

# Electrochemistry

## CHEM 361A: Introduction to Physical Chemistry

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Lecture 14

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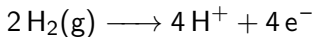
Learning Objective: Define electrochemical reactions and predict which direction is the spontaneous reaction.

References:

- Atkins and de Paula Focus 5I and 5J
- Chang Chapter 10

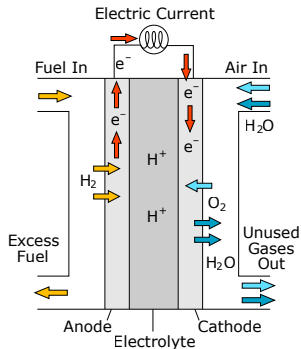
# Electrochemical Reactions

An example of an electrochemical reaction is



These free electrons can then move through a circuit. Therefore, electrochemical reactions **convert chemical energy to electrical energy**. The amount of energy produced by an electrochemical cell is quantified by the Gibbs Free Energy of the reaction:

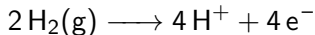
$$W_{no \text{ expansion}} = \Delta G$$



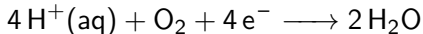
# Electrochemical Reactions

To complete the circuit, there must be a place where the electrons originate and a place they are used.

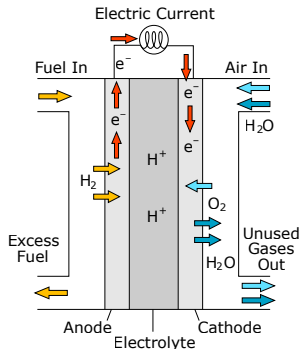
- The **anode** is where electrons are produced (oxidation)



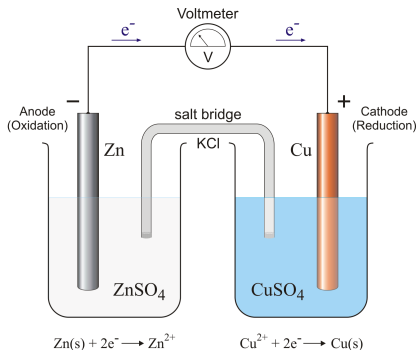
- The **cathode** is where the electrons are used (reduction)



If  $\Delta G < 0$  for these two coupled reactions, then electrical work occurs spontaneously.

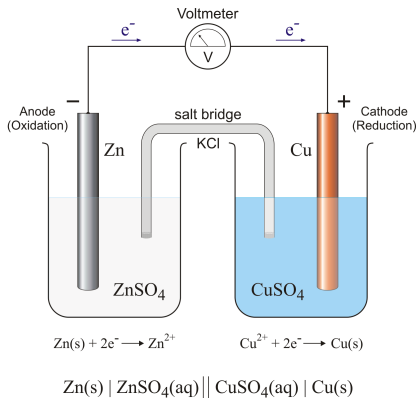


## Daniell Cell



A type of voltaic cell is called a **Daniell Cell**. This setup has an anode and cathode in an electrolyte solution connected by a salt bridge. When the anode and cathode is connected with a wire, electrons will flow from the anode to the cathode.

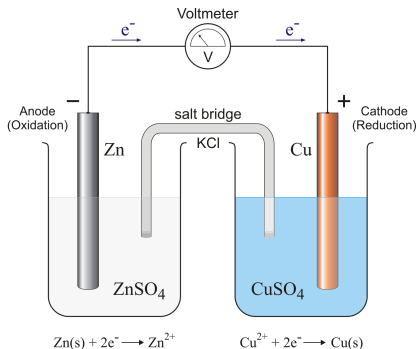
# Daniell Cell Diagram



The Daniell Cell Diagram is given at the bottom of the figure.

- Single vertical lines denotes phase boundaries
- Double vertical lines denote the salt bridge
- The anode side is on the left
- The cathode side is on the right

## Daniell Cell - Electromotive Force



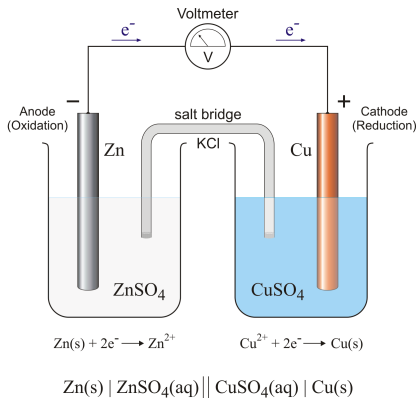
The **electromotive force** ( $E$ ) of the reaction is measured in volts by the voltmeter. The amount of work produced by the cell is the amount of charge moving through the circuit times the potential difference the charges move through. So

$$w = -n \cdot 1.6022 \times 10^{-19} \text{ C} \cdot 6.022 \times 10^{23} \text{ mol}^{-1} \cdot E$$

$$w = -n(96500)E$$

$$w = -nFE$$

# Daniell Cell - Gibbs Free Energy



Recall that  $w_{no\ expansion} = \Delta G$   
therefore

$$\Delta G = -nFE$$

where

- $F$  is Faraday's Constant ( $96500\ \text{C mol}^{-1}$ )
- $n$  is the number of moles of electrons transferred
- $E$  is the electromotive force in volts



# Nernst Equation

Given that there is a direct link between the electromotive force and the Gibbs Free energy we can write

$$\begin{aligned}\Delta G &= \Delta G^{\ominus} + RT \ln Q \\ \frac{\Delta G}{-nF} &= \frac{\Delta G^{\ominus}}{-nF} + \frac{RT}{-nF} \ln Q \\ E &= E^{\ominus} - \frac{RT}{nF} \ln Q\end{aligned}$$

This is the **Nernst Equation**. It represents a more convenient way to determine the spontaneous direction of an electrochemical reaction as it requires a measurement of the electromotive force instead of Gibbs Free Energy.

# Determining $E^\ominus$

Using the Zinc-Copper Daniell Cell reaction



The two half-cell reactions with their standard potentials (taken from a table) are

- Anode:  $\text{Zn(s)} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$   $E^\ominus = 0.7618 \text{ V}$
- Cathode:  $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu(s)}$   $E^\ominus = 0.3419 \text{ V}$

Therefore, the  $E^\ominus$  for the complete reaction is

$$E^\ominus = 0.7618 + 0.3419 = 1.1037 \text{ V}$$

The standard change in Gibbs Free Energy is

$$\Delta G^\ominus = -nFE^\ominus = -2(96500)(1.1037) = -2.13 \times 10^5 \text{ J mol}^{-1}$$

So the spontaneous direction of the electrons to flow is from Zn (anode) to Cu (cathode).

# Summary

- The electromotive force is the potential difference which moves electrons around a circuit.
- This voltage arises from the two half cell reactions and can be used to calculate the  $\Delta G$  of the combined chemical reaction
- The Nernst Equation

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

can be used to calculate the actual electromotive force from a given mixture of reagents through the reaction quotient.