Redox Titrations

Net transfer of electrons during the reaction.
Oxidation numbers of two/more species change.

Satisfies requirements for reactions in quantitation;
a. large K   b. fast reaction

Balancing redox reactions:

1. identify the oxidation & reduction species and/*processes*.
2. balance each of *them* separately for mass, then charge. (H^+, OH^-, H_2O may be needed to balance *for species containing O, H*)
3. multiply half reactions to make the number of electrons the same in both half reactions

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

$$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O$$

$$MnO_4^- + 8H^+ + 5Fe^{+2} = Mn^{+2} + 5Fe^{+3} + 4H_2O$$

Note the changes in oxidation number.

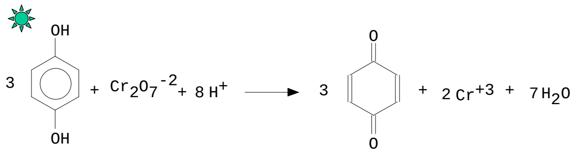
oxidizing agent, oxidant
↓

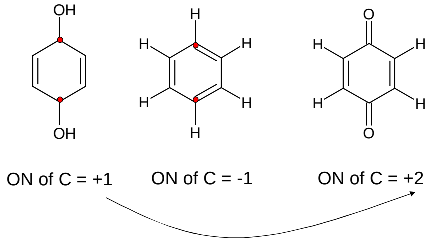
$$Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$$

↑
reducing agent, reductant
↓

$$MnO_4^- + 8H^+ + 5Fe^{+2} = Mn^{+2} + 5Fe^{+3} + 4H_2O$$

↑
oxidizing agent, oxidant





$$MnO_4^- + CH_3OH + H^+ \rightarrow Mn^{+2} + CO_2$$

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{+2} + 4H_2O$$

$$CH_3OH \rightarrow CO_2$$

$$\boxed{H_2O} + CH_3OH \rightarrow CO_2$$

$$H_2O + CH_3OH \rightarrow CO_2 + 6H^+$$

$$H_2O + CH_3OH \rightarrow CO_2 + 6H^+ + 6e$$

$$(MnO_4^- + 8H^+ + 5e \rightarrow Mn^{+2} + 4H_2O) \times 6$$

$$(H_2O + CH_3OH \rightarrow CO_2 + 6H^+ + 6e) \times 5$$

$$6MnO_4^- + 18H^+ + 5CH_3OH \rightarrow 6Mn^{+2} + 19H_2O + 5CO_2$$

$$MnO_4^- + CH_3OH + H^+ \rightarrow Mn^{+2} + CO_2$$

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{+2} + 4H_2O$$

$$CH_3OH \rightarrow CO_2$$

$$H_2O + CH_3OH \rightarrow CO_2$$

$$H_2O + CH_3OH \rightarrow CO_2 + 6H^+$$

$$H_2O + CH_3OH \rightarrow CO_2 + 6H^+ + 6e$$

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$$(H_2O + CH_3OH \rightarrow CO_2 + 6H^+ + 6e) \times 5$$

$$6MnO_4^- + 18H^+ + 5CH_3OH \rightarrow 6Mn^{+2} + 19H_2O + 5CO_2$$

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$$

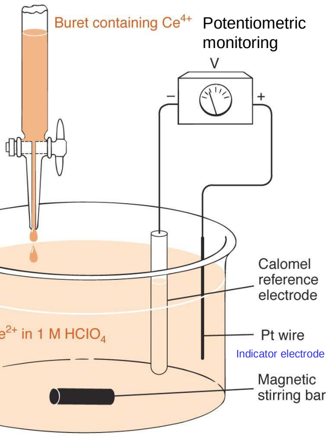
$$Cu \longrightarrow Cu^{+2} + 2e$$

$$NO_3^{-1} + 4H^+ + 3e \longrightarrow NO + 2H_2O$$

$$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

Note some nitrate ions are spectator ions.

$Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$



Electrochemistry (Potentiometry - very abbreviated version):

Electrochemistry deals with reactions, where electrons exchange between species.

Oxidation-reduction reactions:

$Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$

↑ ↑

reduced oxidized in the process

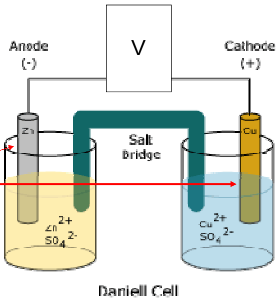
[O] [R]

If this reaction can be made to occur **at two sites**,

→ Electrochemical cell.

Electrochemical Cell – Voltaic Cell

Electrodes



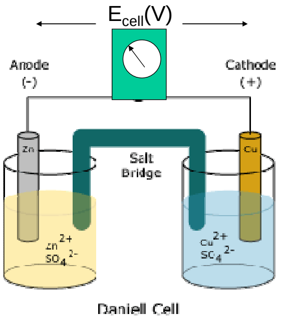
$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$

$Zn \rightarrow Zn^{2+} + 2e$

$Cu^{+2} + 2e \rightarrow Cu$ spontaneous, generates energy.

http://chemistry.about.com/library/weekly/aa082003a.htm

Convention:
Left-[O]
Right-[R]
$E_{cell} > 0$



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oxidation (half) reaction at one site and
reduction (half) reaction at the other site

↓

electrochemical cell = cell

$Fe^{+2} = Fe^{+3} + e$	anode	half reactions
$Ce^{+4} + e = Ce^{+3}$	cathode	

oxidation @ anode and reduction @ cathode

If a chemical species has a propensity to oxidize and another to reduce, combination of them will result in a redox reaction; reaction products - weaker oxidant/reductant.

Inherent propensity of a species to reduce is measured by their standard reduction potentials.

Note: A species that can be reduced easily (a propensity to be reduced) implies the reverse process, i.e. the oxidation is difficult.

Inherent ability to undergo reduction can be gleaned from the standard reduction potential values.

Standard (reduction) potential values of species are expressed referenced to standard proton reduction potential, i.e.

@ 25°C potential for

$2H^{+}(aq, a=1) + e = H_2(g, p=1atm)\ E^0_{H+/H2} = 0.00V$

Electrode potential tables are Standard Reduction Potential tables and the half reaction written as a reduction.

Acceptor Side		Donor Side	
Good Acceptors		*Poor Donors*	
$MnO_4^- + 8H + 5e^-$	=	$Mn^{2+} + 4H_2O$	+1.51
$Cl_2(g) + 2e^-$	=	$2Cl^-$	+1.359
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	=	$2Cr^{3+} + 7H_2O$	+1.33
$O_2 + 4H^+ + 4e^-$	=	$2H_2O$	+1.229
$IO_3^- + 6H^+ + 5e^-$	=	$1/2\ I_2 + 3H_2O$	+1.195
$NO_3^- + 3H^+ + 2e^-$	=	$HNO_2 + H_2O$	+0.94
$Cu^{2+} + I^- + e^-$	=	CuI	+0.86
$Ag^+ + e^-$	=	Ag	+0.799
$Fe^{3+} + e^-$	=	Fe^{2+}	+0.771
$2HgCl_4^{2-} + 2e^-$	=	$Hg_2Cl_2(s) + 6Cl^-$	+0.69
$I_2\ (aq) + 2e^-$	=	$2I^-$	+0.620
$I_3^- + 2e^-$	=	$3I^-$	+0.536
$Cu^{2+} + 2e^-$	=	Cu(s)	+0.337
$Hg_2Cl_2(s) + 2e^-$	=	$2Hg + 2Cl^-$	+0.268
AgCl + e-	=	Ag + Cl-	+0.222

Good e^- acceptor

Poor e^- donor

$MnO_4^- + 8H + 5e^-$	=	$Mn^{2+} + 4H_2O$	+1.51
$Cl_2(g) + 2e^-$	=	$2Cl^-$	+1.359
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	=	$2Cr^{3+} + 7H_2O$	+1.33
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$Cu^{2+} + I^- + e^-$	=	CuI	+0.86
$Ag^+ + e^-$	=	Ag	+0.799
$Fe^{3+} + e^-$	=	Fe^{2+}	+0.771
$2HgCl_4^{2-} + 2e^-$	=	$Hg_2Cl_2(s) + 6Cl^-$	+0.69
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$Hg_2Cl_2(s) + 2e^-$	=	$2Hg + 2Cl^-$	+0.268
AgCl + e-	=	Ag + Cl-	+0.222
$Sn^{4+} + 2e^-$	=	Sn^{2+}	+0.154
$Cu^{2+} + e^-$	=	Cu^+	+0.153
$S_4O_6^{2-} + 2e^-$	=	$2\ S_2O_3^{2-}$	+0.08
$2H^+ + 2e^-$	=	H_2	0.000
$Sn^{2+} + 2e^-$	=	Sn	-0.136
$2CO_2\ (g) + 2H^+ + 2e^-$	=	$H_2C_2O_4$	-0.49
$Zn^{2+} + 2e^-$	=	Zn	-0.763

Poor e^- acceptor

Good e^- donor

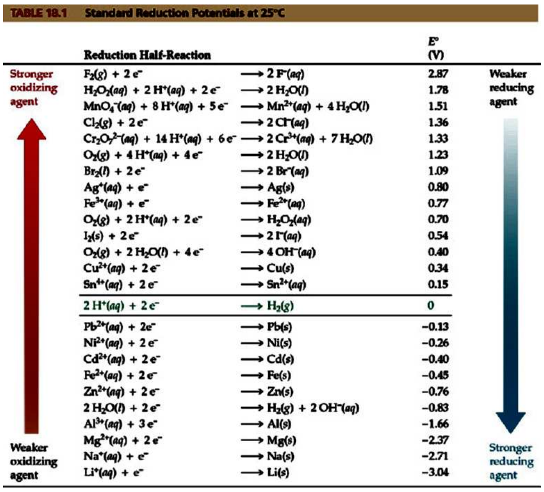


TABLE 18.1 Standard Reduction Potentials at 25°C

Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51
$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09
$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77
$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70
$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54
$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34
$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13
$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26
$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45
$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71
$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04

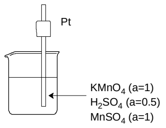
Construction of redox electrodes:

Standard electrodes

Inspect the half reaction, identify the species involved and their physical states.

Mix them up in solution, the activities of each species must be at their standard states (unity). If there are no 'species' that is metallic use a Pt wire (for electrical contact).

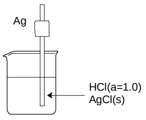
e.g. $MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O$



Notation:
Mn^{+2}(a=1),MnO_4(a=1),H^+(a=1)/Pt

Silver-silver chloride electrode:

AgCl(s) + e = Ag(s) + Cl $^-$(aq)



Notation:
Cl^-(a=1)/AgCl(s)/Ag

Electrodes – non standard:

In non-standard electrodes the concentrations/activity of one or more of the species involved is *not* unity.

E^o_{cell} A measure of the inherent ability for reaction to occur

Consider the redox reaction

$$Fe^{+2} + Ce^{+4} = Fe^{+3} + Ce^{+3}$$

Would this redox reaction occur spontaneously?
How quantitative is this reaction (K=?)?

Calculate E^0_{cell} for the reaction as written; if positive - reaction occurs; spontaneous and if large the K is large.

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

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

half reactions

$E^0_{cell} = E^0_{Ce^{+4}/Ce^{+3}} - E^0_{Fe^{+3}/Fe^{+2}}$ from tables (reduction potentials)

Prediction of the propensity to react, K, related to free energy change,...

$$\Delta G^O = -RT\ln K = \boxed{-nFE^O_{cell}}$$

$$E^O_{cell} = E^O_{reduction.pot.} + E^O_{oxidation.pot.}$$

cathode anode

$E^O_{electrode}$ tabulated as *reduction potentials*

$E^O_{cell} = E^O_{cathode} - E^O_{anode}$ (from tables)

$$E^O_{cell} = E^O_{red.pocess} - E^O_{oxd.process}$$

E^o_{cell}

Consider the redox reaction

$$Fe^{+2} + Ce^{+4} = Fe^{+3} + Ce^{+3}$$

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

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

half reactions

$$E^O_{cell} = E^O_{red.pocess} - E^O_{oxd.process}$$

$$E^O_{cell} = E^O_{cathode} - E^O_{anode}$$

$E^O_{cell} = E^O_{Ce^{+4}/Ce^{+3}} - E^O_{Fe^{+3}/Fe^{+2}}$ (from tables)

$= 1.720 - 0.771 = 0.949V$

(Large and) positive E^o_{cell} processes are good candidates for redox titration reactions; larger E^o_{cell} gives sharper end points (large K values).

Electrode potential (in general); Nernst equation for electrode calculates the propensity for a reduction half reaction to occur when species are at a given set of concentrations. It is a measure of the *reducibility* of the species in solution.

→ $E_{halfrxn} = E_{el} = E_{el}{}^0 - \frac{RT}{nF}\ln(Q)_{el}$

$$E_{rxn} = E_{cell} = E_{cell}{}^0 - \frac{RT}{nF}\ln(Q)_{cell}$$

Q = reaction quotient.

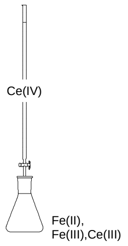
$$oxidized + ne = reduced$$

$$E_{el} = E^0{}_{el} - \frac{RT}{nF}\ln \underbrace{\frac{a_{reduced}}{a_{oxidized}}}_{Q}$$

Note: Q for electrode is for the electrode reaction *written as* a reduction.

Q large for a system ~ E_{el} small (and or negative) implies poor electron acceptor/ implies good electron donor - reducing system (and vice versa)

For the reaction: $Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$



$$E_{cathode} = E_{Ce^{+4}/Ce^{+3}} = E_{Ce^{+4}/Ce^{+3}}{}^{0} - \frac{RT}{nF}\ln\frac{a_{Ce^{+3}}}{a_{Ce^{+4}}}$$

$$E_{anode} = E_{Fe^{+3}/Fe^{+2}} = E_{Fe^{+3}/Fe^{+2}}{}^{0} - \frac{RT}{nF}\ln\frac{a_{Fe^{+2}}}{a_{Fe^{+3}}}$$

Note Q for electrode is for the electrode reaction written as a reduction.

In potential calculated from any one of the two equations above are the same and is called the *solution redox potential*.

Only one equation is useful at a given instant for calculation, however.

During the titration the Q values change in a systematic manner.

$$E_{Ce^{+4}/Ce^{+3}} = E_{Ce^{+4}/Ce^{+4}}{}^{0} - \frac{RT}{nF}\ln\frac{a_{Ce^{+3}}}{a_{Ce^{+4}}}$$

$$E_{Fe^{+3}/Fe^{+2}} = E_{Fe^{+3}/Fe^{+2}}{}^{0} - \frac{RT}{nF}\ln\frac{a_{Fe^{+2}}}{a_{Fe^{+3}}}$$

The solution potential calculated from the perspective of any of the two redox equilibria that exist in the system; is numerically the same.

Measuring the variation of the solution potential allows the monitoring of the progress of the reaction/titration.

To calculate the redox potential in the solution, consider the *appropriate* equilibrium system, it is one of the two equilibria and the one that can be easily handled, arithmetically (mathematically).

Potentials are calculated as reduction potentials (convention).

Need to write the equilibria as reduction equilibria,

e.g. $Fe^{+3} + e = Fe^{+2}$

$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O$

Use Nernst equation.

The solution potential calculated from the perspective of of any redox equilibria that exist in the system is numerically the same.

$$MnO_4^- + 8H^+ + 5Fe^{+2} = Mn^{+2} + 5Fe^{+3} + 4H_2O$$

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

$$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O$$

Use Nernst equation.

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

$$MnO_4^- + 8H^+ + 5e = Mn^{+2} + 4H_2O$$

Either,

$$E_{Fe^{+3}/Fe^{+2}} = E^0{}_{Fe^{+3}/Fe^{+2}} - \frac{RT}{F}\ln\frac{a_{Fe^{+2}}}{a_{Fe^{+3}}}$$

or

$$E_{MnO_4^{-1}/Mn^{+2}} = E^0{}_{MnO_4^{-1}/Mn^{+2}} - \frac{RT}{5F}\ln\frac{a_{Mn^{+2}}}{a_{MnO_4^{-1}}a_{H^+}^8}$$

E_{cell} measures the propensity of a (overall) reaction, where the species are at any given concentration.

$$E_{rxn} = E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln(Q)_{cell}$$

Example 1.

$$MnO_4^-(a_1) + 8H^+(a_2) + 5Fe^{+2}(a_3) = Mn^{+2}(a_4) + 5Fe^{+3}(a_5) + 4H_2O$$

$$E_{cell} = E^0_{cell} - \frac{RT}{5F}\ln\left(\frac{a^2_{Mn^{+2}}a^5_{Fe^{+3}}}{a_{MnO_4^-}a^8_{H^+}a^5_{Fe^{+2}}}\right)$$

$$E_{cell} = E^0_{cell} - \frac{RT}{5F}\ln\left(\frac{a_4^2a_5^5}{a_1a_2^8a_3^5}\right)$$

Example 2 $Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$

$$E_{halfrxn} = E_{el} = E^0_{el} - \frac{RT}{nF}\ln(Q)_{el}$$

$$E_{rxn} = E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln(Q)_{cell}$$

For the two half reactions, E_{el};

$$E_{cathode} = E_{Ce^{+4}/Ce^{+3}} = E^0_{Ce^{+4}/Ce^{+4}} - \frac{RT}{nF}\ln\frac{a_{Ce^{+3}}}{a_{Ce^{+4}}}$$

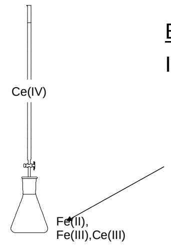
$$E_{anode} = E_{Fe^{+3}/Fe^{+2}} = E^0_{Fe^{+3}/Fe^{+2}} - \frac{RT}{nF}\ln\frac{a_{Fe^{+2}}}{a_{Fe^{+3}}}$$

Pick the process (anodic/cathodic) to follow, judiciously.

Solution potential is determined by Q; changing Q changes the *solution potential*.

The reaction progress is followed by following the redox potential of the solution, which depends on Q, with an oxidation-reduction potential electrode.

For $\boxed{Ce^{+4}} + Fe^{+2} = Ce^{+3} + Fe^{+3}$



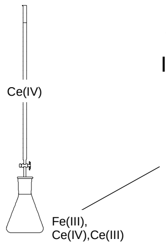
Before eq. point

Indicator reaction

$$E_{Fe^{+3}/Fe^{+2}} = E^0_{Fe^{+3}/Fe^{+2}} - \frac{RT}{nF}\ln\frac{a_{Fe^{+2}}}{a_{Fe^{+3}}}$$

Before eq. point $a_{Ce(IV)}$~ very small, 0; $\frac{a_{Fe^{+2}}}{a_{Fe^{+3}}}$ changes.

$Ce^{+4} + \boxed{Fe^{+2}} = Ce^{+3} + Fe^{+3}$



After eq. point

Indicator reaction

$$E_{Ce^{+4}/Ce^{+3}} = E^0_{Ce^{+4}/Ce^{+3}} - \frac{RT}{nF}\ln\frac{a_{Ce^{+3}}}{a_{Ce^{+4}}}$$

n=1

After eq. point $a_{Fe(II)}$ very small, ~0; $\frac{a_{Ce^{+3}}}{a_{Ce^{+4}}}$ changes.

$\boxed{Ce^{+4} + Fe^{+2}} = Ce^{+3} + Fe^{+3}$

At the eq. point $a_{Fe(II)}, a_{Ce(IV)}$ very small, ~0;

But, $\frac{a'_{Fe^{+2}}}{a'_{Fe^{+3}}} = \frac{a'_{Ce^{+4}}}{a'_{Ce^{+3}}}$ Q $a'_{Ce^{+3}} = a'_{Fe^{+3}}$

$a'_{Ce^{+4}} = a'_{Fe^{+2}}$

a’ concentrations of species at ‘end point’

Considering the redox potential at eq. pt. from both perspectives

$$\rightarrow E_{ep} = E_{Ce^{+4}/Ce^{+3}} = E^0_{Ce^{+4}/Ce^{+3}} - \frac{RT}{nF}\ln\frac{a'_{Ce^{+3}}}{a'_{Ce^{+4}}}$$

$$E_{ep} = E_{Fe^{+3}/Fe^{+2}} = E^0_{Fe^{+3}/Fe^{+2}} - \frac{RT}{nF}\ln\frac{a'_{Fe^{+2}}}{a'_{Fe^{+3}}}$$

$\boxed{Ce^{+4} + Fe^{+2}} = Ce^{+3} + Fe^{+3}$

At the eq. point $a_{Fe(II)}, a_{Ce(IV)}$ very small, ~0;

$\because a'_{Ce^{+3}} = a'_{Fe^{+3}}$ $\frac{a'_{Ce^{+3}}}{a'_{Ce^{+4}}} = \frac{a'_{Fe^{+3}}}{a'_{Fe^{+2}}}$ $\frac{a'_{Ce^{+3}}\,a'_{Fe^{+2}}}{a'_{Ce^{+4}}\,a'_{Fe^{+3}}} = 1$

$a'_{Ce^{+4}} = a'_{Fe^{+2}}$

a’ concentrations of species at ‘end point’

Considering the redox potential at eq. pt. from both perspectives

$$\rightarrow E_{ep} = E_{Ce^{+4}/Ce^{+3}} = E^0_{Ce^{+4}/Ce^{+3}} - \frac{RT}{nF}\ln\frac{a'_{Ce^{+3}}}{a'_{Ce^{+4}}}$$

$$E_{ep} = E_{Fe^{+3}/Fe^{+2}} = E^0_{Fe^{+3}/Fe^{+2}} - \frac{RT}{nF}\ln\frac{a'_{Fe^{+2}}}{a'_{Fe^{+3}}}$$

$$Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$$

$$a'_{Fe^{+3}} = a'_{Ce^{+3}}$$

$$a'_{Fe^{+2}} = a'_{Ce^{+4}}$$

$$\frac{a'_{Fe^{+2}}}{a'_{Fe^{+3}}} = \frac{a'_{Ce^{+4}}}{a'_{Ce^{+3}}}$$

$$\frac{a'_{Ce^{+3}}}{a'_{Ce^{+4}}}\frac{a'_{Fe^{+2}}}{a'_{Fe^{+3}}} = 1$$

$$E_{ep} = E_{Ce^{+4}/Ce^{+3}} = E^0_{Ce^{+4}/Ce^{+3}} - \frac{RT}{nF}\ln\frac{a'_{Ce^{+3}}}{a'_{Ce^{+4}}}$$

$$E_{ep} = E_{Fe^{+3}/Fe^{+2}} = E^0_{Fe^{+3}/Fe^{+2}} - \frac{RT}{nF}\ln\frac{a'_{Fe^{+2}}}{a'_{Fe^{+3}}}$$

Adding the above two equations:

$$2E_{ep} = E^0_{Ce^{+4}/Ce^{+4}} + E^0_{Fe^{+3}/Fe^{+2}} - \frac{RT}{nF}\ln\frac{a'_{Ce^{+3}}}{a'_{Ce^{+4}}} - \frac{RT}{nF}\ln\frac{a'_{Fe^{+2}}}{a'_{Fe^{+3}}}$$

$$2E_{ep} = E^0_{Ce^{+4}/Ce^{+4}} + E^0_{Fe^{+3}/Fe^{+2}} - \frac{RT}{nF}\ln\boxed{\frac{a'_{Ce^{+3}}}{a'_{Ce^{+4}}}\frac{a'_{Fe^{+2}}}{a'_{Fe^{+3}}}}$$

$$2E_{ep} = E^0_{Ce^{+4}/Ce^{+4}} + E^0_{Fe^{+3}/Fe^{+2}} - \frac{RT}{nF}\ln 1$$

Solution potential at equivalence point.

$$E_{ep} = \frac{E^0{}_{Ce^{+4}/Ce^{+3}} + E^0{}_{Fe^{+3}/Fe^{+2}}}{2}$$

In general, where $n_1 \neq n_2$;

$$E_{ep} = \frac{n_1E_1^0 + n_2E_2^0}{n_1 + n_2}$$

The potential of a single electrode is not measurable.

Only differences in potentials can be measured.

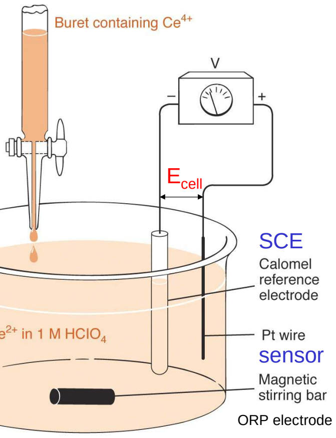
Thus a coupling of the ‘sensor’ electrode with a another *electrode of known, unchanging potential* is employed,
- *standard reference electrode*

$$Ce^{+4} + Fe^{+2} = Ce^{+3} + Fe^{+3}$$

$E_{measured}$=E_{cell}

=E_{sensor}- E_{SCE}

E_{sensor}= E_{cell}- E_{SCE}



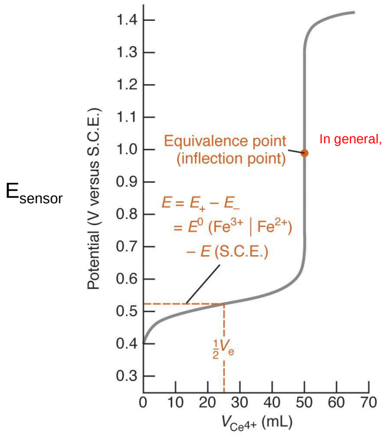
Note: The (reduction) potential of the solution is measured by coupling with a reference electrode, E_{ref} (which remains constant).

E_{cell} = E_{el} - E_{ref}. (convention)

E_{cell} varies in the same fashion as E_{el}.

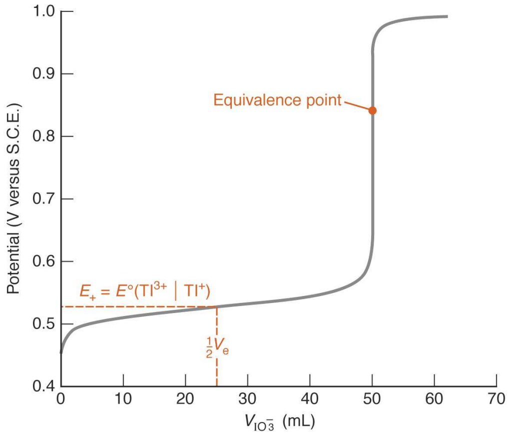
In general, where reaction is not 1:1 and/or the reactions are pH dependent, calculate starting from Nernst Equation.

Study the hand out.



In general, where $n_1 \neq n_2$;

$$E_{ep} = \frac{n_1E_1^0 + n_2E_2^0}{n_1 + n_2}$$



Comparison of titration curves with same titrant $Ce^{+4}(aq)$.

$Fe^{+2} + Ce^{+4} \rightarrow$ $E^0_{Fe(III)} / E^0_{Fe(III)} = 0.68V$

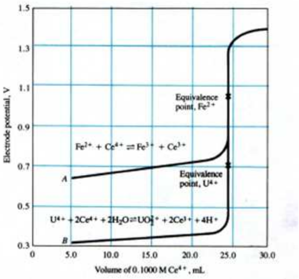
$U^{+4} + Ce^{+4} \rightarrow$ $E^0_{U(IV)} / E^0_{U(VI)} = 0.334$

E^0_{cell} calculation:

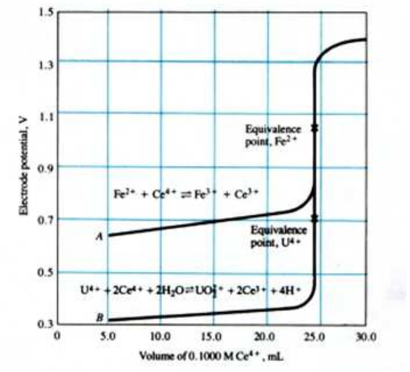
$$E^0_{Ce+4/Ce+3} - E^0_{Fe+3/Fe+2} = E^0_{Ce+4/Ce+3} - 0.680$$

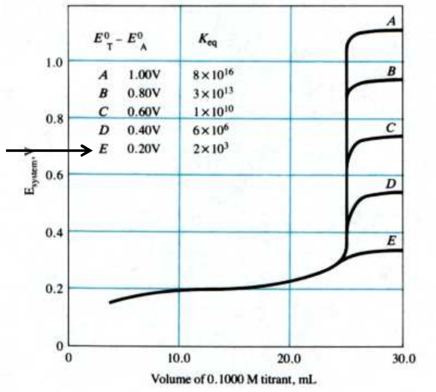
$$E^0_{Ce+4/Ce+3} - E^0_{U+6/U+4} = E^0_{Ce+4/Ce+3} - 0.334$$

$$E^0_{Ce+4/Ce+3} - 0.334 > E^0_{Ce+4/Ce+3} - 0.680$$



E_{cell} change at end point higher if $|E^O_{titrant} - E^O_{analyte}|$ is large. This is also a measure of the 'completeness' (i.e K) of the reaction.





	$E^0_T - E^0_A$	K_{eq}
A	1.00V	8×10^{16}
B	0.80V	3×10^{13}
C	0.60V	1×10^{10}
D	0.40V	6×10^6
E	0.20V	2×10^3

Redox Indicators:

Substances that are reduced and oxidized reversibly, two forms have different colors. It must undergo reduction/ oxidation as well.

In the proximity of the end point, E_{eq}.

In_{ox} + ne = In_{red}
color I color II

$$E = E^{O}_{ind} - \frac{2.303RT}{nF}\log\frac{[In_{red}]}{[In_{oxd}]}$$

$$\frac{[In_{red}]}{[In_{oxd}]}$$

$$\frac{[In_{red}]}{[In_{oxd}]}$$

Must change by 100, at a minimum to detect end point visually. e.g. 0.1 to 10 or vice versa.

In the transition range solution potential measured as An electrode potential must change;

$$E_{el} = \left[E^{O}_{Ind} \pm \frac{0.0592}{n}\right]$$

i.e. $$E_{cell} = \left[E^{O}_{Ind} \pm \frac{0.0592}{n}\right] - E_{ref}$$

The range dictated as $E_{el} = \left[E^{O}_{Ind} \pm \frac{0.0592}{n}\right]$

The indicator standard reduction potential must fall in the range above.

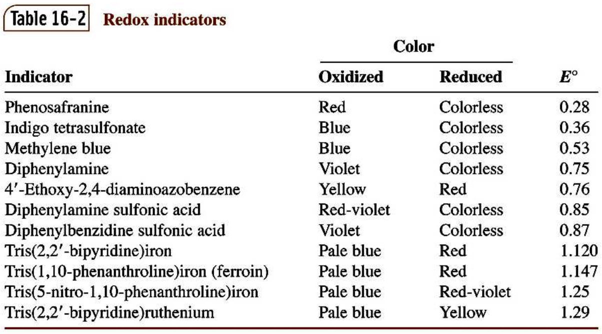
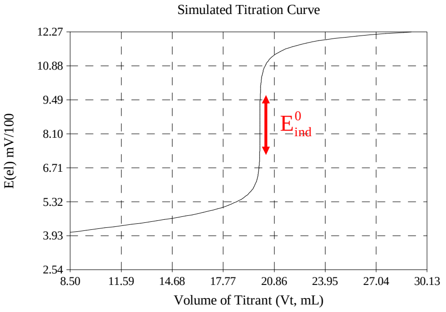


Table 16-2 **Redox indicators**

Indicator	Color: Oxidized	Color: 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

Simulated Titration Curve



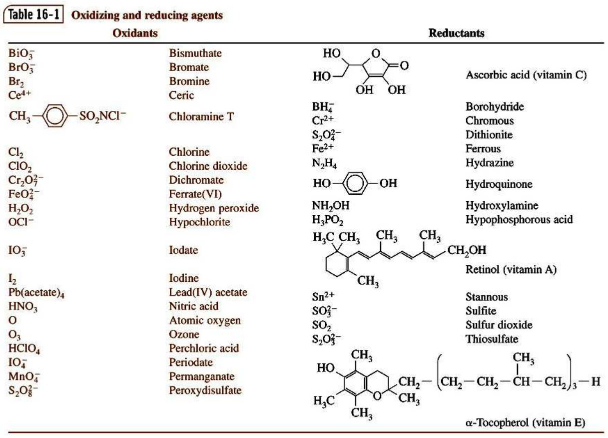


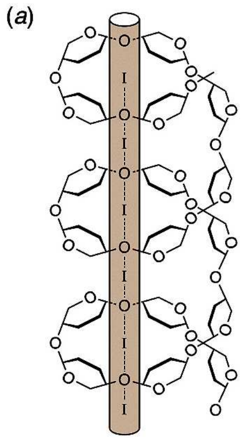
Table 16-1 **Oxidizing and reducing agents**

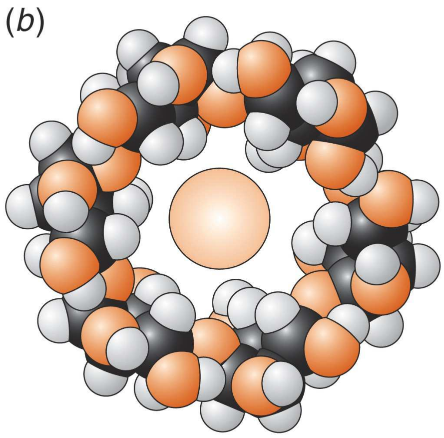
Oxidants		Reductants	
BiO_3^-	Bismuthate		Ascorbic acid (vitamin C)
BrO_3^-	Bromate	BH_4^-	Borohydride
Br_2	Bromine	Cr^{2+}	Chromous
Ce^{4+}	Ceric	$S_2O_4^{2-}$	Dithionite
	Chloramine T	Fe^{2+}	Ferrous
Cl_2	Chlorine	N_2H_4	Hydrazine
ClO_2	Chlorine dioxide		Hydroquinone
$Cr_2O_7^{2-}$	Dichromate	NH_2OH	Hydroxylamine
FeO_4^{2-}	Ferrate(VI)	H_3PO_2	Hypophosphorous acid
H_2O_2	Hydrogen peroxide		Retinol (vitamin A)
OCl^-	Hypochlorite	Sn^{2+}	Stannous
IO_3^-	Iodate	SO_3^{2-}	Sulfite
I_2	Iodine	SO_2	Sulfur dioxide
$Pb(acetate)_4$	Lead(IV) acetate	$S_2O_3^{2-}$	Thiosulfate
HNO_3	Nitric acid		α-Tocopherol (vitamin E)
O	Atomic oxygen		
O_3	Ozone		
$HClO_4$	Perchloric acid		
IO_4^-	Periodate		
MnO_4^-	Permanganate		
$S_2O_8^{2-}$	Peroxydisulfate		

Other ‘indicating’ strategies:

Starch-Iodine complex – for reactions involving I_2.

Self indicators – where one of the reactants is strongly colored, e.g. $KMnO_4$.





Sample Preparation

Some analyte samples must be prepared for a redox titration.

Analyte must be present in the correct oxidation state.

e.g. For analyzing iron with a Sn^{2+}, a reducing titrant all the iron must be present as Fe^{3+} in order to be reduced to Fe^{2+}.

If some iron is already present as Fe^{2+}, then it will not consume titrant and so escapes measurement.

Analyte must be pre-oxidized or pre-reduced to convert the analyte to **a single oxidation state.**

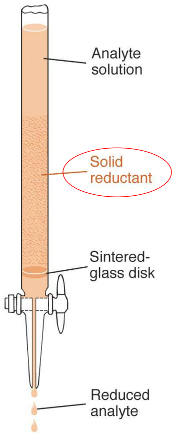
Adjusting oxidation states of analytes:

1. Change oxidation states (oxidation and reduction) by chemical reaction with excess of a pre-adjustment chemical agent.

2. Remove un-reacted chemical agent. (read text)

Examples:
Mn(II) to MnO_4^- (Ag^{+2})
V(V) to V(IV) (H_2SO_3)
Fe(III) to Fe(II) ($SnCl_2$)
Co(II) to Co(III) (H_2O_2)

$CrCl_2$
H_2S
Zn/Hg (Jones reductor)
Walden Reductor



Jones Reductor
Zinc amalgam
(strong)

Walden Reductor
Ag in 1M HCl
(mild/selective)

Granular Cd
(mild/selective)

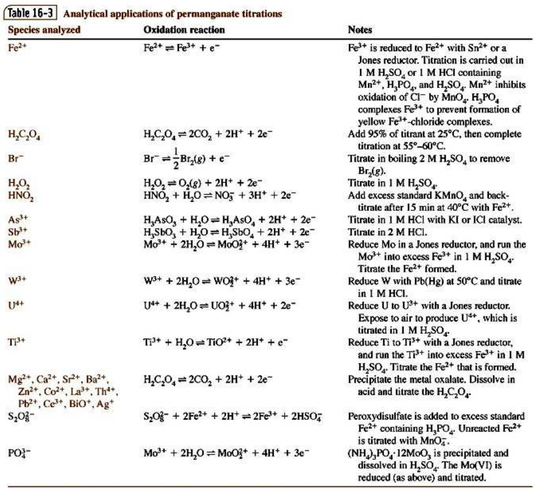


Table 16-3 Analytical applications of permanganate titrations

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.

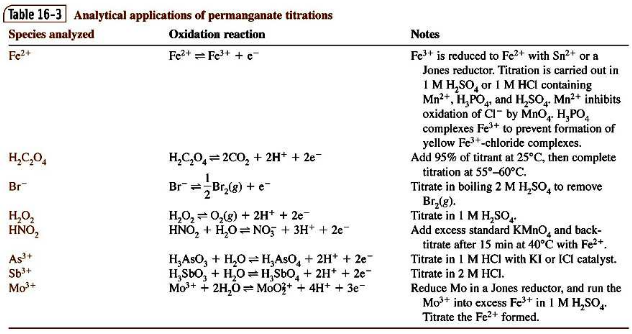


Table 16-3 Analytical applications of permanganate titrations

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.

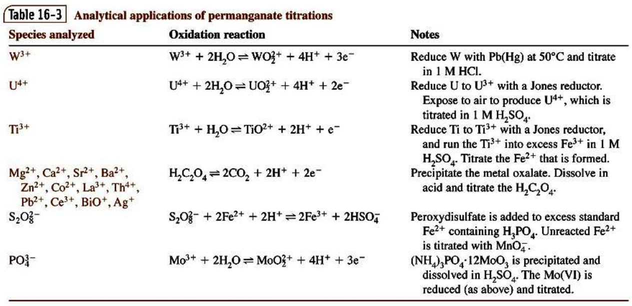


Table 16-3 Analytical applications of permanganate titrations

Species analyzed	Oxidation reaction	Notes
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.

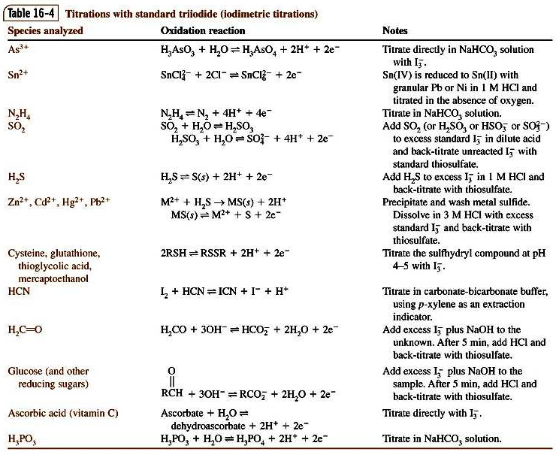


Table 16-4 Titrations with standard triiodide (iodimetric titrations)

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)	$R\overset{\overset{O}{\Vert}}{C}H + 3OH^- \rightleftharpoons RCO_2^- + 2H_2O + 2e^-$	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.

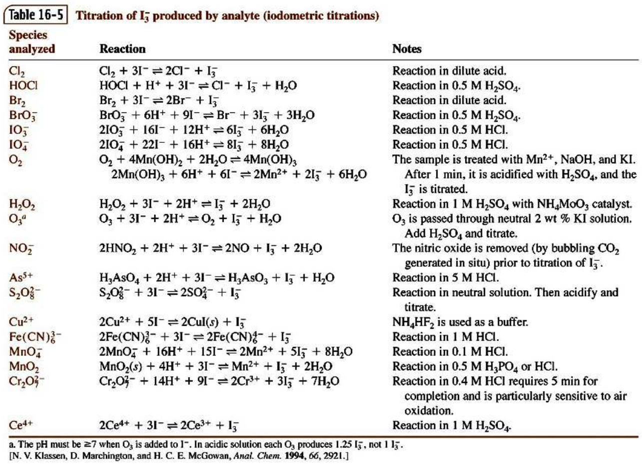


Table 16-5 Titration of I_3^- produced by analyte (iodometric titrations)

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	$O_2 + 4Mn(OH)_2 + 2H_2O \rightleftharpoons 4Mn(OH)_3$ $2Mn(OH)_3 + 6H^+ + 6I^- \rightleftharpoons 2Mn^{2+} + 2I_3^- + 6H_2O$	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 ≥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.]