Lectures- 12

Titrations Based on Redox reactions

Analytical titrations using redox reactions were introduced shortly after the development of acid–base titrimetry. The earliest **Redox titration** took advantage of the oxidizing power of chlorine. In 1787, Claude Berthollet introduced a method for the quantitative analysis of chlorine water (a mixture of Cl_2, HCl, and HOCl) based on its ability to oxidize indigo, a dye that is colorless in its oxidized state. In 1814, Joseph Gay-Lussac developed a similar method for determining chlorine in bleaching powder. In both methods the end point is a change in color. Before the equivalence point the solution is colorless due to the oxidation of indigo. After the equivalence point, however, unreacted indigo imparts a permanent color to the solution.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO_4^-, $Cr_2O_7^{2-}$, and I_2 as oxidizing titrants, and of Fe^{2+} and $S_2O_3^{2-}$ as reducing titrants. Even with the availability of these new titrants, redox titrimetry was slow to develop due to the lack of suitable indicators. A titrant can serve as its own indicator if its oxidized and reduced forms differ significantly in color. For example, the intensely purple MnO_4^- ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colorless. Other titrants require a separate indicator. The first such indicator, diphenylamine, was introduced in the 1920s. Other redox indicators soon followed, increasing the applicability of redox titrimetry.

Redox Titration Curves

To evaluate a redox titration we need to know the shape of its titration curve. In an acid–base titration or a complexation titration, the titration curve shows how the concentration of H_3O^+ (as pH) or M^{n+} (as pM) changes as we add titrant. For a redox titration it is convenient to monitor the titration reaction's potential instead of the concentration of one species.

You may recall from Chapter 6 that the Nernst equation relates a solution's potential to the concentrations of reactants and products participating in the redox reaction. Consider, for example, a titration in which a titrand in a reduced state, A_{red}, reacts with a titrant in an oxidized state, B_{ox}.

$$A_{red} + B_{ox} \rightleftharpoons B_{red} + A_{ox}$$

where A_{ox} is the titrand's oxidized form, and B_{red} is the titrant's reduced form. The reaction's potential, E_{rxn}, is the difference between the reduction potentials for each half-reaction.

$$E_{rxn} = E_{Box/Bred} - E_{Aox/Ared}$$

After each addition of titrant the reaction between the titrand and the titrant reaches a state of equilibrium. Because the potential at equilibrium is zero, the titrand's and the titrant's reduction potentials are identical.

$$E_{Box/Bred} = E_{Aox/Ared}$$

This is an important observation because we can use either half-reaction to monitor the titration's progress.

Before the equivalence point the titration mixture consists of appreciable quantities of the titrand's oxidized and reduced forms. The concentration of unreacted titrant, however, is very small. The potential, therefore, is easier to calculate if we use the Nernst equation for the titrand's half-reaction

$$E_{rxn} = E^o_{A_{ox}/A_{red}} - \frac{RT}{nF} \ln \frac{[A_{red}]}{[A_{ox}]}$$

Note **:** Although the Nernst equation is written in terms of the half-reaction's standard state potential, a matrix-dependent **formal potential**often is used in its place. See Appendix 13 for the standard state potentials and formal potentials for selected half-reactions.

After the equivalence point it is easier to calculate the potential using the Nernst equation for the titrant's half-reaction.

$$E_{rxn} = E^o_{B_{ox}/B_{red}} - \frac{RT}{nF} \ln \frac{[B_{red}]}{[B_{ox}]}$$

Calculating the Titration Curve

Let's calculate the titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$. The reaction in this case is

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightleftharpoons Ce^{3+}(aq) + Fe^{3+}(aq) \qquad 12.1$$

Note

In 1 M $HClO_4$, the formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of Ce^{4+} to $Ce^{3+}$is +1.70 V.

Because the equilibrium constant for reaction 12.1 is very large—it is approximately 6×10^{15}—we may assume that the analyte and titrant react completely.

Note

Step 1: Calculate the volume of titrant needed to reach the equivalence point.

The first task is to calculate the volume of Ce^{4+} needed to reach the titration's equivalence point. From the reaction's stoichiometry we know that

moles Fe^{2+} = moles Ce^{4+}

$M_{Fe} \times V_{Fe} = M_{Ce} \times V_{Ce}$

Solving for the volume of Ce^{4+} gives the equivalence point volume as

$$V_{eq} = V_{Ce} = \frac{M_{Fe}V_{Fe}}{M_{Ce}} = \frac{(0.100\ \text{M})(50.0\ \text{mL})}{(0.100\ \text{M})} = 50.0\ \text{mL}$$

Note

Step 2: Calculate the potential before the equivalence point by determining the concentrations of the titrand's oxidized and reduced forms, and using the Nernst equation for the titrand's reduction half-reaction.

Before the equivalence point, the concentration of unreacted Fe^{2+} and the concentration of Fe^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Fe^{3+}/Fe^{2+} half-reaction.

$$E = E^o_{Fe^{3+}/Fe^{2+}} - \frac{RT}{nF}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = +0.767\text{V} - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]} \qquad 12.2$$

For example, the concentrations of Fe^{2+} and Fe^{3+} after adding 10.0 mL of titrant are

$$[Fe^{2+}] = \frac{\text{initial moles } Fe^{2+} - \text{moles } Ce^{4+} \text{ added}}{\text{total volume}} = \frac{M_{Fe}V_{Fe} - M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}}$$
$$= \frac{(0.100\ \text{M})(50.0\ \text{mL}) - (0.100\ \text{M})(10.0\ \text{mL})}{50.0\ \text{mL} + 10.0\ \text{mL}} = 6.67 \times 10^{-2}\ \text{M}$$

$$[Fe^{3+}] = \frac{\text{moles } Ce^{4+} \text{ added}}{\text{total volume}} = \frac{M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}}$$
$$= \frac{(0.100\ \text{M})(10.0\ \text{mL})}{50.0\ \text{mL} + 10.0\ \text{mL}} = 1.67 \times 10^{-2}\ \text{M}$$

Substituting these concentrations into equation 9.2 gives a potential of

$$E = +0.767\ \text{V} - 0.05916\log\frac{6.67 \times 10^{-2}\ \text{M}}{1.67 \times 10^{-2}\ \text{M}} = +0.731\ \text{V}$$

Note

Step 3: Calculate the potential after the equivalence point by determining the concentrations of the titrant's oxidized and reduced forms, and using the Nernst equation for the titrant's reduction half-reaction.

After the equivalence point, the concentration of Ce^{3+} and the concentration of excess Ce^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Ce^{4+}/Ce^{3+} half-reaction.

$$E = E^o_{Ce^{4+}/Ce^{3+}} - \frac{RT}{nF}\log\frac{[Ce^{3+}]}{[Ce^{4+}]} = +1.70\text{ V} - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]} \qquad 12.3$$

For example, after adding 60.0 mL of titrant, the concentrations of Ce^{3+} and

$$[Ce^{3+}] = \frac{\text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Fe}V_{Fe}}{V_{Fe}+V_{Ce}} = \frac{(0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL}+60.0\text{ mL}} = 4.55\times10^{-3}\text{ M}$$

$$[Ce^{4+}] = \frac{\text{moles } Ce^{4+}\text{ added} - \text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Ce}V_{Ce} - M_{Fe}V_{Fe}}{V_{Fe}+V_{Ce}} = \frac{(0.100\text{ M})(60.0\text{ mL}) - (0.100\text{ M})(50.0\text{ mL})}{50.0\text{ mL}+60.0\text{ mL}} = 9.09\times10^{-3}\text{ M}$$

Ce^{4+} are

Substituting these concentrations into equation 9.3 gives a potential of

$$E = +1.70\text{ V} - 0.05916\log\frac{4.55\times10^{-2}\text{ M}}{9.09\times10^{-3}\text{ M}} = +1.66\text{ V}$$

Note

Step 4: Calculate the potential at the equivalence point.

At the titration's equivalence point, the potential, E_{eq}, in equation 12.2 and equation 12.3 are identical. Adding the equations together to gives

$$2E_{eq} = E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}$$

Because $[Fe^{2+}] = [Ce^{4+}]$ and $[Ce^{3+}] = [Fe^{3+}]$ at the equivalence point, the log term has a value of zero and the equivalence point's potential is

$$E_{eq} = \frac{E^o_{Fe^{3+}/Fe^{2+}} + E^o_{Ce^{4+}/Ce^{3+}}}{2} = \frac{0.767\ V + 1.70\ V}{2} = 1.23\ V$$

Additional results for this titration curve are shown in Table 12.1 and Figure 1.

Table 12.1 Data for the Titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}

Volume of Ce^{4+} (mL)	*E* (V)	Volume Ce^{4+} (mL)	*E* (V)
10.0	0.731	60.0	1.66
20.0	0.757	70.0	1.68
30.0	0.777	80.0	1.69
40.0	0.803	90.0	1.69
50.0	1.23	100.0	1.70

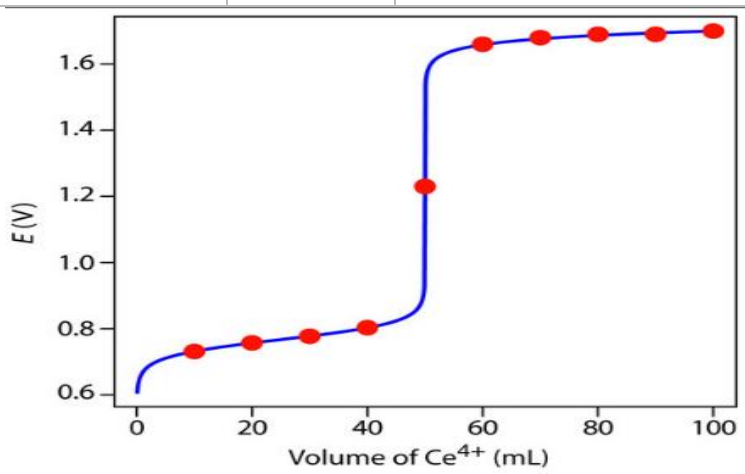


Figure 1 Titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}. The red points correspond to the data in Table 12.1. The blue line shows the complete titration curve.

Practice Exercise 1

Calculate the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{2+} with 0.100 M Tl^{3+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}\ (aq) + Tl^{3+}\ (aq) \rightarrow Sn^{4+}\ (aq) + Tl^{+}\ (aq)$$

Sketching a Redox Titration Curve

To evaluate the relationship between a titration's equivalence point and its end point we need to construct only a reasonable approximation of the exact titration curve. In this section we demonstrate a simple method for sketching a redox titration curve. Our goal is to sketch the titration curve quickly, using as few

calculations as possible. Let's use the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in a matrix of 1 M $HClO_4$.

Note

This is the same example that we used in developing the calculations for a redox titration curve. You can review the results of that calculation in Table 12.1 and Figure 1.

We begin by calculating the titration's equivalence point volume, which, as we determined earlier, is 50.0 mL. Next, we draw our axes, placing the potential, *E*, on the *y*-axis and the titrant's volume on the *x*-axis. To indicate the equivalence point's volume, we draw a vertical line corresponding to 50.0 mL of Ce^{4+}. Figure.2 a shows the result of the first step in our sketch.

Before the equivalence point, the potential is determined by a redox buffer of Fe^{2+} and Fe^{3+}. Although we can easily calculate the potential using the Nernst equation, we can avoid this calculation by making a simple assumption. You may recall from Chapter 6 that a redox buffer operates over a range of potentials that extends approximately ±(0.05916/*n*) unit on either side of $E^o_{Fe^{3+}/Fe^{2+}}$. The potential is at the buffer's lower limit

$$E = E^o_{Fe3+ / Fe2+} - 0.05916$$

when the concentration of Fe^{2+} is 10× greater than that of Fe^{3+}. The buffer reaches its upper potential

$$E = E^o_{Fe3+ /Fe2+} + 0.05916$$

when the concentration of Fe^{2+} is 10× smaller than that of Fe^{3+}. The redox buffer spans a range of volumes from approximately 10% of the equivalence point volume to approximately 90% of the equivalence point volume.

Figure b shows the second step in our sketch. First, we superimpose a ladder diagram for Fe^{2+} on the *y*-axis, using its $E^o_{Fe^{3+}/Fe^{2+}}$ value of 0.767 V and including the buffer's range of potentials. Next, we add points representing the pH at 10% of the equivalence point volume (a potential of 0.708 V at 5.0 mL) and at 90% of the equivalence point volume (a potential of 0.826 V at 45.0 mL).

Note

We used a similar approach when sketching the acid–base titration curve for the titration of acetic acid with NaOH.

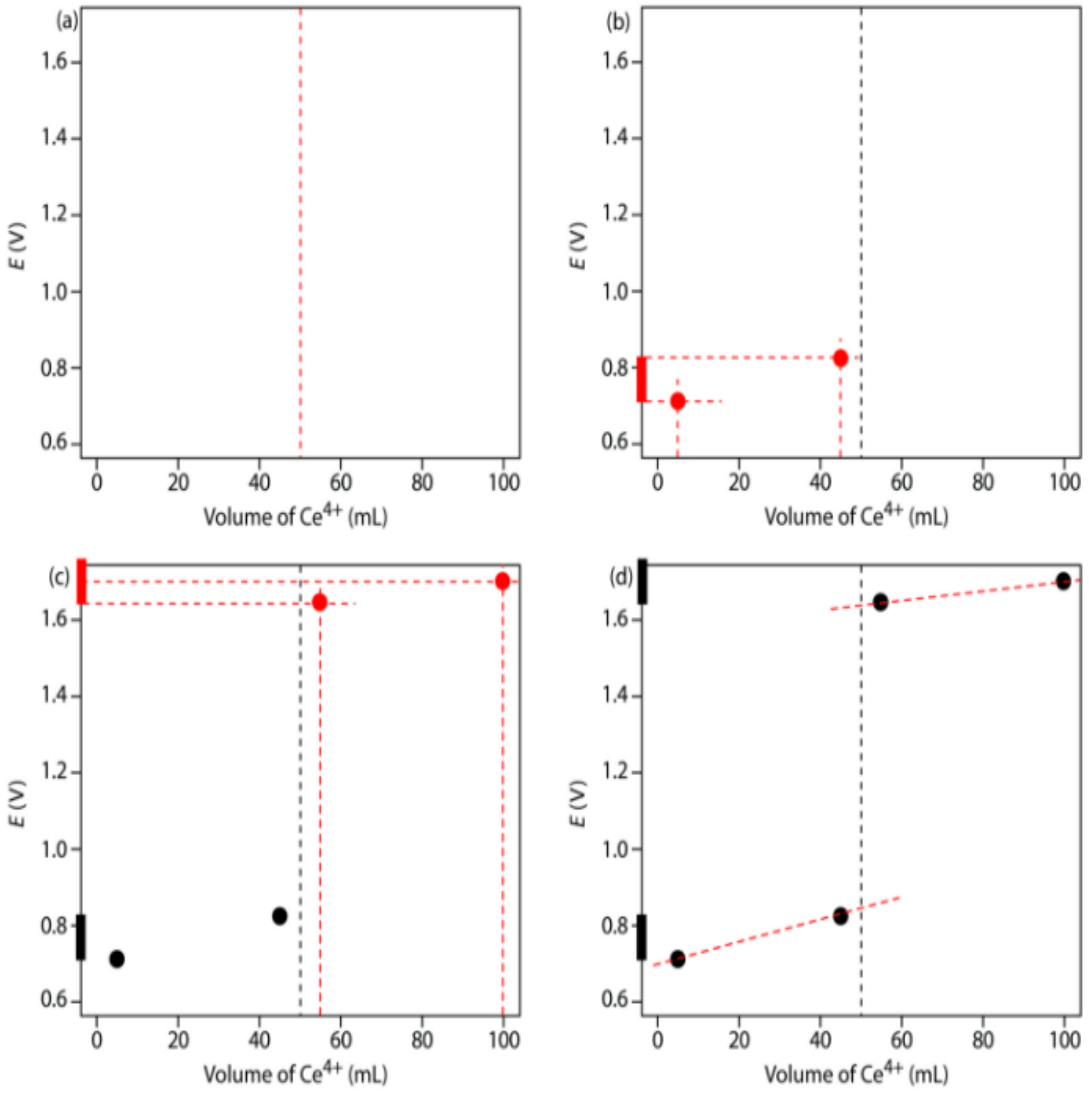
The third step in sketching our titration curve is to add two points after the equivalence point. Here the potential is controlled by a redox buffer of Ce^{3+} and Ce^{4+}.The redox buffer is at its lower limit of $E = E^o_{Ce^{4+}/Ce^{3+}} - 0.05916$ when the titrant reaches 110% of the equivalence point volume and the potential is $E^o_{Ce^{4+}/Ce^{3+}}$ when the volume of Ce^{4+} is $2\times V_{eq}$.

Figure c shows the third step in our sketch. First, we add a ladder diagram for Ce^{4+}, including its buffer range, using its $E^{o}_{Ce^{4+}/Ce^{3+}}$value of 1.70 V. Next, we add points representing the potential at 110% of V_{eq} (a value of 1.66 V at 55.0 mL) and at 200% of V_{eq} (a value of 1.70 V at 100.0 mL).

Note

We used a similar approach when sketching the complexation titration curve for the titration of Mg^{2+} with EDTA.

Next, we draw a straight line through each pair of points, extending the line through the vertical line representing the equivalence point's volume (Figure d). Finally, we complete our sketch by drawing a smooth curve that connects the three straight-line segments (Figure e). A comparison of our sketch to the exact titration curve (Figure f) shows that they are in close agreement.



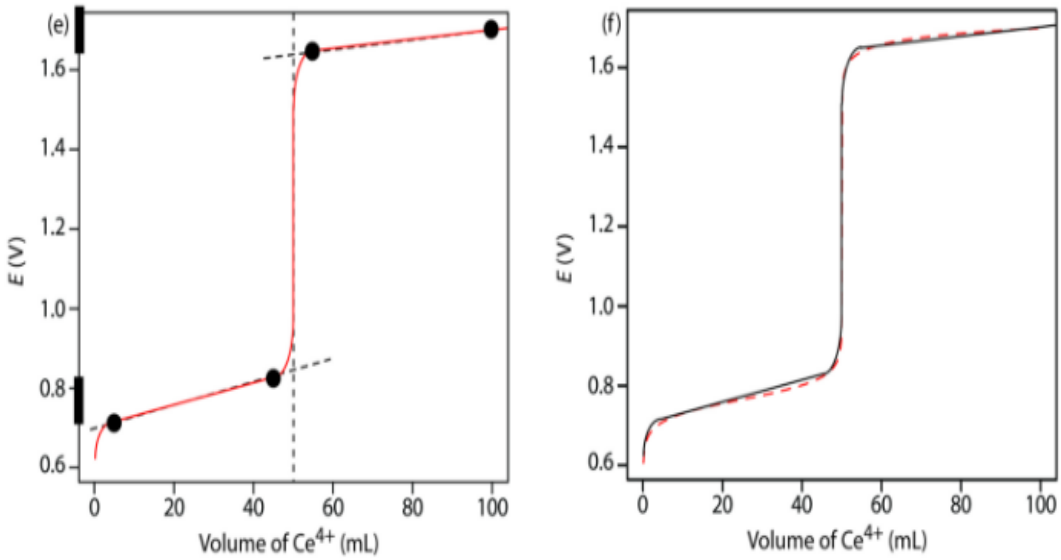


Figure 2 Illustrations showing the steps in sketching an approximate titration curve for the titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+} in 1 M $HClO_4$: (a) locating the equivalence point volume; (b) plotting two points before the equivalence point; (c) plotting two points after the equivalence point; (d) preliminary approximation of titration curve using straight-lines; (e) final approximation of titration curve using a smooth curve; (f) comparison of approximate titration curve (solid black line) and exact titration curve (dashed red line). See the text for additional details.

Practice Exercise 2

Sketch the titration curve for the titration of 50.0 mL of 0.0500 M Sn^{4+} with 0.100 M Tl^{+}. Both the titrand and the titrant are 1.0 M in HCl. The titration reaction is

$$Sn^{2+}(aq) + Tl^{3+}(aq) \rightarrow Sn^{4+}(aq) + Tl^{+}(aq)$$

Compare your sketch to your calculated titration curve from **Practice Exercise 1**

Practice Exercise 1

The volume of Tl^{3+} needed to reach the equivalence point is

$$V_{eq} = V_{Tl} = \frac{M_{Sn}V_{Sn}}{M_{Tl}} = \frac{(0.050\ M)(50.0\ mL)}{0.100\ M} = 25.0\ mL$$

Before the equivalence point, the concentration of unreacted Sn^{2+} and the concentration of Sn^{4+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Sn^{4+}/Sn^{2+} half-reaction.For example, the concentrations of Sn^{2+} and Sn^{4+} after adding 10.0 mL of titrant are

$$[Sn^{2+}] = \frac{(0.050\ M)(50.0\ mL) - (0.100\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL} = 0.0250\ M$$

$$[Sn^{4+}] = \frac{(0.100\ M)(10.0\ mL)}{50.0\ mL + 10.0\ mL} = 0.0167\ M$$

and the potential is

$$E = +0.139\ V - \frac{0.05916}{2}\log\frac{0.0250\ M}{0.0167\ M} = +0.134\ V$$

After the equivalence point, the concentration of Tl^+ and the concentration of excess Tl^{3+} are easy to calculate. For this reason we find the potential using the Nernst equation for the Tl^{3+}/Tl^+ half-reaction. For example, after adding 40.0 mL of titrant, the concentrations of Tl^+ and Tl^{3+} are

$$[Tl^+] = \frac{(0.0500\ M)(50.0\ mL)}{50.0\ mL + 40.0\ mL} = 0.0278\ M$$

$$[Tl^{3+}] = \frac{(0.100\ M)(40.0\ mL) - (0.0500\ M)(50.0\ mL)}{50.0\ mL + 40.0\ mL} = 0.0167\ M$$

and the potential is

$$E = +0.77\ V - \frac{0.05916}{2}\log\frac{0.0278\ M}{0.0167\ M} = +0.76\ V$$

At the titration's equivalence point, the potential, E_{eq}, potential is

$$E_{eq} = \frac{0.139\ V + 0.77\ V}{2} = 0.45\ V$$

Some additional results are shown here.

Vol. of Tl^{3+} (mL)	*E* (V)	Vol. of Tl^{3+} (mL)	*E* (V)
5	0.121	30	0.75
10	0.134	35	0.75
15	0.144	40	0.76
20	0.157	45	0.76
25	0.45	50	0.76

References

- Modern Analytical Chemistry by David Harvey (DePauw University)
- Fundametal of Analytical Chemistry by Skoog