Ch 16: Redox Titrations
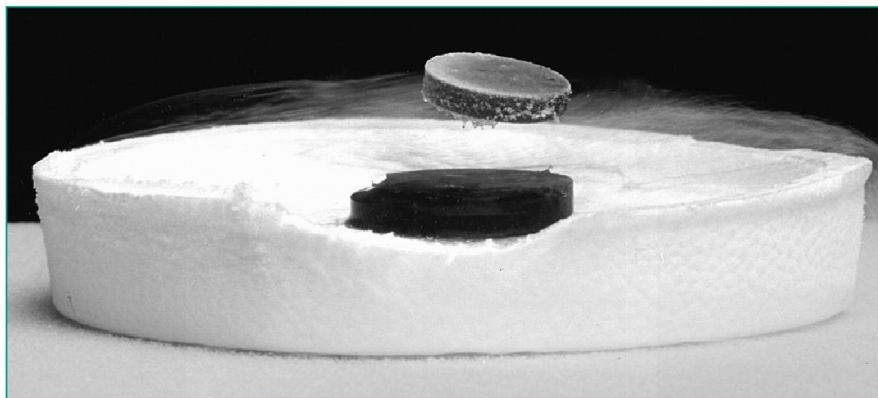

**Redox titrations are essential in measuring the chemical composition of a superconductor ($YBa_2Cu_3O_7$ - 2/3 Cu^{2+} and 1/3 the unusual Cu^{3+})**

Table 16-1   Oxidizing and reducing agents

Oxidants		Reductants
BiO_3^-	Bismuthate	
BrO_3^-		
Br_2		
Ce^{4+}		
$CH_3-\bigcirc$		
Cl_2		
ClO_2		
$Cr_2O_7^{2-}$		
FeO_4^{2-}		
H_2O_2		
$Fe^{2+} + H_2$		acid
OCl^-		
IO_3^-		
I_2		
Pb(acetate)		
HNO_3		
O		
O_2		
O_3		
$HClO_4$		
IO_4^-		
MnO_4^-	Permanganate	
$S_2O_8^{2-}$	Peroxydisulfate	

I_2	Iodine
$Pb(acetate)_4$	Lead(IV) acetate
HNO_3	Nitric acid
O	Atomic oxygen
O_2	Dioxygen (oxygen)
O_3	Ozone
$HClO_4$	Perchloric acid
IO_4^-	Periodate
MnO_4^-	Permanganate

α-Tocopherol (vitamin E)

Table 16-1
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KMnO$_4$ Titrations

$8H^+ + MnO_4^- + 5e^- = Mn^{2+} + 4H_2O$ $E^o = +1.51V$
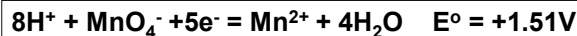
permanganate is one of the strongest oxidizing agents available

Table 16-2 *Analytical applications of permanganate titrations*

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.

|		
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$_2$SO$_4$.
T^{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$_2$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$^+$	$H_2C_2O_4 \rightleftharpoons 2CO_2 + 2H^+ + 2e^-$	Precipitate the metal oxalate. Dissolve in acid and titrate the H$_2$C$_2$O$_4$.
S$_2$O$_8^{2-}$	$S_2O_8^{2-} + 2Fe^{2+} + 2H^+ \rightleftharpoons 2Fe^{3+} + 2HSO_4^-$	Peroxydisulfate is added to excess standard Fe^{2+} containing H$_3$PO$_4$. Unreacted Fe^{2+} is titrated with MnO$_4^-$.
PO$_4^{3-}$	$Mo^{3+} + 2H_2O \rightleftharpoons MoO_2^+ + 4H^+ + 3e^-$	(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.

Preliminary Sample Treatment
(from "Quantitative Analysis", 6th ed., Day and Underwood, 1991, p. 297)

The iron in iron ore is usually both Fe^{2+} and Fe^{3+}, so a reducing agent such as tin(II) chloride is used to convert it entirely to Fe^{2+}.

Step 1: $Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}$ where the Sn^{2+} is added in excess

Step 2: The excess Sn^{2+} that didn't react will react with the KMnO$_4$, so it is removed by treating with HgCl$_2$:

$2HgCl_2 + Sn^{2+} \rightarrow Hg_2Cl_2(s) + Sn^{4+} + 2Cl^-$
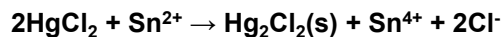
Step 3: To prevent the reaction of Cl$^-$ with KMnO$_4$, the Zimmerman-Reinhardt reagent is added. This reagent contains Mn^{2+} to prevent the oxidation of Cl$^-$ and H$_3$PO$_4$ prevents the formation of Fe^{3+}-chloride complexes as the titration proceeds.

KMnO$_4$ Standardization Using Na$_2$C$_2$O$_4$

It takes 38.29 mL of a permanganate solution to titrate 0.2587 g of preimary standard NaC$_2$O$_4$ (M = 133.999). What is the molarity of the permanganate?

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$
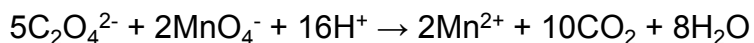
Determination of %Fe in an Ore

A 0.4857 g iron ore sample was dissolved in concentrated acid and reduced to Fe^{2+} using SnCl$_2$. 41.21 mL of 0.01963 M MnO4- was required to titrate the sample. Calculate the %Fe in the ore.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$
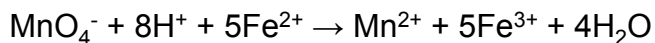
Formal Potentials

Redox System	Standard Potential	Formal Potential	Solution
$Ce^{4+} + e^- = Ce^{3+}$	---	1.23 1.44 1.61 1.7	1 M HCl 1 M H_2SO_4 1 M HNO_3 1 M $HClO_4$
$Fe^{3+} + e^- = Fe^{2+}$	+0.771	0.68 0.700 0.767	1 M H_2SO_4 1 M HCl 1 M $HClO_4$
$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	+1.33	1.00 1.05 1.08 1.08 1.15 1.03	1 M HCl 2 M HCl 3 M HCl 0.5 M H_2SO_4 4 M H_2SO_4 1 M $HClO_4$
$H_3AsO_4 + 2H^+ + 2e^- = H_3AsO_3 + H_2O$	+0.559	0.557 0.557	1 M HCl 1 M $HClO_4$
$Cr^{3+} + e^- = Cr^{2+}$	-0.42	-0.38	1 M $HClO_4$
$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15	0.14	1 M HCl

Theory of Redox Titrations (Sec 16-1)

Titration reaction example -
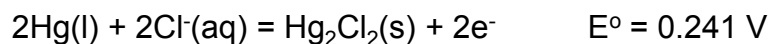
$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$
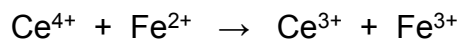
titrant   analyte

After the titration, most of the ions in solution are Ce^{3+} and Fe^{3+}, but there will be equilibrium amounts of Ce^{4+} and Fe^{2+}. All 4 of these ions undergoe redox reactions with the electrodes used to follow the titration. These redox reactions are used to calculate the potential developed during the titration.
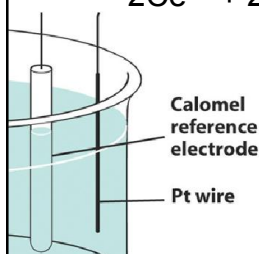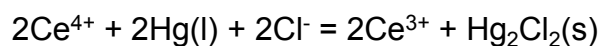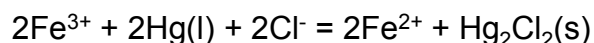

Buret containing Ce^{4+}

V

Calomel reference electrode

Pt wire

Magnetic stirring bar

Fe^{2+} in 1 M $HClO_4$
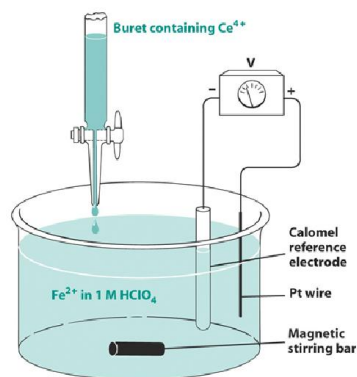
Saturated Calomel Reference Electrode half-reaction:

$$2Hg(l) + 2Cl^-(aq) = Hg_2Cl_2(s) + 2e^- \qquad E^o = 0.241 \text{ V}$$

Pt electrode half-reactions:

$$Fe^{3+} + e^- = Fe^{2+} \qquad E^{o'} = 0.767 \text{ V*}$$

$$Ce^{4+} + e^- = Ce^{3+} \qquad E^{o'} = 1.70 \text{ V*}$$
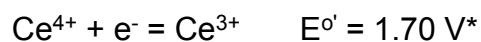
The net cell reaction can be described in two equivalent ways:

$$2Fe^{3+} + 2Hg(l) + 2Cl^- = 2Fe^{2+} + Hg_2Cl_2(s)$$

$$2Ce^{4+} + 2Hg(l) + 2Cl^- = 2Ce^{3+} + Hg_2Cl_2(s)$$

Calomel reference electrode

Pt wire

* formal potential in 1.0 M $HClO_4$

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1. Before the Equivalence Point

It's easier to use the Fe half-reaction because we know how much was originally present and how much remains for each aliquot of added titrant (otherwise, using Ce would require a complicated equilibrium to solve for).

$$E = E_+ - E_-$$

$$= \left[0.767V - 0.0592 \ \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \right] - 0.241V$$

Nernst equation for
$Fe^{3+} + e^- = Fe^{2+}$ (n=1)
$E^o = 0.767V$

$E_- = $ Sat'd Calomel Electrode voltage (E_{SCE})

$$= 0.526V - 0.0592 \ \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

We're only going to calculate the potential at the half-equivalence point where $[Fe^{2+}] = [Fe^{3+}]$:

$$E_{1/2} = 0.526V - 0.0592 \ \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \quad 0$$

$E_{1/2}$ = 0.526V or more generally for the half-equivalence point:

$E_{1/2} = E_+ - E_-$ where $E_+ = E^o$ (since the log term went to zero) and $E_- = E_{SCE}$

$E_{1/2} = E^o - E_{SCE}$

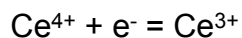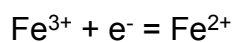## 2. At the Equivalence Point

$Ce^{3+} + Fe^{3+} = Ce^{4+} + Fe^{2+}$ (reverse of the titration reaction)
titrant   analyte

from the reaction stoichiometry, at the eq. pt. -

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

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

the two ½ reactions are at equilibrium with the Pt electrode -

   $Fe^{3+} + e^- = Fe^{2+}$

   $Ce^{4+} + e^- = Ce^{3+}$

so the Nernst equations are -

$$E_+ = E^0_{Fe} - 0.0592 \ \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \qquad E_+ = E^o_{Ce} - 0.0592 \ \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$E_+ = E^0_{Fe} - 0.0592 \; \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_+ = E^o_{Ce} - 0.0592 \; \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

adding the two equations together gives -

$$2E_+ = E^o_{Fe} + E^o_{Ce} - 0.0592 \; \log \frac{[Fe^{2+}]}{[Fe^{3+}]} - 0.0592 \; \log \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

$$2E_+ = E^o_{Fe} + E^o_{Ce} - 0.0592 \; \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Ce^{3+}]}{[Ce^{4+}]}$$

and since $[Ce^{3+}] = [Fe^{3+}]$ and $[Ce^{4+}] = [Fe^{2+}]$

$$2E_+ = E^o_{Fe} + E^o_{Ce} - 0.0592 \; \log \frac{[Fe^{2+}]}{[Fe^{3+}]} \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

$$2E_+ = E^o_{Fe} + E^o_{Ce} - 0.0592 \; \log \frac{[\cancel{Fe^{2+}}]}{[\cancel{Fe^{3+}}]} \frac{[\cancel{Fe^{3+}}]}{[\cancel{Fe^{2+}}]}$$

$$2E_+ = E^o_{Fe} + E^o_{Ce}$$

$$E_+ = \frac{E^o_{Fe} + E^o_{Ce}}{2} = \frac{0.767 + 1.70}{2} = \frac{2.467}{2} = 1.23V$$

$$E_+ = \frac{E^0_{titrant} + E^0_{analyte}}{2}$$

More generally, this is the cathode potential at the eq. pt. for <u>any</u> redox reaction where the number of electrons in each half reaction is equal.

$$E_{e.p.} = E_+ - E_- = E_+ - E_{SCE} = 1.23 - 0.241 = 0.99V$$

Figure (top slide)

Potential (V vs. S.C.E.) — y-axis: 0.3 to 1.5

Volume of titrant (mL) — x-axis: 0 to 70

$Fe^{2+} + Ce^{4+}$

Equivalence point for $Fe^{2+} + Ce^{4+}$ titration

Equivalence point for $Fe^{2+} + Tl^{3+}$ titration

$E = E°(Fe^{3+} | Fe^{2+}) - E(S.C.E.)$

$\frac{1}{2}V_e$

$Fe^{2+} + Tl^{3+}$
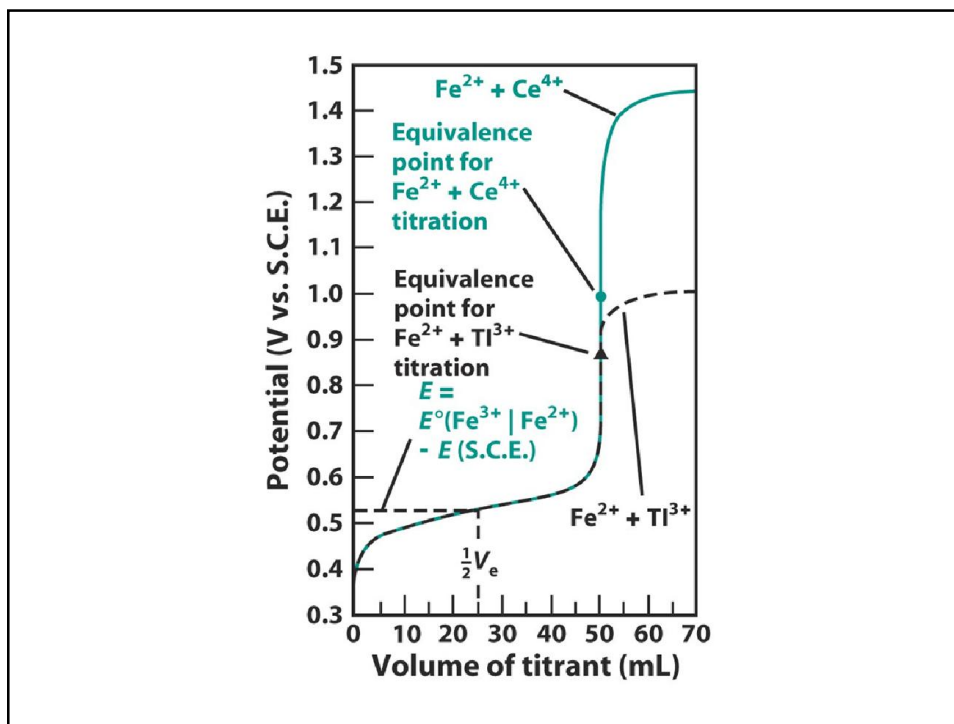
Equivalence Point Potentials
*Use these equations with **Standard Reduction Potentials**!*

1. Equal number of electrons

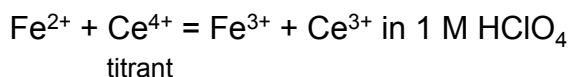$$E_+ = \frac{E^0_{titrant} + E^0_{analyte}}{2}$$

2. Unequal number of electrons (m = #e's cathode ½ rxn, n = #e's anode ½ rxn)

$$E_+ = \frac{mE^0_{titrant} + nE^0_{analyte}}{m+n}$$

8

Examples

1. Equal number of electrons

   $Fe^{2+} + Ce^{4+} = Fe^{3+} + Ce^{3+}$ in 1 M $HClO_4$
      titrant

2. Unequal number of electrons

   $Sn^{4+} + 2Cr^{2+} = Sn^{2+} + 2Cr^{3+}$ in 1 M HCl
      titrant
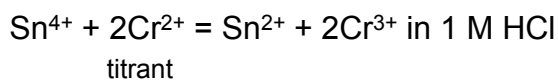
$KMnO_4$ is its own indicator, and electrodes can be used also, in which case the eq. pt. is obtained by calculating the 2nd derivative. Otherwise, an indicator is chosen that changes color at the eq. pt. potential.

TABLE **16-1**   Redox indicators

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