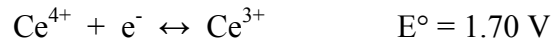


Chapter 16 Redox Titrations

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+} .



Therefore,

Titration reaction

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

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

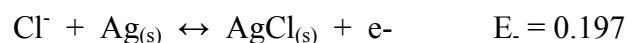
Lets use a reference electrode to follow the course of the titration. We will use the titration solution as one half cell and a reference electrode (in this example I will use the Ag/AgCl ref. electrode) as another half cell.

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.

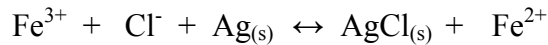
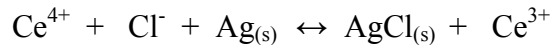
At the cathode



At the anode



Overall cell reaction



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

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

$$E_- = 0.197 \text{ V}$$

$$E_{\text{cell}} = E_+ - E_-$$

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

$$[\text{Fe}^{2+}] = \{(50.00 \text{ ml}) \cdot (0.0500 \text{ M}) - (2.00 \text{ ml}) \cdot (0.1000 \text{ M})\} / (52.00 \text{ ml})$$
$$= 0.04423 \text{ M}$$

$$[\text{Fe}^{3+}] = (2.00 \text{ ml}) \cdot (0.1000 \text{ M}) / (52.00 \text{ ml})$$
$$= 0.003846 \text{ M}$$

$$E_{\text{cell}} = 0.797 - 0.05916 \log(0.04423/0.003846) - 0.197 = 0.537 \text{ V}$$

Ecell @ 10.00 ml added

$$[\text{Fe}^{2+}] = \{(50.00 \text{ ml}) \cdot (0.0500 \text{ M}) - (10.00 \text{ ml}) \cdot (0.1000 \text{ M})\} / (60.00 \text{ ml})$$
$$= 0.0250 \text{ M}$$

$$[\text{Fe}^{3+}] = (10.00 \text{ ml}) \cdot (0.1000 \text{ M}) / (60.00 \text{ ml})$$
$$= 0.016667 \text{ M}$$

$$E_{\text{cell}} = 0.797 - 0.05916 \log(0.0250/0.016667) - 0.197 = 0.590 \text{ V}$$

Ecell @ 12.50 ml added

$$E_{\text{cell}} = 0.797 - 0.197 = 0.600 \text{ V}$$

Ecell @ 18.00 ml added

$$[\text{Fe}^{2+}] = \{(50.00 \text{ ml}) \cdot (0.0500 \text{ M}) - (18.00 \text{ ml}) \cdot (0.1000 \text{ M})\} / (78.00 \text{ ml})$$
$$= 0.0089743 \text{ M}$$

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

$$E_{\text{cell}} = 0.797 - 0.05916 \log(0.00897/0.02308) - 0.197 = 0.624 \text{ V}$$

Ecell @ 25.00 ml added (the equiv. point)

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

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

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

$$E_+ = (E_+^\circ(\text{Ce}) + E_+^\circ(\text{Fe}))/2 = 1.25 \text{ V}$$

$$E_{\text{cell}} = 1.25 - 0.197 = 1.05 \text{ V}$$

After the equiv. point

Ecell @ 35.00 ml added

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

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

$$E_{\text{cell}} = 1.70 - 0.05916 \log(0.02941/0.01177) - 0.197 = 1.11 \text{ V}$$

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 ($1/2V_e$ is often = $E^0(\text{analyte})$)
- 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 (Ti^+ 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 $\Delta E^0 \geq 0.2 \text{ V}$

Redox indicators

Table 16.2

Working range = $E^\circ \pm 0.05916/n$ 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^- $E^\circ = 1.507$ V

Ammonium hexanitratocerate(IV)

Ce^{4+} $E^\circ = 1.47$ V in 1 F HCl

Potassium dichromate

$Cr_2O_7^{2-}$ $E^\circ = 1.36$ V

Methods involving iodine

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

Iodimetry

Use a standardized solution of I_3^- as a titrant

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

Ex. Ascorbic acid (vit. C) $E^\circ = 0.390$ V

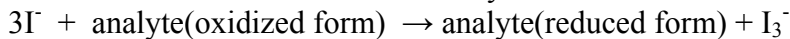
$I_3^- + \text{ascorbate} \rightarrow 3I^- + \text{dehydroascorbate} + 2H^+$ (pg 365)

Starch indicator: I_3^- forms a dark blue complex with starch

Add starch at the beginning of titration

Iodometry

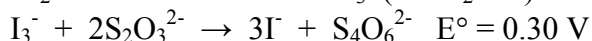
Add excess I^- to a solution of the analyte



then titrate I_3^- with standard a thiosulfate solution

(back titration)

Analysis of Cl_2 $E^\circ = 1.396 \text{ V}$

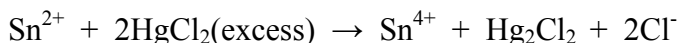
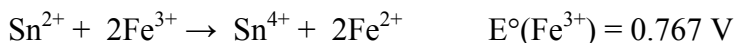


Due a pre-titration to get a rough idea of the equiv. pt., then for the “real” titration and starch just before reaching equiv. pt.

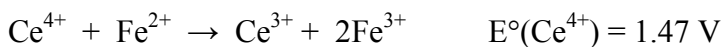
Preoxidation / Pre-reduction

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+} $E^\circ(Sn^{2+}) = 0.139 \text{ V}$



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

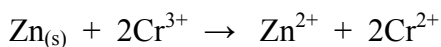


Jones reductor

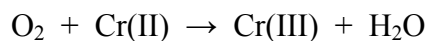
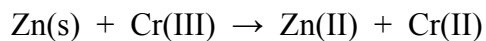
Solid zinc metal as the reductor

For example

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



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



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



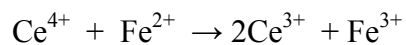
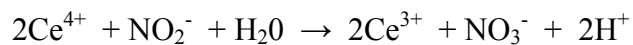
Fe^{2+} is stable in acid

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



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+} .



$$\begin{aligned} \text{mmole Ce}^{4+} \text{ needed to titrate NO}_2^- &= \\ (50.0 \text{ ml}) \cdot (0.1186 \text{ M}) - (31.13 \text{ ml}) \cdot (0.04289 \text{ M}) &= 4.59483 \text{ mmol Ce}^{4+} \end{aligned}$$

$$\begin{aligned} (\text{mmol NO}_2^-)_{\text{dil}} &= (4.59483 \text{ mmol Ce}^{4+}) \cdot (1 \text{ mmol NO}_2^- / 2 \text{ mmol Ce}^{4+}) \\ &= 2.29742 \text{ mmol NO}_2^- \end{aligned}$$

$$\begin{aligned} (\text{mmol NO}_2^-)_{\text{sample}} &= (2.29742 \text{ mmol NO}_2^-) \cdot (500.0 / 25.00) \\ &= 45.94 \text{ mmol NO}_2^- \end{aligned}$$

$$\begin{aligned} \text{mg G} &= (45.94 \text{ mmol NO}_2^-) \cdot (68.995 \text{ mg NaNO}_2 / \text{mmol NO}_2^-) \\ &= 3170.2 \text{ mg NaNO}_2 = 3.1702 \text{ g NaNO}_2 \end{aligned}$$

$$\% \text{ NaNO}_2 = (3.1702 \text{ g NaNO}_2) / (4.030 \text{ g sample}) \cdot 100 = 78.67 \%$$