dissolve it in exactly \( V_{\text{dissolved}} = 100 \text{ mL} \) in a volumetric flask
- Pipette exactly \( V_{\text{aliquote}} = 25 \text{ mL} \) for each of your titration
- Dilute the pipetted amount to about 50 mL (the exact amount is irrelevant)
- Titrate this solution with your \( \text{Ce}^{4+} \) solution and determine the number of moles of Fe in your initial unknown

\[
n_{\text{Fe}^{2+}} = C_{\text{Ce}^{4+}} \times V_{\text{end-point}}^{\text{Ce}} \times \frac{V_{\text{dissolved}}}{V_{\text{aliquote}}} = 4 \times C_{\text{Ce}^{4+}} \times V_{\text{end-point}}^{\text{Ce}}
\]

- You will have 2-4 values of \( V_{\text{end-point}}^{\text{Ce}} \); use them to calculate the uncertainty \( \Delta V_{\text{end-point}}^{\text{Ce}} \). You may neglect errors in measuring \( V_{\text{dissolved}} \) and \( V_{\text{aliquote}} \).

- The weight fraction of Fe in your unknown and its uncertainty can now be calculated.

\[
\alpha_{\text{Fe}^{2+}} = \frac{\text{mass}_{\text{Fe}}}{\text{mass}_{\text{unknown}}} = \frac{n_{\text{Fe}^{2+}} \times MW_{\text{Fe}}}{\text{mass}_{\text{unknown}}} = 4 \times C_{\text{Ce}^{4+}} \times V_{\text{end-point}}^{\text{Ce}} \times MW_{\text{Fe}}
\]

\[
\Delta \alpha_{\text{Fe}^{2+}} = \alpha_{\text{Fe}^{2+}} \times \sqrt{\left( \frac{\Delta C_{\text{Ce}^{4+}}}{C_{\text{Ce}^{4+}}} \right)^2 + \left( \frac{\Delta V_{\text{end-point}}^{\text{Ce}}}{V_{\text{end-point}}^{\text{Ce}}} \right)^2}
\]

(We have neglected the error in weighing your unknown sample in this example)