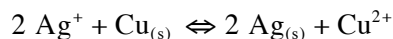


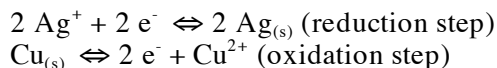
USING ELECTRODE POTENTIALS

I. Measuring Equilibrium Constants with Redox Reactions

A. Consider the reaction:



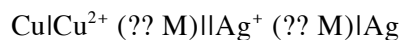
with associated half-reactions:



B. The equilibrium constant for this reaction is given by:

$$K_{eq} = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

C. The reaction above is the same as the galvanic cell:



D. If this galvanic cell completely discharges to reach equilibrium,

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{Ag}} - E_{\text{Cu}} = 0$$

which means:

$$E_{\text{Ag}} = E_{\text{Cu}}$$

Substituting for each from the Nernst equation:

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

After rearrangement:

$$\frac{2(E_{\text{Ag}}^0 - E_{\text{Cu}}^0)}{0.0592} = \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = \log K_{eq} \Rightarrow K_{eq} = 4 \cdot 10^{15}$$

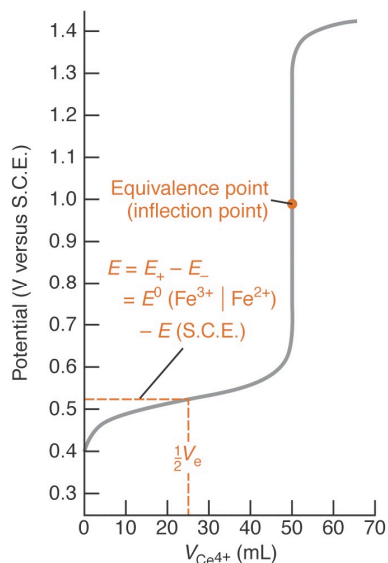
1. Note that since the equilibrium constant is so large, the equilibrium lies heavily toward the right (i.e., the reaction is essentially complete).

2. Similar calculations are possible for other systems.

II. Oxidation-Reduction Titrations

A. When an oxidation-reduction (redox) reaction is used to measure an analyte, the titrations usually follow the electrode potential as a function of titrant (or analyte) concentration.

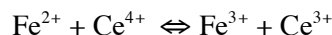
B. Since the electrode potential is a log function of the concentrations, it behaves as a "p" function.



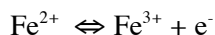
C. We will discuss the redox titrations in terms of a specific reaction and look at the calculations for each of the different regions of the titration curve. This would include:

1. Initially (before any titrant was added).
2. Before equivalence.
3. At the equivalence point.
4. After equivalence.

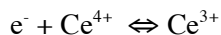
D. The specific reaction to consider: titration of iron(II) with cerium(IV)



1. Oxidation half-reaction:



2. Reduction half-reaction:



E. General comments about redox titrations and titration reactions.

1. The reactions must be fully reversible (i.e., the system must be at equilibrium at all times through the titration).
2. To be fully reversible means that:

$$E_{\text{system}} = E_{\text{Ce}} = E_{\text{Fe}} = E_{\text{indicator}} \text{ and } \Delta E_{\text{cell}} = 0$$

a. The equilibrium concentration ratios of the oxidized and reduced forms of the two species are such that their attraction for electrons are identical.

b. The Nernst equation applies.

3. Data from the titration can be used to calculate the titration curve using the Nernst equation for either the cerium(IV) or the iron(II) half-reactions.

4. In practice, for this kinds of example:

- Before equivalence, the Fe(III) and Fe(II) concentrations are used to calculate the E_{system} .
- After equivalence, Ce(III) and Ce(IV) concentrations are used to calculate the E_{system} .
- At equivalence, simplifying assumptions are made based upon the stoichiometric relationships to calculate the E_{system} .

F. Details of the titration: 50.00 mL of 0.05000 M Fe^{2+} is titrated with 0.1000 M Ce^{4+} in a medium containing 1.0 M H_2SO_4 (thus the **formal potentials** can be used from the appendix in the back of the textbook).

G. Derivation/calculation of the titration curve:

1. Initial region: no Ce(IV) has been added

- Since the amount of Fe^{3+} cannot be calculated (and is essentially zero), and the amount of Ce^{3+} is zero, the *potential cannot be calculated*.
- Some amount of reaction must occur before numbers can be plugged into the Nernst equation.

2. Before equivalence: assume 5.00 mL of Ce^{4+} solution have been added

$$[\text{Fe}^{3+}] = \frac{5\text{mL} \cdot 0.1\text{M}}{50\text{mL} + 5\text{mL}} = \frac{0.5\text{mmoles}}{55\text{mL}}$$

$$[\text{Fe}^{2+}] = \frac{(50\text{mL} \cdot 0.1\text{M}) - (5\text{mL} \cdot 0.1\text{M})}{50\text{mL} + 5\text{mL}} = \frac{2\text{mmoles}}{55\text{mL}}$$

$$E_{\text{system}} = E_{\text{Fe}} = E_{\text{Fe}}^f - \frac{0.0592}{1} \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 0.68 - 0.036 = 0.64\text{V}$$

3. At equivalence: All the iron(II) is converted to iron(III); all the cerium(IV) is converted to cerium(III)

a. Note that at the equivalence point:

$$\begin{aligned} [\text{Fe}^{3+}] &= [\text{Ce}^{3+}] \\ [\text{Fe}^{2+}] &= [\text{Ce}^{4+}] \implies \text{a very small amount!!} \end{aligned}$$

b. The system potential can be calculated by combining the Nernst equations for **both** species as follows:

$$E_{\text{system}} = E_{\text{Ce}} = E_{\text{Ce}}^f - \frac{0.0592}{1} \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

$$E_{system} = E_{Fe} = E_{Fe}^f - \frac{0.0592}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Adding the two equations together:

$$E_{system} = \frac{E_{Ce}^f + E_{Fe}^f}{2} = \frac{1.44 + 0.68}{2} = 1.06V$$

4. Beyond the equivalence point: assume 25.10 mL of cerium(IV) have been added

- The iron(II) is completely titrated.
- The cerium(III) and cerium(IV) concentrations must be used to calculate the potential of the system.
- Note that the number of moles of cerium(III) is equal to the number of moles of iron(II) originally present in the sample.
- Cerium(IV) present is due to the excess cerium(IV) added past equivalence.
- The system potential is calculated as follows:

$$[Ce^{3+}] = \frac{\# \text{ moles } Fe^{2+} \text{ originally}}{\text{total volume}} = \frac{50mL \cdot 0.05M}{50mL + 25.1mL} = \frac{2.5 \text{ mmoles}}{75.1mL}$$

$$[Ce^{4+}] = \frac{\# \text{ moles } Ce^{4+} \text{ past equivalence}}{\text{total volume}} = \frac{0.1mL \cdot 0.1M}{50mL + 25.1mL} = \frac{0.01 \text{ mmoles}}{75.1mL}$$

Substituting into the Nernst equation:

$$E_{system} = E_{Ce} = E_{Ce}^f - \frac{0.0592}{1} \log \frac{[Ce^{3+}]}{[Ce^{4+}]} = 1.44 - 0.14 = 1.30 V$$

III. Effects of System Variables on Redox Titrations

- The system potential ordinarily is independent of dilution.
 - Volume typically cancels out in the Nernst equation.
 - Usually, increased concentrations do not increase the magnitude of the change at equivalence.
- The larger the difference in standard electrode potential, the more complete the reaction.
 - If the difference is large, K_{eq} will be large.
 - The equivalence transition will be large.