CH 302 – Unit 5 Review 2

ELECTROCHEMICAL APPLICATIONS, NON-STANDARD CELLS

ECIS is open (course instructor surveys)

Please do mine + comment

They are funny

And make me happy ☺

Unit 5 Outline: Electrochemistry

I. Understand fundamental redox reactions
   - Balancing redox reactions
   - Assigning oxidation numbers
   - Identifying the roles of the different species in the reaction

II. Combine half-reactions into standard cells (voltaic and electrolytic)
   - Important: Electrolytic applications (electrolysis and electroplating)

III. Apply the concepts of electrochemical cells to non-standard conditions
   - Concentration Cells
   - Nernst Potential

IV. Complete the storylines of thermodynamics and equilibrium by converting electrical potential into K and ΔG.

V. Common applications of batteries
   - Primary and secondary cells
   - Fuel Cells

Unit 5 Equations

$\frac{\text{moles } e^-}{\text{mol product}}$

1. Electrochemical Cell Potential

$$\varepsilon^\circ_{cell} = \varepsilon^\circ_{cathode} - \varepsilon^\circ_{anode}$$

2. Faraday's Law, plating a metal, electrolysis

$$\frac{I \cdot t}{n \cdot F} = \text{moles created}$$

$\frac{\text{mole } e^-}{\text{rxn}}$

3. Convert between electrical potential (ε) and free energy/ maximum electrical work (ΔG)

$$\Delta G = -nF\varepsilon \qquad \Delta G^\circ = -nF\varepsilon^\circ$$

4. Convert between electrical potential (ε) and the equilibrium constant (K)

$$\varepsilon^\circ = \frac{RT}{nF}\ln K \qquad \boxed{\varepsilon^\circ = \frac{0.05916}{n}\log K}$$

5. Non-standard Cell Potential

$$\cancel{\varepsilon = \varepsilon^\circ - \frac{RT}{nF}\ln Q} \qquad \boxed{\varepsilon = \varepsilon^\circ - \frac{0.05916}{n}\log Q}$$

Electrochemical Cell Definitions

1. **Anode**: the site of oxidation (An Ox) ; gives electrons to the wire
2. **Cathode**: the site of reduction (Red Cat) ; takes in electrons from the wire
3. Voltage: the difference in potential per unit charge (J/C or V); a measurement of the “pulling power” on the electrons
4. **Voltaic Cell (Galvanic Cell)**: an electrochemical cell with a positive standard cell potential ; the redox reaction of the cell occurs without an external power source (spontaneous) ; $\varepsilon^\circ_{cathode} > \varepsilon^\circ_{anode}$ (reduction potentials)

   work is done by system

   $\Delta G < 0$

   $\varepsilon^\circ > 0$

   $K > 1$

5. **Electrolytic Cell:** an electrochemical cell with a negative standard cell potential ; the redox reaction of the cell relies on an external power source (non-spontaneous) $\varepsilon^\circ_{cathode} < \varepsilon^\circ_{anode}$ (reduction potentials)

   work is done on system

   $\Delta G > 0$

   $\varepsilon^\circ < 0$

   $K < 1$

6. Shorthand Notation:

   anode|anodic solution ||cathodic solution | cathode

The Electrochemical Cell Summary

	voltaic cells	electrolytic cells
free energy, Δ*G*	negative (–)	positive (+)
potential, *E*	positive (+)	negative (–)
push/pull of electrons	from the chemical reactions of the two half-reactions	from an external electrical power source
anode	negative (–)	positive (+)
cathode	positive (+)	negative (–)

In **all** electrochemical cells, the electrons travel from the site of oxidation (anode) to the site of reduction (cathode). The main difference is that voltaic cells are spontaneous cells, **where the redox reaction drives the current**. In an electrolytic cell, the redox reaction is non-spontaneous. **Therefore, the push/pull of current is driven by an external power source.**

Conceptual Summary: Standard Cells

STD. Electrical Potential ε°	Free Energy ΔG°	Equilibrium Constant K	Spontaneous?
Positive	Negative	Greater than 1	Yes
Negative	Positive	Less than 1	No
Zero	Zero	Equal to 1	At Equilibrium

↑ Concentration Cell

Tough Shorthand Notation

anode | anodic solution || cathodic solution | cathode

$\mathrm{Al} | \mathrm{Al^{3+}} || \mathrm{Cu^{2+}} | \mathrm{Cu}$

$\mathrm{Pt} | \mathrm{H_2} | \mathrm{H^+} || \mathrm{Cu^{2+}} | \mathrm{Cu}$

$\mathrm{Al} | \mathrm{Al^{3+}} || \mathrm{Cr^{3+}}, \mathrm{Cr^{2+}} | \mathrm{C\ (graphite)}$

$\mathrm{Ag} | \mathrm{Ag^+} || \underbrace{\mathrm{Cl^-\ (aq)} | \mathrm{AgCl\ (s)} | \mathrm{Ag\ (s)}}$

$e^- + \mathrm{AgCl} \rightarrow \mathrm{Ag} + \mathrm{Cl^-}$

← reduction table

Faraday's Law

Two common applications of electrolytic cells are electroplating and electrolysis

Here our "n" value represents the moles of electron in the half-reaction that produces the desired product

$$\frac{C}{S} \leftarrow A \qquad\qquad S$$

$$\frac{\overset{A}{I}\cdot \overset{S}{t}}{n\cdot F} = \underline{\text{moles created}} = \frac{\text{charge applied}}{\text{charge per mol product}}$$

$$n\cdot F \rightarrow \frac{\text{moles } e^-}{\text{mol prod}} \times \frac{C}{\text{mol } e^-}$$

Exam Question

What is the mass of aluminum (Al, 26.98 g/mol) formed when 18 A is run through the following cell for 8.0 hours?

$$\cancel{\mathrm{Cu}|\mathrm{Cu}^{2+}||}\,\mathrm{Al}^{3+}|\ \mathrm{Al}$$

$$\mathrm{Al}^{3+} + 3e^- \longrightarrow \mathrm{Al}$$

$n = 3$

$$\frac{d \times t}{n \times F} = \frac{18 \times (8 \times 60 \times 60)}{3 \times 96485}$$

$= 1.79$ mol Al

$\times\, 26.98$ g/mol

$= 48$ g

$* \; PV = nRT \; *$

→ 273.15 K
1 atm

$$\frac{I \times t}{n \cdot F} = mol\ Cl_2$$

Electrolysis Question

What is the volume of $Cl_2(g)$ produced at STP by the electrolysis of concentrated sodium chloride if 7.00 A are passed through the solution for 6 hours? The reaction is shown below:

$$V = \frac{0.7835 \times 0.08206 \times 273.15}{1}$$

2~~Na~~$Cl(aq)$ ~~$+ 2H_2O(l)$~~ $\rightleftharpoons$ ~~$2NaOH(aq) + H_2(g)$~~ $+ Cl_2(g)$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$V = 17.56\ L$

$$\frac{7 \times (6 \times 60 \times 60)}{2 \times 96485} = 0.7835\ mol$$

Free Energy and Electrical Work

1. **There is a simple relationship between free energy and electrical potential:**

$$\Delta G = -\overbrace{nF}^{\left(\frac{\text{charge}}{\text{rxn}}\right) \times \left(\frac{J}{C}\right)}\mathcal{E}$$

2. **This equation can be applied to tell us about the capacity for an electrochemical system to do work:**

$$\underline{w = -q \cdot \mathcal{E}}$$

3. These values are ideal, meaning we are calculating the maximum electrical work, **or the maximum reversible non-expansion work.**

4. **This relationship provides an effective way of determining the capacity for a chemical system to do work when we do not have a change in gas moles (no change in volume)**

Electrochemical Work

Consider the following cell at standard conditions (E˚ = 0.75 V) :

$$\underbrace{Al | Al^{3+}}_{3e^-} || \underbrace{Cr^{2+} | Cr}_{2e^-} \Big\} 6e^-$$

What is the value of ΔG˚? Is work done on the system or being applied to the system?

$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

$$-434182.5\ J = -6 \times 96485 \times 0.75$$

$$\hookrightarrow -434\ kJ$$

by system

$\Delta G < 0,\ \mathcal{E}^\circ > 0,\ K > 1$

Electrical Potential and Equilibrium

Now that we know the relationship between electrical potential and free energy:

$$\Delta G^\circ = -nF\mathcal{E}^\circ \quad = \quad \Delta G^\circ = -RT\ln K$$

We can very clearly connect the dots between free energy and the equilibrium constant, K:

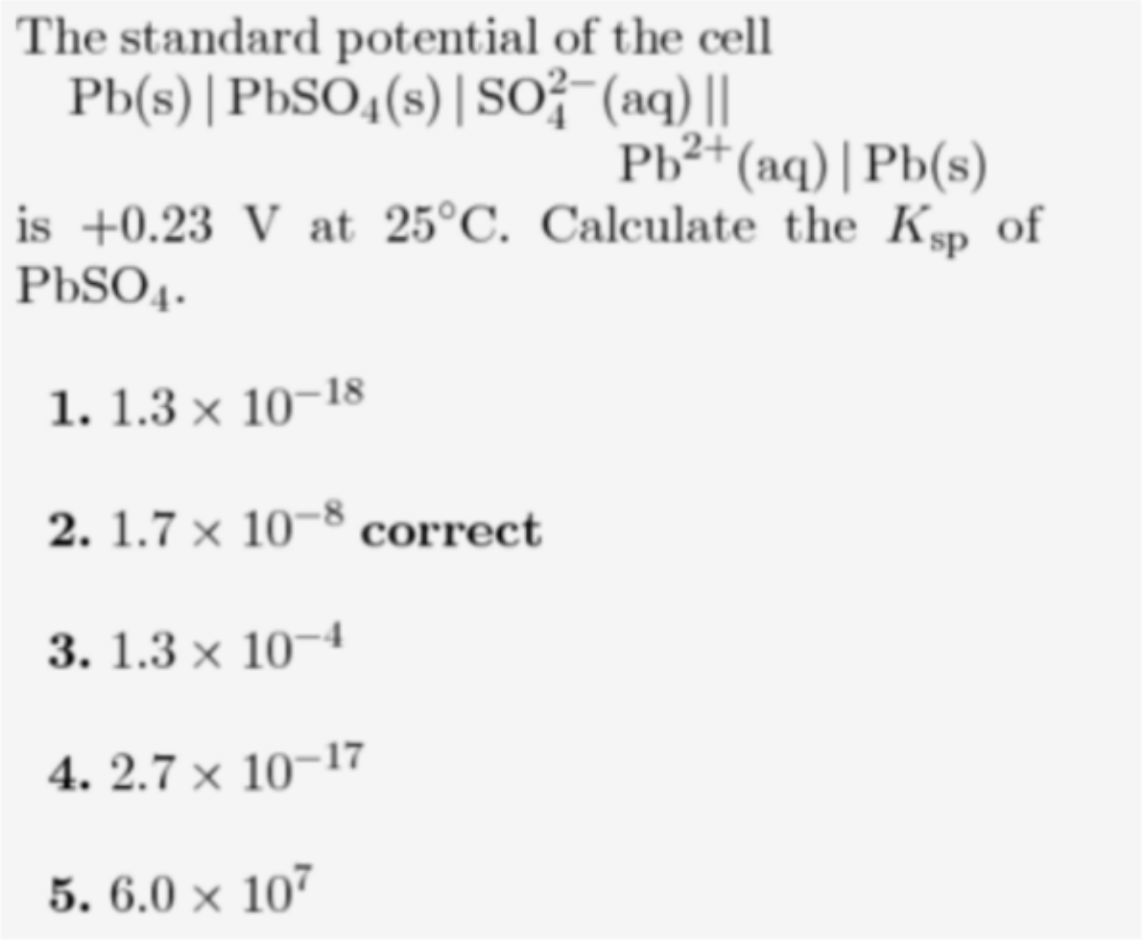
$$\mathcal{E}^\circ = \frac{RT}{nF}\ln K$$

$$\underbrace{\mathcal{E}^\circ = \frac{0.05916}{n}\log K}$$

Equilibrium Calculations

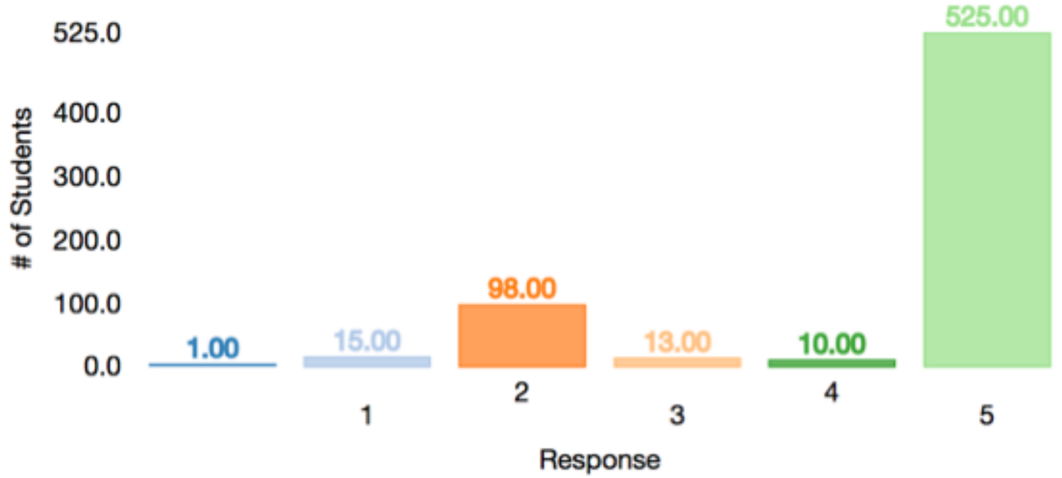
$$10^{\frac{0.23\times n}{0.05916}} = K$$

$$= 6\times 10^{7}$$



The standard potential of the cell
$Pb(s)\,|\,PbSO_4(s)\,|\,SO_4^{2-}(aq)\,||\,Pb^{2+}(aq)\,|\,Pb(s)$
is +0.23 V at 25°C. Calculate the K_{sp} of $PbSO_4$.

1. 1.3×10^{-18}
2. 1.7×10^{-8} **correct**
3. 1.3×10^{-4}
4. 2.7×10^{-17}
5. 6.0×10^{7}



$$\mathcal{E}^\circ = \frac{0.05916}{n}\log K$$

$PbSO_4 \rightarrow Pb^{2+} + SO_4^{2-}$

Equilibrium Calculations

The standard potential of the cell

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is +0.23 V at 25°C. Calculate the K_{sp} of $PbSO_4$.

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[✓ 2.] 1.7×10^{-8} **correct**
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5. 6.0×10^{7}

$\cancel{Pb} + SO_4^{2-} \rightarrow PbSO_4 + \cancel{2e^-}$

$Pb^{2+} + \cancel{2e^-} \rightarrow \cancel{Pb}$

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

Non-Standard Cells Electrical Potential

You can use Q to determine the non-standard potential with the Nernst Equation:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF}\ln Q$$

OR:

$$\boxed{\mathcal{E} = \mathcal{E}^\circ - \overbrace{\frac{0.05916}{n}}^{\text{adjustment to std conditions}}\log Q}$$

Remember how Q works (and remember that Q depends only on aqueous and gaseous species!):

- Q is the given concentrations (or pressures) of the products raised to the power of their coefficients divided by the reactants raised to the power of their coefficients.
- If you add product, your voltage drops
- If you add reactant, your voltage increases

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.05916}{n}\log \underline{\underline{Q}}$$

Non-Standard Cell Potential

Consider the following cell at standard conditions:

$Pb(s)\ |\ PbSO_4(s)\ |\ SO_4^{2-}\ ||\ H^+(aq)\ |\ H_2(g)\ |\ Pt$

How does each of the following change the voltage:

I. Increase partial pressure of hydrogen $Q\uparrow,\ \mathcal{E}\downarrow$

II. Add sodium sulfate to the anode compartment $Q\downarrow,\ \mathcal{E}\uparrow$

III. Decrease the pH $pH\downarrow\ [H^+]\uparrow\ Q\downarrow,\ \mathcal{E}\uparrow$

$$Q = \frac{P_{H_2}}{[SO_4^{2-}][H^+]^2}$$

Overview Question

Suppose you create a battery out of nickel and cadmium with the following half-reactions:

$\hookrightarrow (+)$

$Cd^{2+} + 2e^{-} \rightarrow Cd$ -0.40V

$Ni^{2+} + 2e^{-} \rightarrow Ni$ -0.23V

$$Cd \rightarrow Cd^{2+} + 2e^{-}$$
$$Ni^{2+} + 2e^{-} \rightarrow Ni$$
$$\overline{Cd + Ni^{2+} \rightarrow Ni + Cd^{2+}}$$

What are the values of 1) E°, 2) ΔG°, and 3) K?

What is the ratio of Cd^{2+} : Ni^{2+} when your battery reaches equilibrium?

$$\mathcal{E}^{\circ}_{cell} = \mathcal{E}^{\circ}_{cat} - \mathcal{E}^{\circ}_{an}$$

1) $+0.17V = -0.23V - (-0.40V)$

$$\Delta G^{\circ} = -nF\mathcal{E}^{\circ}$$

2) $-32804J = -(2)(96485)(0.17) \longrightarrow -32.8\,kJ$

$$\mathcal{E}^{\circ} = \frac{0.05916}{n}\log K = \frac{RT}{nF}\ln K$$

3) $10^{\frac{0.17 \cdot 2}{0.05916}} = 5.6 \times 10^{5}$

@ EQ when

$Q = K$

$$\frac{Cd^{2+}}{Ni^{2+}} = Q$$

OR solve.....

$$\cancel{\mathcal{E}} = \mathcal{E}^{\circ} - \frac{0.05916}{n}\log Q$$
$=0$

$$E = E^{\circ} - \frac{0.05916}{n} \log Q \qquad Q = \frac{P_{H_2}}{[SO_4^{2-}][H^+]^2}$$

Non-Standard Calculations

If E° for the following cell is 0.36 V at 25°C, what is the value of E for the conditions given:

$Pb(s)\ |\ PbSO_4(s)\ |\ SO_4^{2-}(aq,\ 0.60\ M)\ ||\ H^+(aq,\ 1.6\ M)\ |\ H_2(g,\ 0.08\ atm)\ |\ Pt$

$$0.40V = 0.36V - \frac{0.05916}{2} \log \frac{0.08}{0.6 \times 1.6^2}$$

The Concentration Cell

A concentration cell is simply a cell that has identical half-reactions and achieves a positive cell potential by having a favorable Q-value in the Nernst Equation.

$$reduction: \mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu}\ (0.34\mathrm{V})$$

$$oxidation: \mathrm{Cu} \rightarrow Cu^{2+} + 2e^-(\text{-}0.34\mathrm{V})$$

$$\varepsilon^\circ_{\text{cell}} = \varepsilon^\circ_{\text{reduction}} + \varepsilon^\circ_{\text{oxidation}}$$

$$\varepsilon^\circ_{\text{cell}} = 0\mathrm{V}$$

$$\mathrm{Cu}^{2+} + \mathrm{Cu} \rightarrow \mathrm{Cu}^{2+} + \mathrm{Cu}$$

$$\mathcal{E} = \underset{=0}{\cancel{\mathcal{E}^\circ}} - \frac{0.05916}{n}\log Q$$

$$\frac{[\mathrm{Cu}^{2+}]_{\text{anode}}}{[\mathrm{Cu}^{2+}]_{\text{cathode}}}$$

The Concentration Cell

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$$\varepsilon^{\circ}_{\mathrm{cell}} = \varepsilon^{\circ}_{\mathrm{reduction}} + \varepsilon^{\circ}_{\mathrm{oxidation}}$$

$$\varepsilon^{\circ}_{\mathrm{cell}} = 0\mathrm{V}$$

$$\mathcal{E} = \underset{=0V}{\cancel{\mathcal{E}^{\circ}}} - \frac{0.05916}{n}\log Q$$

You can maximize ε by minimizing Q:

1. Increasing the concentration of Cu^{2+} in the cathode compartment
2. Decreasing the concentration of Cu^{2+} in the anode compartment

$$\mathcal{E} = \mathcal{E}^\circ - \frac{0.05916}{n}\log Q$$

$2H^+ + 2e^- \to H_2$

$H_2 \to 2H^+ + 2e^-$

Concentration Cell Question

An electrochemical cell is created out of two SHE compartments (shown below). What is the pH of the anode compartment if the measured potential is 0.12 V?

Pt | H_2 (1 atm)| H^+ (???) || H^+ (1M)| H_2 (1 atm)| Pt

$$0.12V = 0 - \frac{0.05916}{\cancel{2}}\log[H^+_{anode}]^{\cancel{2}}$$

$$\frac{0.12V}{0.05916} = -\log[H^+] = pH = 2.03$$

$$pH = -\log[H^+], \quad \log x^2 = 2\log x$$