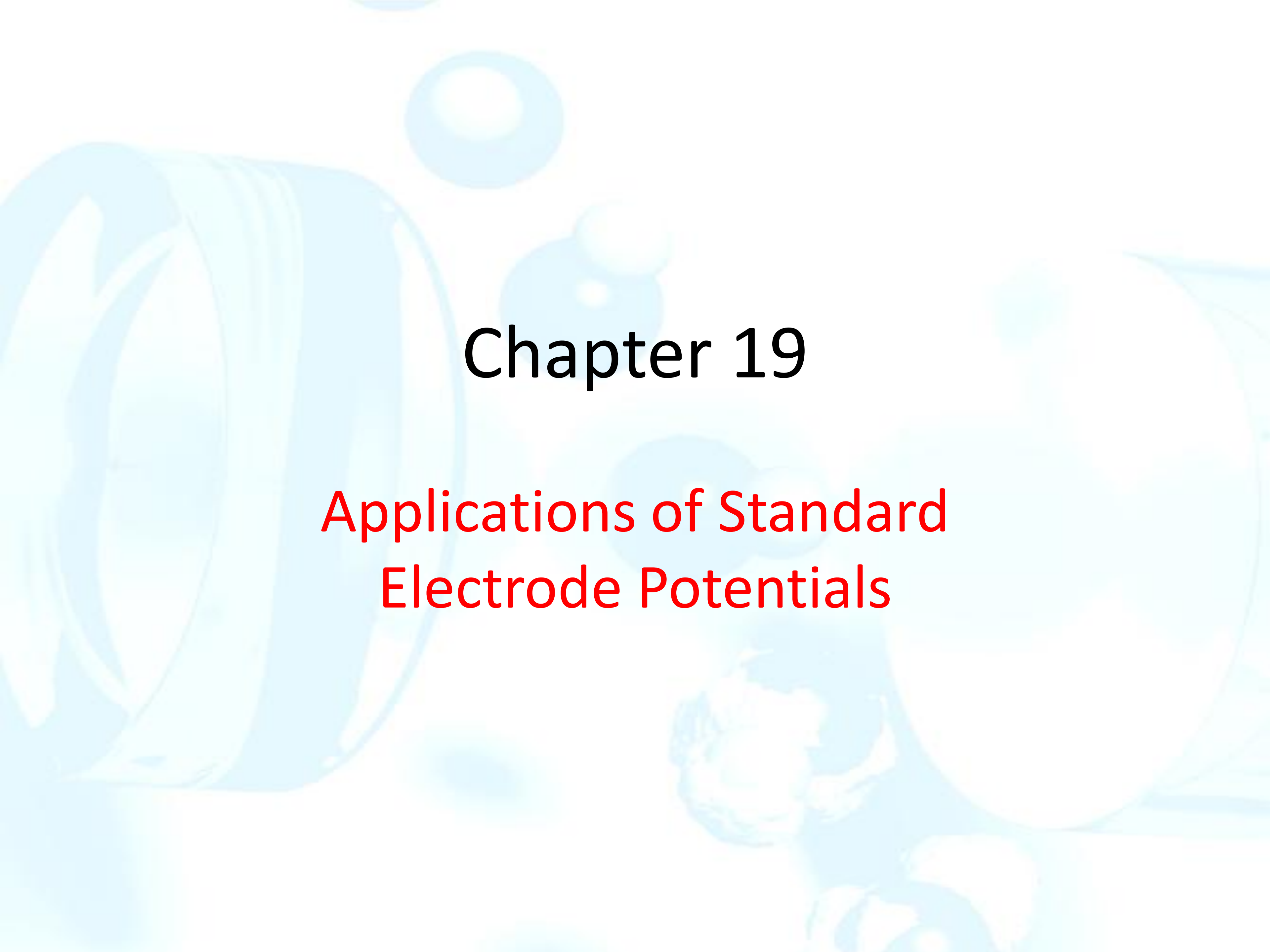


Chapter 19

Applications of Standard Electrode Potentials

Calculating potentials of electrochemical cells

The thermodynamic potential of an electrochemical cell is the difference between the electrode potential of the right-hand electrode and the electrode potential of the left-hand electrode:

$$E_{\mathrm{cell}} = E_{\mathrm{right}} - E_{\mathrm{left}}$$

The equation is valid when the liquid junction potential is absent or minimal.

EXAMPLE 19-1

Calculate the thermodynamic potential of the following cell and the free energy change associated with the cell reaction:

$$\mathrm{Cu}|\mathrm{Cu}^{2+}(0.0200\ \mathrm{M})\,\|\,\mathrm{Ag}^{+}(0.0200\ \mathrm{M})|\mathrm{Ag}$$

Note that this cell is the galvanic cell shown in Figure 18-2a.

Solution

The two half-reactions and standard potentials are

$$\mathrm{Ag}^{+} + e^{-} \rightleftharpoons \mathrm{Ag}(s) \qquad E^{0} = 0.799\ \mathrm{V} \tag{19-2}$$

$$\mathrm{Cu}^{2+} + 2e^{-} \rightleftharpoons \mathrm{Cu}(s) \qquad E^{0} = 0.337\ \mathrm{V} \tag{19-3}$$

The electrode potentials are

$$E_{\mathrm{Ag}^{+}/\mathrm{Ag}} = 0.799 - 0.0592 \log \frac{1}{0.0200} = 0.6984\ \mathrm{V}$$

$$E_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = 0.337 - \frac{0.0592}{2} \log \frac{1}{0.0200} = 0.2867\ \mathrm{V}$$

We see from the cell diagram that the silver electrode is the right-hand electrode and the copper electrode is the left-hand electrode. Therefore, application of Equation 19-1 gives

$$E_{\mathrm{cell}} = E_{\mathrm{right}} - E_{\mathrm{left}} = E_{\mathrm{Ag}^{+}/\mathrm{Ag}} - E_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = 0.6984 - 0.2867 = +0.412\ \mathrm{V}$$

The free energy change ΔG for the reaction $\mathrm{Cu}(s) + 2\mathrm{Ag}^{+} \rightleftharpoons \mathrm{Cu}^{2+} + \mathrm{Ag}(s)$ is found from

$$\Delta G = -nFE_{\mathrm{cell}} = -2 \times 96485\ \mathrm{C} \times 0.412\ \mathrm{V} = -79{,}503\ \mathrm{J}\ (18.99\ \mathrm{kcal})$$

EXAMPLE 19-2

Calculate the potential for the cell

$$\mathrm{Ag}|\mathrm{Ag}^{+}(0.0200\ \mathrm{M})\,\|\,\mathrm{Cu}^{2+}(0.0200\ \mathrm{M})|\mathrm{Cu}$$

Solution

The electrode potentials for the two half-reactions are identical to the electrode potentials calculated in Example 19-1, that is,

$$E_{\mathrm{Ag}^{+}/\mathrm{Ag}} = 0.6984\ \mathrm{V} \qquad \text{and} \qquad E_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = 0.2867\ \mathrm{V}$$

In contrast to the previous example, however, the silver electrode is on the left, and the copper electrode is on the right. Substituting these electrode potentials into Equation 19-1 gives

$$E_{\mathrm{cell}} = E_{\mathrm{right}} - E_{\mathrm{left}} = E_{\mathrm{Cu}^{2+}/\mathrm{Cu}} - E_{\mathrm{Ag}^{+}/\mathrm{Ag}} = 0.2867 - 0.6984 = -0.412\ \mathrm{V}$$

EXAMPLE 19-3

Calculate the potential of the following cell and indicate the reaction that would occur spontaneously if the cell were short-circuited (see Figure 19-1).

$$\text{Pt}|\text{U}^{4+}(0.200\text{ M}),\ \text{UO}_2^{\ 2+}(0.0150\text{ M}),\ \text{H}^+(0.0300\text{ M})\ \|$$
$$\text{Fe}^{2+}(0.0100\text{ M}),\ \text{Fe}^{3+}(0.0250\text{ M})|\text{Pt}$$

Solution

The two half-reactions are

$$\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} \qquad E^0 = +0.771\text{ V}$$

$$\text{UO}_2^{\ 2+} + 4\text{H}^+ + 2e^- \rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O} \qquad E^0 = +0.334\text{ V}$$

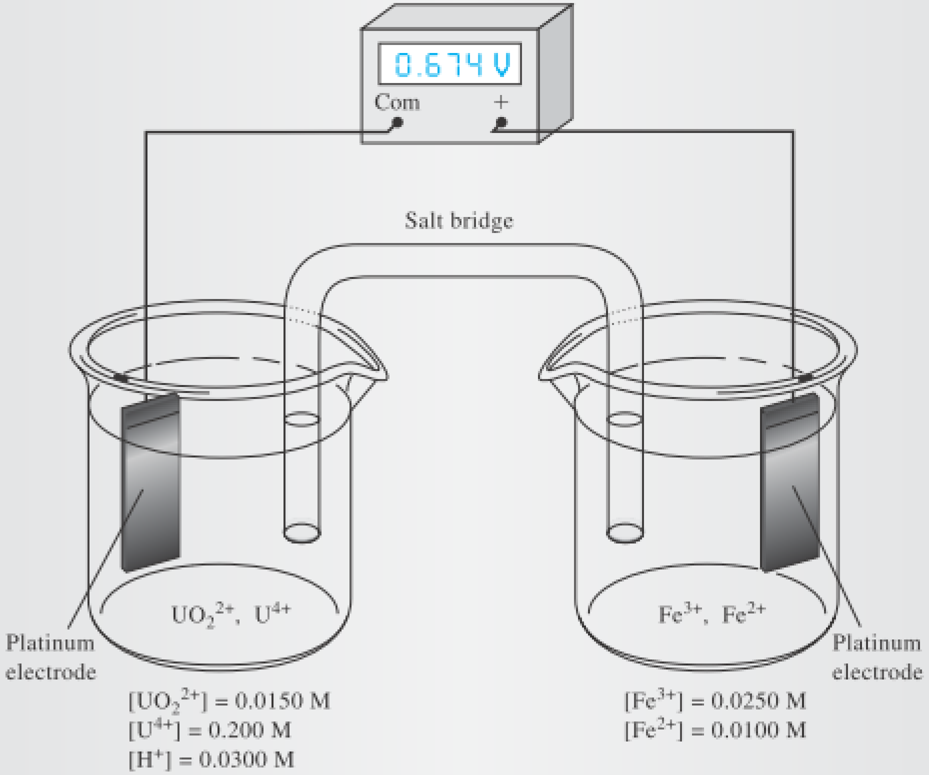
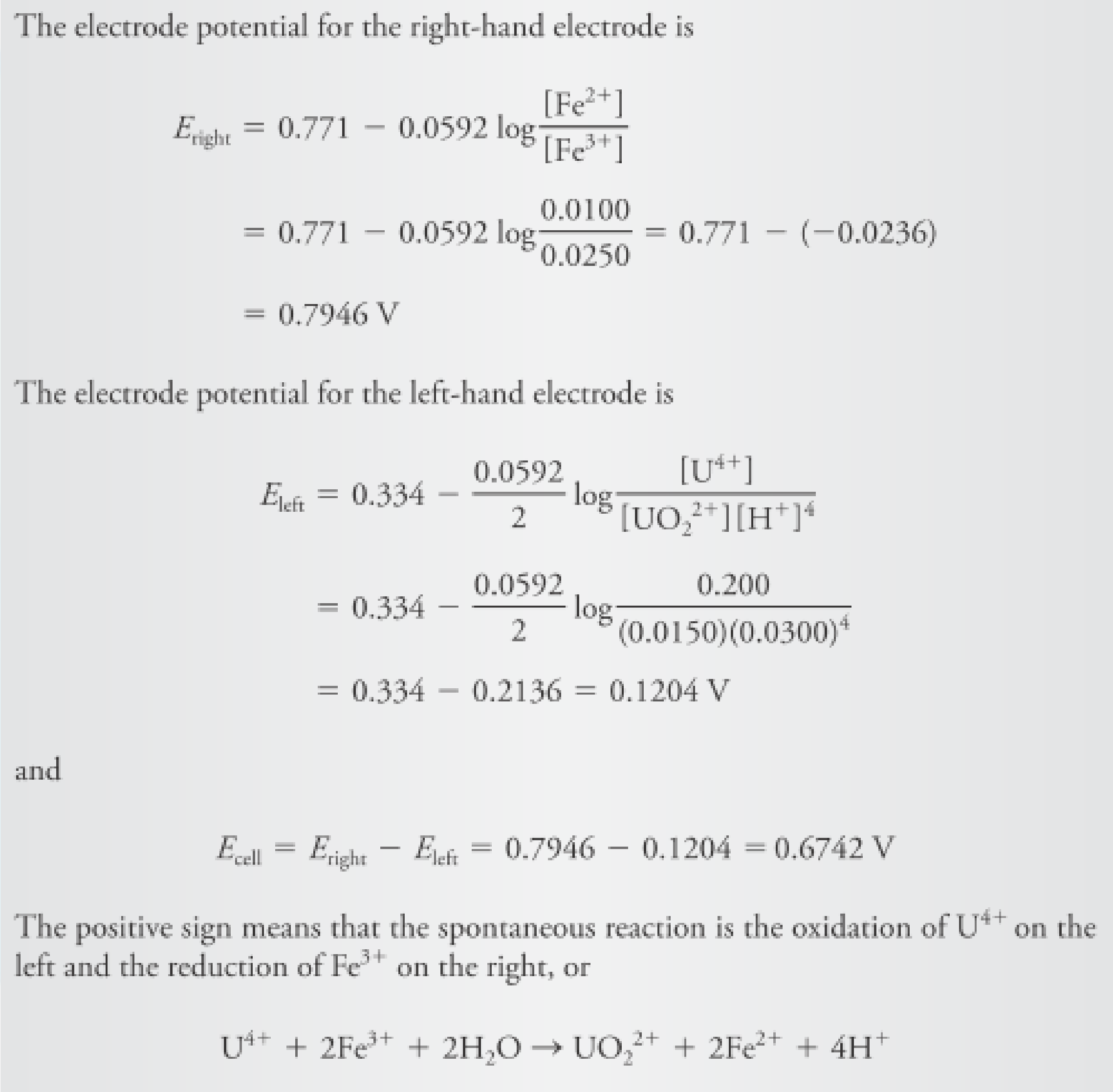


Figure 19-1 Cell for Example 19-3.



The electrode potential for the right-hand electrode is

$$E_{\text{right}} = 0.771 - 0.0592 \log\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$= 0.771 - 0.0592 \log\frac{0.0100}{0.0250} = 0.771 - (-0.0236)$$

$$= 0.7946 \text{ V}$$

The electrode potential for the left-hand electrode is

$$E_{\text{left}} = 0.334 - \frac{0.0592}{2} \log\frac{[\text{U}^{4+}]}{[\text{UO}_2{}^{2+}][\text{H}^+]^4}$$

$$= 0.334 - \frac{0.0592}{2} \log\frac{0.200}{(0.0150)(0.0300)^4}$$

$$= 0.334 - 0.2136 = 0.1204 \text{ V}$$

and

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = 0.7946 - 0.1204 = 0.6742 \text{ V}$$

The positive sign means that the spontaneous reaction is the oxidation of U^{4+} on the left and the reduction of Fe^{3+} on the right, or

$$\text{U}^{4+} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2{}^{2+} + 2\text{Fe}^{2+} + 4\text{H}^+$$

EXAMPLE 19-4

Calculate the cell potential for

$$\text{Ag}|\text{AgCl(sat'd), HCl(0.0200 M)}|\text{H}_2\text{(0.800 atm), Pt}$$

Note that this cell does not require two compartments (nor a salt bridge) because molecular H_2 has little tendency to react directly with the low concentration of Ag^+ in the electrolyte solution. This is an example of a **cell without liquid junction** (see **Figure 19-2**).

Solution

The two half-reactions and their corresponding standard electrode potentials are (see Table 18-1).

$$2H^+ + 2e^- \rightleftharpoons H_2(g) \qquad E^0_{H^+/H_2} = 0.000\ V$$

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- \qquad E^0_{AgCl/Ag} = 0.222\ V$$

The two electrode potentials are

$$E_{\text{right}} = 0.000 - \frac{0.0592}{2}\log\frac{p_{H_2}}{[H^+]^2} = -\frac{0.0592}{2}\log\frac{0.800}{(0.0200)^2}$$

$$= -0.0977\ V$$

$$E_{\text{left}} = 0.222 - 0.0592\log[Cl^-] = 0.222 - 0.0592\log 0.0200$$

$$= 0.3226\ V$$

The cell potential is thus

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = -0.0977 - 0.3226 = -0.420\ V$$

The negative sign indicates that the cell reaction as considered

$$2H^+ + 2Ag(s) \rightarrow H_2(g) + 2AgCl(s)$$

is nonspontaneous. In order to get this reaction to occur, we would have to apply an external voltage and construct an electrolytic cell.

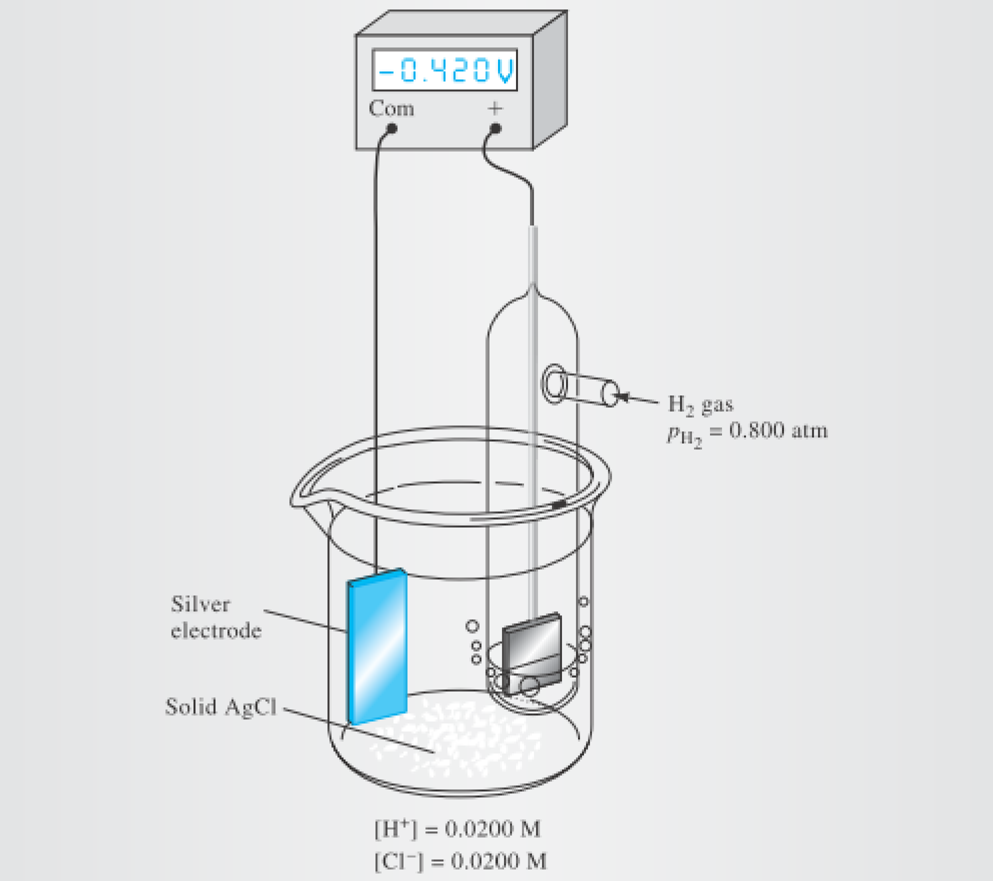


Figure 19-2 Cell without liquid junction for Example 19-4.

EXAMPLE 19-5

Calculate the potential for the following cell using (a) concentrations and (b) activities:

$$\mathrm{Zn}\,|\,\mathrm{ZnSO_4}(x\ \mathrm{M}),\ \mathrm{PbSO_4}(\text{sat'd})\,|\,\mathrm{Pb}$$

where $x = 5.00 \times 10^{-4}, 2.00 \times 10^{-3}, 1.00 \times 10^{-2}, 5.00 \times 10^{-2}$.

Solution

(a) In a neutral solution, little HSO_4^- is formed, and we can assume that

$$[\mathrm{SO_4^{2-}}] = c_{\mathrm{ZnSO_4}} = x = 5.00 \times 10^{-4}\ \mathrm{M}$$

The half-reactions and standard electrode potentials are (see Table 18-1).

$$\mathrm{PbSO_4}(s) + 2e^- \rightleftharpoons \mathrm{Pb}(s) + \mathrm{SO_4^{2-}} \qquad E^0_{\mathrm{PbSO_4/Pb}} = -0.350\ \mathrm{V}$$

$$\mathrm{Zn^{2+}} + 2e^- \rightleftharpoons \mathrm{Zn}(s) \qquad E^0_{\mathrm{Zn^{2+}/Zn}} = -0.763\ \mathrm{V}$$

The lead electrode potential is

$$E_{\mathrm{PbSO_4/Pb}} = E^0_{\mathrm{PbSO_4/Pb}} - \frac{0.0592}{2}\log\,[\mathrm{SO_4^{2-}}]$$

$$= -0.350 - \frac{0.0592}{2}\log(5.00 \times 10^{-4}) = -0.252\ \mathrm{V}$$

The zinc electrode potential is

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{0.0592}{2}\log\frac{1}{[Zn^{2+}]}$$

$$= -0.763 - \frac{0.0592}{2}\log\frac{1}{5.00 \times 10^{-4}} = -0.860\ V$$

The cell potential is thus

$$E_{cell} = E_{right} - E_{left} = E_{PbSO_4/Pb} - E_{Zn^{2+}/Zn} = -0.252 - (-0.860) = 0.608\ V$$

Cell potentials at the other concentrations can be calculated in the same way. Their values are given in **Table 19-1**.

(b) To calculate activity coefficients for Zn^{2+} and $[SO_4^{2-}]$, we must first find the ionic strength of the solution using Equation 10-1:

$$\mu = \frac{1}{2}[5.00 \times 10^{-4} \times (2)^2 + 5.00 \times 10^{-4} \times (2)^2] = 2.00 \times 10^{-3}$$

In Table 10-2, we find and $\alpha_{SO_4^{2-}} = 0.4$ nm and $\alpha_{Zn^{2+}} = 0.6$ nm. If we substitute these values into Equation 10-5, we find that

$$-\log \gamma_{SO_4^{2-}} = \frac{0.51 \times (2)^2 \sqrt{2.00 \times 10^{-3}}}{1 + 3.3 \times 0.4\sqrt{2.00 \times 10^{-3}}} = 8.61 \times 10^{-2}$$

$$\gamma_{SO_4^{2-}} = 0.820$$

Repeating the calculations for Zn^{2+}, we find that

$$\gamma_{Zn^{2+}} = 0.825$$

The Nernst equation for the lead electrode is now

$$E_{\mathrm{PbSO_4/Pb}} = E^0_{\mathrm{PbSO_4/Pb}} - \frac{0.0592}{2}\log \gamma_{\mathrm{SO_4^{2-}}} c_{\mathrm{SO_4^{2-}}}$$

$$= -0.350 - \frac{0.0592}{2}\log(0.820 \times 5.00 \times 10^{-4}) = -0.250\ \mathrm{V}$$

and for the zinc electrode, we have

$$E_{\mathrm{Zn^{2+}/Zn}} = E^0_{\mathrm{Zn^{2+}/Zn}} - \frac{0.0592}{2}\log \frac{1}{\gamma_{\mathrm{Zn^{2+}}} c_{\mathrm{Zn^{2+}}}}$$

$$= -0.763 - \frac{0.0592}{2}\log \frac{1}{0.825 \times 5.00 \times 10^{-4}} = -0.863\ \mathrm{V}$$

Finally, we find the cell potential from

$$E_{\mathrm{cell}} = E_{\mathrm{right}} - E_{\mathrm{left}} = E_{\mathrm{PbSO_4/Pb}} - E_{\mathrm{Zn^{2+}/Zn}} = -0.250 - (-0.863) = 0.613\ \mathrm{V}$$

Values for other concentrations and experimentally determined potentials for the cell are found in Table 19-1.

TABLE 19-1

Effect of Ionic Strength on the Potential of a Galvanic Cell*

Concentration $ZnSO_4$, M	Ionic Strength, μ	(a) *E*, Based on Concentrations	(b) *E*, Based on Activities	*E*, Experimental Values†
5.00×10^{-4}	2.00×10^{-3}	0.608	0.613	0.611
2.00×10^{-3}	8.00×10^{-3}	0.573	0.582	0.583
1.00×10^{-2}	4.00×10^{-2}	0.531	0.550	0.553
2.00×10^{-2}	8.00×10^{-2}	0.513	0.537	0.542
5.00×10^{-2}	2.00×10^{-1}	0.490	0.521	0.529

EXAMPLE 19-6

Calculate the potential required to initiate deposition of copper from a solution that is 0.010 M in $CuSO_4$ and contains sufficient H_2SO_4 to give a pH of 4.00.

Solution

The deposition of copper necessarily occurs at the cathode, which according to IUPAC convention is the right-hand-electrode. Since there is no more easily oxidizable species than water in the system, O_2 will evolve at the anode. The two half-reactions and their corresponding standard electrode potentials are (see Table 18-1):

$$\mathrm{Cu^{2+}} + 2\mathrm{e^-} \rightleftharpoons \mathrm{Cu}(s) \qquad E^0_{\mathrm{AgCl/Ag}} = +0.337\ \mathrm{V\ (right)}$$

$$\mathrm{O_2}(g) + 4\mathrm{H^+} + 4\mathrm{e^-} \rightleftharpoons 2\mathrm{H_2O} \qquad E^0_{\mathrm{O_2/H_2O}} = +1.229\ \mathrm{V\ (left)}$$

The electrode potential for the Cu electrode is

$$E_{\mathrm{Cu^{2+}/Cu}} = +0.337 - \frac{0.0592}{2}\log\frac{1}{0.010} = +0.278\ \mathrm{V}$$

If O_2 is evolved at 1.00 atm, the electrode potential for the oxygen electrode is

$$E_{\mathrm{O_2/H_2O}} = +1.229 - \frac{0.0592}{4}\log\frac{1}{p_{\mathrm{O_2}}[\mathrm{H^+}]^4}$$

$$= +1.229 - \frac{0.0592}{4}\log\frac{1}{(1\ \mathrm{atm})(1.00 \times 10^{-4})^4} = +0.992\ \mathrm{V}$$

and the cell potential is thus

$$E_{\mathrm{cell}} = E_{\mathrm{right}} - E_{\mathrm{left}} = E_{\mathrm{Cu^{2+}/Cu}} - E_{\mathrm{O_2/H_2O}} = +0.278 - 0.992 = -0.714\ \mathrm{V}$$

The negative sign shows that the cell reaction

$$2\mathrm{Cu^{2+}} + 2\mathrm{H_2O} \rightarrow \mathrm{O_2}(g) + 4\mathrm{H^+} + 2\mathrm{Cu}(s)$$

is nonspontaneous and that, to cause copper to be deposited according to the following reaction, we must apply a negative potential slightly greater than −0.714 V.

19B Determining standard potentials experimentally

None of the standard potentials can be measured directly in the laboratory.

Any electrode system in which the reactants and products are at unit activity or pressure, such as the SHE, are hypothetical electrodes.

There is no way to prepare solutions containing ions whose activities are exactly 1.

EXAMPLE 19-7

D. A. MacInnes[1] found that a cell similar to that shown in Figure 19-2 had a potential of 0.52053 V. The cell is described by the following notation:

$$\text{Pt, H}_2(1.00\text{ atm})\,|\,\text{HCl}(3.215 \times 10^{-3}\text{ M}), \text{AgCl(sat'd)}\,|\,\text{Ag}$$

Calculate the standard electrode potential for the half-reaction

$$\text{AgCl}(s) + e^- \rightleftharpoons \text{Ag}(s) + \text{Cl}^-$$

Solution

In this example, the electrode potential for the right-hand electrode is

$$E_{\text{right}} = E^0_{\text{AgCl}} - 0.0592 \log (\gamma_{\text{Cl}^-})(c_{\text{HCl}})$$

where γ_{Cl^-} is the activity coefficient of Cl^-. The second half-cell reaction is

$$\text{H}^+ + e^- \rightleftharpoons \frac{1}{2}\text{H}_2(g)$$

and

$$E_{\text{left}} = E^0_{\text{H}^+/\text{H}_2} - \frac{0.0592}{1} \log \frac{p^{1/2}_{\text{H}_2}}{(\gamma_{\text{H}^+})(c_{\text{HCl}})}$$

The cell potential is then the difference between these two potentials

$$
\begin{aligned}
E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} \\
&= [E^0_{\text{AgCl}} - 0.0592 \log (\gamma_{\text{Cl}^-})(c_{\text{HCl}})] - \left[E^0_{\text{H}^+/\text{H}_2} - 0.0592 \log \frac{p^{1/2}_{\text{H}_2}}{(\gamma_{\text{H}^+})(c_{\text{HCl}})}\right] \\
&= E^0_{\text{AgCl}} - 0.0592 \log (\gamma_{\text{Cl}^-})(c_{\text{HCl}}) - 0.000 - 0.0592 \log \frac{(\gamma_{\text{H}^+})(c_{\text{HCl}})}{p^{1/2}_{\text{H}_2}}
\end{aligned}
$$

Notice that we have inverted the terms in the second logarithmic term. We now combine the two logarithmic terms to find that

$$E_{\text{cell}} = 0.52053 = E^0_{\text{AgCl}} - 0.0592 \log \frac{(\gamma_{\text{H}^+})(\gamma_{\text{Cl}^-})(c_{\text{HCl}})^2}{p^{1/2}_{\text{H}_2}}$$

The activity coefficients for H^+ and Cl^- can be calculated from Equation 10-5 using 3.215×10^{-3} M for the ionic strength μ. These values are 0.945 and 0.939, respectively. If we substitute these values of the activity coefficients and the experimental data into the equation above and rearrange the equation, we obtain

$$
\begin{aligned}
E^0_{\text{AgCl}} &= 0.52053 + 0.0592 \log \frac{(0.945)(0.939)(3.215 \times 10^{-3})^2}{1.00^{1/2}} \\
&= 0.2223 \approx 0.222 \text{ V}
\end{aligned}
$$

MacInnes found the mean for this and similar measurements at other concentrations to be 0.222 V.

19C Calculating redox equilibrium constants

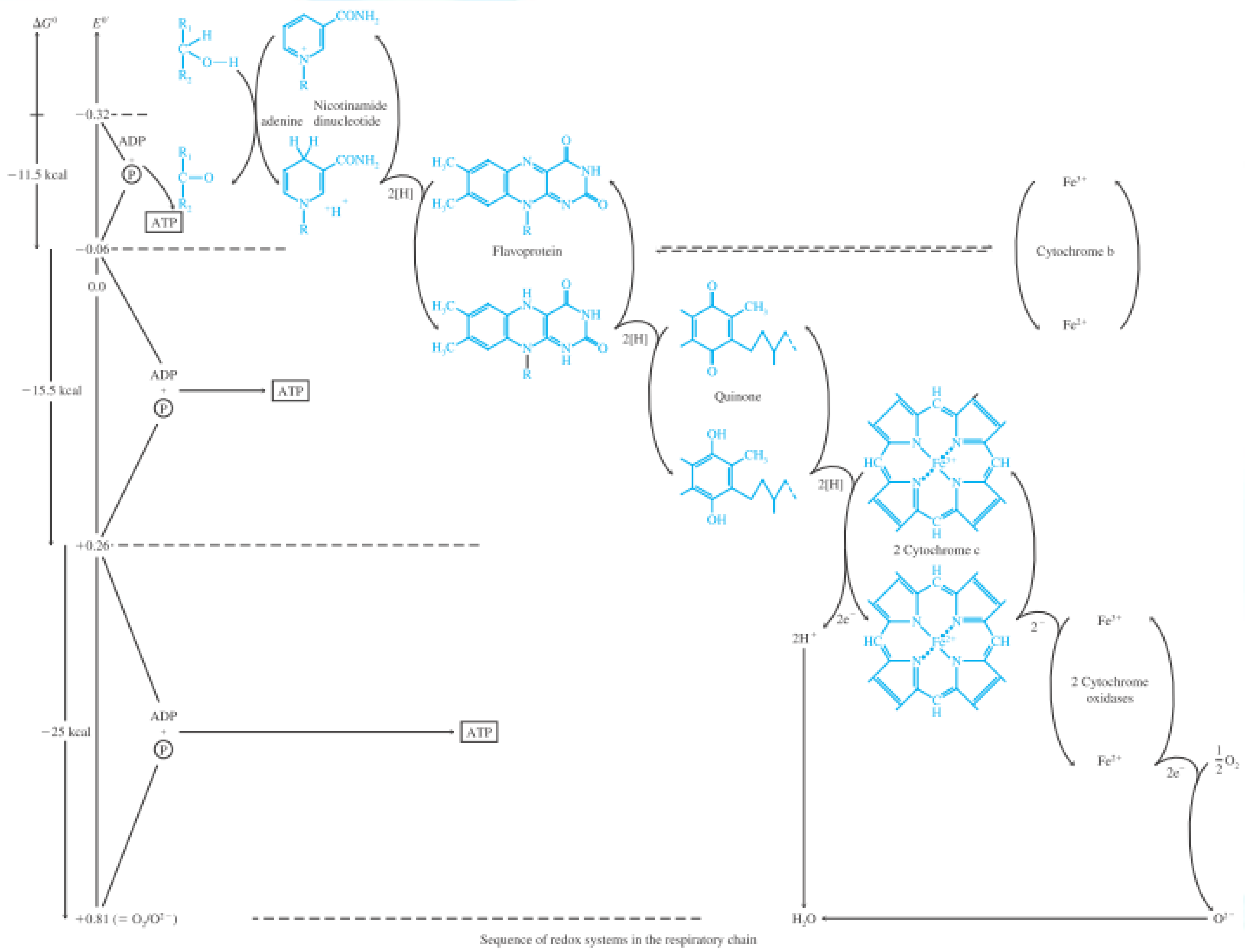


Figure 19F-1 Redox systems in the respiratory chain. P = phosphate ion. (From P. Karlson, *Introduction to Modern Biochemistry*, New York: Academic Press, 1963. With permission.)

Consider the reaction: $Cu(s) + 2Ag^{+} \Leftrightarrow Cu^{+2} + 2Ag(s)$

The equilibrium constant for this reaction is

$$K_{eq} = [Cu^{+2}]/[Ag^{+}]^{2}$$

The cell potential at any given instant is

$$E_{cell} = E_{right} - E_{left} = E_{Ag+/Ag} - E_{Cu+2/Cu}$$

As the reaction proceeds, the concentration of Cu(II) ions increases, and the concentration of Ag(I) ions decreases.

At equilibrium, $E_{cell} = E_{left} = E_{Ag} = E_{cu}$

The electrode potentials for all half-reactions in an oxidation/reduction system are equal.

Substituting Nernst expressions for the two electrode potentials:

$$E^{0}_{Ag} - \frac{0.0592}{2}\log\frac{1}{[Ag^{+}]^{2}} = E^{0}_{Cu} - \frac{0.0592}{2}\log\frac{1}{[Cu^{+2}]}$$

$$E^0_{Ag} - E^0_{Cu} = \frac{0.0592}{2}\log\frac{1}{[Ag^+]^2} - \frac{0.0592}{2}\log\frac{1}{[Cu^{+2}]}$$

$$E^0_{Ag} - E^0_{Cu} = \frac{0.0592}{2}\log\frac{1}{[Ag^+]^2} + \frac{0.0592}{2}\log\frac{[Cu^{+2}]}{1}$$

$$\frac{2(E^0_{Ag} - E^0_{Cu})}{0.0592} = \log\frac{[Cu^{+2}]}{[Ag^+]^2} = \log K_{eq}$$

$$\log K_{eq} = \frac{nE^0_{cell}}{0.0592} = \frac{n(E^0_{right} - E^0_{left})}{0.0592}$$

EXAMPLE 19-8

Calculate the equilibrium constant for the reaction shown in Equation 19-4.

Solution

Substituting numerical values into Equation 19-8 yields

$$\log K_{eq} = \log \frac{[Cu^{2+}]}{[Ag^+]^2} = \frac{2(0.799 - 0.337)}{0.0592} = 15.61$$

$$K_{eq} = \text{antilog } 15.61 = 4.1 \times 10^{15}$$

EXAMPLE 19-9

Calculate the equilibrium constant for the reaction

$$2Fe^{3+} + 3I^- \rightleftharpoons 2Fe^{2+} + I_3^-$$

Solution

In Appendix 5, we find

$$2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+} \qquad E^0 = 0.771 \text{ V}$$

$$I_3^- + 2e^- \rightleftharpoons 3I^- \qquad E^0 = 0.536 \text{ V}$$

We have multiplied the first half-reaction by 2 so that the number of moles of Fe^{3+} and Fe^{2+} will be the same as in the balanced overall equation. We write the

Nernst equation for Fe^{3+} based on the half-reaction for a 2-electron transfer, that is,

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

and

$$E_{I_3^-/I^-} = E^0_{I_3^-/I^-} - \frac{0.0592}{2}\log\frac{[I^-]^3}{[I_3^-]}$$

At equilibrium, the electrode potentials are equal, and

$$E_{Fe^{3+}/Fe^{2+}} = E_{I_3^-/I^-}$$

$$E^0_{Fe^{3+}/Fe^{2+}} - \frac{0.0592}{2}\log\frac{[Fe^{2+}]^2}{[Fe^{3+}]^2} = E^0_{I_3^-/I^-} - \frac{0.0592}{2}\log\frac{[I^-]^3}{[I_3^-]}$$

This equation rearranges to

$$\frac{2(E^0_{Fe^{3+}/Fe^{2+}} - E^0_{I_3^-/I^-})}{0.0592} = \log\frac{[Fe^{2+}]^2}{[Fe^{3+}]^2} - \log\frac{[I^-]^3}{[I_3^-]}$$

$$= \log\frac{[Fe^{2+}]^2}{[Fe^{3+}]^2} + \log\frac{[I_3^-]}{[I^-]^3}$$

$$= \log\frac{[Fe^{2+}]^2[I_3^-]}{[Fe^{3+}]^2[I^-]^3}$$

Notice that we have changed the sign of the second logarithmic term by inverting the fraction. Further arrangement gives

$$\log \frac{[\mathrm{Fe}^{2+}]^2[\mathrm{I}_3^-]}{[\mathrm{Fe}^{3+}]^2[\mathrm{I}^-]^3} = \frac{2(E^0_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} - E^0_{\mathrm{I}_3^-/\mathrm{I}^-})}{0.0592}$$

Recall, however, that in this instance the concentration terms are *equilibrium concentrations,* and

$$\log K_{\mathrm{eq}} = \frac{2(E^0_{\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}} - E^0_{\mathrm{I}_3^-/\mathrm{I}^-})}{0.0592} = \frac{2(0.771 - 0.536)}{0.0592} = 7.94$$

$$K_{\mathrm{eq}} = \text{antilog } 7.94 = 8.7 \times 10^7$$

We round the answer to two figures because $\log K_{\mathrm{eq}}$ contains only two significant figures (the two to the right of the decimal point).

EXAMPLE 19-10

Calculate the equilibrium constant for the reaction

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightleftharpoons 5MnO_2(s) + 4H^+$$

Solution

In Appendix 5, we find

$$2MnO_4^- + 8H^+ + 6e^- \rightleftharpoons 2MnO_2(s) + 4H_2O \qquad E^0 = +1.695\ V$$
$$3MnO_2(s) + 12H^+ + 6e^- \rightleftharpoons 3Mn^{2+} + 6H_2O \qquad E^0 = +1.23\ V$$

Again, we have multiplied both equations by integers so that the numbers of electrons are equal. When this system is at equilibrium,

$$E^0_{MnO_4^-/MnO_2} = E^0_{MnO_2/Mn^{2+}}$$

$$1.695 - \frac{0.0592}{6}\log\frac{1}{[MnO_4^-]^2[H^+]^8} = 1.23 - \frac{0.0592}{6}\log\frac{[Mn^{2+}]^3}{[H^+]^{12}}$$

If we invert the log term on the right and rearrange, we obtain

$$\frac{6(1.695 - 1.23)}{0.0592} = \log\frac{1}{[MnO_4^-]^2[H^+]^8} + \log\frac{[H^+]^{12}}{[Mn^{2+}]^3}$$

If we invert the log term on the right and rearrange, we obtain

$$\frac{6(1.695 - 1.23)}{0.0592} = \log \frac{1}{[MnO_4^-]^2[H^+]^8} + \log \frac{[H^+]^{12}}{[Mn^{2+}]^3}$$

Adding the two log terms gives

$$\frac{6(1.695 - 1.23)}{0.0592} = \log \frac{[H^+]^{12}}{[MnO_4^-]^2[Mn^{2+}]^3[H^+]^8}$$

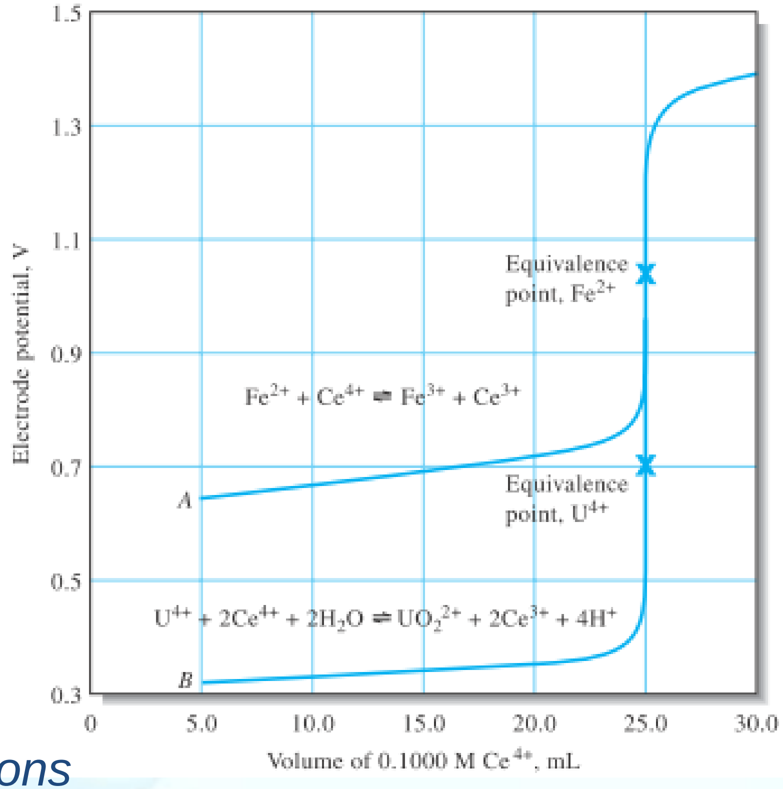
$$47.1 = \log \frac{[H^+]^4}{[MnO_4^-]^2[Mn^{2+}]^3} = \log K_{eq}$$

$$K_{eq} = \text{antilog } 47.1 = 1 \times 10^{47}$$

Note that the final result has only one significant figure.

19D Constructing redox titration curves

- There is a logarithmic relationship between electrode potential and concentration of the analyte or titrant.
- Hence, redox titration curves are similar in appearance to those for other types o titrations in which a p-function is plotted as the ordinate.



19D-1 Electrode Potentials during Redox Titrations

Consider the redox titration of iron(II) with a standard solution of cerium(IV).

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

The electrode potentials for the two half- reactions are always identical.

$$E_{Ce+4/Ce+3} = E_{Fe+3/Fe+2} = E_{system}$$

E_{system} is the potential of the system.*

The titration mixture of the reaction can be treated as part of the hypothetical cell:

SHE|| Ce^{+4},Ce^{+3},Fe^{+3},Fe^{+2}| Pt

Equivalence-Point Potentials

At the equivalence point, the concentration of cerium(IV) and iron(II) are minute; however, equivalence-point potentials are easily obtained.

$$E_{eq} = E^0_{Ce+4/Ce+3} - \frac{0.0592}{1}\log\frac{[Ce^{+3}]}{[Ce^{+4}]} \qquad E_{eq} = E^0_{Fe+3/Fe+2} - \frac{0.0592}{1}\log\frac{[Fe^{+2}]}{[Fe^{+3}]}$$

$$2E_{eq} = E^0_{Fe+3/Fe+2} + E^0_{Ce+4/Ce+3} - \frac{0.0592}{1}\log\frac{[Ce^{+3}][Fe^{+2}]}{[Ce^{+4}][Fe^{+3}]}$$

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

EXAMPLE 19-11

Derive an expression for the equivalence-point potential in the titration of 0.0500 M U^{4+} with 0.1000 M Ce^{4+}. Assume both solutions are 1.0 M in H_2SO_4.

$$U^{4+} + 2Ce^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2Ce^{3+} + 4H^+$$

Solution

In Appendix 5, we find

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad E^0 = 0.334\ \mathrm{V}$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0'} = 1.44\ \mathrm{V}$$

Now, we use the formal potential for Ce^{4+} in 1.0 M H_2SO_4.

Proceeding as in the cerium(IV)/iron(II) equivalence-point calculation, we write

$$E_{eq} = E^0_{UO_2^{2+}/U^{4+}} - \frac{0.0592}{2}\log\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

$$E_{eq} = E^{0'}_{Ce^{4+}/Ce^{3+}} - \frac{0.0592}{1}\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

In order to combine the log terms, we must multiply the first equation by 2 to give

$$2E_{eq} = 2E^0_{UO_2^{2+}/U^{4+}} - 0.0592\log\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

Adding this equation to the previous equation leads to

$$3E_{eq} = 2E^0_{UO_2^{2+}/U^{4+}} + E^{0'}_{Ce^{4+}/Ce^{3+}} - 0.0592\log\frac{[U^{4+}][Ce^{3+}]}{[UO_2^{2+}][Ce^{4+}][H^+]^4}$$

But, at equivalence,

$$[\mathrm{U}^{4+}] = [\mathrm{Ce}^{4+}]/2$$

and

$$[\mathrm{UO_2}^{2+}] = [\mathrm{Ce}^{3+}]/2$$

Substituting these equations gives on rearranging

$$E_{\mathrm{eq}} = \frac{2E^0_{\mathrm{UO_2{}^{2+}/U^{4+}}} + E^{0'}_{\mathrm{Ce^{4+}/Ce^{3+}}}}{3} - \frac{0.0592}{3}\log\frac{2\cancel{[\mathrm{Ce}^{4+}]}\cancel{[\mathrm{Ce}^{3+}]}}{2\cancel{[\mathrm{Ce}^{3+}]}\cancel{[\mathrm{Ce}^{4+}]}[\mathrm{H}^+]^4}$$

$$= \frac{2E^0_{\mathrm{UO_2{}^{2+}/U^{4+}}} + E^{0'}_{\mathrm{Ce^{4+}/Ce^{3+}}}}{3} - \frac{0.0592}{3}\log\frac{1}{[\mathrm{H}^+]^4}$$

We see that, in this titration, the equivalence-point potential is pH dependent.

19D-2 The Titration Curve

- Consider the titration of 50.00 mL of 0.0500 M Fe^{+2} with 0.1000 M Ce^{+4} in a medium that is 1.0 M in H2SO4

$$Ce^{+4} + e^{-} \leftrightarrow Ce^{+3} \qquad E^{01} = 1.44V$$

$$Fe^{+3} + e^{-} \leftrightarrow Fe^{+2} \qquad E^{01} = 0.68V$$

- *Initial Potential*

There is not enough information to calculate an initial potential.

- *Potential after the Addition of 5.00 mL of Cerium(IV)*

When oxidant is added, Ce+3 and Fe+3 are formed. The equilibrium concentration of Fe(III) is equal to its molar analytical concentration minus the molar equilibrium concentration of the unreacted Ce(IV).

$$[Fe^{+3}] = \frac{5.00mL \times 0.1M}{50.00mL + 5.00mL} - [Ce^{+4}] = \left(\frac{0.5}{55.00}\right)M - [Ce^{+4}]$$

$$[Fe^{+2}] = (\frac{2.00}{55.00})M + [Ce^{+4}]$$

Until the end point, Nerst equation for iron is used

$$E_{eq} = E^{0}_{Fe+3/Fe+2} - \frac{0.0592}{1}\log\frac{[Fe^{+2}]}{[Fe^{+3}]}$$

Equivalence-Point Potential

From the two formal potentials, we get E_{eq} =1.06 V

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

Potential after E.P.   Adding 25.10 mL of Cerium(IV)

The molar concentrations of Ce(III), Ce(IV), and Fe(III) are easily computed at this point, but that for Fe(II) . Therefore, *Esystem computations based on the* cerium half-reaction are more convenient. The concentrations of the two cerium ion species are

$[Ce^{3+}]$ = 25.00 x 0.1000 /75.10   = 2.500 / 75.10 M

$[Ce^{4+}]$ =(25.10 x 0.1000 - 50.00 x 0.0500) / 75.10 = 0.010 / 75.10 M

Substitution into the Nernst equation for the cerium couple gives

$$E_{eq} = E^0_{Ce+4/Ce+3} - \frac{0.0592}{1} \log \frac{[Ce^{+3}]}{[Ce^{+4}]} \qquad E_{eq} = 1.30 \text{ V}$$

TABLE 19-2

Electrode Potential versus SHE in Titrations with 0.100 M Ce^{4+}

Reagent Volume, mL	Potential, V, vs. SHE*		
	50.00 mL of 0.0500 M Fe^{2+}		50.00 mL of 0.02500 M U^{4+}
5.00	0.64		0.316
15.00	0.69		0.339
20.00	0.72		0.352
24.00	0.76		0.375
24.90	0.82		0.405
25.00	**1.06**	← **Equivalence Point** →	**0.703**
25.10	1.30		1.30
26.00	1.36		1.36
30.00	1.40		1.40

*H_2SO_4 concentration is such that $[H^+] = 1.0$ throughout.

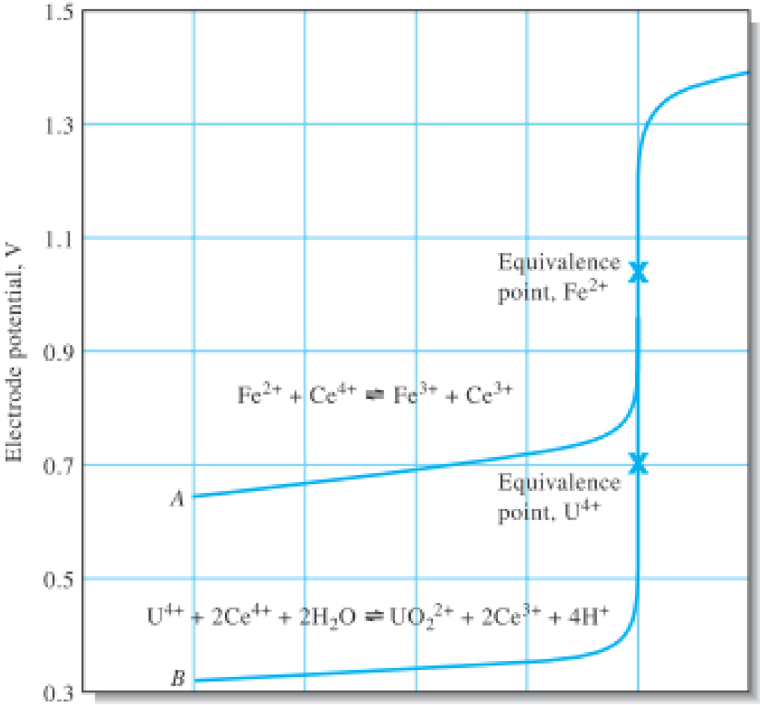


Figure 19-3 Titration curves for 0.1000 M Ce^{4+} titration. *A*: Titration of 50.00 mL of 0.05000 M Fe^{2+}. *B*: Titration of 50.00 mL of 0.02500 M U^{4+}.

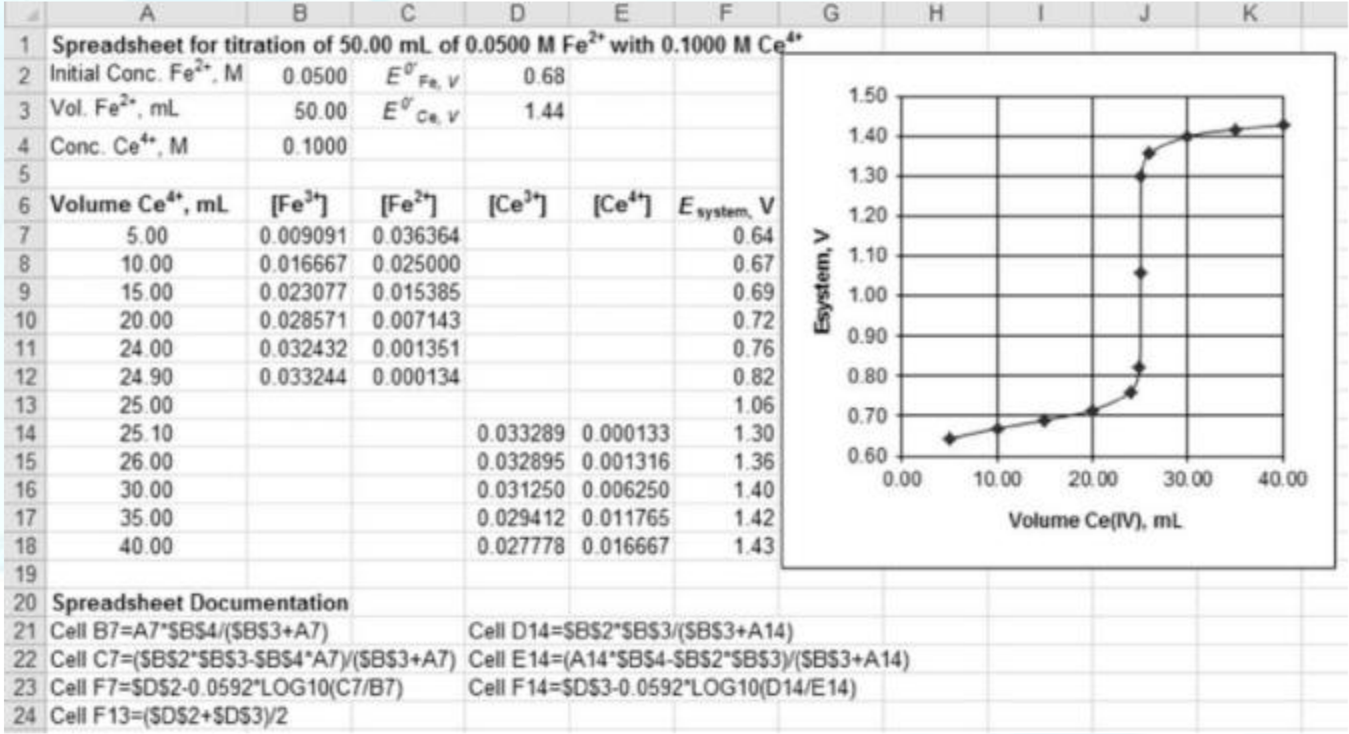
EXAMPLE 19-12

Calculate data and construct a titration curve for the reaction of 50.00 mL of 0.02500 M U^{4+} with 0.1000 M Ce^{4+}. The solution is 1.0 M in H_2SO_4 throughout the titration (for the sake of simplicity, assume that $[H^+]$ for this solution is also about 1.0 M).

Solution

The analytical reaction is

$$U^{4+} + 2Ce^{4+} + 2H_2O \rightleftharpoons UO_2^{2+} + 2Ce^{3+} + 4H^+$$



	A	B	C	D	E	F
1	**Spreadsheet for titration of 50.00 mL of 0.0500 M Fe^{2+} with 0.1000 M Ce^{4+}**					
2	Initial Conc. Fe^{2+}, M	0.0500	$E^{0'}_{Fe}$, V	0.68		
3	Vol. Fe^{2+}, mL	50.00	$E^{0'}_{Ce}$, V	1.44		
4	Conc. Ce^{4+}, M	0.1000				
5						
6	**Volume Ce^{4+}, mL**	**$[Fe^{3+}]$**	**$[Fe^{2+}]$**	**$[Ce^{3+}]$**	**$[Ce^{4+}]$**	**E_{system}, V**
7	5.00	0.009091	0.036364			0.64
8	10.00	0.016667	0.025000			0.67
9	15.00	0.023077	0.015385			0.69
10	20.00	0.028571	0.007143			0.72
11	24.00	0.032432	0.001351			0.76
12	24.90	0.033244	0.000134			0.82
13	25.00					1.06
14	25.10			0.033289	0.000133	1.30
15	26.00			0.032895	0.001316	1.36
16	30.00			0.031250	0.006250	1.40
17	35.00			0.029412	0.011765	1.42
18	40.00			0.027778	0.016667	1.43
19						
20	**Spreadsheet Documentation**					
21	`Cell B7=A7*$B$4/($B$3+A7)`			`Cell D14=$B$2*$B$3/($B$3+A14)`		
22	`Cell C7=($B$2*$B$3-$B$4*A7)/($B$3+A7)`			`Cell E14=(A14*$B$4-$B$2*$B$3)/($B$3+A14)`		
23	`Cell F7=$D$2-0.0592*LOG10(C7/B7)`			`Cell F14=$D$3-0.0592*LOG10(D14/E14)`		
24	`Cell F13=($D$2+$D$3)/2`					

And, in Appendix 5, we find

$$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O \qquad E^0 = 0.334\text{ V}$$

$$Ce^{4+} + e^- \rightleftharpoons Ce^{3+} \qquad E^{0'} = 1.44\text{ V}$$

Potential after Adding 5.00 mL of Ce^{4+}

$$\begin{aligned}\text{original amount } U^{4+} &= 50.00\ \cancel{\text{mL }U^{4+}} \times 0.02500\ \frac{\text{mmol } U^{4+}}{\cancel{\text{mL }U^{4+}}}\\ &= 1.250\text{ mmol } U^{4+}\end{aligned}$$

$$\begin{aligned}\text{amount } Ce^{4+}\text{ added} &= 5.00\ \cancel{\text{ml }Ce^{4+}} \times 0.1000\ \frac{\text{mmol } Ce^{4+}}{\cancel{\text{mL }Ce^{4+}}}\\ &= 0.5000\text{ mmol } Ce^{4+}\end{aligned}$$

$$\begin{aligned}\text{amount } U^{4+}\text{ remaining} &= 1.250\text{ mmol } U^{4+} - 0.2500\ \cancel{\text{mmol }UO_2^{2+}}\\ &\quad\times \frac{1\text{ mmol } U^{4+}}{\cancel{1\text{ mmol }UO_2^{2+}}}\\ &= 1.000\text{ mmol } U^{4+}\end{aligned}$$

$$\text{total volume of solution} = (50.00 + 5.00)\text{mL} = 55.00\text{ mL}$$

$$\text{concentration } U^{4+}\text{ remaining} = \frac{1.000\text{ mmol } U^{4+}}{55.00\text{ mL}}$$

$$\begin{aligned}\text{concentration } UO_2^{2+}\text{ formed} &= \frac{0.5000\ \cancel{\text{mmol }Ce^{4+}} \times \dfrac{1\text{ mmol } UO_2^{2+}}{2\ \cancel{\text{mmol }Ce^{4+}}}}{55.00\text{ mL}}\\ &= \frac{0.2500\text{ mmol } UO_2^{2+}}{55.00\text{ mL}}\end{aligned}$$

Applying the Nernst equation for UO_2^{2+}, we obtain

$$E = 0.334 - \frac{0.0592}{2}\log\frac{[U^{4+}]}{[UO_2^{2+}][H^+]^4}$$

$$= 0.334 - \frac{0.0592}{2}\log\frac{[U^{4+}]}{[UO_2^{2+}](1.00)^4}$$

Substituting concentrations of the two uranium species gives

$$E = 0.334 - \frac{0.0592}{2}\log\frac{1.000\text{ mmol } U^{4+}/\cancel{55.00\text{ mL}}}{0.2500\text{ mmol } UO_2^{2+}/\cancel{55.00\text{ mL}}}$$

$$= 0.316\text{ V}$$

Other preequivalence-point data, calculated in the same way, are given in the third column in Table 19-2.

Equivalence-Point Potential

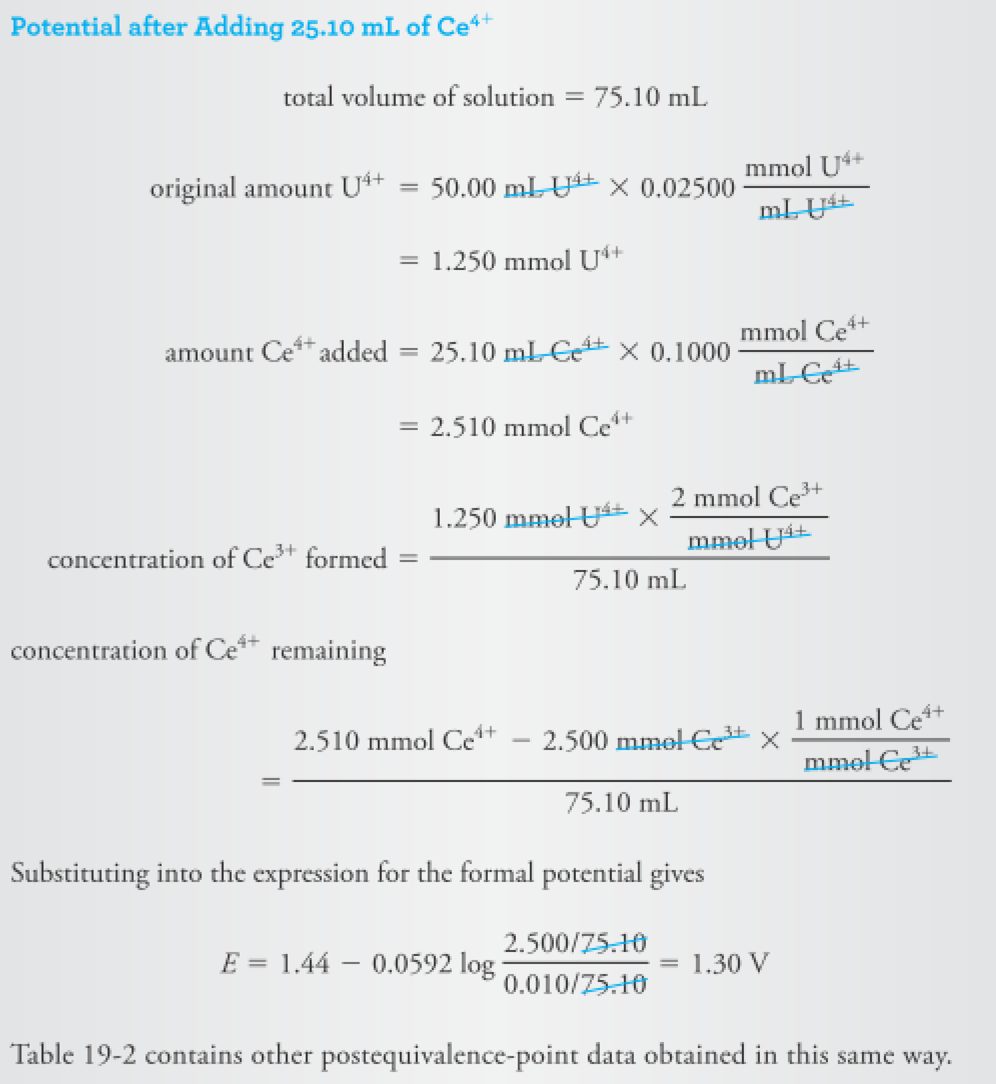
Following the procedure shown in Example 19-11, we obtain

$$E_{eq} = \frac{(2E^0_{UO_2^{2+}/U^{4+}} + E^{0'}_{Ce^{4+}/Ce^{3+}})}{3} - \frac{0.0592}{3}\log\frac{1}{[H^+]^4}$$

Substituting gives

$$E_{eq} = \frac{2 \times 0.334 + 1.44}{3} - \frac{0.0592}{3}\log\frac{1}{(1.00)^4}$$

$$= \frac{2 \times 0.334 + 1.44}{3} = 0.703\text{ V}$$



Potential after Adding 25.10 mL of Ce^{4+}

$$\text{total volume of solution} = 75.10\text{ mL}$$

$$\begin{aligned}\text{original amount U}^{4+} &= 50.00\ \cancel{\text{mL U}^{4+}} \times 0.02500\ \frac{\text{mmol U}^{4+}}{\cancel{\text{mL U}^{4+}}}\\ &= 1.250\text{ mmol U}^{4+}\end{aligned}$$

$$\begin{aligned}\text{amount Ce}^{4+}\text{ added} &= 25.10\ \cancel{\text{mL Ce}^{4+}} \times 0.1000\ \frac{\text{mmol Ce}^{4+}}{\cancel{\text{mL Ce}^{4+}}}\\ &= 2.510\text{ mmol Ce}^{4+}\end{aligned}$$

$$\text{concentration of Ce}^{3+}\text{ formed} = \frac{1.250\ \cancel{\text{mmol U}^{4+}} \times \dfrac{2\text{ mmol Ce}^{3+}}{\cancel{\text{mmol U}^{4+}}}}{75.10\text{ mL}}$$

concentration of Ce^{4+} remaining

$$= \frac{2.510\text{ mmol Ce}^{4+} - 2.500\ \cancel{\text{mmol Ce}^{3+}} \times \dfrac{1\text{ mmol Ce}^{4+}}{\cancel{\text{mmol Ce}^{3+}}}}{75.10\text{ mL}}$$

Substituting into the expression for the formal potential gives

$$E = 1.44 - 0.0592 \log \frac{2.500/\cancel{75.10}}{0.010/\cancel{75.10}} = 1.30\text{ V}$$

Table 19-2 contains other postequivalence-point data obtained in this same way.

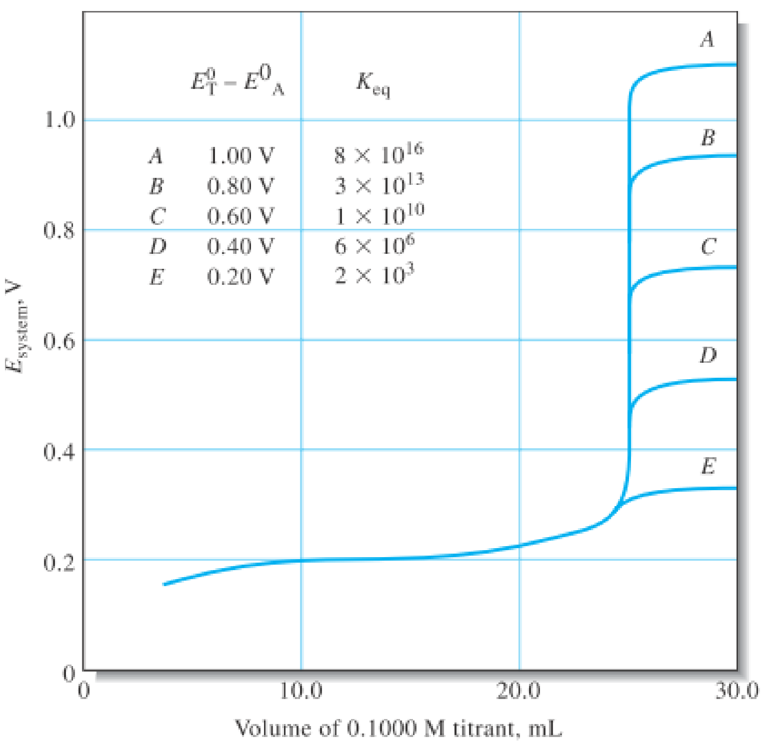
Effect of Variables on Redox Titration Curves

Reactant Concentration

Titration curves for oxidation/reduction reactions are usually independent of analyte and reagent concentrations.

Completeness of the Reaction

Figure 19-5 Effect of titrant electrode potential on reaction completeness. The standard electrode potential for the analyte (E_A^0) is 0.200 V; starting with curve *A*, standard electrode potentials for the titrant (E_T^0) are 1.20, 1.00, 0.80, 0.60, and 0.40, respectively. Both analyte and titrant undergo a one-electron change.



19E Oxidation/reduction Indicators

Two types of chemical indicators are used for obtaining end points for oxidation/reduction titrations:

General Redox Indicators

These indicators change color on being oxidized or reduced. The half-reaction responsible for color change is:

$$In_{ox} + ne^- \Leftrightarrow In_{red}$$

If the indicator reaction is reversible,

$$E = E^0_{Inox/Inred} - \frac{0.0592}{n}\log\frac{[In_{red}]}{[In_{ox}]}$$

The potential change required to produce the full color change of a typical general indicator can be expressed as:

$$E = E^0_{\ln} \pm \frac{0.0592}{n}$$

TABLE 19-3

Selected Oxidation/Reduction Indicators*

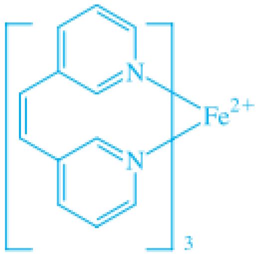
Indicator	Color		Transition Potential, V	Conditions
	Oxidized	Reduced		
5-Nitro-1,10-phenanthroline iron(II) complex	Pale blue	Red-violet	+1.25	1 M H_2SO_4
2,3'-Diphenylamine dicarboxylic acid	Blue-violet	Colorless	+1.12	7-10 M H_2SO_4
1,10- Phenanthroline iron(II) complex	Pale blue	Red	+1.11	1 M H_2SO_4
5-Methyl 1,10-phenanthroline iron(II) complex	Pale blue	Red	+1.02	1 M H_2SO_4
Erioglaucin A	Blue-red	Yellow-green	+0.98	0.5 M H_2SO_4
Diphenylamine sulfonic acid	Red-violet	Colorless	+0.85	Dilute acid
Diphenylamine	Violet	Colorless	+0.76	Dilute acid
p-Ethoxychrysoidine	Yellow	Red	+0.76	Dilute acid
Methylene blue	Blue	Colorless	+0.53	1 M acid
Indigo tetrasulfonate	Blue	Colorless	+0.36	1 M acid
Phenosafranine	Red	Colorless	+0.28	1 M acid

*Data in part from I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis,* 2nd ed., Vol. 1, p. 140, New York: Interscience, 1942.

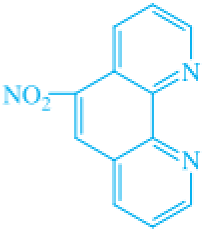
Iron(II) Complexes of Orthophenanthrolines

A class of organic compounds known as 1,10-phenanthrolines, or orthophenanthrolines, form stable complexes with iron(II) and certain other ions.

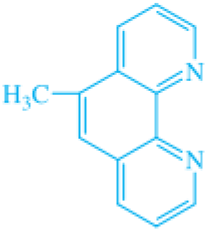
Three orthophenanthroline molecules combine with each iron ion to yield a complex.



ferroin $(phen)_3Fe^{2+}$



5-nitro-1, 10-phenanthroline



5-methyl-1, 10-phenanthroline

The complexed iron in ferroin undergoes a reversible oxidation/reduction reaction:

$$(phen)_3Fe^{+3} + e^- \Leftrightarrow (phen)_3Fe^{+2}$$

Starch/Iodine Solutions

Starch, which forms a blue complex with triiodide ion, is a widely used specific indicator in oxidation/reduction reactions involving iodine as an oxidant or iodide ion as a reductant.

Specific Indicators

The best-known specific indicator is starch, which forms a dark blue complex with triiodide ion.

Potassium thiocyanate is another specific indicator which may be used in the titration of iron(III) with solutions of titanium(III) sulfate.

19F Potentiometric end points

The end points for many oxidation/reduction titrations can be observed by making the solution of the analyte part of the cell

reference electrode || analyte solution | Pt