

Unit 4: Review 3

FARADAY'S LAW, FREE ENERGY, EQUILIBRIUM, NON-STANDARD CELLS

Equations for today

1. Faraday's Law, plating a metal

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

2. Convert between electrical potential (\mathcal{E}) and free energy (ΔG)

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

3. Convert between electrical potential (\mathcal{E}) and the equilibrium constant (K)

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

4. Non-standard Cell Potential

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

Faraday's Law

Last week we said that electrolytic cells can be very important to create a metal from its ions.

- We can run an electrolytic cell by inputting voltage with a power source
- In an experimental setting, it's more reasonable to calculate the amount of moles using current, time, and a little bit of information about the overall reaction (number of moles, Faraday's constant):

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

Exam Question

What is the mass of lead formed when 18 A is run through the following cell for 8 hours?



Homework Question

What is the volume of $\text{Cl}_2(\text{g})$ produced at STP by the electrolysis of concentrated sodium chloride if 7.00 A are passed through the solution for 6 hours?



Free Energy and Electrical Work

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

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

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

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

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)

Electrical Potential and Equilibrium

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

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

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

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

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

Non-Standard Cells Electrical Potential

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

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln Q \quad \text{OR:} \quad \mathcal{E} = \mathcal{E}^\circ - \frac{0.05916}{n} \log Q$$

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

Homework Question

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



Homework Question

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




What are the values of E° , ΔG° , and K ?

What is the ratio of $\text{Cd}^{2+} : \text{Ni}^{2+}$ when your battery dies?

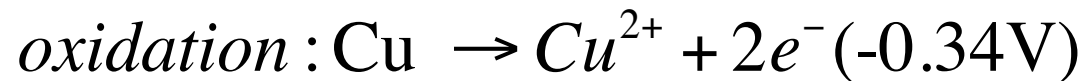
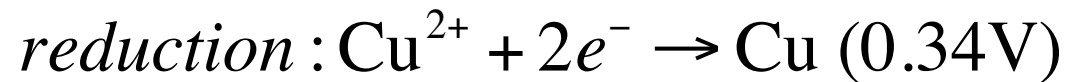
Conceptual Summary: Standard Cells

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

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.



$$\begin{aligned}\epsilon^{\circ}_{\text{cell}} &= \epsilon^{\circ}_{\text{reduction}} + \epsilon^{\circ}_{\text{oxidation}} \\ \epsilon^{\circ}_{\text{cell}} &= 0\text{V}\end{aligned}$$

$$\epsilon = \cancel{\epsilon^{\circ}}_{=0\text{V}} - \frac{0.05916}{n} \log Q$$

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

$$\frac{\text{Amps} \cdot \text{s}}{n \cdot F} = \text{moles created}$$

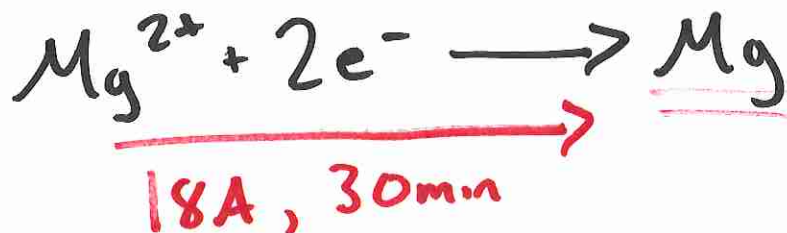
$$n \cdot F$$

moles e^- 96485

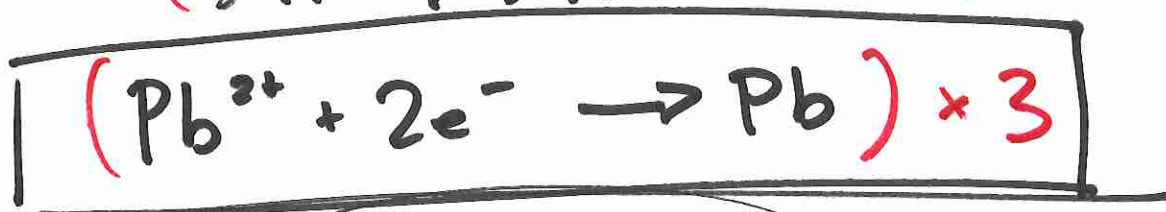
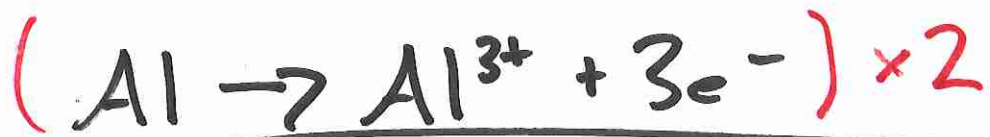
Usually interchangeable

$$\frac{\left(\frac{C}{s}\right) \cdot (s)}{\left(\frac{\text{moles } e^-}{\text{rxn}}\right) \cdot \left(\frac{C}{\text{mole } e^-}\right)} = \text{rxns run}$$

Example



$$\frac{18 \cdot (60 \cdot 30)}{2e^- \cdot (96485)} = \underline{\underline{1.7 \text{ moles}}}$$



$6e^{-}$ total

$$\frac{18 A \cdot (60 \cdot 60 \cdot 8)}{6e^{-} \cdot 96485} = \underline{\underline{0.90 \text{ reactions run}}}$$

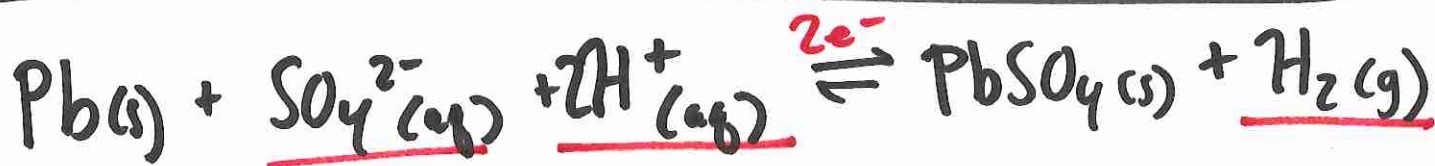


$$\textcircled{1} \quad 0.90 \text{ reactions} \times \frac{3 \text{ mols Pb}}{\text{reaction}} = \underline{\underline{2.70 \text{ mols Pb}}}$$

$$\textcircled{2} \quad \frac{18 A \cdot (60 \cdot 60 \cdot 8)}{2e^{-} \cdot 96485} = \underline{\underline{2.69 \text{ mols Pb}}}$$

$$2.69 \text{ mols} \times 207.2 = \boxed{556.6 \text{ g}}$$

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



$$Q = \frac{P_{\text{H}_2} \rightarrow \text{atm}}{[\text{SO}_4^{2-}] [\text{H}^+]^2 \rightarrow M}$$

$$n = 2$$

$$\xi^{\circ} = 0.36 \text{ V}$$

$$\xi = 0.36 \text{ V} - \left(\frac{0.05916}{2} \right) \log \left(\frac{0.08}{0.6 \cdot (1.6)^2} \right)$$

$$= 0.40 \text{ V}$$

Battery: $\mathcal{E}^{\circ} > 0$

$$\mathcal{E}_{\text{cell}}^{\circ} = \mathcal{E}_{\text{cathode}}^{\circ} - \mathcal{E}_{\text{anode}}^{\circ}$$

(+)

↑

more positive

↑

more negative

$$\boxed{0.17\text{V} = -0.23 - (-0.40)}$$



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

$$\boxed{-33\text{kJ} =}$$

$$\frac{2e^{-} \cdot 96485 \cdot 0.17}{1000}$$

$$\mathcal{E}^{\circ} = \frac{0.05916}{n} \log K, \quad K = 10^{\frac{\mathcal{E}^{\circ} \cdot n}{0.05916}}$$

$$\boxed{= 5.6 \times 10^5}$$

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

↓
↓
↓
↓

0V
0.17V
=2

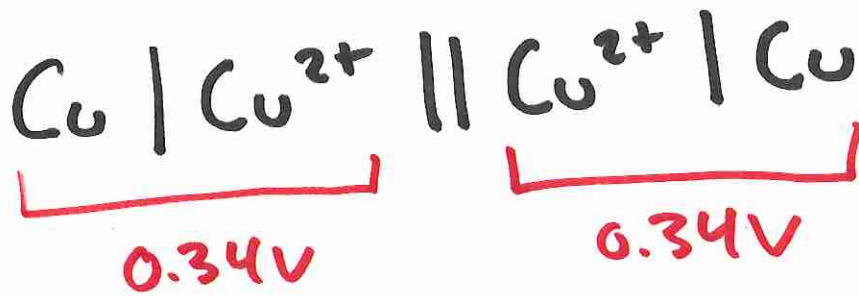
$$0.17V = \frac{0.05916}{2} \log Q$$

$$\frac{0.17 \cdot 2}{0.05916} = \log \frac{[Cd^{2+}]}{[Ni^{2+}]}$$

$$10^{\frac{0.17 \cdot 2}{0.05916}} = Q$$

$$= 5.6 \times 10^5$$

Dead = @ equilibrium



$$\xi^{\circ} = 0$$

$$\xi = \cancel{\xi^{\circ}} - \frac{0.05916}{n} \log Q$$

\downarrow
 0V

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

