Ch. 15: Redox Titrations

Outline:

- 15-1 The Shape of a Redox Curve
- 15-2 Finding the Endpoint
- 15-3 Adjustment of Analyte Oxidation State
- 15-4 Oxidation with Potassium Permanganate
- 15-5 Oxidation with Ce$^{4+}$
- 15-6 Oxidation with Potassium Dichromate
- 15-7 Methods Involving Iodine

Updated Nov. 30, 2011
The Shape of a Redox Curve

Consider the titration of iron(II) with standard cerium(IV), monitored potentiometrically with Pt and calomel electrodes.

\[ \text{Titration reaction:} \quad \text{Ce}^{4+} + \text{Fe}^{2+} \rightarrow \text{Ce}^{3+} + \text{Fe}^{3+} \]

for which \( K \approx 10^{16} \) in 1 M HClO\(_4\). Therefore, each mole of ceric ion oxidizes 1 mol of ferrous ion rapidly and quantitatively. The titration reaction creates a mixture of Ce\(^{4+}\), Ce\(^{3+}\), Fe\(^{2+}\) and Fe\(^{3+}\).

At the Pt (indicator) electrode

\[ \text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} \quad E^\circ = 0.767 \text{ V} \]

\[ \text{Ce}^{4+} + e^- \rightleftharpoons \text{Ce}^{3+} \quad E^\circ = 1.70 \text{ V} \]

The potentials are the formal potentials that apply in 1 M HClO\(_4\). The Pt indicator electrode responds to the relative activities of Ce\(^{4+}\) and Ce\(^{3+}\) or Fe\(^{3+}\) and Fe\(^{2+}\).
Region 1: Before the Equivalence Point

Prior to the equivalence point, excess unreacted Fe$^{2+}$ remains in solution, and Ce$^{4+}$ is completely consumed to form Ce$^{3+}$ and Fe$^{3+}$. [Fe$^{n+}$] are easy to find; [Ce$^{n+}$] not so much! Calculate the cell voltage from the iron half-reaction at the Pt electrode:

\[
E = E_+ - E_-
\]

\[
E = \left[ 0.767 - 0.059 \times 16 \log \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \right) \right] - 0.241
\]

\[
E = 0.526 - 0.059 \times 16 \log \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \right)
\]

A special point is at the equivalence point, where \( V = \frac{1}{2} V_e \), and \([Fe^{3+}] = [Fe^{2+}]\). In this case, the log term is 0, and \( E_+ = E^\circ \) for the Fe$^{3+}$ | Fe$^{2+}$ couple (analogous to the point in a pH titration where at \( V = \frac{1}{2} V_e \), the pH = pK$_a$).

The voltage at zero titrant volume cannot be calculated, because we do not know how much Fe$^{3+}$ is present (i.e., if \([Fe^{3+}] = 0\), voltage = \(-\infty\)). There must be some Fe$^{3+}$ in each reagent (impurity, etc.) - the voltage could never be lower than that needed to reduce the solvent.
Region 2: At the Equivalence Point

Exactly enough Ce$^{4+}$ has been added to react with all the Fe$^{2+}$. Virtually all cerium is in the form Ce$^{3+}$, and virtually all iron is in the form Fe$^{3+}$. Tiny amounts of Ce$^{4+}$ and Fe$^{2+}$ are present at equilibrium (due to the reverse form of our initial reaction).

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

These reactions are both in equilibrium at the Pt electrode. At the equivalence point, it is convenient to use both reactions to describe the cell voltage. The Nernst equations are

\[
E_+ = 0.767 - 0.05916 \log\left(\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}\right)
\]

\[
E_+ = 1.70 - 0.05916 \log\left(\frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}\right)
\]

Neither of these equations alone allows us to find $E_+$, because we do not know exactly what tiny concentrations of Fe$^{2+}$ and Ce$^{4+}$ are present.
Region 2: At the Equivalence Point, 2

We can solve the four simultaneous equations by first adding the two Nernst equations:

\[ 2E_+ = 0.767 + 1.70 - 0.059 \times 16 \log \left( \frac{[Fe^{2+}]}{[Fe^{3+}]} \right) - 0.059 \times 16 \log \left( \frac{[Ce^{3+}]}{[Ce^{4+}]} \right) \]

\[ 2E_+ = 2.467 - 0.059 \times 16 \log \left( \frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]} \right) \]

Because \([Ce^{3+}] = [Fe^{3+}]\) and \([Ce^{4+}] = [Fe^{2+}]\) at the EP, the ratio of concentrations in the log term is unity. Therefore, the logarithm is 0 and

\[ 2E_+ = 2.467 \ V \implies E_+ = 1.23 \ V \]

The cell voltage is

\[ E = E_+ - E(\text{calomel}) = 1.23 - 0.241 = 0.99 \ V \]

In this particular titration, the equivalence-point voltage is independent of the concentrations and volumes of the reactants.
Region 2: After the Equivalence Point

Virtually all iron atoms are Fe$^{3+}$. The moles of Ce$^{3+}$ equal the moles of Fe$^{3+}$, and there is a known excess of unreacted Ce$^{4+}$. Because we know both [Ce$^{3+}$] and [Ce$^{4+}$], it is convenient to use the Ce half-reaction to describe the chemistry at the Pt electrode:

\[
E = E_+ - E(\text{calomel}) = \left[ 1.70 - 0.059 \times 16 \log \left( \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right) \right] - 0.241
\]

At the special point when \( V = 2V_e \), [Ce$^{3+}$] = [Ce$^{4+}$] and \( E_+ = E^\circ(\text{Ce}^{4+}|\text{Ce}^{3+}) = 1.70 \text{ V} \).

Before \( V_e \), the indicator electrode potential is fairly steady near \( E^\circ(\text{Fe}^{3+}|\text{Fe}^{2+}) = 0.77 \text{V} \).

At \( V_e \), there is a rapid rise in voltage.

After \( V_e \), the indicator electrode potential levels off near \( E^\circ(\text{Ce}^{4+}|\text{Ce}^{3+}) = 1.70 \text{ V} \).
Potentiometric Redox Titration

e.g., Titrate 100.0 mL of 0.0500 M Fe\(^{2+}\) with 0.100 M Ce\(^{4+}\). The equivalence point occurs when \(V_e = 50.0\) mL. Calculate the cell voltage at 36.0, 50.0, and 63.0 mL.

**At 36.0 mL:** This is 36.0/50.0 of the way to the EP. Therefore, 36.0/50.0 of the iron is in the form Fe\(^{3+}\) and 14.0/50.0 is in the form Fe\(^{2+}\). Putting \([\text{Fe}^{2+}] / [\text{Fe}^{3+}] = 14.0/36.0\) below gives

\[
E = 0.526 - 0.5916 \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) = 0.526 - 0.5916 \log \left( \frac{14}{36} \right) = 0.550 \text{ V}
\]

**At 50.0 mL:** The cell voltage at the equivalence point is 0.99 V, regardless of the concentrations of reagents for this particular titration.

\[
E = E_+ - E(\text{calomel}) = 1.23 - 0.241 = 0.99 \text{ V}
\]

**At 63.0 mL:** The first 50.0 mL of cerium were converted into Ce\(^{3+}\). There is an excess of 13.0 mL of Ce\(^{4+}\), so \([\text{Ce}^{3+}] / [\text{Ce}^{4+}] = 50.0/13.0\). Then:

\[
E = E_+ - E(\text{calomel}) = \left[ 1.70 - 0.5916 \log \left( \frac{[\text{Ce}^{2+}]}{[\text{Ce}^{3+}]} \right) \right] = \left[ 1.70 - 0.5916 \log \left( \frac{50}{13} \right) \right] = 1.424 \text{ V}
\]
Shapes of Redox Titrations Curves

The voltage at any point in the Fe/Ce titration (left curve) depends only on the ratio of reactants; concentrations do not figure in any calculations (should be independent of dilution!). The curve features a steep rise in voltage at the EP, where \([\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 1\). The Fe/Ce curve is also symmetric about the EP, since the stoichiometry of the reaction is 1:1.

The curve for the titration of \(\text{Tl}^+\) with \(\text{IO}_3^-\) in 1.00 M HCl (right curve) is not symmetric about the EP, since the reactant stoichiometry is 2:1 instead of 1:1.

\[
\text{IO}_3^- + 2\text{Tl}^+ + 2\text{Cl}^- + 6\text{H}^+ \rightarrow \text{ICl}_2^- + 2\text{Tl}^{3+} + 3\text{H}_2\text{O}
\]

Note in both instances, you cannot calculate a potential for zero titrant (rather a very small volume is used).
Finding the End Point

As in acid-base titrations, indicators and electrodes are commonly used to find the end point of a redox titration.

If one uses electrodes, one can plot $E$ as a function of $V$, and the EP is found at the maximum of the first derivative of the plot, $\Delta E/\Delta V$, or the zero crossing of the second derivative, $\Delta(\Delta E/\Delta V)/\Delta V$, which can be easily displayed on an Excel spreadsheet.

A very accurate way of finding the EP involves the Gran plot, which is a graph of $V \cdot 10^{-nE/0.05916}$ versus $V$, which should be a straight line with x-intercept $= V_e$.

Gran plot for titration of Fe$^{2+}$ by Ce$^{4+}$ (in Exercise 15-D). The line was fit to the four points shown by circles. In the function on the ordinate, the value of $n$ is 1. Numerical values were multiplied by $10^{10}$ for ease of display. Multiplication does not change the x-intercept.
Redox Indicators

A redox indicator is a compound that changes colour when it goes from its oxidized to its reduced state. The indicator ferroin changes from pale blue (almost colourless) to red.

To predict the potential range over which the indicator colour will change, we first write a Nernst equation for the indicator.

\[
In(\text{oxidized}) + ne^- \rightleftharpoons In(\text{reduced})
\]

\[
E = E^\circ - \frac{0.05916}{n} \log\left(\frac{[In(\text{reduced})]}{[In(\text{oxidized})]}\right)
\]

As with acid base indicators:

Colour of \( In(\text{reduced}) \) observed when: \[ \frac{[In(\text{reduced})]}{[In(\text{oxidized})]} \gtrsim \frac{10}{1} \]

Colour of \( In(\text{oxidized}) \) observed when: \[ \frac{[In(\text{reduced})]}{[In(\text{oxidized})]} \lessapprox \frac{1}{10} \]
If the quotients from the previous slide are inserted in the Nernst equation, we get the range over which the colour change will occur:

\[ E = \left( E^\circ \pm \frac{0.05916}{n} \right) \text{volts} \]

For ferroin, with \( E^\circ = 1.147 \) V, we expect the colour change to occur in the approximate range 1.088 V to 1.206 V with respect to the SHE. With a saturated calomel reference electrode, the indicator transition range will be

\[
\begin{align*}
\left( \text{Indicator transition range versus calomel electrode (S.C.E.)} \right) &= \left( \text{Transition range versus standard hydrogen electrode (S.H.E.)} \right) - E(\text{calomel}) \\
&= (1.088 \text{ to } 1.206) - (0.241) \\
&= 0.847 \text{ to } 0.965 \text{ V (versus S.C.E.)}
\end{align*}
\]

The larger the difference in standard potential between titrant and analyte, the greater the break in the titration curve at the equivalence point.

**Feasible:** \( \geq 0.2 \) V difference between analyte and titrant (potentiometric detection, not sharp)

**Satisfactory or better:** \( \geq 0.4 \) V difference between analyte and titrant (colour indicator by eye is normally fine for this.)
Redox Indicators, 3

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

A redox indicator changes colour over a range of $\pm(59/n)$ mV, centred at $E^\circ$ for the indicator. $n$ is the number of electrons in the indicator half-reaction. The indicator transition range should overlap the steep part of the titration curve.
The Starch-Iodine Complex

Starch is the indicator of choice for redox titrations involving iodine, because it forms an intense blue complex with iodine. Starch is not a redox indicator; it responds specifically to the presence of I₂, not to a change in redox potential.

(a) Structure of the repeating unit of amylose (a polymer of the sugar α-D-glucose). (b) Schematic structure of the starch-iodine complex. The amylose chain forms a helix around I₆ units, which have a deep blue colour. (c) View down the starch helix, showing iodine inside the helix.

Starch is readily biodegraded, so it should be freshly dissolved or the solution should contain a preservative, such as Hgl₂ (~1 mg/100 mL) or thymol. A hydrolysis product of starch is glucose, which is a reducing agent (partially hydrolyzed starch solution can be a source of error).
Adjustment of the analyte oxidation state

Sometimes we need to adjust the oxidation state of analyte before it can be titrated. For example, Mn$^{2+}$ can be preoxidized to MnO$_4^-$ and then titrated with standard Fe$^{2+}$. Prereduction of reagents is also a possibility. Preadjustment must be quantitative, and you must eliminate excess preadjustment reagent so that it will not interfere in the subsequent titration.

Preoxidation techniques

Peroxydisulfate ($S_2O_8^{2-}$, also called persulfate) is a strong oxidant that requires Ag$^+$ as a catalyst. Excess $S_2O_8^{2-}$ can be easily destroyed after the reaction by boiling.

\[
S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{2-} + SO_4^{2-} + Ag^{2+}
\]

These oxidants are used for: Mn$^{2+} \rightarrow$ MnO$_4^-;$ Ce$^{3+} \rightarrow$ Ce$^{4+};$ VO$^{2+}$ to VO$_2^+;$ Cr$_2$O$_7^{2-}$

Silver (II) oxide (AgO) dissolves in concentrated mineral acids to give Ag$^{2+}$ (similar oxidizing strength to $S_2O_8^{2-}$); XS Ag$^{2+}$ can be removed by boiling. Solid sodium bismuthate (NaBiO$_3$) is similar to both $S_2O_8^{2-}$ and Ag$^{2+}$; it can be removed by filtration.

Hydrogen peroxide ($H_2O_2$) is a good oxidant in basic solutions, and easily disproportionates in boiling water. It can transform Co$^{2+} \rightarrow$ Co$^{3+},$ Fe$^{2+} \rightarrow$ Fe$^{3+}$ and Mn$^{2+} \rightarrow$ MnO$_2$. In acidic solution, it can reduce Cr$_2$O$_7^{2-}$ to Cr$^{3+}$ and MnO$_4^-$ to Mn$^{2+}$.

\[
2H_2O_2 \xrightarrow{\text{boiling}} O_2 + 2H_2O
\]
Adjustment of the analyte oxidation state, 2

Prereduction techniques

*Stannous chloride* (SnCl$_2$) will reduce Fe$^{3+}$ to Fe$^{2+}$ in hot HCl. Excess reductant is destroyed by adding excess HgCl$_2$. The Fe$^{2+}$ is then titrated with an oxidant.

$\text{Sn}^{2+} + 2\text{HgCl}_2 \rightarrow \text{Sn}^{4+} + \text{Hg}_2\text{Cl}_2 + 2\text{Cl}^-$

*Chromous chloride* is a powerful reductant sometimes used to prereduce analyte to a lower oxidation state. Excess Cr$^{2+}$ is oxidized by atmospheric O$_2$. *Sulphur dioxide* and *hydrogen sulphide* are mild reducing agents that can be expelled by boiling an acidic solution after the reduction is complete.

An important prereduction technique uses a column packed with a solid reducing agent. To the left is shown a *Jones reductor*, which contains zinc coated with *zinc amalgam*. An *amalgam* is a solution of anything in mercury, which is prepared by mixing granular Zn with 2 wt% aqueous HgCl$_2$ for 10 min and then washing with water.

You can reduce Fe$^{3+}$ to Fe$^{2+}$ by passage through a Jones reductor, using 1 M H$_2$SO$_4$ as solvent. Wash the column well with water and titrate the combined washings with standard, Ce$^{4+}$, or Cr$_2$O$_7^{2-}$.
Oxidation with KMnO₄

Potassium permanganate (KMnO₄) is a strong oxidant with an intense violet colour. In strongly acidic solutions (pH ≲1), it is reduced to colourless Mn²⁺.

\[
\text{MnO}_4^- + 8H^+ + 5e^- \rightleftharpoons \text{Mn}^{2+} + 4H_2O \quad E^\circ = 1.507 \text{ V}
\]

Permanganate  \hspace{0.5cm} \text{Manganous}

In neutral or alkaline solution, the product is the brown solid, MnO₂.

\[
\text{MnO}_4^- + 4H^+ + 3e^- \rightleftharpoons \text{MnO}_2(s) + 2H_2O \quad E^\circ = 1.692 \text{ V}
\]

Manganese dioxide

In strong basic solution (e.g., 2M NaOH), the green manganate ion is produced:

\[
\text{MnO}_4^- + e^- \rightleftharpoons \text{MnO}_4^{2-} \quad E^\circ = 0.56 \text{ V}
\]

Manganate

For titrations in strongly acidic solution, KMnO₄ serves as its own indicator because the product, Mn²⁺, is colourless.

**Note:** that KMnO₄ is not a primary standard, as traces of MnO₂ are invariably present. It must be standardized by titration of sodium oxalate (Na₂C₂O₄) or pure electrolytic iron wire.
## Oxidation with KMnO₄, 2

<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Oxidation reaction</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe²⁺</td>
<td>Fe²⁺ ⇌ Fe³⁺ + e⁻</td>
<td>Fe³⁺ is reduced to Fe²⁺ with Sn²⁺ or a Jones reductor. Titration is carried out in 1 M H₂SO₄ or 1 M HCl containing Mn²⁺, H₃PO₄, and H₂SO₄. Mn²⁺ inhibits oxidation of Cl⁻ by MnO₄⁻. H₃PO₄ complexes Fe³⁺ to prevent formation of yellow Fe³⁺-chloride complexes.</td>
</tr>
<tr>
<td>H₂C₂O₄</td>
<td>H₂C₂O₄ ⇌ 2CO₂ + 2H⁺ + 2e⁻</td>
<td>Add 95% of titrant at 25°C, then complete titration at 55°C–60°C.</td>
</tr>
<tr>
<td>Br⁻</td>
<td>Br⁻ ⇌ ½ Br₂(g) + e⁻</td>
<td>Titrator in boiling 2 M H₂SO₄ to remove Br₂(g).</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>H₂O₂ ⇌ O₂(g) + 2H⁺ + 2e⁻</td>
<td>Titrator in 1 M H₂SO₄.</td>
</tr>
<tr>
<td>HNO₂</td>
<td>HNO₂ + H₂O ⇌ NO₃⁻ + 3H⁺ + 2e⁻</td>
<td>Add excess standard KMnO₄ and back-titrator after 15 min at 40°C with Fe²⁺.</td>
</tr>
<tr>
<td>As³⁺</td>
<td>H₃AsO₃ + H₂O ⇌ H₃AsO₄ + 2H⁺ + 2e⁻</td>
<td>Titrator in 1 M HCl with KI or ICl catalyst.</td>
</tr>
<tr>
<td>Sb³⁺</td>
<td>H₃SbO₃ + H₂O ⇌ H₃SbO₄ + 2H⁺ + 2e⁻</td>
<td>Titrator in 2 M HCl.</td>
</tr>
<tr>
<td>Mo³⁺</td>
<td>Mo³⁺ + 2H₂O ⇌ MoO₂²⁺ + 4H⁺ + 3e⁻</td>
<td>Reduce Mo in a Jones reductor, and run the Mo³⁺ into excess Fe³⁺ in 1 M H₂SO₄. Titrator the Fe²⁺ formed.</td>
</tr>
<tr>
<td>W³⁺</td>
<td>W³⁺ + 2H₂O ⇌ WO₂²⁺ + 4H⁺ + 3e⁻</td>
<td>Reduce W with Pb(Hg) at 50°C and titrate in 1 M HCl.</td>
</tr>
<tr>
<td>U⁴⁺</td>
<td>U⁴⁺ + 2H₂O ⇌ UO₂²⁺ + 4H⁺ + 2e⁻</td>
<td>Reduce U to U³⁺ with a Jones reductor. Expose to air to produce U⁴⁺, which is titrated in 1 M H₂SO₄.</td>
</tr>
<tr>
<td>Ti³⁺</td>
<td>Ti³⁺ + H₂O ⇌ TiO²⁺ + 2H⁺ + e⁻</td>
<td>Reduce Ti to Ti³⁺ with a Jones reductor, and run the Ti³⁺ into excess Fe³⁺ in 1 M H₂SO₄. Titrator the Fe²⁺ that is formed.</td>
</tr>
<tr>
<td>Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Zn²⁺, Co²⁺, La³⁺, Th⁴⁺, Pb²⁺, Ce³⁺, BiO⁺, Ag⁺</td>
<td>H₂C₂O₄ ⇌ 2CO₂ + 2H⁺ + 2e⁻</td>
<td>Precipitate the metal oxalate. Dissolve in acid and titrate the H₂C₂O₄.</td>
</tr>
<tr>
<td>S²O₅²⁻, S₂O₅²⁻, BiO⁺, Ag⁺</td>
<td>S₂O₅²⁻ + 2Fe²⁺ + 2H⁺ ⇌ 2Fe³⁺ + 2HSO₄⁻</td>
<td>Peroxydisulfate is added to excess standard Fe²⁺ containing H₃PO₄. Unreacted Fe²⁺ is titrated with MnO₄⁻.</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>Mo³⁺ + 2H₂O ⇌ MoO₂²⁺ + 4H⁺ + 3e⁻</td>
<td>(NH₄)₃PO₄ · 12MoO₃ is precipitated and dissolved in H₂SO₄. The Mo(VI) is reduced (as above) and titrated.</td>
</tr>
</tbody>
</table>
Oxidation with Ce\(^{4+}\)

Reduction of Ce\(^{4+}\) to Ce\(^{3+}\) proceeds cleanly in acidic solutions. The aquo ion, Ce(H\(_2\)O)\(_n\)\(^{4+}\), probably does not exist, because Ce(IV) binds anions (ClO\(_4^-\), SO\(_4^{2-}\), NO\(_3^-\), Cl\(^-\)). Variation of the Ce\(^{4+}\) \text{ vs } Ce\(^{3+}\) formal potential with the medium indicates these interactions:

\[
Ce^{4+} + e^- \rightleftharpoons Ce^{3+}
\]

\[
\text{Formal potential:} \begin{cases} 
1.70 \text{ V in } 1 \text{ F HClO}_4 \\
1.61 \text{ V in } 1 \text{ F HNO}_3 \\
1.47 \text{ V in } 1 \text{ F HCl} \\
1.44 \text{ V in } 1 \text{ F H}_2\text{SO}_4
\end{cases}
\]

Ce\(^{4+}\) is yellow and Ce\(^{3+}\) is colourless, but the colour change is not distinct enough for cerium to be its own indicator. Ferroin and other substituted phenanthroline redox indicators are well suited to titrations with Ce\(^{4+}\). Ce\(^{4+}\) can be used in place of KMnO\(_4\) in most procedures.

Primary-standard-grade ammonium hexanitratocerate(IV), (NH\(_4\))\(_2\)Ce(NO\(_3\))\(_6\), can be dissolved in 1 M H\(_2\)SO\(_4\) and used directly. Although the oxidizing strength of Ce\(^{4+}\) is greater in HClO\(_4\) or HNO\(_3\), these solutions undergo slow photochemical decomposition with concomitant oxidation of water. Ce\(^{4+}\) in H\(_2\)SO\(_4\) is stable indefinitely, despite the fact that the reduction potential of 1.44 V is great enough to oxidize H\(_2\)O to O\(_2\).
Methods involving iodine

Iodimetry: A reducing analyte is titrated with iodine (to produce I⁻)
Iodometry: An oxidizing analyte is added to excess I⁻ to produce iodine, which is then titrated with standard thiosulfate solution.

Molecular iodine is only slightly soluble in water (1.3 × 10⁻³ M at 20°C), but its solubility is enhanced by complexation with iodide.

\[
\text{I}_2(aq) + I^- \rightleftharpoons I_3^- \hspace{1cm} K = 7 \times 10^2
\]

Iodine Iodide Triiodide

A typical 0.05 M solution of I₃⁻ for titrations is prepared by dissolving 0.12 mol of KI plus 0.05 mol of I₂ in 1 L of water. When we speak of using iodine as a titrant, we almost always mean that we are using a solution of I₂ plus excess I⁻.

A solution made from
1.5 mM I₂ + 1.5 mM KI in water contains:

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Molarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9 mM I₂</td>
<td>5 μM I₅⁻</td>
</tr>
<tr>
<td>0.9 mM I⁻</td>
<td>40 nM I₆⁻</td>
</tr>
<tr>
<td>0.6 mM I₃⁻</td>
<td>0.3 μM HOI</td>
</tr>
</tbody>
</table>
Starch Indicator

As described earlier, starch is used as an indicator for iodine. In a solution with no other coloured species, it is possible to see the colour of ~5 μM I$_3^-$.

With starch, the limit of detection is extended by about a factor of 10.

In iodimetry (titration with I$_3^-$), starch can be added at the beginning of the titration. The first drop of excess I$_3^-$ after the equivalence point causes the solution to turn dark blue.

In iodometry, I$_3^-$ is present throughout the reaction up to the EP. Starch should not be added until right before the EP (as detected visually, by fading of the I$_3^-$); otherwise, some iodine tends to remain bound to starch particles after the equivalence point is reached.

Iodometric Titration.

I$_3^-$ solution (left). I$_3^-$ solution before end point in titration with S$_2$O$_3^{2-}$ (left centre). I$_3^-$ solution immediately before end point with starch indicator present (right centre). At the end point (right).
Prep and Standardization of $I_3^-$ Solutions

Triiodide ($I_3^-$) is prepared by dissolving solid $I_2$ in excess KI. Sublimed $I_2$ is pure enough to be a primary standard, but it is seldom used as a standard because it evaporates while it is being weighed. Instead, the approximate amount is rapidly weighed, and the solution of $I_3^-$ is standardized with a pure sample of analyte or $Na_2S_2O_3$.

Acidic solutions of $I_3^-$ are unstable because the excess $I^-$ is slowly oxidized by air:

\[
6I^- + O_2 + 4H^+ \rightarrow 2I_3^- + 2H_2O
\]

In neutral solutions, oxidation is insignificant in the absence of heat, light, and metal ions. At pH 11, triiodide disproportionates to hypoiodous acid (HOI), iodate, and iodide.

Another way to prepare standard $I_3^-$ is to add a known quantity of the primary standard potassium iodate ($KIO_3$) to a small excess of KI, followed by addition of excess strong acid (giving pH $\approx 1$) to produce $I_3^-$ by quantitative reverse disproportionation.

\[
IO^- + 8I^- + 6H^+ \rightleftharpoons 3I_3^- + 3H_2O
\]

Freshly acidified iodate plus iodide can be used to standardize thiosulfate. However, $I_3^-$ must be used immediately or it will be oxidized by air.
Use of Sodium Thiosulphate

*Sodium thiosulfate* is the almost universal titrant for triiodide. In neutral or acidic solution, triiodide oxidizes thiosulfate to *tetrathionate*:

\[ \text{I}_3^- + 2\text{S}_2\text{O}_3^{2-} \rightarrow 3\text{I}^- + \text{O} = \text{S} - \text{S} - \text{S} - \text{S} = \text{O} \]

Thiosulfate

\[
\begin{array}{c}
\text{O} \\
\text{S} - \text{S} - \text{S} - \text{S} = \text{O} \\
\text{O} \\
\end{array}
\]

Tetrathionate

In basic solution, \(\text{I}_3^-\) disproportionates to \(\text{I}^-\) and \(\text{HOI}\), which can oxidize \(\text{S}_2\text{O}_3^{2-}\) to \(\text{SO}_4^{2-}\); hence the reaction above should be carried out below pH 9. The common form of thiosulfate, \(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}\), is not pure enough to be a primary standard. Instead, thiosulfate is usually standardized by reaction with a fresh solution of \(\text{I}_3^-\) prepared from \(\text{KIO}_3\) plus \(\text{KI}\).

A stable solution of \(\text{Na}_2\text{S}_2\text{O}_3\) can be prepared by dissolving the reagent in freshly boiled distilled water. Dissolved \(\text{CO}_2\) makes the solution acidic and promotes disproportionation of \(\text{S}_2\text{O}_3^{2-}\):

\[ \text{S}_2\text{O}_3^{2-} + \text{H}^+ \rightleftharpoons \text{HSO}_3^- + \text{S}(s) \]

Bisulfite  Sulfur

Thiosulfate solutions should be stored in the dark. Addition of 0.1 g of sodium carbonate per litre maintains the pH in an optimum range for stability. Three drops of chloroform should also be added to each bottle of thiosulfate solution to help prevent bacterial growth.
Analytical Applications of Iodine

Reducing agents can be titrated directly with standard in the presence of starch, until reaching the intense blue starch-iodine end point. e.g., the iodimetric determination of vitamin C:

\[
\text{Ascorbic acid (vitamin C)} + I^- + H_2O \rightarrow \text{Dehydroascorbic acid}^{25} + 3I^- + 2H^+
\]

Oxidizing agents can be treated with excess I\(^-\) to produce I\(_3^-\). The iodometric analysis is completed by titrating the liberated I\(_3^-\) with standard thiosulfate. Starch is not added until just before the end point.

There are loads of applications for both iodimetric and iodometric titrations!
**Titrations with standard I$_3^-$ (iodimetric)**

<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Oxidation reaction</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>As$^{3+}$</td>
<td>$\text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^-$</td>
<td>Titrate directly in NaHCO$_3$ solution with I$_3^-$.&lt;br&gt;Sn(IV) is reduced to Sn(II) with granular Pb or Ni in 1 M HCl and titrated in the absence of oxygen.</td>
</tr>
<tr>
<td>Sn$^{2+}$</td>
<td>$\text{SnCl}_2^- + 2\text{Cl}^- \rightleftharpoons \text{SnCl}_2^{2-} + 2\text{e}^-$</td>
<td></td>
</tr>
<tr>
<td>$\text{N}_2\text{H}_4$</td>
<td>$\text{N}_2\text{H}_4 \rightleftharpoons \text{N}_2 + 4\text{H}^+ + 4\text{e}^-$</td>
<td>Titrate in NaHCO$_3$ solution.</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>$\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$&lt;br&gt;$\text{H}_2\text{SO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{e}^-$</td>
<td>Add SO$_2$ (or H$_2$SO$_3$ or HSO$_3^-$ or SO$_3^{2-}$) to excess standard I$_3^-$ in dilute acid and back-titrate unreacted I$_3^-$ with standard thiosulfate.</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$\text{H}_2\text{S} \rightleftharpoons \text{S(s)} + 2\text{H}^+ + 2\text{e}^-$</td>
<td>Add H$_2$S to excess I$_3^-$ in 1 M HCl and back-titrate with thiosulfate.</td>
</tr>
<tr>
<td>Zn$^{2+}$, Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$</td>
<td>$\text{M}^{2+} + \text{H}_2\text{S} \rightarrow \text{MS}(s) + 2\text{H}^+$&lt;br&gt;$\text{MS}(s) \rightleftharpoons \text{M}^{2+} + \text{S} + 2\text{e}^-$</td>
<td>Precipitate and wash metal sulfide.&lt;br&gt;Dissolve in 3 M HCl with excess standard I$_3^-$ and back-titrate with thiosulfate.</td>
</tr>
<tr>
<td>Cysteine, glutathione, thioglycolic acid, mercaptoethanol</td>
<td>$2\text{RSH} \rightleftharpoons \text{RSSR} + 2\text{H}^+ + 2\text{e}^-$</td>
<td>Titrate the sulfhydryl compound at pH 4–5 with I$_3^-$.</td>
</tr>
<tr>
<td>HCN</td>
<td>$\text{I}_2 + \text{HCN} \rightleftharpoons \text{ICN} + \text{I}^- + \text{H}^+$</td>
<td>Titrate in carbonate-bicarbonate buffer, using $p$-xylene as an extraction indicator.</td>
</tr>
<tr>
<td>H$_2$C=O</td>
<td>$\text{H}_2\text{CO} + 3\text{OH}^- \rightleftharpoons \text{HCO}_2^- + 2\text{H}_2\text{O} + 2\text{e}^-$</td>
<td>Add excess I$_3^-$ plus NaOH to the unknown.&lt;br&gt;After 5 min, add HCl and back-titrate with thiosulfate.</td>
</tr>
<tr>
<td>Glucose (and other reducing sugars)</td>
<td>$\text{RCH} + 3\text{OH}^- \rightleftharpoons \text{RCO}_2^- + 2\text{H}_2\text{O} + 2\text{e}^-$</td>
<td>Add excess I$_3^-$ plus NaOH to the sample. After 5 min, add HCl and back-titrate with thiosulfate.</td>
</tr>
<tr>
<td>Ascorbic acid (vitamin C)</td>
<td>Ascorbate + H$_2$O $\rightleftharpoons$ dehydroascorbate + 2H$^+$ + 2e$^-$</td>
<td>Titrate directly with I$_3^-$.</td>
</tr>
<tr>
<td>H$_3$PO$_3$</td>
<td>$\text{H}_3\text{PO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{PO}_4 + 2\text{H}^+ + 2\text{e}^-$</td>
<td>Titrate in NaHCO$_3$ solution.</td>
</tr>
</tbody>
</table>
# Titrations of $I_3^-$ from analyte (iodometric)

<table>
<thead>
<tr>
<th>Species analyzed</th>
<th>Reaction</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cl}_2$</td>
<td>$\text{Cl}_2 + 3\text{I}^- \rightleftharpoons 2\text{Cl}^- + \text{I}_3^-$</td>
<td>Reaction in dilute acid.</td>
</tr>
<tr>
<td>$\text{HOCI}$</td>
<td>$\text{HOCI} + \text{H}^+ + 3\text{I}^- \rightleftharpoons \text{Cl}^- + \text{I}_3^- + \text{H}_2\text{O}$</td>
<td>Reaction in 0.5 M $\text{H}_2\text{SO}_4$.</td>
</tr>
<tr>
<td>$\text{Br}_2$</td>
<td>$\text{Br}_2 + 3\text{I}^- \rightleftharpoons 2\text{Br}^- + \text{I}_3^-$</td>
<td>Reaction in dilute acid.</td>
</tr>
<tr>
<td>$\text{BrO}_3^-$</td>
<td>$\text{BrO}_3^- + 6\text{H}^+ + 9\text{I}^- \rightleftharpoons \text{Br}^- + 3\text{I}_3^- + 3\text{H}_2\text{O}$</td>
<td>Reaction in 0.5 M $\text{H}_2\text{SO}_4$.</td>
</tr>
<tr>
<td>$\text{IO}_3^-$</td>
<td>$2\text{IO}_3^- + 16\text{I}^- + 12\text{H}^+ \rightleftharpoons 6\text{I}_3^- + 6\text{H}_2\text{O}$</td>
<td>Reaction in 0.5 M HCl.</td>
</tr>
<tr>
<td>$\text{IO}_4^-$</td>
<td>$2\text{IO}_4^- + 22\text{I}^- + 16\text{H}^+ \rightleftharpoons 8\text{I}_3^- + 8\text{H}_2\text{O}$</td>
<td>Reaction in 0.5 M HCl.</td>
</tr>
<tr>
<td>$\text{O}_2$</td>
<td>$\text{O}_2 + 4\text{Mn(OH)}_2 + 2\text{H}_2\text{O} \rightleftharpoons 4\text{Mn(OH)}_3 + 2\text{Mn}_2\text{O}_4^2^- + 2\text{H}_2\text{O}$</td>
<td>The sample is treated with $\text{Mn}^{2+}$, NaOH, and KI. After 1 min, it is acidified with $\text{H}_2\text{SO}_4$, and the $\text{I}_3^-$ is titrated.</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2$</td>
<td>$\text{H}_2\text{O}_2 + 3\text{I}^- + 2\text{H}^+ \rightleftharpoons \text{I}_3^- + 2\text{H}_2\text{O}$</td>
<td>Reaction in 1 M $\text{H}_2\text{SO}_4$ with NH$_4$MoO$_3$ catalyst. $\text{O}_3$ is passed through neutral 2 wt% KI solution. Add $\text{H}_2\text{SO}_4$ and titrate.</td>
</tr>
<tr>
<td>$\text{O}_3^a$</td>
<td>$\text{O}_3 + 3\text{I}^- + 2\text{H}^+ \rightleftharpoons \text{O}_2 + \text{I}_3^- + \text{H}_2\text{O}$</td>
<td>The nitric oxide is removed (by bubbling CO$_2$ generated in situ) prior to titration of $\text{I}_3^-$.</td>
</tr>
<tr>
<td>$\text{NO}_2^-$</td>
<td>$2\text{HNO}_2 + 2\text{H}^+ + 3\text{I}^- \rightleftharpoons 2\text{NO} + \text{I}_3^- + 2\text{H}_2\text{O}$</td>
<td>Reaction in 5 M HCl.</td>
</tr>
<tr>
<td>$\text{As}^{5+}$</td>
<td>$\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 3\text{I}^- \rightleftharpoons \text{H}_3\text{AsO}_3^- + \text{I}_3^- + \text{H}_2\text{O}$</td>
<td>Reaction in neutral solution. Then acidify and titrate.</td>
</tr>
<tr>
<td>$\text{S}_2\text{O}_5^{2-}$</td>
<td>$\text{S}_2\text{O}_5^{2-} + 3\text{I}^- \rightleftharpoons 2\text{SO}_4^{2-} + \text{I}_3^- $</td>
<td>$\text{NH}_4\text{HF}_2$ is used as a buffer.</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}$</td>
<td>$2\text{Cu}^{2+} + 5\text{I}^- \rightleftharpoons 2\text{CuI} + \text{I}_3^- $</td>
<td>Reaction in 1 M HCl.</td>
</tr>
<tr>
<td>$\text{Fe(CN)}_6^{3-}$</td>
<td>$2\text{Fe(CN)}_6^{3-} + 3\text{I}^- \rightleftharpoons 2\text{Fe(CN)}_6^{4-} + \text{I}_3^- $</td>
<td>Reaction in 0.1 M HCl.</td>
</tr>
<tr>
<td>$\text{MnO}_4^-$</td>
<td>$2\text{MnO}_4^- + 16\text{H}^+ + 15\text{I}^- \rightleftharpoons 2\text{Mn}^{2+} + 5\text{I}_3^- + 8\text{H}_2\text{O}$</td>
<td>Reaction in 0.5 M $\text{H}_3\text{PO}_4$ or HCl.</td>
</tr>
<tr>
<td>$\text{MnO}_2$</td>
<td>$\text{MnO}_2(s) + 4\text{H}^+ + 3\text{I}^- \rightleftharpoons \text{Mn}^{2+} + 3\text{I}_3^- + 2\text{H}_2\text{O}$</td>
<td>Reaction in 0.4 M HCl requires 5 min for completion and is particularly sensitive to air oxidation.</td>
</tr>
<tr>
<td>$\text{Cr}_2\text{O}_7^{2-}$</td>
<td>$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 9\text{I}^- \rightleftharpoons 2\text{Cr}^{3+} + 3\text{I}_3^- + 7\text{H}_2\text{O}$</td>
<td>Reaction in 1 M $\text{H}_2\text{SO}_4$.</td>
</tr>
<tr>
<td>$\text{Ce}^{4+}$</td>
<td>$2\text{Ce}^{4+} + 3\text{I}^- \rightleftharpoons 2\text{Ce}^{3+} + \text{I}_3^- $</td>
<td></td>
</tr>
</tbody>
</table>

\* The pH must be $\geq 7$ when $\text{O}_3$ is added to $\Gamma$. In acidic solution, each $\text{O}_3$ produces 1.25 $\text{I}_3^-$, not 1 $\text{I}_3^-$. [N. V. Klassen, D. Marchington, and H. C. E. McGowan, Anal. Chem. 1994, 66, 2921.]