Ch. 15: Redox Titrations

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- 15-2 Finding the Endpoint
- 15-3 Adjustment of Analyte Oxidation State
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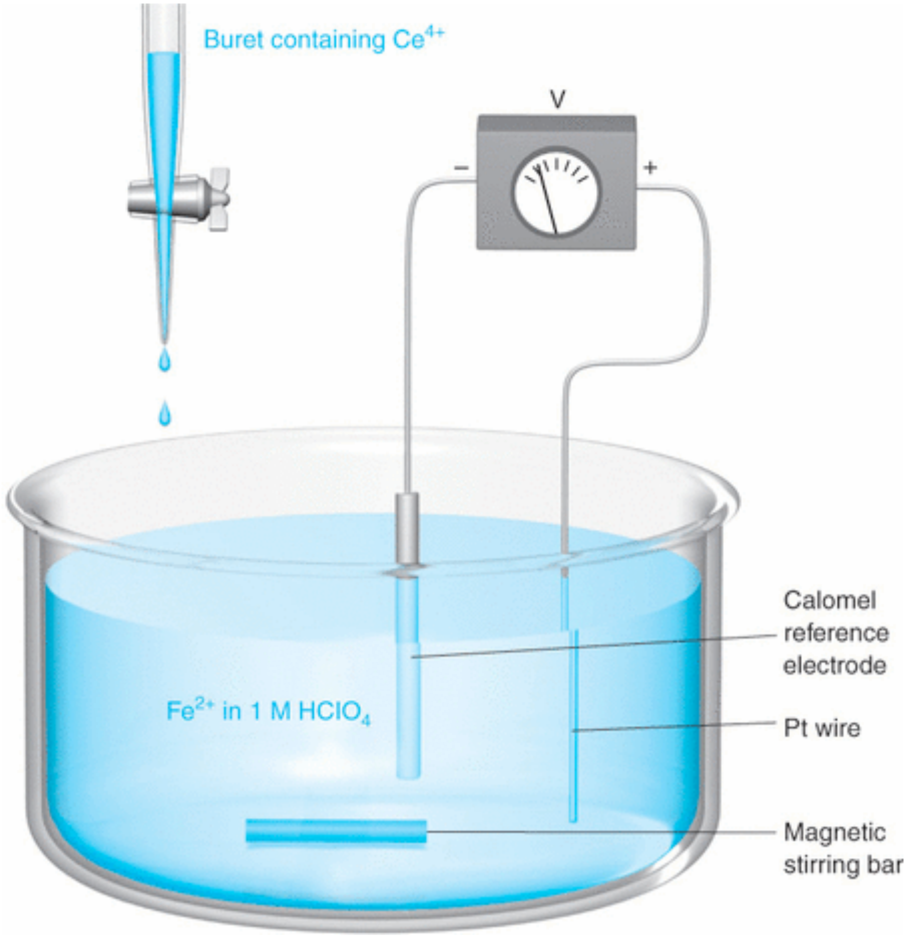
Updated Nov. 30, 2011

The Shape of a Redox Curve

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

Titration reaction:	Ce^{4+}	+	Fe^{2+}	→	Ce^{3+}	+	Fe^{3+}
	Ceric titrant		Ferrous analyte		Cerous		Ferric

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

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^\circ = 0.767\ V$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^\circ = 1.70\ V$$

The potentials are the formal potentials that apply in 1 M HClO4. 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 Ce4+ is completed 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:

$$E = E_+ - E_-$$

$$E = \left[\underset{\substack{\uparrow \\ \text{Formal potential for Fe}^{3+} \\ \text{reduction in} \\ \text{1 M HClO}_4}}{0.767} - 0.059\,16 \log\left(\frac{[\mathrm{Fe}^{2+}]}{[\mathrm{Fe}^{3+}]}\right)\right] - \underset{\substack{\uparrow \\ \text{Potential of} \\ \text{saturated calomel} \\ \text{electrode}}}{0.241}$$

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

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).

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

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

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

$$E_+ = 0.767 - 0.059\,16 \log\left(\frac{[Fe^{2+}]}{[Fe^{3+}]}\right)$$

$$E_+ = 1.70 - 0.059\,16 \log\left(\frac{[Ce^{3+}]}{[Ce^{4+}]}\right)$$

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:

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

$$2E_+ = 2.46_7 - 0.059\,16 \log\left(\frac{[\mathrm{Fe}^{2+}][\mathrm{Ce}^{3+}]}{[\mathrm{Fe}^{3+}][\mathrm{Ce}^{4+}]}\right)$$

$$\log a + \log b = \log ab$$
$$-\log a - \log b = -\log ab$$

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

$$2E_+ = 2.46_7\ \mathrm{V} \Rightarrow E_+ = 1.23\ \mathrm{V}$$

The cell voltage is

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

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:

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

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

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

At V_e, there is a rapid rise in voltage.

After V_e, the indicator electrode potential levels off near $E°(Ce^{4+}|Ce^{3+}) = 1.70$ 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 $[Fe^{2+}]/[Fe^{3+}]$ = 14.0/36.0 below gives

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

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.

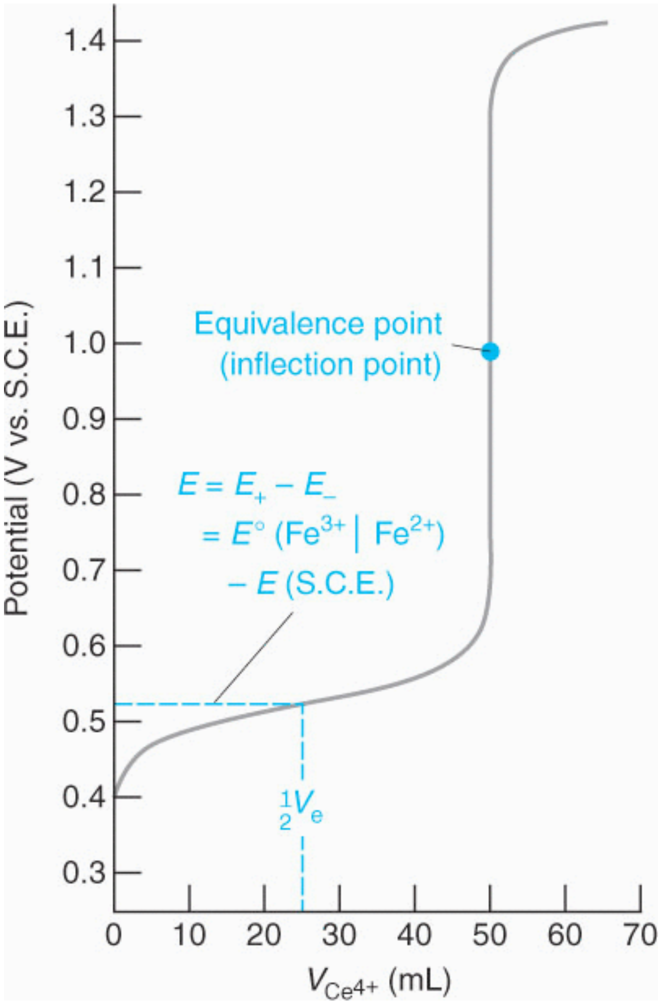
$$E = E_{+} - E(\mathrm{calomel}) = 1.23 - 0.241 = 0.99\ \mathrm{V}$$

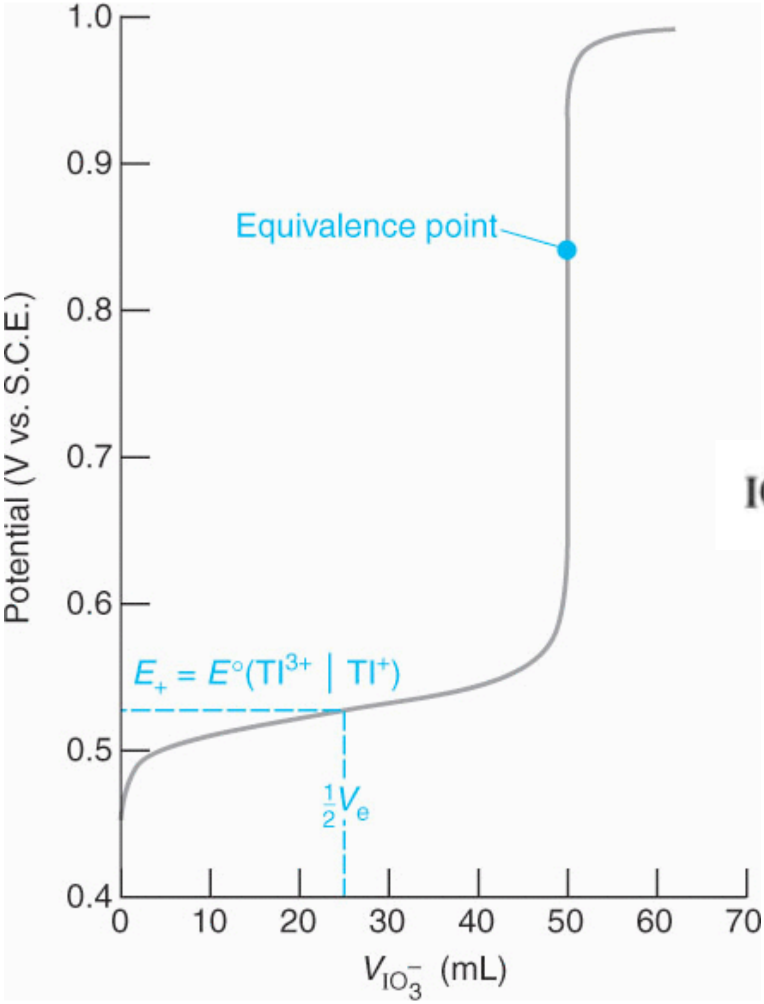
At 63.0 mL: The first 50.0 mL of cerium were converted into Ce^{3+}. There is an excess of 13.0 mL of Ce^{4+}, so $[Ce^{3+}]/[Ce^{4+}]$ = 50.0/13.0. Then:

$$E = E_{+} - E(\mathrm{calomel}) = \left[1.70 - 0.5916\log\left(\frac{[\mathrm{Ce}^{2+}]}{[\mathrm{Ce}^{3+}]}\right)\right] = \left[1.70 - 0.5916\log\left(\frac{50}{13}\right)\right] = 1.424\ \mathrm{V}$$

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 $[Fe^{2+}]/[Fe^{3+}] = 1$. 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 Tl^+ with IO3- in 1.00 M HCl (**right curve**) is not symmetric about the EP, since the reactant stoichiometry is 2:1 instead of 1:1.

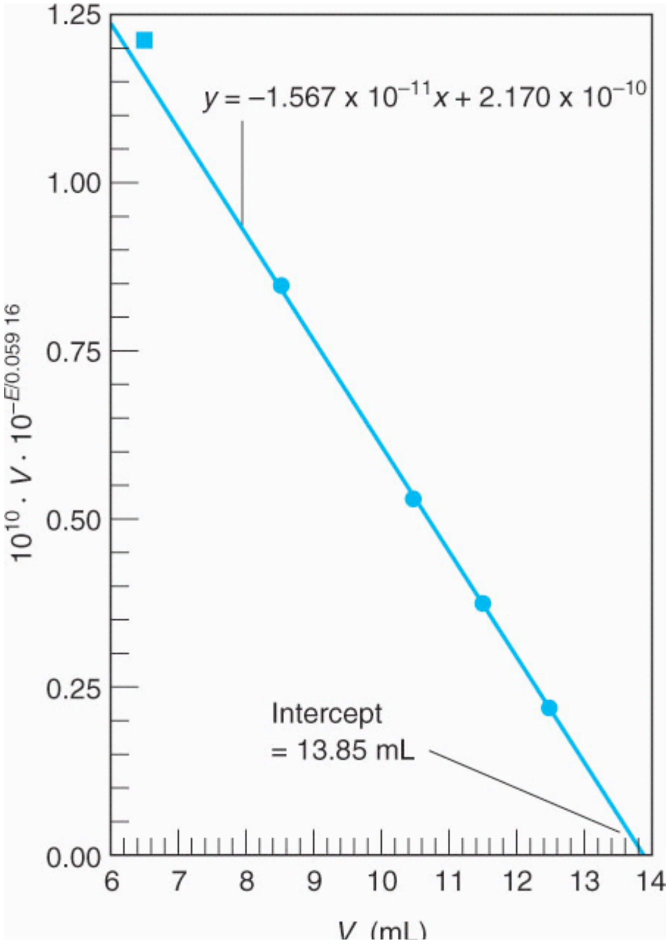
$$IO_3^- + 2Tl^+ + 2Cl^- + 6H^+ \rightarrow ICl_2^- + 2Tl^{3+} + 3H_2O$$

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.

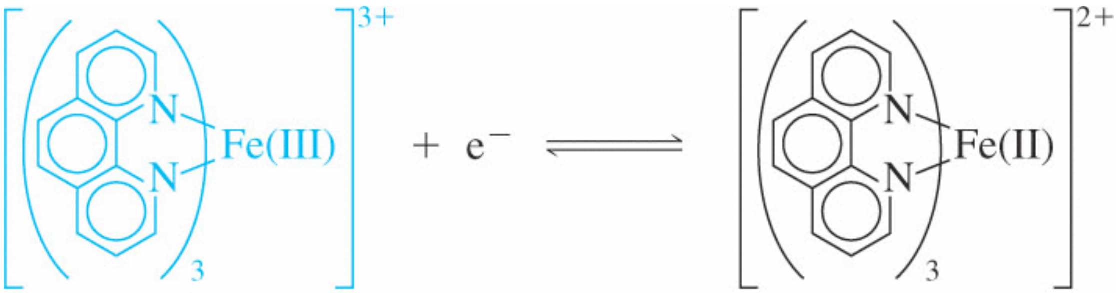


A very accurate way of finding the **EP** involves the *Gran plot*, which is a graph of $V \cdot 10^{-nE/0.05916}$ versus V, which should be a straight line with x-intercept = V_e.

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.



Oxidized ferroin
(pale blue)
In(oxidized)

Reduced ferroin
(red)
In(reduced)

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

$$\mathrm{In(oxidized)} + ne^- \rightleftharpoons \mathrm{In(reduced)}$$

$$E = E^\circ - \frac{0.059\,16}{n}\log\left(\frac{[\mathrm{In(reduced)}]}{[\mathrm{In(oxidized)}]}\right)$$

As with acid base indicators:

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

Colour of In(oxidized) observed when: $\frac{[\mathrm{In(reduced)}]}{[\mathrm{In(oxidized)}]} \lesssim \frac{1}{10}$

Redox Indicators, 2

If the quotients from the previous slide are inserted in the Nernst equation, we get the range over which the colour change will occur:

$$E = \left(E^\circ \pm \frac{0.059\,16}{n}\right)\text{volts}$$

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

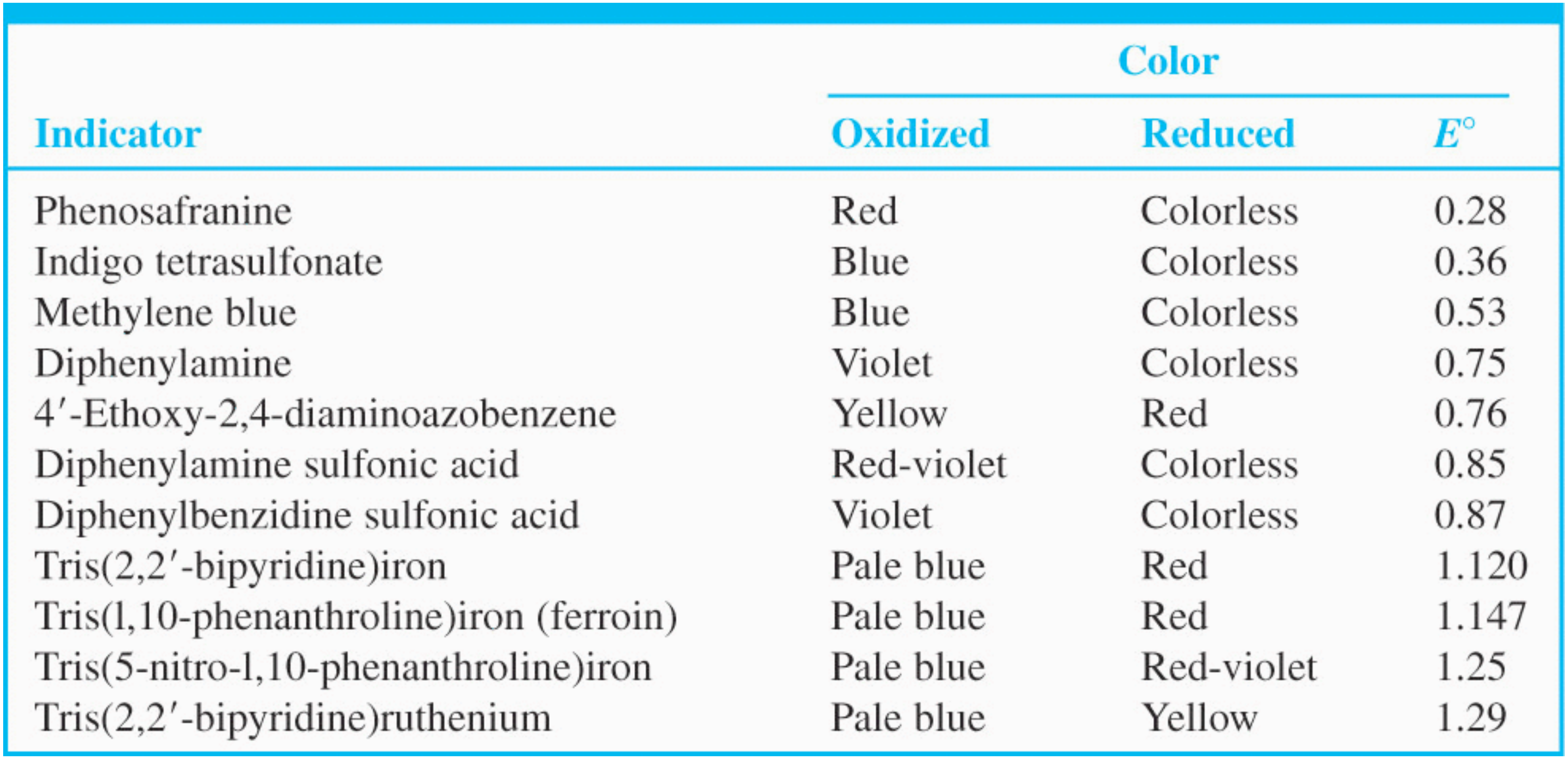
$$\begin{aligned}\begin{pmatrix}\text{Indicator transition}\\ \text{range versus calomel}\\ \text{electrode (S.C.E.)}\end{pmatrix} &= \begin{pmatrix}\text{Transition range}\\ \text{versus standard hydrogen}\\ \text{electrode (S.H.E.)}\end{pmatrix} - E(\text{calomel})\\ &= (1.088 \text{ to } 1.206) - (0.241)\\ &= 0.847 \text{ to } 0.965 \text{ V (versus S.C.E.)}\end{aligned}$$

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

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

Satisfactory or better: ≥ 0.4 V difference between analyte and titrant (colour indicator by eye is normally fine for this.

Redox Indicators, 3

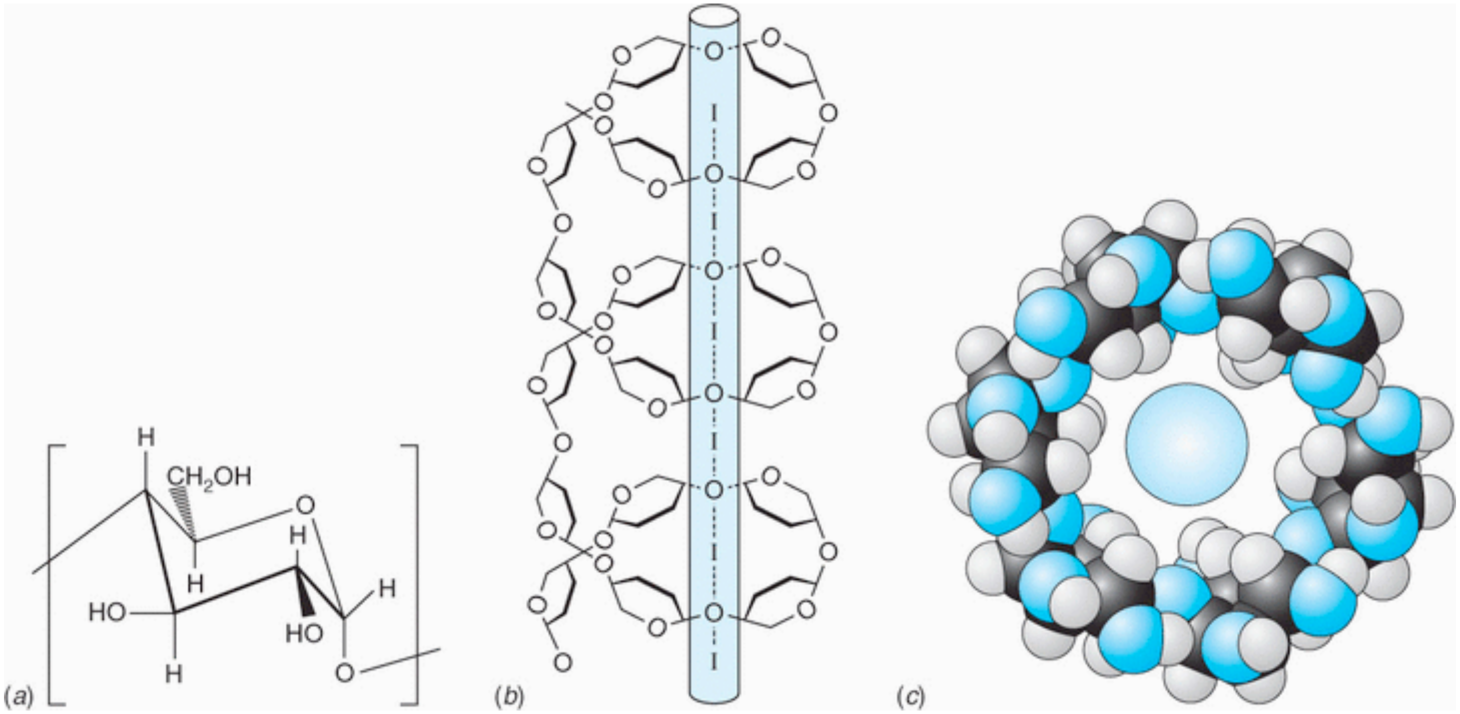


	Color		
Indicator	**Oxidized**	**Reduced**	$E°$
Phenosafranine	Red	Colorless	0.28
Indigo tetrasulfonate	Blue	Colorless	0.36
Methylene blue	Blue	Colorless	0.53
Diphenylamine	Violet	Colorless	0.75
4′-Ethoxy-2,4-diaminoazobenzene	Yellow	Red	0.76
Diphenylamine sulfonic acid	Red-violet	Colorless	0.85
Diphenylbenzidine sulfonic acid	Violet	Colorless	0.87
Tris(2,2′-bipyridine)iron	Pale blue	Red	1.120
Tris(1,10-phenanthroline)iron (ferroin)	Pale blue	Red	1.147
Tris(5-nitro-1,10-phenanthroline)iron	Pale blue	Red-violet	1.25
Tris(2,2′-bipyridine)ruthenium	Pale blue	Yellow	1.29

A redox indicator changes colour over a range of ±(59/*n*) mV, centred at $E°$ 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 I_2, 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 I_6 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 HgI_2 (~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 <u>you must eliminate excess preadjustment reagent so that it will not interfere in the subsequent titration.</u>

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.

$$S_2O_8^{2-} + Ag^+ \rightarrow SO_4^{2-} + \underbrace{SO_4^- + Ag^{2+}}_{\text{Two powerful oxidants}} \qquad 2S_2O_8^{2-} + 2H_2O \xrightarrow{\text{boiling}} 4SO_4^{2-} + O_2 + 4H^+$$

These oxidants are used for: $Mn^{2+} \rightarrow MnO_4^-$; $Ce^{3+} \rightarrow Ce^{4+}$; VO^{2+} to VO_2^+; $Cr_2O_7^{2-}$

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 $Cr_2O_7^{2-}$ 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

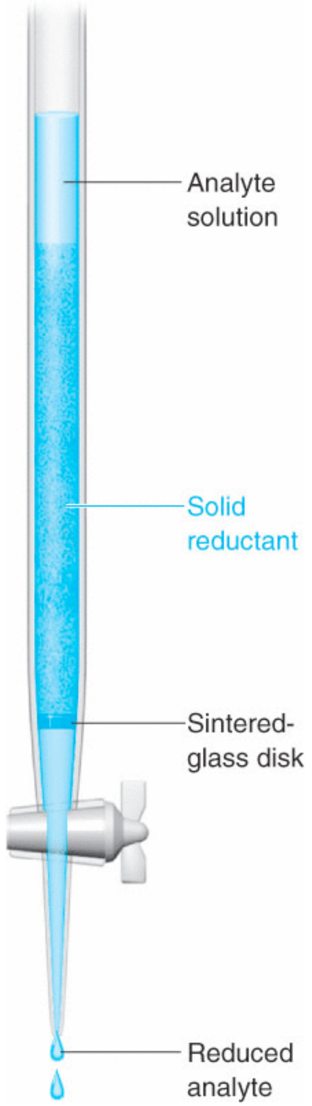
Stannous chloride ($SnCl_2$) will reduce Fe^{3+} to Fe^{2+} in hot HCl. Excess reductant is destroyed by adding excess $HgCl_2$. The Fe^{2+} is then titrated with an oxidant.

$$Sn^{2+} + 2HgCl_2 \rightarrow Sn^{4+} + Hg_2Cl_2 + 2Cl^-$$

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 hy*drogen 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_2SO_4 as solvent. Wash the column well with water and titrate the combined washings with standard , Ce^{4+}, or $Cr_2O_7^{2-}$.



Oxidation with $KMnO_4$

Potassium permanganate ($KMnO_4$) is a strong oxidant with an **intense violet colour**. In strongly acidic solutions (pH ≲1), it is reduced to colourless Mn^{2+}

$$\underset{\text{Permanganate}}{MnO_4^-} + 8H^+ + 5e^- \rightleftharpoons \underset{\text{Manganous}}{Mn^{2+}} + 4H_2O \qquad E^\circ = 1.507\text{ V}$$

In neutral or alkaline solution, the product is the **brown solid, MnO_2**.

$$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons \underset{\substack{\text{Manganese}\\ \text{dioxide}}}{MnO_2(s)} + 2H_2O \qquad E^\circ = 1.692\text{ V}$$

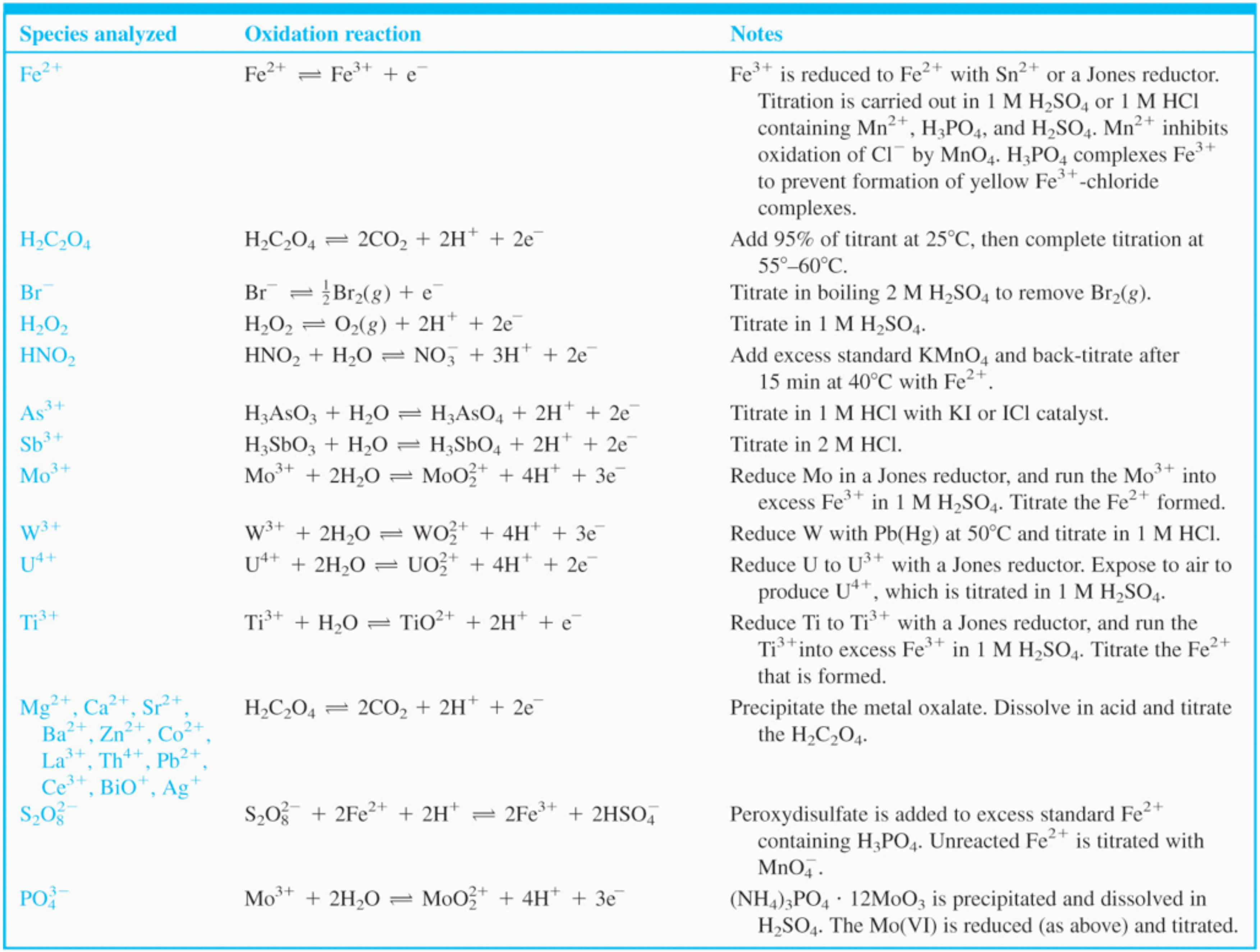
In strong basic solution (e.g., 2M NaOH), the **green manganate ion** is produced:

$$MnO_4^- + e^- \rightleftharpoons \underset{\text{Manganate}}{MnO_4^{2-}} \qquad E^\circ = 0.56\text{ V}$$

For titrations in strongly acidic solution, $KMnO_4$ serves as its own indicator because the product, Mn^{2+}, is colourless.

Note: that $KMnO_4$ is not a primary standard, as traces of MnO_2 are invariably present. It must be standardized by titration of sodium oxalate ($Na_2C_2O_4$) or pure electrolytic iron wire.

Oxidation with $KMnO_4$, 2



Species analyzed	Oxidation reaction	Notes
Fe^{2+}	$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$	Fe^{3+} is reduced to Fe^{2+} with Sn^{2+} or a Jones reductor. Titration is carried out in 1 M H_2SO_4 or 1 M HCl containing Mn^{2+}, H_3PO_4, and H_2SO_4. Mn^{2+} inhibits oxidation of Cl^- by MnO_4. H_3PO_4 complexes Fe^{3+} to prevent formation of yellow Fe^{3+}-chloride complexes.
$H_2C_2O_4$	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Add 95% of titrant at 25°C, then complete titration at 55°–60°C.
Br^-	$Br^- \rightleftharpoons \frac{1}{2}Br_2(g) + e^-$	Titrate in boiling 2 M H_2SO_4 to remove $Br_2(g)$.
H_2O_2	$H_2O_2 \rightleftharpoons O_2(g) + 2H^+ + 2e^-$	Titrate in 1 M H_2SO_4.
HNO_2	$HNO_2 + H_2O \rightleftharpoons NO_3^- + 3H^+ + 2e^-$	Add excess standard $KMnO_4$ and back-titrate after 15 min at 40°C with Fe^{2+}.
As^{3+}	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$	Titrate in 1 M HCl with KI or ICl catalyst.
Sb^{3+}	$H_3SbO_3 + H_2O \rightleftharpoons H_3SbO_4 + 2H^+ + 2e^-$	Titrate in 2 M HCl.
Mo^{3+}	$Mo^{3+} + 2H_2O \rightleftharpoons MoO_2^{2+} + 4H^+ + 3e^-$	Reduce Mo in a Jones reductor, and run the Mo^{3+} into excess Fe^{3+} in 1 M H_2SO_4. Titrate the Fe^{2+} formed.
W^{3+}	$W^{3+} + 2H_2O \rightleftharpoons WO_2^{2+} + 4H^+ + 3e^-$	Reduce W with Pb(Hg) at 50°C and titrate in 1 M HCl.
U^{4+}	$U^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 4H^+ + 2e^-$	Reduce U to U^{3+} with a Jones reductor. Expose to air to produce U^{4+}, which is titrated in 1 M H_2SO_4.
Ti^{3+}	$Ti^{3+} + H_2O \rightleftharpoons TiO^{2+} + 2H^+ + e^-$	Reduce Ti to Ti^{3+} with a Jones reductor, and run the Ti^{3+} into excess Fe^{3+} in 1 M H_2SO_4. Titrate the Fe^{2+} that is formed.
Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Co^{2+}, La^{3+}, Th^{4+}, Pb^{2+}, Ce^{3+}, BiO^+, Ag^+	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Precipitate the metal oxalate. Dissolve in acid and titrate the $H_2C_2O_4$.
$S_2O_8^{2-}$	$S_2O_8^{2-} + 2Fe^{2+} + 2H^+ \rightleftharpoons 2Fe^{3+} + 2HSO_4^-$	Peroxydisulfate is added to excess standard Fe^{2+} containing H_3PO_4. Unreacted Fe^{2+} is titrated with MnO_4^-.
PO_4^{3-}	$Mo^{3+} + 2H_2O \rightleftharpoons MoO_2^{2+} + 4H^+ + 3e^-$	$(NH_4)_3PO_4 \cdot 12MoO_3$ is precipitated and dissolved in H_2SO_4. The Mo(VI) is reduced (as above) and titrated.

Oxidation with Ce^{4+}

Reduction of Ce^{4+} to Ce^{3+} proceeds cleanly in acidic solutions. The aquo ion, $Ce(H_2O)_n^{4+}$, probably does not exist, because Ce(IV) binds anions (ClO_4^-, SO_4^{2-}, NO_3^-, Cl^-). Variation of the $Ce^{4+} | Ce^{3+}$ formal potential with the medium indicates these interactions:

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad \text{Formal potential} \begin{cases} 1.70 \text{ V in } 1 \text{ F } HClO_4 \\ 1.61 \text{ V in } 1 \text{ F } HNO_3 \\ 1.47 \text{ V in } 1 \text{ F } HCl \\ 1.44 \text{ V in } 1 \text{ F } H_2SO_4 \end{cases}$$

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), $(NH_4)_2Ce(NO_3)_6$, can be dissolved in 1 M H_2SO_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_2SO_4 is stable indefinitely, despite the fact that the reduction potential of 1.44 V is great enough to oxidize H_2O 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.

$$\underset{\text{Iodine}}{I_2(aq)} + \underset{\text{Iodide}}{I^-} \rightleftharpoons \underset{\text{Triiodide}}{I_3^-} \qquad K = 7 \times 10^2$$

A typical 0.05 M solution of I_3^- for titrations is prepared by dissolving 0.12 mol of KI plus 0.05 mol of I_2 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 I_2 plus excess I^-.

A solution made from
1.5 mM I_2 + 1.5 mM KI in water contains:

0.9 mM I_2
0.9 mM I^-
0.6 mM I_3^-
5 µM I_5^-
40 nM I_6^{2-}
0.3 µM HOI

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 $S_2O_3^{2-}$ (**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.

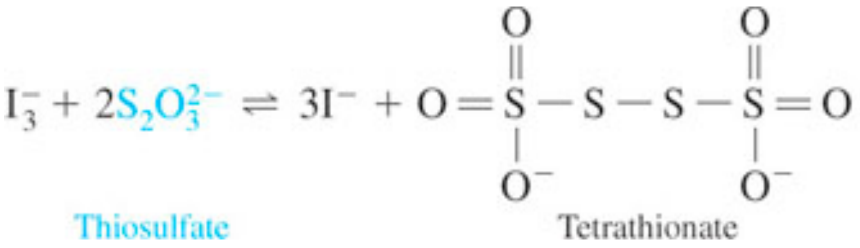
Another way to prepare standard I_3^- is to add a known quantity of the primary standard potassium iodate (KIO_3) to a small excess of KI, followed by addition of excess strong acid (giving pH ≈ 1) to produce I_3^- by quantitative *reverse disproportionation*.

$$IO_3^- + 8I^- + 6H^+ \rightleftharpoons 3I_3^- + 3H_2O$$

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*:



$$I_3^- + \underset{\text{Thiosulfate}}{2S_2O_3^{2-}} \rightleftharpoons 3I^- + \underset{\text{Tetrathionate}}{O=\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{S}}-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{S}}=O}$$

In basic solution, I_3^- disproportionates to I^- and HOI, which can oxidize $S_2O_3^{2-}$ to SO_4^{2-}; hence the reaction above should be carried out below pH 9. The common form of thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, is not pure enough to be a primary standard. Instead, thiosulfate is usually standardized by reaction with a fresh solution of I_3^- prepared from KIO_3 plus KI.

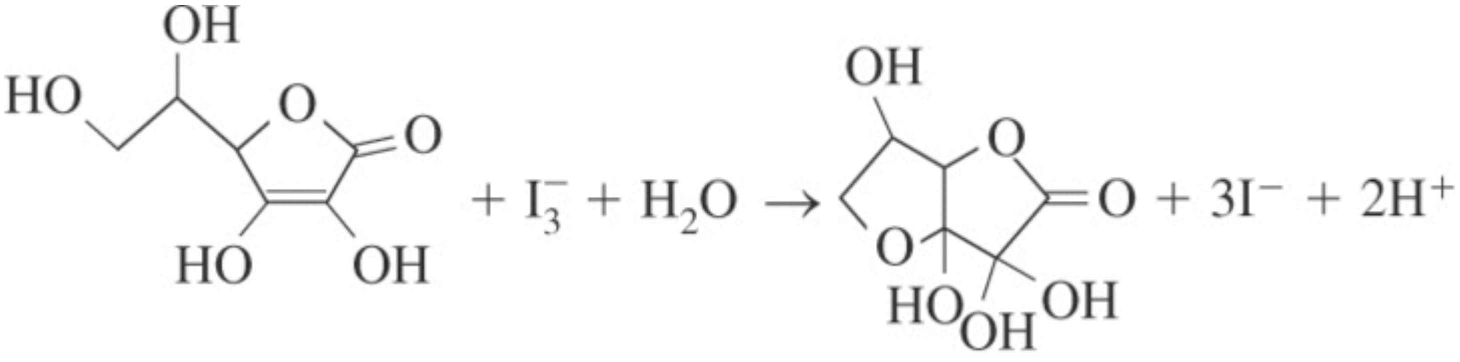
A stable solution of $Na_2S_2O_3$ can be prepared by dissolving the reagent in freshly boiled distilled water. Dissolved CO_2 makes the solution acidic and promotes disproportionation of $S_2O_3^{2-}$:

$$S_2O_3^{2-} + H^+ \rightleftharpoons \underset{\text{Bisulfite}}{HSO_3^-} + \underset{\text{Sulfur}}{S(s)}$$

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**:



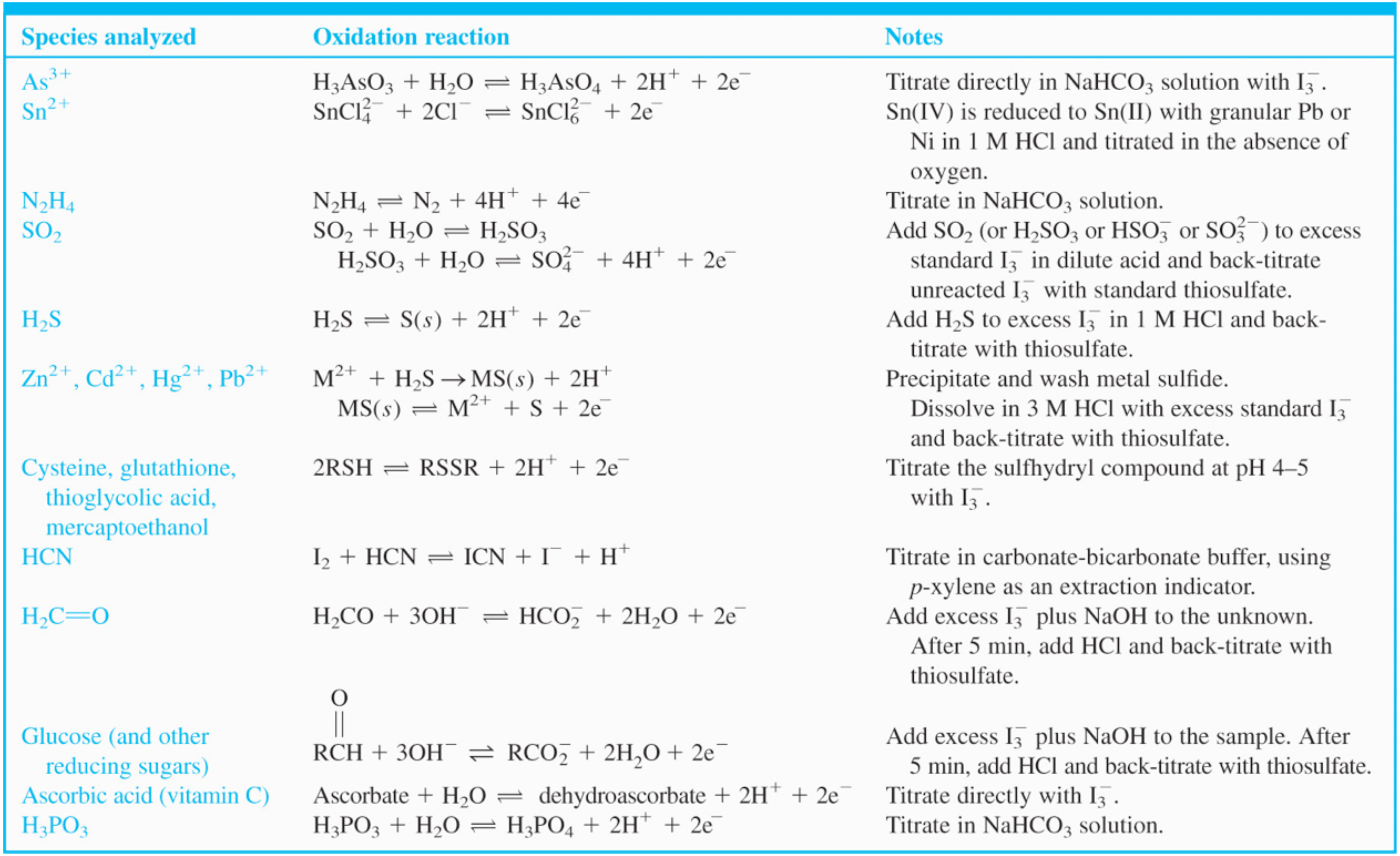
Ascorbic acid
(vitamin C)

Dehydroascorbic
acid[25]

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.

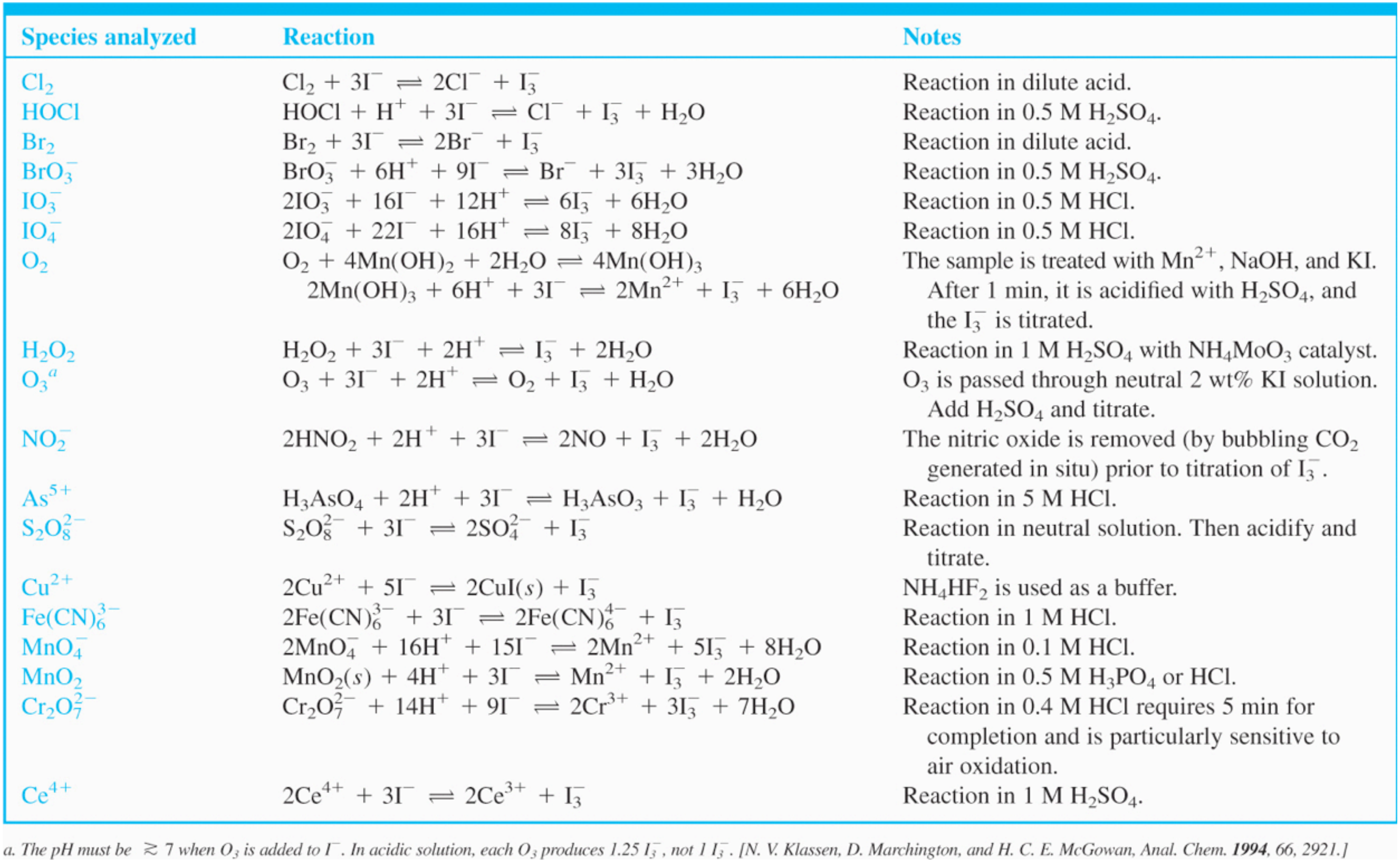
There are loads of applications for both iodimetric and iodometric titrations!

Titrations with standard I_3^- (iodimetric)



Species analyzed	Oxidation reaction	Notes
As^{3+}	$H_3AsO_3 + H_2O \rightleftharpoons H_3AsO_4 + 2H^+ + 2e^-$	Titrate directly in $NaHCO_3$ solution with I_3^-.
Sn^{2+}	$SnCl_4^{2-} + 2Cl^- \rightleftharpoons SnCl_6^{2-} + 2e^-$	Sn(IV) is reduced to Sn(II) with granular Pb or Ni in 1 M HCl and titrated in the absence of oxygen.
N_2H_4	$N_2H_4 \rightleftharpoons N_2 + 4H^+ + 4e^-$	Titrate in $NaHCO_3$ solution.
SO_2	$SO_2 + H_2O \rightleftharpoons H_2SO_3$ $H_2SO_3 + H_2O \rightleftharpoons SO_4^{2-} + 4H^+ + 2e^-$	Add SO_2 (or H_2SO_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.
H_2S	$H_2S \rightleftharpoons S(s) + 2H^+ + 2e^-$	Add H_2S to excess I_3^- in 1 M HCl and back-titrate with thiosulfate.
Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}	$M^{2+} + H_2S \rightarrow MS(s) + 2H^+$ $MS(s) \rightleftharpoons M^{2+} + S + 2e^-$	Precipitate and wash metal sulfide. Dissolve in 3 M HCl with excess standard I_3^- and back-titrate with thiosulfate.
Cysteine, glutathione, thioglycolic acid, mercaptoethanol	$2RSH \rightleftharpoons RSSR + 2H^+ + 2e^-$	Titrate the sulfhydryl compound at pH 4–5 with I_3^-.
HCN	$I_2 + HCN \rightleftharpoons ICN + I^- + H^+$	Titrate in carbonate-bicarbonate buffer, using *p*-xylene as an extraction indicator.
$H_2C{=}O$	$H_2CO + 3OH^- \rightleftharpoons HCO_2^- + 2H_2O + 2e^-$	Add excess I_3^- plus NaOH to the unknown. After 5 min, add HCl and back-titrate with thiosulfate.
Glucose (and other reducing sugars)	$R\overset{\overset{\displaystyle O}{\|}}{C}H + 3OH^- \rightleftharpoons RCO_2^- + 2H_2O + 2e^-$	Add excess I_3^- plus NaOH to the sample. After 5 min, add HCl and back-titrate with thiosulfate.
Ascorbic acid (vitamin C)	Ascorbate $+ H_2O \rightleftharpoons$ dehydroascorbate $+ 2H^+ + 2e^-$	Titrate directly with I_3^-.
H_3PO_3	$H_3PO_3 + H_2O \rightleftharpoons H_3PO_4 + 2H^+ + 2e^-$	Titrate in $NaHCO_3$ solution.

Titrations of I_3^- from analyte (iodometric)



Species analyzed	Reaction	Notes
Cl_2	$Cl_2 + 3I^- \rightleftharpoons 2Cl^- + I_3^-$	Reaction in dilute acid.
HOCl	$HOCl + H^+ + 3I^- \rightleftharpoons Cl^- + I_3^- + H_2O$	Reaction in 0.5 M H_2SO_4.
Br_2	$Br_2 + 3I^- \rightleftharpoons 2Br^- + I_3^-$	Reaction in dilute acid.
BrO_3^-	$BrO_3^- + 6H^+ + 9I^- \rightleftharpoons Br^- + 3I_3^- + 3H_2O$	Reaction in 0.5 M H_2SO_4.
IO_3^-	$2IO_3^- + 16I^- + 12H^+ \rightleftharpoons 6I_3^- + 6H_2O$	Reaction in 0.5 M HCl.
IO_4^-	$2IO_4^- + 22I^- + 16H^+ \rightleftharpoons 8I_3^- + 8H_2O$	Reaction in 0.5 M HCl.
O_2	$O_2 + 4Mn(OH)_2 + 2H_2O \rightleftharpoons 4Mn(OH)_3$ $2Mn(OH)_3 + 6H^+ + 3I^- \rightleftharpoons 2Mn^{2+} + I_3^- + 6H_2O$	The sample is treated with Mn^{2+}, NaOH, and KI. After 1 min, it is acidified with H_2SO_4, and the I_3^- is titrated.
H_2O_2	$H_2O_2 + 3I^- + 2H^+ \rightleftharpoons I_3^- + 2H_2O$	Reaction in 1 M H_2SO_4 with NH_4MoO_3 catalyst.
O_3[a]	$O_3 + 3I^- + 2H^+ \rightleftharpoons O_2 + I_3^- + H_2O$	O_3 is passed through neutral 2 wt% KI solution. Add H_2SO_4 and titrate.
NO_2^-	$2HNO_2 + 2H^+ + 3I^- \rightleftharpoons 2NO + I_3^- + 2H_2O$	The nitric oxide is removed (by bubbling CO_2 generated in situ) prior to titration of I_3^-.
As^{5+}	$H_3AsO_4 + 2H^+ + 3I^- \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$	Reaction in 5 M HCl.
$S_2O_8^{2-}$	$S_2O_8^{2-} + 3I^- \rightleftharpoons 2SO_4^{2-} + I_3^-$	Reaction in neutral solution. Then acidify and titrate.
Cu^{2+}	$2Cu^{2+} + 5I^- \rightleftharpoons 2CuI(s) + I_3^-$	NH_4HF_2 is used as a buffer.
$Fe(CN)_6^{3-}$	$2Fe(CN)_6^{3-} + 3I^- \rightleftharpoons 2Fe(CN)_6^{4-} + I_3^-$	Reaction in 1 M HCl.
MnO_4^-	$2MnO_4^- + 16H^+ + 15I^- \rightleftharpoons 2Mn^{2+} + 5I_3^- + 8H_2O$	Reaction in 0.1 M HCl.
MnO_2	$MnO_2(s) + 4H^+ + 3I^- \rightleftharpoons Mn^{2+} + I_3^- + 2H_2O$	Reaction in 0.5 M H_3PO_4 or HCl.
$Cr_2O_7^{2-}$	$Cr_2O_7^{2-} + 14H^+ + 9I^- \rightleftharpoons 2Cr^{3+} + 3I_3^- + 7H_2O$	Reaction in 0.4 M HCl requires 5 min for completion and is particularly sensitive to air oxidation.
Ce^{4+}	$2Ce^{4+} + 3I^- \rightleftharpoons 2Ce^{3+} + I_3^-$	Reaction in 1 M H_2SO_4.

a. The pH must be $\gtrsim 7$ when O_3 is added to I^-. In acidic solution, each O_3 produces 1.25 I_3^-, not 1 I_3^-. [N. V. Klassen, D. Marchington, and H. C. E. McGowan, Anal. Chem. ***1994****, 66, 2921.]*