Chapter 16
Redox Titrations

In general:
Determining the amount of reductant in a sample through titration with a strong oxidant.

Example: Analysis of $Fe^{2+,}$ titration with Ce^{4+}.

$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$ $\quad E° = 1.70$ V

$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ $\quad E° = 0.767$ V

Therefore,

Titration reaction

$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$ is a highly favorable rxn and will effectively go to completion.

$K = [Ce^{3+}][Fe^{3+}]/[Fe^{2+}][Ce^{4+}] = 10^{(nE°/0.05916)} = 10^{16}$

Lets use a reference electrode to follow the course of the titration. We will use the titration solution as one half cell and a reference electrode (in this example I will use the Ag/AgCl ref. electrode) as another half cell.

We can describe the reduction reaction **of the electrochemical cell** in terms of the Ce^{4+} or the Fe^{3+}, which ever is most convenient.

At the cathode

$Ce^{4+} + e^- \leftrightarrow Ce^{3+}$ $\quad E° = 1.70$ V

$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$ $\quad E° = 0.767$ V

At the anode

$Cl^- + Ag_{(s)} \leftrightarrow AgCl_{(s)} + e-$ $\quad E_{-} = 0.197$

Overall cell reaction

$$Ce^{4+} + Cl^- + Ag_{(s)} \leftrightarrow AgCl_{(s)} + Ce^{3+}$$

$$Fe^{3+} + Cl^- + Ag_{(s)} \leftrightarrow AgCl_{(s)} + Fe^{2+}$$

The cell current is very low, so it is not significantly altering (changing) the concentrations of $[Ce^{3+}]$, $[Ce^{4+}]$, $[Fe^{2+}]$, and $[Fe^{3+}]$. The cell voltage is being used to measure the concentrations of these species.

$E_+ = 1.70 - 0.05916 \log([Ce^{3+}]/[Ce^{4+}]) = 0.797 - 0.05916 \log([Fe^{2+}]/[Fe^{3+}])$
$E_- = 0.197$ V
$E_{cell} = E_+ - E_-$

Keep going with this example
Titrate 50.00 ml of 0.0500 M Fe^{2+} with 0.100 M Ce^{4+}

Equivalence point: 25.00 ml Ce^{4+}

Ecell @ 0.00 ml added (not trivial)

Ecell @ 2.00 ml added

$[Fe^{2+}]$ = {(50.00 ml)*(0.0500 M) – (2.00 ml)*(0.1000 M)} / (52.00 ml)
= 0.04423 M
$[Fe^{3+}]$ = (2.00 ml)*(0.1000 M) / (52.00 ml)
= 0.003846 M

Ecell = 0.797 - 0.05916 log(0.04423/0.003846) - 0.197 = 0.537 V

Ecell @ 10.00 ml added

$[Fe^{2+}]$ = {(50.00 ml)*(0.0500 M) – (10.00 ml)*(0.1000 M)} / (60.00 ml)
= 0.0250 M
$[Fe^{3+}]$ = (10.00 ml)*(0.1000 M) / (60.00 ml)
= 0.016667 M

Ecell = 0.797 - 0.05916 log(0.0250/0.016667) - 0.197 = 0.590 V

Ecell @ 12.50 ml added

Ecell = 0.797 - 0.197 = 0.600 V

Ecell @ 18.00 ml added

$[Fe^{2+}]$ = {(50.00 ml)*(0.0500 M) – (18.00 ml)*(0.1000 M)} / (78.00 ml)
= 0.0089743 M

$[Fe^{3+}]$ = (18.00 ml)*(0.1000 M) / (78.00 ml)
= 0.0230769 M

Ecell = 0.797 - 0.05916 log(0.00897/0.02308) - 0.197 = 0.624 V

Ecell @ 25.00 ml added (the equiv. point)

$E_+ = 1.70 - 0.05916 \log([Ce^{3+}]/[Ce^{4+}]) = 0.797 - 0.05916 \log([Fe^{2+}]/[Fe^{3+}])$

$2E_+ = E_+°(Ce) + E_+°(Fe) - 0.05916 \log ([Ce^{3+}][Fe^{2+}]/[Ce^{4+}][Fe^{3+}])$

At the equiv. pt. $[Ce^{3+}] = [Fe^{2+}]$, and $[Ce^{4+}] = [Fe^{3+}]$

$E_+ = (E_+°(Ce) + E_+°(Fe))/2 = 1.25$ V

Ecell = 1.25 – 0.197 = 1.05 V

After the equiv. point

Ecell @ 35.00 ml added

$[Ce^{3+}]$ = {(50.00 ml)*(0.0500 M)/(85.00 ml)
= 0.02941 M

$[Ce^{4+}]$ = (10.00 ml)*(0.1000 M) / (85.00 ml)
= 0.011765 M

Ecell = 1.70 - 0.05916 log(0.02941/0.01177) - 0.197 = 1.11 V

Chapter 16 redox titrations

Titrant – usually a strong oxidant

Analyte – acts as the reductant

Goal – determine concentration of the endpoint by adding just enough titrant to react with the analyte

Detecting the endpoint

- choose an appropriate re-dox indicator (changes color in the potential range corresponding to the expected equiv point
- follow the titration with an indicator electrode (analogous to a pH meter for a/b)

wed lecture – we learned how to predict the cell voltage (that would be read from the voltmeter of the indicator electrode)

You can write E^+ in terms of the half cells for either the analyte or the titrant, both are always true. The one we choose to apply is out of convenience.

- before equiv point (expression for E+ written in terms of analyte) special point (1/2Ve is often = E^0(analyte))
- after equiv pt (expression for E^+ written in terms of analyte)
- at equiv point (math trick, add together multiples of both the E^+ titrant expression and the E^+ analyte expression)

shape of a re-dox titration curve

pg 353, compare fig 16-3 (Tl^+ with IO_3^-) with 16-2 (Fe^{2+} with Ce^{4+})
symmetry of the equivalence point

The titration curve break will be sharper for larger differences in E^0. However, redox titration can be successfully performed with $\Delta E^0 \geq 0.2$ V

Redox indicators
Table 16.2
Working range = $E° \pm 0.05916/n$ V

Redox titrations using an oxidant as a titrant

Standard solutions of reductants are generally not stable in air (oxidation by O_2). Therefore, you must do experiment in a glove box under pure nitrogen.
Major exception: Fe^{2+} in acid

Intro (determining oxidation states of metals)

Most common titrants

Potassium permanganate
MnO_4^- $E° = 1.507$ V

Ammonium hexanitratocerate(IV)
Ce^{4+} $E° = 1.47$ V in 1 F HCl

Potassium dichromate
$Cr_2O_7^{2-}$ $E° = 1.36$ V

Methods involving iodine

$I_3^- + 2e^- \rightarrow 3I^-$ $E° = 0.535$ V

Iodimetry

Use a standardized solution of I_3^- as a titrant

I_3^- + analyte(reduced form) $\rightarrow$ $3I^-$ + analyte(oxidized form)

Ex. Ascorbic acid (vit. C) $E° = 0.390$ V

I_3^- + ascorbate $\rightarrow$ $3I^-$ + dehydyoascorbate + $2H^+$ (pg 365)

Starch indicator: I_3^- forms a dark blue complex with starch
Add starch at the beginning of titration

Iodometry

Add excess I^- to a solution of the analyte
$3I^- + \text{analyte(oxidized form)} \rightarrow \text{analyte(reduced form)} + I_3^-$
then titrate I_3^- with standard a thiosulfate solution
(back titration)
Analysis of Cl_2 $E° = 1.396$ V

$Cl_2 + \text{excess } I^- \rightarrow 2Cl^- + I_3^-$ (no Cl_2 left)

$I_3^- + 2S_2O_3^{2-} \rightarrow 3I^- + S_4O_6^{2-}$ $E° = 0.30$ V

Due a pre-titration to get a rough idea of the equiv. pt., then for the "real" titration and starch just before reaching equiv. pt.

Preoxidation / Pre-reduction

Convert all of the analyte into its most reduced form and destroy any excess reducing agent.

Example: $SnCl_2$ used to reduce Fe^{3+} to Fe^{2+} $E°(Sn^{2+}) = 0.139$ V

$Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}$ $E°(Fe^{3+}) = 0.767$ V

$Sn^{2+} + 2HgCl_2(\text{excess}) \rightarrow Sn^{4+} + Hg_2Cl_2 + 2Cl^-$

Then titrate the Fe^{2+} with strong oxidant Ce^{4+}

$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + 2Fe^{3+}$ $E°(Ce^{4+}) = 1.47$ V

Jones reductor

Solid zinc metal as the reductor

For example
Using Zn(s) to reduce Cr^{3+} $E°(Zn^{2+}) = -0.764$
$E°(Cr^{3+}) = -0.408$

$Zn_{(s)} + 2Cr^{3+} \rightarrow Zn^{2+} + 2Cr^{2+}$

but most reduced analytes are reoxidized by atmospheric oxygen. For instance Cr(II), Ti(III), V(II)

$Zn(s) + Cr(III) \rightarrow Zn(II) + Cr(II)$

$O_2 + Cr(II) \rightarrow Cr(III) + H_2O$

Titrate into an acidic solution of Fe^{3+}

$Fe^{3+} + Cr(II) \rightarrow Fe^{2+} + Cr(III)$ $\quad E°(Fe^{3+}) = 0.767$ V

Fe^{2+} is stable in acid

Titrate Fe^{2+} with strong oxidant (Ce^{4+})

$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$ $\quad E°(Ce^{4+}) = 1.47$ V

Problem 16.19

4.030 g solid containing only $NaNO_2$ and $NaNO_3$. Given the following data calculate the wt. % $NaNO_2$ in the sample. The sample is dissolved in 500 ml vol. A 25.00 ml aliquot is added to 50.00 ml of 0.1186 M Ce^{4+} and given time to react. The excess Ce^{4+} is back titrated with 31.13 ml of 0.04289 M Fe^{2+}.

$$2Ce^{4+} + NO_2^- + H_20 \rightarrow 2Ce^{3+} + NO_3^- + 2H^+$$

$$Ce^{4+} + Fe^{2+} \rightarrow 2Ce^{3+} + Fe^{3+}$$

mmole Ce^{4+} needed to titrate NO_2^- =
(50.0 ml)*(0.1186 M) – (31.13 ml)*(0.04289 M) = 4.59483 mmol Ce^{4+}

$(\text{mmol } NO_2^-)_{dil}$ = (4.59483 mmol Ce^{4+})(1 mmol NO_2^-/2 mmol Ce^{4+})
= 2.29742 mmol NO_2^-

$(\text{mmol } NO_2^-)_{sample}$ = (2.29742 mmol NO_2^-)*(500.0/25.00)
= 45.94 mmol NO_2^-

mg G = (45.94 mmol NO_2^-)*(68.995 mg $NaNO_2$/mmol NO_2^-)
= 3170.2 mg $NaNO_2$ = 3.1702 g $NaNO_2$

% $NaNO_2$ = (3.1702 g $NaNO_2$)/(4.030 g sample)*100 = 78.67 %