Related concept
Potentiometric titration, redox reaction, Nernst equation, quantitative analysis.

Principle
In a potentiometric titration, the equivalence point is detected by monitoring the electromotive force (e. m. f.) of an electrochemical cell formed by an indicator electrode coupled with a convenient reference electrode. The potential of the indicator electrode, and hence the e. m. f. of the cell, is a measure of the activity (approximately the concentration) of the ionic species in the electrolyte solution.

Material
- 1 Volumetric flask, 500 ml
- 1 Set balance TE 3102S and software, 230 V
- 1 Weighing dishes, 85 x 85 x 7 mm
- 1 Graduated pipette, 25 ml
- 1 Volumetric pipette, 10 ml
- 1 Pipettor
- 1 Graduated cylinder, 250 ml
- 1 Funnel, d = 80 mm
- 1 Funnel, d = 55 mm
- 1 Pasteur pipettes
- 1 Rubber bulbs
- 1 Wash bottle, 500 ml
- 1 Iron-II sulphate, 500 g
- 1 Cerium-IV disulphate, 25 g
- 1 Sulphuric acid, 95 – 98 %, 500 ml
- 1 Water, distilled, 5 l
- 1 PC with USB interface, Windows XP or higher

Fig. 1: Experimental set up.
Volumetric redox titration: Cerimetry with Cobra4

Safety instructions

When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing. Please refer to the appendix for detailed safety instructions.

Tasks

1. Perform a potentiometric titration on the iron(II)/cerium(IV) redox system with a 0.1 molar iron(II) sulphate solution to determine the factor for cerium(IV) sulphate solution.
2. Determine the concentration of an unknown iron(II) solution.
3. Discuss the general form of the titration curve in terms of the Nernst equation.

Set-up and preparation

- Prepare the solutions required for the experiment as follows:
  - 0.1 molar Ce(SO₄)₂ solution: Pour 200 ml of distilled water into a 1000 ml beaker, add a magnetic stirrer bar and place the beaker on the magnetic stirrer. Using a graduated pipette, carefully add 11.2 ml of concentrated sulphuric acid to the distilled water under continuous agitation to achieve an approximately 1 molar sulphuric acid solution. Dissolve 20.215 g of cerium(IV) sulphate (Ce(SO₄)₂ · 4 H₂O) quantitatively in this acid to accelerate the dissolution process, heat the solution slightly. When the cerium salt has dissolved completely, allow this solution to cool down and then transfer it quantitatively to a 500 ml volumetric flask. Make up to the mark with distilled water.
  - 0.1 molar FeSO₄ solution: Weigh 2.78 g of iron(II)sulphate (FeSO₄ · 7 H₂O) into a 100 ml volumetric flask, add some distilled water to dissolve it, then make up to the mark with distilled water.

- Set up the experiment as shown in Fig. 1.
- Connect the Cobra4 Sensor-Unit Chemistry and the Cobra4 Drop Counter to the Cobra4 Wireless-Links.
- Attach them to the retort stand with the holders for Cobra4 and right angle clamps.
- Use the BNC adapter to connect the electrodes to the Cobra4 Sensor-Unit Chemistry.
- Start the PC and connect the Cobra4 Wireless Manager with a USB socket of the computer.
- After the Cobra4 Wireless-Links have been switched on, the sensors are automatically recognized. Some ID numbers (01 and 02) are allocated to them now, which are indicated in the display of the particular Cobra4 Wireless-Link.
- Call up the “Measure” programme.
- Click the “Unknown titration volume” button and confirm with “OK”.
- Boot the experiment “Potentiometric titration” (experiment > open experiment). The measurement parameters for this experiment are loaded now.
- Pipette 10 ml of the 0.1 molar iron(II)sulphate solution into a 250 ml glass beaker and dilute to a total volume of 150 ml.
- Add a magnetic stirrer bar and place the beaker on the magnetic stirrer.
- Attach the burette to the support rod of the magnetic stirrer and fill it with 0.1 molar cerium(IV) sulphate solution.
- Immerse the reference electrode and the platinum electrode carefully in the solution and ensure that the magnetic stirrer bar is free to rotate.
- Adjust the magnetic stirrer to a medium stirring speed (Note: The stirrer bar must not touch the electrode).
- Start the measurement with ●.
- Add the cerium(IV) sulphate solution until a total of 20 ml has been added.
- Stop the measurement by pressing ■.
- Send all data to “measure” (see Fig. 2).
- Save the measurement (File> Save measurement as…).

Fig. 3: Potentiometric redox titration curve for the Fe(II)/Ce(IV) system.

- Fig. 3 shows the graph as it is presented by the programme when the measurement is stopping.

**Theory and evaluation**
The potentiometric redox titration performed here involves the oxidation of iron(II) by the oxidising agent cerium(IV) according to

\[
\text{Fe}^{2+}(aq) + \text{Co}^{4+}(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{Co}^{3+}(aq)
\]

The potential of a platinum indicator electrode in contact with a solution of these ions will clearly vary as the titration proceeds. To monitor these changes, a second reference electrode (here Ag \((s)\) | AgCl \((s)\) | Cl\(^-\) \((aq)\)) is immersed in the solution to complete the electrical circuit. The cell can be expressed in terms of the Fe\(^{3+}\), Fe\(^{2+}\) couple.

\[
\text{Ag} \,(s)\ | \ AgCl \,(s) \ | \ KCl \,(aq,3M) \ | \ F_{3+}(aq) \ | \ F_{2+}(aq) \ | \ Pt
\]

Later in terms of the Ce\(^{4+}\), Ce\(^{3+}\) couple

\[
\text{Ag} \,(s)\ | \ AgCl \,(s) \ | \ KCl \,(aq,3M) \ | \ Ce^{4+}(aq) \ | \ Ce^{2+}(aq) \ | \ Pt
\]

The dependence of the potential of the indicator electrode on the activities of the various ionic species in solution is given by the following equivalent Nernst equations
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\[ E_{Fe^{3+}, Fe^{2+}} = E_{Fe^{3+}, Fe^{2+}} + \frac{RT}{F} \ln \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \]  
(1a)

\[ E_{Ce^{4+}, Ce^{3+}} = E_{Ce^{4+}, Ce^{3+}} + \frac{RT}{F} \ln \frac{a_{Ce^{4+}}}{a_{Ce^{3+}}} \]  
(1b)

The cell e. m. f. is thus expressible as

\[ E = E_{Fe^{3+}, Fe^{2+}} - E_{Ag \mid AgCl \mid Cl^-} \]

\[ = E_{Fe^{3+}, Fe^{2+}} + \frac{RT}{F} \ln \frac{c_{Fe^{3+}}}{c_{Fe^{2+}}} - E_{Ag \mid AgCl \mid Cl^-} \]  
(2a)

\[ E = E_{Ce^{4+}, Ce^{3+}} - E_{Ag \mid AgCl \mid Cl^-} \]

\[ = E_{Ce^{4+}, Ce^{3+}} + \frac{RT}{F} \ln \frac{c_{Ce^{4+}}}{c_{Ce^{3+}}} - E_{Ag \mid AgCl \mid Cl^-} \]  
(2b)

in which, for the sake of simplicity, ionic activities have been replaced by ionic concentrations.

Up until the equivalence point (at which an exactly stoichiometric amount of sample has been added to the titrant) changes in the electrical potential of the solution, and hence in the e. m. f. of the cell, are effectively controlled by Eq. 2a, since the Ce(IV) ions added are continually consumed in the redox reaction. After the equivalence point practically all the Fe(II) in solution has been oxidised and the solution potential is now determined by the concentration ratio \( c(\text{Ce}^{4+}) / c(\text{Ce}^{3+}) \). The equivalence point is thus discernible as a rapid rise in the solution potential form that of the Fe\(^{3+}\), Fe\(^{2+}\) couple to that of the Ce\(^{4+}\), Ce\(^{3+}\) couple. To get shown the equivalence point of the curve you have to press \( \frac{1}{z} \) in the „measure“ programme. In the now appearing window (see Fig. 4) the values for the equivalence point are shown under “Results”. The point of equivalence can be shown in the curve by choosing “Visualize results” (see Fig. 5).

Fig. 4: Window which appears after pressing the button for calculating the point of equivalence.
The detailed shape of the E versus V curve recorded here is characteristic of potentiometric titrations. At the equivalence point we have $c(\text{Ce}^{4+}) = c(\text{Fe}^{3+})$ and $c(\text{Ce}^{3+}) = c(\text{Fe}^{2+})$.

By replacing the Ce concentration $c_{\text{Ce}}$ in Eq. 2b we obtain:

$$E = E^{\ominus\text{Ce}^{4+},\text{Ce}^{3+}} + \frac{RT}{F} \ln \frac{c_{\text{Fe}^{2+}}}{c_{\text{Fe}^{3+}}} - E_{\text{Ag} | \text{AgCl} | \text{Cl}^-}$$

(3)

and from this:

$$E = E^{\ominus\text{Ce}^{4+},\text{Ce}^{3+}} + \frac{RT}{F} \ln \frac{c_{\text{Fe}^{3+}}}{c_{\text{Fe}^{2+}}} - E_{\text{Ag} | \text{AgCl} | \text{Cl}^-}$$

(4)

Readjusting this for $\ln (c(\text{Fe}^{3+}) / c(\text{Fe}^{2+}))$ and insertion in Eq. 2a gives:

$$2E = E_{\text{Fe}^{3+},\text{Fe}^{2+}} + E^{\ominus\text{Ce}^{4+},\text{Ce}^{3+}} - 2E_{\text{Ag} | \text{AgCl} | \text{Cl}^-}$$

(5)

And, after dividing by 2:

$$E = \frac{1}{2} \ln (E_{\text{Fe}^{3+},\text{Fe}^{2+}} + E_{\text{Ce}^{4+},\text{Ce}^{3+}}) - E_{\text{Ag} | \text{AgCl} | \text{Cl}^-}$$

(6)

It follows then that the e. m. f. of the cell at the equivalence point is independent of the reaction concentrations.

With the following standard electrode potentials:
and the referential potential of the $\text{Ag}_\text{(s)} \mid \text{AgCl}_\text{(s)} \mid \text{Cl}^- \text{(aq)}$ electrode at 20 °C:

$$E_{\text{Ag} \mid \text{AgCl} \mid \text{Cl}^-} = 0.210 \text{ V}$$

the equivalence point is expected to correspond to a cell potential of 0.98 V.

The standardisation factor $f$ for the 0.1 M cerium(IV) sulphate solution, which corrects for any discrepancy between the formal concentration (0.1 M) and the actual concentration, is expressed as:

$$f = \frac{10}{V_1} \quad (7)$$

$V_1 = \text{Volume of cerium(IV) solution consumed for 10 ml of the 0.1 M iron(II) solution}$

The concentration of the unknown iron(II) sulphate solution is obtained by:

$$c_{\text{Fe}^{2+}} = \frac{c_{\text{Ce}^{4+}} \cdot f \cdot V_2}{V_3} \quad (8)$$

$c_{\text{Fe}^{2+}} = \text{Concentration of the unknown iron(II) sulphate solution}$

$c_{\text{Ce}^{4+}} = \text{Concentration of the cerium(IV) sulphate solution}$

$f = \text{Factor for the cerium(IV) sulphate solution}$

$V_2 = \text{Total volume of the cerium(IV) sulphate solution}$

$V_3 = \text{Volume of the titrated unknown iron(II) sulphate solution}$

Addition of $x$ ml of 0.1 M Ce(IV) sulphate solution corresponds to the addition of $x \cdot 10^{-4} \text{ mol Ce(IV) cations}$ and, since the equilibrium for the reaction lies well to the product side, results in the formation of $x \cdot 10^{-4} \text{ mol Fe(III) cations}$.

Initially $10^{-3} \text{ mol Fe(II) cations}$ are present in a total sample volume of 150 ml. The concentration of Fe(III) cations following the addition of $x$ ml of titrant is thus

$$c_{\text{Fe}^{3+}} = \frac{0.1 \cdot x}{150 + x} \quad (9)$$

and that of Fe(II) cations
According to Eq. 2a a plot of the cell e. m. f. against ln \( \frac{c(\text{Fe}^{3+})}{c(\text{Fe}^{2+})} \) should be a straight line of gradient 25.3 mV (at 20 °C) up to the equivalence point.

To obtain a presentation of this, mark the second part of the titration curve, including the equivalence point, after pressing \( \text{f} \) in the menu bar (see Fig. 6).

Use the function \( \text{f} \) to cut this area (see fig. 7).

In addition, delete the value for V 0 ml in the data table. (right mouse click > to choose “data table” > to press \( \text{f} \)).

Now you can have the diagram calculated with \( \text{Calculate} \).

For this, set the parameters as given in Fig. 8 and press “Calculate”.

\[
C_{\text{Fe}^2+} = \frac{1 - 0.1 \cdot x}{150 + x}
\]  

(10)
Fig. 8: Setting for channel modification.

Fig. 9 shows the resulting plot.

- The plot shows an approximately straight line form which verifies the use of the Nernst equation to describe the behaviour of the potentiometric titration performed here.
- You can have the slope of the curve shown by pressing \( \text{fig. 10} \). After that you have to put the two shown points on the nearly straight line (see Fig. 10).
When you divide the value for $\Delta y$ by the value for $\Delta x$ from the upper right box (see Fig. 11) you get the slope.

![Figure 11: Box with values for two points on the nearly straight line.](image)

**Data and results**

From Fig. 3 you can see that the equivalence point occurs at $V = 10.12 \text{ ml}$, which corresponds to a cell e. m. f. of 815 mV. The discrepancy between this value and the calculated value of 980 mV may be due to a number of factors. The reference electrode potential may have a potential somewhat different to the value of 210 mV assumed above. The possibility of an impure iron(II) sulphate sample already contaminated by the presence of iron(III) may also be of relevance. Also the response of the $\text{Fe}^{3+}$, $\text{Fe}^{2+}$ and $\text{Ce}^{4+}$, $\text{Ce}^{3+}$ redox couples to dissolved oxygen in the solutions has not been taken into account.

The graphically determined value for the slope of the approximately is here 22.2 mV. The difference between this value and the literature value (25.3 mV at 20°C) can be explained with the temperature dependence of the e.m.f.

**Disposal**

Do not dispose of heavy-metal-containing waste via household waste.

**Appendix**

<table>
<thead>
<tr>
<th>Hazard symbol, signal word</th>
<th>Hazard statements</th>
<th>Precautionary statements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron-II sulphate</td>
<td></td>
<td>P305 + 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing. P302 + 352: IF ON SKIN: Wash with soap and water</td>
</tr>
<tr>
<td></td>
<td>H302: Harmful if swallowed.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H319: Causes serious eye irritation.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H315: Causes skin irritation</td>
<td></td>
</tr>
<tr>
<td>Cerium-IV disulphate</td>
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</tbody>
</table>

![Hazard symbol](image)
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<table>
<thead>
<tr>
<th>Warning</th>
<th>H315: Causes skin irritation.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H319: Causes serious eye irritation.</td>
</tr>
<tr>
<td></td>
<td>H335: May cause respiratory irritation.</td>
</tr>
</tbody>
</table>

**Sulphuric acid 95 _ 98 %**

| Warning | H314: Causes severe skin burns and eye damage. |

| P261: Avoid breathing dust/fume/gas/mist/vapours/spray. |
| P305 + 351 +338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing. |

| P280: Wear protective gloves/protective clothing/eye protection/face protection. |
| P301 + 330 +331: IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. |
| P309 + 310: IF exposed or you feel unwell: Immediately call a POISON CENTER or doctor/physician. |
| P305 * 351 + 338: IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses if present and easy to do. continue rinsing. |