

Fundamentals of Analytical Chemistry

Chapter 19
Applications of Standard
Electrode Potentials

Problems

- 4, 6, 8, 11, 15

Calculations of Equilibrium Constants

- From thermodynamics, we know that at equilibrium, $\Delta G = 0$
- Also, $\Delta G = -nFE$
 - Since both n and F are greater than zero, it means that at equilibrium, $E = 0$
- $Q =$ mass action quotient
 - At equilibrium (by definition) $Q = K$

Calculation of Equilibrium Constants

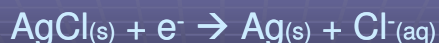
$$\begin{aligned} \text{We know } E &= E^\circ - \frac{0.05916}{n} \log Q \\ \therefore \text{At equilibrium } 0 &= E^\circ - \frac{0.05916}{n} \log K \\ \text{Rearranging; } E^\circ &= \frac{0.05916}{n} \log K \\ \therefore \frac{nE^\circ}{0.05916} &= \log K \\ K &= 10^{nE^\circ/0.05916} \end{aligned}$$

Calculation of Equilibrium Constants

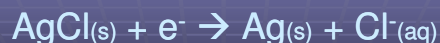
- E° is a *standard cell* potential
 - NOT a $\frac{1}{2}$ cell potential
 - NOT a cell potential under non-standard conditions

Calculation of Standard Cell Potentials

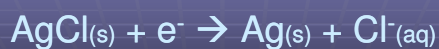
- Standard cell potentials can be calculated for many cells involving slightly soluble metal salts
 - In these cases, the electrochemical process involved the reduction of the metal ion
 - If we can calculate the underlying ion concentration, we can calculate the standard $\frac{1}{2}$ cell potential
 - Must know K_{sp}



- 'Driving' $\frac{1}{2}$ reaction is the reduction of Ag
 - $\text{Ag}^+ + e^- \rightarrow \text{Ag}$
 - Note that there is no change in the oxidation state of chlorine
 - Under standard conditions, all species are at unit activity.
 - AgCl and Ag are under standard conditions when there is 'some' present
 - Cl⁻ is at unit activity when the concentration is such that the activity is 1 (assume $\gamma_{\text{Cl}^-} = 1$)



- For $\text{AgCl} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$
 - $K_{\text{sp}} = 1.8 \times 10^{-10}$
 - This IS NOT the same as the $\frac{1}{2}$ reaction!!!
 - Ag⁺ rather than Ag as the product
 - NO electron exchange
 - If $K_{\text{sp}} = [\text{Ag}^+] * [\text{Cl}^-]$ and by definition $[\text{Cl}^-] = 1$
 - $K_{\text{sp}} = [\text{Ag}^+]$



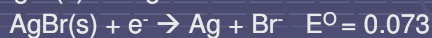
- From the Nernst equation for the reduction of silver
 - $E = E^\circ - (0.05916/n) \log (1/K_{\text{sp}})$
 - $E = 0.799 - (0.05916/1) \log (1/1.8 \times 10^{-10})$
 - $E = 0.223$
- But since these conditions came from the standard conditions for the above reaction, $E^\circ = 0.223\text{V}$

Calculation of K_{sp} values

- Consider $\text{AgBr}(s) \rightleftharpoons \text{Ag}^+ + \text{Br}^-$
 - Not normally considered an electrochemical process
 - K is a *state function*
 - Independent of the path used to derive the value
 - If we can write the reaction as a redox process, we can calculate E° , and from that we can calculate K

Calculation of K_{sp} values

For $\text{AgBr}(s) \rightleftharpoons \text{Ag}^+ + \text{Br}^-$



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$E^\circ_{\text{cell}} = 0.073 - 0.799 = -0.726$$

$$\log K = n E^\circ_{\text{cell}} / 0.05916 = (1)(-0.726) / 0.05916$$

$$K = 5.3 \times 10^{-13}$$

Potentiometric Titrations

- For a potentiometric titration curve, we plot volume of titrant (x-axis) vs $\frac{1}{2}$ cell potential (y-axis) vs. the SHE
 - We can measure the $\frac{1}{2}$ cell potential for either the cathode and anode
 - During a titration reaction, the overall cell potential is zero
 - Cathodic $\frac{1}{2}$ cell potential has to equal the anodic $\frac{1}{2}$ cell potential

Potentiometric Titration

- We must also determine the reaction!

Consider the titration of 50.0 mL of 0.050 M Sn^{2+} with 0.020 M MnO_4^- in 1M H_2SO_4

What is the reaction?

Potentiometric Titration

- For permanganate, the only viable $\frac{1}{2}$ reaction for titration is reduction to Mn^{2+}
 - $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \leftrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$
- For tin, there are a couple of $\frac{1}{2}$ reactions
 - $\text{Sn}^{2+} + 2\text{e}^- \leftrightarrow \text{Sn}$
 - $\text{Sn}^{4+} + 2\text{e}^- \leftrightarrow \text{Sn}^{2+}$
- What is the reaction?

Potentiometric Titration

- Two things we MUST remember
 - We have to have an oxidation and a reduction $\frac{1}{2}$ reaction combined for our overall reaction
 - The REACTANTS are MnO_4^- and Sn^{2+}
 - One of the reactants MUST be listed as a product in the reduction $\frac{1}{2}$ reactions
 - When we reverse that reaction, we get redox and the proper reactants.



Potentiometric Titration

- At every point *except one* along the titration curve, we will have enough information to calculate the $\frac{1}{2}$ cell potential from either the titrant or analyte
 - Before the equivalence point, the analyte is in excess
 - After the equivalence point, the titrant is in excess

Potentiometric Titration

- At the equivalence point

$$E_{\frac{1}{2}} = \frac{n_c E_c^O + n_a E_a^O}{n_c + n_a}$$

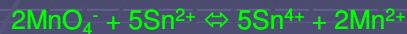
- This equation will work ONLY if
 - No pH dependence OR
 - pH = 0
- Will not work with non 1:1 stoichiometry between the oxidized and reduced forms in the $\frac{1}{2}$ reaction
 - $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

Potentiometric Titration

- Consider the titration of 50.0 mL of 0.050 M Sn^{2+} with 0.020 M MnO_4^- (assume $[\text{H}^+] = 1\text{M}$)
 - Before the equivalence point
 - Sn^{2+} is in excess
 - $\frac{1}{2}$ reaction – $\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$
 - Note that the $\frac{1}{2}$ reaction is shown as a reduction for purposes of calculation using the Nernst equation.
 - After the equivalence point
 - MnO_4^- is in excess
 - $\frac{1}{2}$ reaction – $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

50.0 mL of 0.050 M Sn^{2+} with
0.020 M MnO_4^- ($[\text{H}^+] = 1\text{M}$)

After 10.00 mL of titrant is added:



I	0.20	2.50	0	0
Δ	-0.20	-0.50	+0.50	+0.20
F	~0	2.00	0.50	0.20

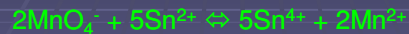
Using $\text{Sn}^{4+} + 2\text{e}^- \rightarrow \text{Sn}^{2+}$

$$E = 0.154 - (0.05916/2) * \log[(2.00/60)/(0.50/60)]$$

$$E = 0.136 \text{ V}$$

50.0 mL of 0.050 M Sn^{2+} with
0.020 M MnO_4^- ($[\text{H}^+] = 1\text{M}$)

After 50.00 mL of titrant is added:



I	1.00	2.50	0	0
Δ	-1.00	-2.50	+2.50	+1.00
F	~0	~0	2.50	1.00

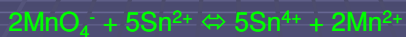
Equivalence Point

$$E = [(5*1.51) + (2*0.154)] / (5+2)$$

$$E = 1.12 \text{ V}$$

50.0 mL of 0.050 M Sn^{2+} with
0.020 M MnO_4^- ($[\text{H}^+] = 1\text{M}$)

After 70.00 mL of titrant is added:



I	1.40	2.50	0	0
Δ	-1.00	-2.50	+2.50	+1.00
F	0.40	~0	2.50	1.00

Using $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$

$$E = 1.51 - (0.05916/5) * \log[(1.00*120) / (0.40/120)(1^8)]$$

$$E = 1.31 \text{ V}$$