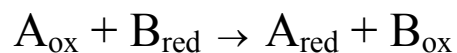


Redox Titrations

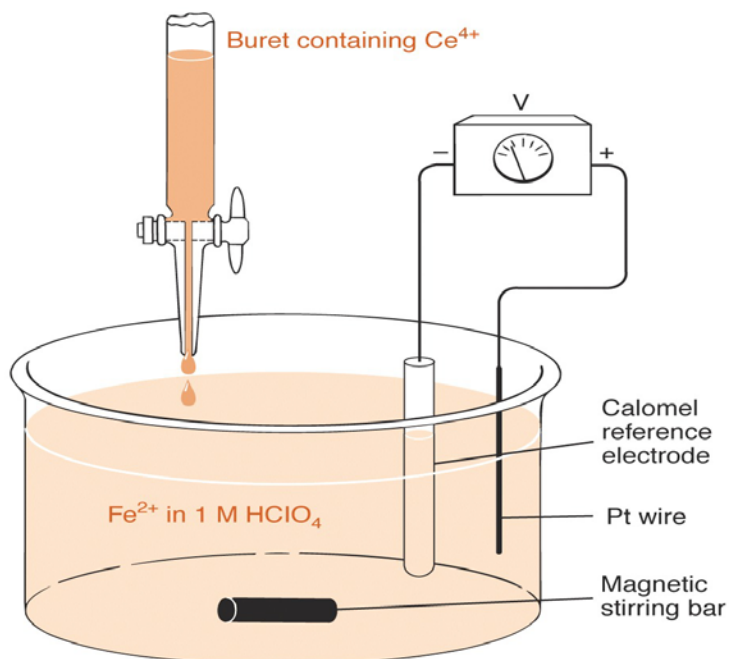
-the oxidation/reduction reaction between analyte and titrant

-titrants are commonly oxidizing agents, although reducing titrants can be used

-the equivalence point is based upon:



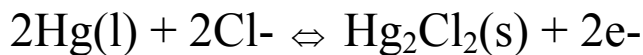
Rx'n goes to completion after each addition of titrant –
Potentiometric Titration:



Titration reaction:



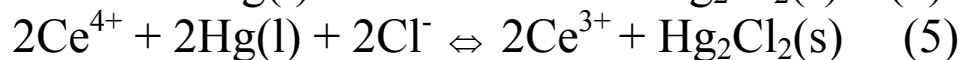
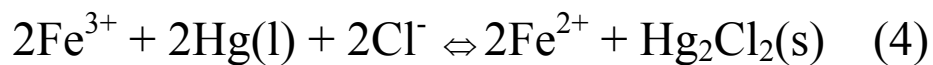
Reference half-reaction:



At the Pt indicator electrode (Indicator half-reaction)



Cell reactions (in 1 M HClO₄):



Relationships

- Cell reactions are not the same as the titration reaction
- May describe the cell voltage with either (4) or (5) or both

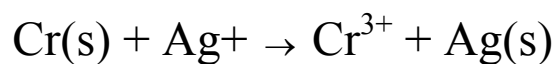
Balancing Redox Reactions

Balance:

-atoms

-# of electrons transferred

Example:

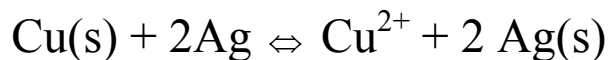


1. Write the half reactions:

2. Balance the electrons:

3. Recombine

Equilibrium constants for oxidation-reduction reactions



$$K_{\text{eq}} = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

Galvanic cell:

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{Ag}^+} - E_{\text{Cu}^{2+}}$$

Under equilibrium conditions, the potential of the cell becomes zero, thus can write:

$$E_{\text{cell}} = 0 = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{Ag}^+} - E_{\text{Cu}^{2+}}$$

or

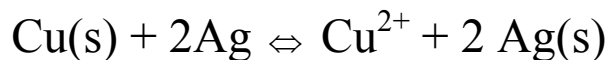
$$E_{\text{cathode}} = E_{\text{anode}} = E_{\text{Ag}^+} = E_{\text{Cu}^{2+}}$$

-Also when in equilibrium, electrode potentials of all systems are identical:

$$E_{\text{Ox1}} = E_{\text{Ox2}} = E_{\text{Ox3}} = E_{\text{Ox4}}$$

Where $E_{\text{Ox1}} \dots$ are electrode potentials for the four half-reactions

Calculating Equilibrium Constants



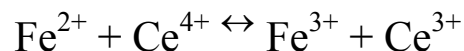
$$E^0_{\text{Ag}^+} - \frac{0.0592}{2} \log \frac{1}{[\text{Ag}^+]^2} = E^0_{\text{Cu}^{2+}} - \frac{0.0592}{2} \log \frac{1}{[\text{Cu}^{2+}]}$$

$$\begin{aligned} E^0_{\text{Ag}^+} - E^0_{\text{Cu}^{2+}} &= \frac{0.0592}{2} \log \frac{1}{[\text{Ag}^+]^2} - \frac{0.0592}{2} \log \frac{1}{[\text{Cu}^{2+}]} \\ &= \frac{2(E^0_{\text{Ag}^+} - E^0_{\text{Cu}^{2+}})}{0.0592} = \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = \log K_{\text{eq}} \end{aligned}$$

Ex: Calculate the equilibrium constant:

$$\begin{aligned} \log K_{\text{eq}} &= \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = \frac{2(0.799 - 0.337)}{0.0592} \\ &= 15.6 \\ K_{\text{eq}} &= \text{antilog } 15.6 = 4.1 \times 10^{15} = 4 \times 10^{15} \end{aligned}$$

Redox Titration Curves



$$E_{\text{Ce}^{4+}} = E_{\text{Fe}^{3+}} = E_{\text{system}}$$

$$E_{\text{In}} = E_{\text{Ce}^{4+}} = E_{\text{Fe}^{3+}} = E_{\text{system}}$$

Equivalence Point Potentials



$$1. \quad E_{\text{eq}} = E_{\text{Ce}^{4+}}^0 - \frac{0.0592}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

$$2. \quad E_{\text{eq}} = E_{\text{Fe}^{3+}}^0 - \frac{0.0592}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$2E_{\text{eq}} = E_{\text{Ce}^{4+}}^0 + E_{\text{Fe}^{3+}}^0 - \frac{[\text{Ce}^{3+}][\text{Fe}^{2+}]}{[\text{Ce}^{4+}][\text{Fe}^{3+}]} \quad (1)$$

Definition of e.p. requires that:

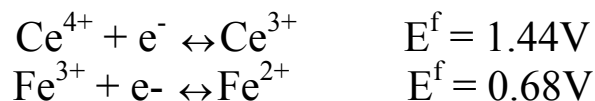
$$\begin{aligned} [\text{Fe}^{3+}] &= [\text{Ce}^{3+}] \\ [\text{Fe}^{2+}] &= [\text{Ce}^{4+}] \end{aligned}$$

$$2E_{\text{eq}} = E_{\text{Ce}^{4+}}^0 + E_{\text{Fe}^{3+}}^0 - \frac{0.0592}{1} \log \frac{[\text{Ce}^{3+}][\text{Ce}^{4+}]}{[\text{Ce}^{4+}][\text{Ce}^{3+}]} = E_{\text{Ce}^{4+}}^0 + E_{\text{Fe}^{3+}}^0$$

$$E_{\text{eq}} = \frac{E_{\text{Ce}^{4+}}^0 + E_{\text{Fe}^{3+}}^0}{2} \quad (2)$$

The Derivation of Titration Curves

Titration of 50.00 mL of 0.05000 M Fe^{2+} with 0.1000 M Ce^{4+} in a solution that is 1.0 M in H_2SO_4 at all times.



1. Initial potential – Ce and Fe^{3+} only present in very small amounts.

2. Potential after addition of 5.00 mL of Ce^{4+}

$$[\text{Fe}^{3+}] = \frac{5.00 \times 0.1000}{50.00 + 5.00} - [\text{Ce}^{4+}] \approx \frac{0.500}{55.00}$$

$$[\text{Fe}^{2+}] = \frac{50.00 \times 0.05000 - 5.00 \times 0.1000}{55.00} + [\text{Ce}^{4+}] \approx \frac{2.000}{55.00}$$

Substitution into Nernst equation:

$$E_{\text{system}} = +0.68 - \frac{0.0592}{1} \log \frac{2.00/55.00}{0.500/55.00} = 0.64\text{V}$$

E.P. potential

$$E_{\text{eq}} = \frac{E_{\text{Ce}^{4+}}^f + E_{\text{Fe}^{3+}}^f}{2} = \frac{1.44 + 0.68}{2} = 1.06\text{V}$$

3. Potential after addition of 25.10 mL of Ce^{4+}

$[\text{Fe}^{2+}]$ = amt of Ce^{4+} left unreacted, therefore added to $C_{\text{Ce}^{4+}}$ calculated from the volumes of the two solutions and subtracted from $C_{\text{Ce}^{3+}}$

Conc of two cerium ion species:

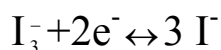
$$[\text{Ce}^{3+}] = \frac{25.00 \times 0.1000}{75.10} - [\text{Fe}^{2+}] \approx \frac{2.500}{75.10}$$

$$\begin{aligned} E &= +1.44 - \frac{0.0592}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} = +1.44 - \frac{0.0592}{1} \log \frac{2.500/75.00}{0.010/75.10} \\ &= +1.30 \text{ V} \end{aligned}$$

Effect of system variables on redox titration curves

Concentration – independent of analyte and reagent concentrations.

Exception: Electrode potentials dependent upon dilution



$$E = E^0 - \frac{0.0592}{2} \log \frac{[\text{I}^-]^3}{[\text{I}_3^-]}$$

num-mol/L³, denom-mol/L

Completeness of reaction – the change in E_{system} in the e.p. region becomes larger as the reaction becomes more concentrated.

Redox indicators

- specific indicators – react with one of the participants in the titration to produce a color, e.g. thiocyanate
- Oxidation-reduction indicators- respond to the potential of the system rather than to the appearance or disappearance of some species during the course of the titration, e.g. methylene blue

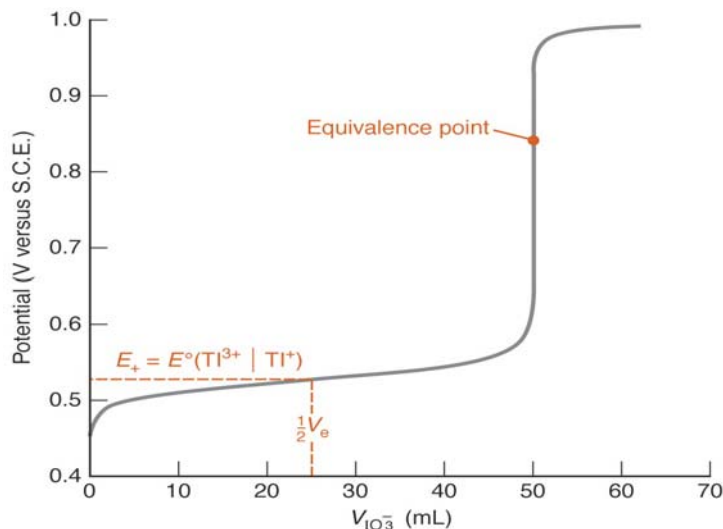
Color changes will occur over the range:

$$E = (E^0 \pm \frac{0.05916}{n})Volts$$

where n = # of electrons in the indicator half-reaction

-larger diff in std potential between titrant and analyte, the sharper the break in the titration curve at the e.p.

≥ 0.2 V, best detected potentiometrically



Gran plot

- more accurate way to use potentiometric data
- uses data well before e.p. (V_e) to locate V_e

For the oxidation of Fe^{2+} to Fe^{3+} , the potential prior to V_e is:

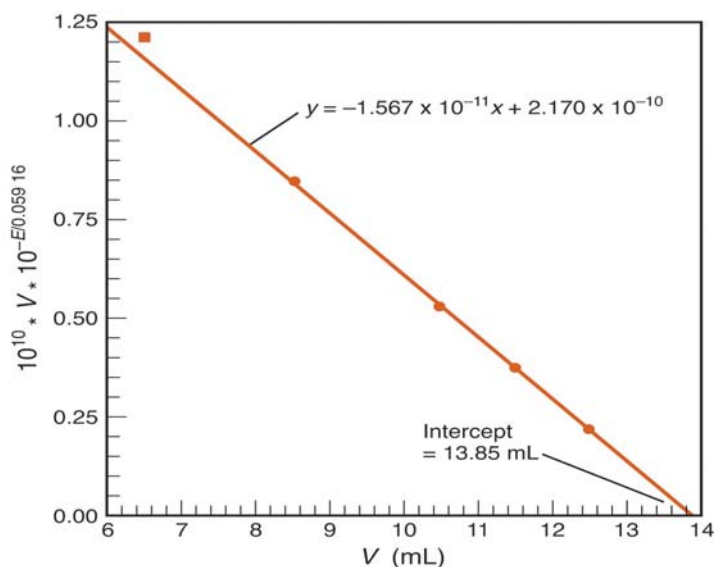
$$E = [E^{0'} - 0.05916 \log\left(\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}\right)] - E_{\text{ref}}$$

where, $E^{0'}$ = formal potential for $\text{Fe}^{3+} | \text{Fe}^{2+}$ and E_{ref} is the potential of the reference electrode.

If vol of analyte = V_0 and the vol of titrant = V , and if reaction goes to completion with each addition of titrant:

$$[\text{Fe}^{2+}] / [\text{Fe}^{3+}] = (V_e - V)$$

$$V \underset{y}{10^{-nE/0.05916}} = V_e \underset{b}{10^{-n(E_{\text{ref}} - E^{0'})/0.05916}} - V \underset{x}{10^{-n(E_{\text{ref}} - E^{0'})/0.05916}} \underset{m}{}$$



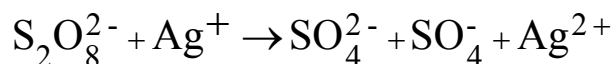
Adjustment of Analyte Oxidation State

-before titration, e.g. Mn^{2+} preoxidized to MnO_4^-

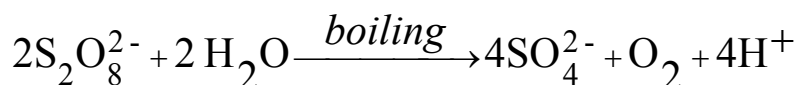
-excess preadjustment reagent must be destroyed so that it will not interfere in subsequent titration

Preoxidation

-powerful oxidants can be removed after preoxidation, e.g. peroxydisulfate ($\text{S}_2\text{O}_8^{2-}$) – requires Ag^+ as a catalyst.



Excess reagent destroyed:



Prereduction

-Stannous chloride (SnCl_2) will reduce Fe^{3+} to Fe^{2+} in hot HCl

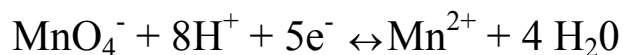
Excess reductant is then destroyed:



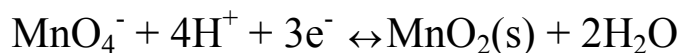
Oxidation with Potassium Permanganate

-strong oxidant, violet color

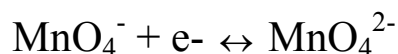
In strongly acidic solutions, reduced to colorless Mn^{2+} :



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



In strongly alkaline solution (2 M NaOH), green manganate is produced:



Tales 16.3.....see below

Note: permanganate solutions are unstable, therefore not a primary standard.



Permanganate must be *standardized* for example with oxalate;



Overall:



Initially the reaction is slow but is catalyzed by Mn^{2+} so becomes more rapid.

Can also standardize with **arsenic (III) oxide**



The reaction of As (III) with permanganate ion takes place without complications in acidic medium if a trace of an iodine compound (for example potassium iodate) is added as a catalyst.

The reaction generally carried out in HCl rather than H_2SO_4 in the latter a brown green coloration occurs due to formation of a manganese arsenate compound

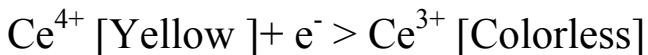
Table 16-3 Analytical applications of permanganate titrations

| Species analyzed | Oxidation reaction | Notes |
|--|---|---|
| Fe ²⁺ | $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + \text{e}^-$ | Fe ³⁺ is reduced to Fe ²⁺ with Sn ²⁺ or a Jones reductor. Titration is carried out in 1 M H ₂ SO ₄ or 1 M HCl containing Mn ²⁺ , H ₃ PO ₄ , and H ₂ SO ₄ . Mn ²⁺ inhibits oxidation of Cl ⁻ by MnO ₄ ⁻ . H ₃ PO ₄ complexes Fe ³⁺ to prevent formation of yellow Fe ³⁺ -chloride complexes. |
| H ₂ C ₂ O ₄ | $\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ | Add 95% of titrant at 25°C, then complete titration at 55°–60°C. |
| Br ⁻ | $\text{Br}^- \rightleftharpoons \frac{1}{2}\text{Br}_2(\text{g}) + \text{e}^-$ | Titrate in boiling 2 M H ₂ SO ₄ to remove Br ₂ (g). |
| H ₂ O ₂ | $\text{H}_2\text{O}_2 \rightleftharpoons \text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^-$ | Titrate in 1 M H ₂ SO ₄ . |
| HNO ₂ | $\text{HNO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NO}_3^- + 3\text{H}^+ + 2\text{e}^-$ | Add excess standard KMnO ₄ and back-titrate after 15 min at 40°C with Fe ²⁺ . |
| As ³⁺ | $\text{H}_3\text{AsO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2\text{e}^-$ | Titrate in 1 M HCl with KI or ICl catalyst. |
| Sb ³⁺ | $\text{H}_3\text{SbO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{SbO}_4 + 2\text{H}^+ + 2\text{e}^-$ | Titrate in 2 M HCl. |
| Mo ³⁺ | $\text{Mo}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_2^{2+} + 4\text{H}^+ + 3\text{e}^-$ | Reduce Mo in a Jones reductor, and run the Mo ³⁺ into excess Fe ³⁺ in 1 M H ₂ SO ₄ . Titrate the Fe ²⁺ formed. |
| W ³⁺ | $\text{W}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{WO}_2^{2+} + 4\text{H}^+ + 3\text{e}^-$ | Reduce W with Pb(Hg) at 50°C and titrate in 1 M HCl. |
| U ⁴⁺ | $\text{U}^{4+} + 2\text{H}_2\text{O} \rightleftharpoons \text{UO}_2^{2+} + 4\text{H}^+ + 2\text{e}^-$ | Reduce U to U ³⁺ with a Jones reductor. Expose to air to produce U ⁴⁺ , which is titrated in 1 M H ₂ SO ₄ . |
| Ti ³⁺ | $\text{Ti}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{TiO}^{2+} + 2\text{H}^+ + \text{e}^-$ | Reduce Ti to Ti ³⁺ with a Jones reductor, and run the Ti ³⁺ into excess Fe ³⁺ in 1 M H ₂ SO 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 ⁺ | $\text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ | Precipitate the metal oxalate. Dissolve in acid and titrate the H ₂ C ₂ O ₄ . |
| S ₂ O ₈ ²⁻ | $\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} + 2\text{H}^+ \rightleftharpoons 2\text{Fe}^{3+} + 2\text{HSO}_4^-$ | Peroxydisulfate is added to excess standard Fe ²⁺ containing H ₃ PO ₄ . Unreacted Fe ²⁺ is titrated with MnO ₄ ⁻ . |
| PO ₄ ³⁻ | $\text{Mo}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{MoO}_2^{2+} + 4\text{H}^+ + 3\text{e}^-$ | (NH ₄) ₃ PO ₄ ·12MoO ₃ is precipitated and dissolved in H ₂ SO ₄ . The Mo(VI) is reduced (as above) and titrated. |

KMnO₄ can serve as own indicator, since product Mn²⁺ is colorless.

Cerium(IV)

Strong oxidant > Ce(III)



Note however that the color change not good enough for it to act as self indicator.

Ce(IV) not found in acid solution as simple aqua ion .. forms complexes.

Dichromate reactions

Dichromate ion is an *oxidizing* agent



Dichromate has replace permanganate in many analyses ... notably iron (II)... it can be prepared as a standard solution and so avoids the need to standardize as is the case with permanganate.

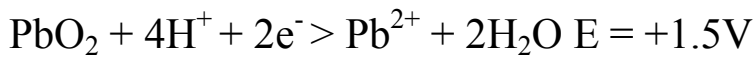
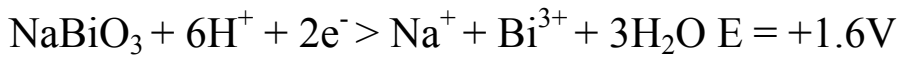
Iodine Methods



Value for E is intermediate can therefore be reduced or oxidized...iodine can be reduced to iodide by for example As(III), Sn(II) whilst iodide can be oxidized to iodine by for example permanganate. Use of iodide as titrant..practical problems ..so add excess potassium iodide and titrate the liberated iodine with for example standard thiosulphate solution

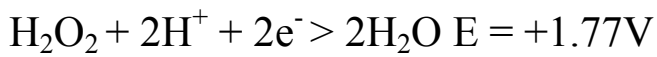
Miscellaneous Oxidizing agents

Sodium bismuthate and *lead (IV) oxide* are strong oxidizing agents.



Hydrogen peroxide

... strong oxidant even in alkaline conditions.



Excess peroxide may be removed by boiling...decomposes

Ex: Derive a titration curve for the titration of 50.00 mL of 0.02500 M U^{4+} with 0.1000 M Ce^{4+}