Potentiometry example:

Assume two solutions, one containing 0.01 M potassium dichromate, $1.0 \times 10^{-6}$ M chromium III from chromium III sulfate and 0.7 M hydrogen ion and one containing 0.012 M iron II sulfate and $1.0 \times 10^{-6}$ M iron III from iron III sulfate. Answer each question below assuming a temperature of 25 °C and that:

A. The two solutions are contained in separate beakers joined by a salt bridge with an inert electrode (such as platinum) immersed in each solution.

B. The two solutions are contained (no dilution) in a single beaker with a saturated calomel electrode and an inert electrode (e.g., Pt) immersed in the solution.

Relevant information:

$\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$: $E^\circ = +1.33$ V
$\text{Fe}^{3+}/\text{Fe}^{2+}$: $E^\circ = +0.77$ V
For SCE: $E_{\text{ref}} = +0.244$ V
Potentiometry example:

1. Sketch the experimental setup for A.
2. Write the shorthand notation for A.
3. Write and balance the expected equation.
4. Identify the electrodes at which oxidation and reduction are likely to occur.
5. Identify the anode and cathode (part A).
6. Calculate the potential of each half cell.
7. Calculate the cell potential (i.e., the cell potential that would be measured by a high impedance voltmeter before any reaction has occurred).
8. What is the cell potential when the primary reaction reaches equilibrium?
9. Calculate the equilibrium constant for the redox reaction.
10. Calculate the iron (II) concentration when the primary reaction is at equilibrium.
11. Calculate the difference between the initial and equilibrium cell potentials.
12. Comment on the relative magnitudes of changes in the iron (II) concentration and the cell potential from initial to equilibrium conditions.
13. Why do small changes in cell potential frequently represent very large changes in concentration? (hint: use Nernst equation)
14. Comment on the relevance of points 11 and 12 to the reliability of potentials required for direct measurement applications of potentiometry.
15. Why are high-impedance (resistance) voltmeters used to measure cell potentials? Why not use a low-impedance voltmeter?
1. Sketch of experimental set-up (Part A):

2. Shorthand notation for A:

\[ \text{Pt|Fe}^{2+}(0.012), \text{Fe}^{3+}(1 \times 10^{-6})||\text{Cr}_2\text{O}_7^{2-}(0.01), \text{Cr}^{3+}(1 \times 10^{-6}), \text{H}^+(0.7)|\text{Pt} \]
3. Write and balance the equation:

half reaction method:

(1) \( \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \)

(2) \(-6(\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+})\)

(3) \( \text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O} \)

(1) - (2) = (3)

Write as a reduction to match \(E^0\), add \(\text{H}_2\text{O}\) to balance \(\text{O}\), \(\text{H}^+\) to balance \(\text{H}\), and \(\text{e}^-\) to balance total charge.

Multiply each reaction by the appropriate number to achieve equal numbers of transferred electrons for each reaction.

Subtract half reaction with lesser \(E^0\) from reaction with greater \(E^0\) to get the balanced equation for the spontaneous reaction.

4. Identify the electrodes:

oxidation \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \), left electrode
reduction \( \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \), right electrode
5. Identify the anode and cathode (part A).

oxidation takes place at the anode (left electrode)

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+}, \text{left electrode} \]

reduction takes place at the cathode (right electrode)

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}, \text{right electrode} \]

6. Calculate the potential of each half cell.

\[ \text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}: \quad E^\circ = +1.33 \text{ V} \]
\[ \text{Fe}^{3+}/\text{Fe}^{2+}: \quad E^\circ = +0.77 \text{ V} \]

These voltages apply to unit activities of reactants and products (not this situation). we turn to Nernst

\[
E = E^\circ + \frac{0.0592}{1} \log \left( \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right) \\
E = 0.77 - \frac{0.0592}{1} \log \left( \frac{0.012}{1 \times 10^{-6}} \right) = 0.53V
\]

\[
E = 1.33 - \frac{0.0592}{6} \log \left( \frac{[\text{Cr}^{3+}]}{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^4} \right) \\
E = 1.33 - \frac{0.0592}{6} \log \left( \frac{(10^{-6})^2}{(10^{-2})(0.7)^4} \right) = 1.41V
\]
7. Calculate the cell potential (i.e., the cell potential that would be measured by a high impedance voltmeter before any reaction has occurred).

\[ E_{cell} = E_{cathode} - E_{anode} = E_{right} - E_{left} \]
\[ = 1.41 \text{V} - 0.53 \text{V} = 0.88 \text{V} \]

Reaction is spontaneous as written for the initial conditions.

8. What is the cell potential when the primary reaction reaches equilibrium?

\[ \Delta G^\circ = -nF E_{cell}^\circ = -RT \ln K_{eq} \]
\[ E_{cell}^\circ = \frac{RT}{nF} \ln K_{eq} \]

At equilibrium, \( E=0 \).

\[ E = E^\circ - \frac{RT}{nF} \ln K = 0 \]
9. Calculate the equilibrium constant for the redox reaction.

\[ E_{\text{cell}} = E_{Cr}^\circ - E_{Fe}^\circ - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2[Fe^{3+}]^6}{[Cr_2O_7^{2-}][Fe^{2+}]^8[H^+]^{14}} \]

\[ 0 = E_{Cr}^\circ - E_{Fe}^\circ - \frac{0.059}{6} \log K \quad \text{at equilibrium} \]

\[ \log K = \frac{6(E_{Cr}^\circ - E_{Fe}^\circ)}{0.059} \]

\[ K = 10^{\frac{6(E_{Cr}^\circ - E_{Fe}^\circ)}{0.059}} = 10^{\frac{6(0.56)}{0.059}} = 8.9 \times 10^{56} \]

In general,

\[ K = 10^{\frac{n(\Delta E^\circ)}{0.059}} = 10^{16.9n(\Delta E^\circ)} \]

Therefore, small changes in \( \Delta E^\circ \) lead to very large changes in \( K \).
10. Calculate the iron (II) concentration when the primary reaction is at equilibrium.

\[
\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightleftharpoons 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}
\]

\[
E_{cell} = 0 = E_{Cr}^\circ - E_{Fe}^\circ - \frac{0.059}{6} \log \frac{[\text{Cr}^{3+}]^2[\text{Fe}^{3+}]^6}{[\text{Cr}_2\text{O}_7^{2-}]^2[\text{Fe}^{2+}]^6[\text{H}^+]^{14}}
\]

where all are equilibrium concentrations

\[
K = 10^{\frac{6(E_{Cr}^\circ - E_{Fe}^\circ)}{0.059}} = 10^{\frac{6(0.56)}{0.059}} = 8.9 \times 10^{56}
\]

initial concentrations:

\[
C_0^{\text{dichromate}} = 0.01\text{M}
\]

\[
C_0^{\text{Cr}^3+} = 1.0 \times 10^{-6}\text{M}
\]

\[
C_0^{\text{H}^+} = 0.7\text{M}
\]

\[
C_0^{\text{Fe}^{2+}} = 0.012\text{M}
\]

\[
C_0^{\text{Fe}^{3+}} = 1.0 \times 10^{-6}\text{M}
\]

Note that \(\text{Cr}_2\text{O}_7^{2-}\) is in stoichiometric excess relative to \(\text{Fe}^{2+}\) and the \(K\) value is so large that we can conclude that virtually all \(\text{Fe}^{2+}\) is converted to \(\text{Fe}^{3+}\).
Therefore,

\[
[\text{Fe}^{3+}]_{eq} \approx 1 \times 10^{-6} \text{ M} + 0.012 \text{ M} \approx 0.012 \text{ M}
\]

\[
[\text{Cr}^{3+}]_{eq} \approx 1 \times 10^{-6} \text{ M} + (2/6)(0.012 \text{ M}) \approx 0.004 \text{ M}
\]

\[
[\text{Cr}_2\text{O}_7^{2-}]_{eq} \approx 0.01 \text{ M} - (1/6)(0.012 \text{ M}) \approx 0.008 \text{ M}
\]

\[
[\text{H}^+]_{eq} \approx 0.7 \text{ M} - (14/6)(0.012 \text{ M}) \approx 0.672 \text{ M}
\]

\[
0 = E^{\circ}_{\text{Cr}} - E^{\circ}_{\text{Fe}} - \frac{0.059}{6}\log\left(\frac{(0.004)^2(0.012)^6}{(0.008)[\text{Fe}^{2+}]^6(0.672)^{14}}\right)
\]

solving for \([\text{Fe}^{2+}]_{eq} = 3.5 \times 10^{-12} \text{ M}\)

11. Calculate the difference between the initial and equilibrium cell potentials.

\[
E_{\text{cell, initial}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{right}} - E_{\text{left}}
\]

\[
= 1.41 \text{ V} - 0.53 \text{ V} = 0.88 \text{ V}
\]

\[
E_{\text{cell, equil.}} = 0 \quad \Delta = 0.88 \text{ V}
\]

12. Comment on the relative magnitudes of changes in the iron (II) concentration and the cell potential from initial to equilibrium conditions.

\[
C^{\circ}_{\text{Fe}^{2+}} = 0.012 \text{ M} ; [\text{Fe}^{2+}]_{eq} = 3.5 \times 10^{-12} \text{ M}
\]

> 9 order of magnitude change in concentration with 0.88 V change in voltage. (wow)
13. Why do small changes in cell potential frequently represent very large changes in concentration? (hint: use Nernst equation)

\[
E_{cell} = E^\circ_{Cr} - E^\circ_{Fe} - \frac{0.059}{6} \log \frac{[Cr^{3+}]^2[Fe^{3+}]^6}{[Cr_2O_7^{2-}][Fe^{2+}]^6[H^+]^{14}}
\]

\[
C^\circ_{\text{dichromate}} = 0.01 \text{M} \\
C^\circ_{Cr^{3+}} = 1.0 \times 10^{-6} \text{ M} \\
C^\circ_{H^+} = 0.7 \text{ M} \\
C^\circ_{Fe^{2+}} = 0.012 \text{ M} \\
C^\circ_{Fe^{3+}} = 1.0 \times 10^{-6} \text{ M}
\]

\[
[Fe^{3+}]_{eq} \approx 1 \times 10^{-6} \text{ M} + 0.012 \text{ M} \approx 0.012 \text{ M} \\
[Cr^{3+}]_{eq} \approx 1 \times 10^{-6} \text{ M} + (2/6)(0.012 \text{ M}) \approx 0.004 \text{ M} \\
[Cr_2O_7^{2-}]_{eq} \approx 0.01 \text{ M} - (1/6)(0.012 \text{ M}) \approx 0.008 \text{ M} \\
[H^+]_{eq} \approx 0.7 \text{ M} - (14/6)(0.012 \text{ M}) \approx 0.672 \text{ M} \\
[Fe^{2+}]_{eq} = 3.5 \times 10^{-12} \text{ M}
\]

Near equilibrium, all species except Fe^{2+} are present at relatively high concentrations. Small absolute changes in these concentrations will give rise to small relative concentration changes. Small absolute changes in Fe^{2+}, however, can give rise to large relative changes….
Therefore,

\[
\frac{[Cr^{3+}]^2[Fe^{3+}]^6}{[Cr_2O_7^{2-}][H^+]^{14}}
\]

can be regarded as a constant, C, near equilibrium.

\[
E_{cell,1} = E_{Cr}^\circ - E_{Fe}^\circ - \frac{0.059}{6} \log C \left( \frac{1}{[Fe^{2+}]^6} \right)
\]

\[
E_{cell,2} = E_{Cr}^\circ - E_{Fe}^\circ - \frac{0.059}{6} \log C \left( \frac{1}{[Fe^{2+}]^6} \right)
\]

\[
E_{cell,1} - E_{cell,2} = \Delta E = -0.059 \left( \log \left( \frac{Fe^{2+}_2}{Fe^{2+}_1} \right) \right)
\]

\[
\left( \frac{Fe^{2+}_2}{Fe^{2+}_1} \right) = 10^{-\frac{\Delta E}{0.059}}
\]

The concentration ratio is an exponential function of the change in potential. Therefore, small changes in potential correspond to large changes in concentration.

e.g., if \( \Delta E = 0.1 \) V, \( [Fe^{2+}_2]/[Fe^{2+}_1] = 49 \)
14. Comment on the relevance of points 11 and 12 to the reliability of potentials required for direct measurement applications of potentiometry.

Small voltage error $\rightarrow$ large concentration error

(However, there are very large relative changes in relative concentrations of reactants and products near the equivalence point in redox titration, which allows for the identification of equivalence points using an indicator or by monitoring voltage. See redox and potentiometric titrations.)

15. Why are high-impedance (resistance) voltmeters used to measure cell potentials? Why not use a low-impedance voltmeter?

Once current can flow, the reactants will proceed toward equilibrium thereby changing the voltage between the electrodes.

$V=IR$ or $I = V/R$, current flow is minimized with a high resistance meter.

A low impedance voltmeter would allow for significant current flow.
Let’s look at Part B:
B. The two solutions are contained (no dilution) in a single beaker with a saturated calomel electrode and an inert electrode (e.g., Pt) immersed in the solution.

Relevant information:

\[
\begin{align*}
\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}: & \quad E^\circ = +1.33 \text{ V} \\
\text{Fe}^{3+}/\text{Fe}^{2+}: & \quad E^\circ = +0.77 \text{ V} \\
\text{For SCE:} & \quad E_{\text{ref}} = +0.244 \text{ V}
\end{align*}
\]

\[
\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \rightleftharpoons 2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}
\]

The reaction quickly reaches equilibrium. What is the potential of this cell?
We know the potential of the SCE, we need to determine the potential at the Pt electrode where at equilibrium, $E_{Cr}$ and $E_{Fe}$ are equal.

We can use the Nernst equation to calculate either $E_{Cr}$ or $E_{Fe}$. Both calculations will give the same result. However, the $[Fe^{2+}]_{eq}$ is very small (3.5x10^{-12} M) and is subject to relatively large uncertainty. Therefore, it is more convenient to use the Cr couple.

$\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}: \quad E^\circ = +1.33 \text{ V}$

$$
\begin{align*}
[\text{Cr}^{3+}]_{eq} & \approx 1 \times 10^{-6} \text{ M} + (2/6)(0.012 \text{ M}) \quad \approx 0.004 \text{ M} \\
[\text{Cr}_2\text{O}_7^{2-}]_{eq} & \approx 0.01 \text{ M} - (1/6)(0.012 \text{ M}) \quad \approx 0.008 \text{ M} \\
[H^+]_{eq} & \approx 0.7 \text{ M} - (14/6)(0.012 \text{ M}) \quad \approx 0.672 \text{ M}
\end{align*}
$$

$$
E = 1.33 - \frac{0.0592}{6} \log \frac{[\text{Cr}^{3+}]^3}{[\text{Cr}_2\text{O}_7^{2-}][H^+]^{14}} \\
E = 1.33 - \frac{0.0592}{6} \log \frac{(0.004)^2}{(0.008)(0.672)^{14}} = 1.333 \text{ V}
$$

(Coincidentally very close to $E^\circ$)

$E_{cell} = E_{Cr} - E_{SCE} = 1.333 - 0.244 = 1.086 \text{ V}$