

**General Chemistry 1412**  
**Spring 2008**  
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## Lecture Notes

### Chapter 21 (21.1-21.25)

#### Suggested Problems ()

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## Introduction

Electrochemistry deals with chemical reactions produced by electric current and chemical reactions producing electricity.

There are two main types of electrochemical reactions;

**Electrolytic cells**, where electricity from an external source causes a nonspontaneous chemical reaction.

**Voltaic cells**, where a spontaneous chemical reaction produces electricity and can be directed toward an external circuit.

Recall the **definition of electricity is literally the flow of electrons**. So every time you plug in your iPod or cell phone to charge electrons are flowing!!

*All electrochemical reactions involve the transfer of electrons and are Reduction-Oxidation (Redox) reactions!!*

Let's take a minute to review Redox reactions, how to identify which compounds are being reduced and which are being oxidized, the reducing agents and oxidizing agents, and direction of electron flow.

## Electrical Conduction

Now let's apply this to a cell.

## Electrodes

*The cathode is defined as the electrode at which reduction occurs (electrons are gained).*

*The anode is defined as the electrode at which oxidation occurs (electrons are lost).*

Here is the confusing part...either electrode can positive or negative!!

Also, the electrodes may or may not participate in the reaction!!

## Electrolytic Cells

Nonspontaneous chemical reactions (reactant favoring) occurring when electrical energy is applied are called **electrolysis**.

The electrodes are often inert in electrolysis so they do not become involved in the reaction taking place.

### **The electrolysis of sodium chloride (molten)**

Solid sodium chloride (table salt) does not conduct electricity, but molten sodium chloride is an excellent conductor of electricity.

Let's draw a sodium chloride cell;

When direct current (dc) is applied a pale green gas is liberated, and a silver white metal is produced on one of the electrodes.

What is happening?

- Electrons are used on the cathode, the reduction of  $\text{Na}^+$  to  $\text{Na}$ .
- Electrons are produced on the anode, the oxidation of  $\text{Cl}^-$ .
- Electrons are thus flowing from the anode to the cathode.
- The dc source is forcing electrons to move from the positive to the negative electrode. Remember this is nonspontaneous!!

**Thus the anode is the positive cell and the cathode is the negative cell in all electrolytic cells!!**

The commercial application of this process utilizes the Downs cell in order to keep metallic sodium and gaseous chlorine from coming in contact and reacting. This is the primary method for producing metallic sodium.

### **The electrolysis of sodium chloride (aqueous)**

What if devise the same Redox reaction, but with aqueous sodium chloride instead of pure sodium chloride?

Let's draw it out.

$\text{H}_2$  gas is liberated at one electrode and the solution turns basic.

$\text{Cl}_2$  gas is liberated at the other electrode.

Let's draw the reaction.

- The overall cell produces  $\text{H}_2$  gas,  $\text{Cl}_2$  gas, and  $\text{NaOH}$ .
- The  $\text{Cl}^-$  is oxidized on the anode, which is positive.
- The  $\text{H}_2$  is reduced at the cathode, which is negative.
- The  $\text{Na}$  is a spectator ion through out the reaction.
- The dc is forcing electrons to flow from the anode to the cathode, just as in the previous example.

We will take a look at why the water is cleaved rather than the sodium reduced a little later in the chapter, as well as how to predict this in aqueous solutions.

### **The electrolysis of sodium sulfate (aqueous)**

Exposure of an aqueous solution of  $\text{NaSO}_4$  to dc electrolysis results in the direct cleavage of water to form  $\text{H}_2$  gas and  $\text{O}_2$  gas.

Let's draw the cell

Let's write out the reaction.

- Hydrogen is being reduced to form  $\text{H}_2$  gas at the cathode.
- Oxygen is being oxidized to form  $\text{O}_2$  gas at the anode.
- The  $\text{NaSO}_4$  is again a spectator molecule, aiding in the conductivity of electricity in water.

### **Coulometry and Faraday's Law of Electrolysis**

If you recall in chapter 5 of the text, we learned that Michael Faraday studied electrolysis of molecules extensively and actually quantified the relationship between amount of electricity and amount of reaction.

He concluded,

*The amount of the substance which undergoes oxidation and reduction at each electrode is directly proportional to the amount of electricity passed through the cell.*

In fact, this quantity is defined as a faraday,

*One faraday is the amount of electricity corresponding to the passage (gaining and losing) of one mole of electrons.*

Let's compare this to the coulomb (C).

The study of this relationship between amount of reaction to amount of current is called coulometry.

Let's work a problem

### **Commercial Applications**

We can see how several gases are produced electrolytically, as well as the production of group 1A and 2A metals. There is another large commercial application in electroplating metals on the surface of other object.

For example,

Now, what about cells in which chemical reactions spontaneously produce electricity....

### **Voltaic and Galvanic Cells**

These types of cell in which electricity is produced instead of required are called voltaic or galvanic cells. These are cells in which the Redox reaction produces electricity. If the two halves of the reaction are separated, requiring the electrons to flow through an external circuit, the electricity can be stored and used. We can see this in our everyday batteries.

### **The construction of voltaic cells**

Let's draw out a simplified cell.

In this case the two half reactions are kept separate until connected through a piece of wire. We can insert a voltmeter to study the potential difference, or an ammeter to measure the current flow.

*Recall that voltage is defined as the potential difference between two electrodes; a measure of the chemical potential to occur.*

*And, an ampere is a unit of electrical current,  $1C/s$ .*

In order to complete the circuit a salt bridge is added to connect the two solutions. This is a medium in which ions slowly pass.

A salt bridge must do three things;

- Allow electrical contact between the two cells.
- Prevents mixing of the two cells.
- Maintains the balance of electrons to neutrality in each half cell as ions flow in and out of each cell.

**If the solution in each half cell is 1M and 1atm for gases this is a standard cell.**

## **The zinc/copper cell**

Let's take a step back and remember a Redox reaction from Chapter 4, the addition of Zn wire to a solution of  $\text{CuSO}_4$ .

Let's write it out

Now let's take this a step further.....

What if we separate the reactants and connect them through a circuit?

Let's draw out an example, the Daniell cell

The initial voltage of the cell is 1.100V and is called the standard potential of this cell.

Let's write out each half reaction.

Recall electrons are released at the anode and consumed at the cathode.

The Zn electrode is the oxidized and is therefore the anode, in which we can expect to lose some of the mass of the electrode as Zn is oxidized to  $\text{Zn}^{2+}$  and is released into solution.

The Cu electrode is therefore being reduced and is the cathode. We can expect to see a gain in the mass of the electrode as the  $\text{Cu}^{2+}$  in solution is reduced to Cu and plates onto the electrode.

The flow through the wire is then from anode to cathode, as in all electrochemical cells. In all voltaic cells, the electrons flow spontaneously from the negative to positive electrode!!

This is tricky!!

Let's compare two simple cells,

**Electrolytic**

Electrons are being *forced* to flow from positive to negative

**Voltaic**

Electrons are *spontaneously* flowing from negative to positive

***Thus the flow is opposite for these cells!!***

## The copper/silver cell

Another example of a common voltaic cell is the Redox reaction of copper and silver. Let's draw this out.

The standard potential for this reaction is 0.462V.  
Notice the role of copper has changed, why is this?

## Standard Electrode Potentials

Recall the last two examples, the Zn/Cu cell and the Cu/Ag cell. The standard potentials were different, the Zn/Cu cell was 1.100V and the Cu/Ag cell was 0.462V. What does this difference mean?

*The magnitude of the standard potential indicates the driving force for the reaction as written, so therefore the higher the potential the greater the driving force from reactants to products.*

In order to predict this driving force we must consider the relative strengths of both the reducing agent and the oxidizing agent in the overall reaction.

## **The standard hydrogen electrode**

Because Redox reactions must work together with both reduction and oxidation occurring at the same time, we can not actually calculate the standard potential of each half cell alone.

Instead, an arbitrary standard was established using the standard hydrogen electrode (SHE).

Let's draw this cell

**The standard hydrogen electrode is arbitrarily assigned a potential of exactly 0 V.**

By using the SHE as one cell and any other standard electrode half cell, we can thus measure the voltage of the system, but since the SHE contributes 0V, the total voltage is the standard electrode potential for the other half cell.

What does the standard mean?

To keep things relative, all standard cell potentials are always presented for each half cell as the reduction partner of the reaction.

## **The zinc-SHE cell**

Let's write out the half reactions for a specific example,

Now let's draw the cells together in a circuit.

- The initial voltage reading of the cell is 0.763V.
- The mass of the Zn electrode decreases.
- Gaseous H<sub>2</sub> is produced.

Let's calculate the standard potential for this cell,

In this case the SHE is the cathode and the Zn electrode is the anode. But we agreed to write standard half cell potentials as the reduction potential...even though zinc is oxidized. So, we write the reverse reaction.

***The standard potential for the Zn half cell is thus represented as a negative number, -0.763V.***

Let's look at this a couple of different ways;

The copper-SHE cell

Another example of using a SHE to calculate the standard potential of a half cell reaction is the copper-SHE cell.

Let's draw this out.

In this case  $\text{Cu}^{2+}$  is being reduced and therefore the  $E^\circ_{\text{cell}} = 0.337\text{V}$  and is positive.  
Or written as “electron pressures”,

## **Standard electrode potentials and uses**

Many of these cells have been studied and a list of standard electrode potentials has been developed and published, see page 810.

Let's look at the table and make some general observations and correlations from the data.

## **Half reactions**

These same principles apply if the electrode is not a reactive species in the half cell, but both reactants are ions in solution with an inert electrode.

For this example, let's look back at the electrolysis of aqueous sodium chloride.

Recall the observed reaction,

Now let's compare the reduction of sodium and hydrogen using the table of standard reduction potentials.

### **Corrosion and protection**

Another useful application of the standard electrode potentials is to predict corrosion reactions. Ordinary corrosion is a Redox reaction and can be costly in our everyday lives and uses of metal objects, however one technique to protecting metals from corrosion is to look at the standard electrode potentials and choose a more reactive metal to reverse the process and act as a sacrificial metal.

For example,

## Effect of Concentration and Partial Pressures on Electrode Potentials

What if our cell solution isn't 1 M? Or our partial gas pressure isn't 1 M? Can we still calculate cell potentials for conditions deviating from standard conditions?

Of course!! We must consider first the overall reaction's energy and spontaneity (hint), and then we can incorporate different concentrations of reactants and products.

Recall, in Chapter 17 we discussed Gibbs free energy and how it related to reactions. We summarized the concept in the following equation;

Isn't an electrochemical reaction similar to those studied in Chapter 17?  
In fact standard electrode potential and Gibbs free energy are related!!

### The relationship of $E^{\circ}_{cell}$ , $\Delta G^{\circ}$ , and $K$

Since the Redox reactions we have been studying are in theory reversible and eventually come to some equilibria, it is reasonable to see there is a standard relationship between Gibbs free energy and cell potentials.

In fact, if you know one of these variables, you can calculate the other two.  
Let's work a problem.

But, we still haven't the question of *non*-standard conditions.  
Gibbs free energy gives us this relationship again.

Recall that K and Q have the same concept with different concentrations, so  
Recall, **the reaction quotient, Q**, is in the form of an equilibrium constant, but the  
concentrations are not necessarily at equilibrium. (Refer to page 667 of the text for more  
detail)

The reaction quotient is a way to measure essentially, where the reaction is in terms of  
amounts of reactants left and products formed in the reaction. Is it just starting or is it  
almost done?

The equation is

Using the reaction quotient lets us calculate the energy associated with that chemical  
reaction, at a specific concentration.

Lucky for us all of this has been studied and an equation was derived from Walther  
Nernst, a German physicist and chemist.

### **The Nernst equation**

The Nernst equation ...

**If the temperature is 25 °C, the equation becomes.**

Let's work a problem

We can also use the Nernst equation to calculate the electrode potential for half cells *not* under standard conditions.

In fact, this approach is favorable sometimes because the standard electrode potentials for many half cells are known.

If calculating a half cell electrode potential.....the equation becomes.

Let's work a problem

Let's take a look at the equation again.

We have seen how to solve for E, but what else can we do with this reaction?

This equation has very important everyday uses!! First, this is the reaction behind the pH meter.

This equation is also used to calculate the potentials across our cell membranes!! Our cell membranes utilize ion channels and the Nernst equation is used to calculate the potentials associated with those channels.

For a demonstration of this equation in relation to cell membranes check out...

<http://www.nernstgoldman.physiology.arizona.edu:80/launch/>

Also, for a Nernst equation calculator check out...

[http://www.csupomona.edu/~seskandari/physiology/physiological\\_calculators/nernst\\_potential.html](http://www.csupomona.edu/~seskandari/physiology/physiological_calculators/nernst_potential.html)

### **Determining cell concentrations**

We have just used the Nernst equation to predict the voltage (E) of a cell with known concentrations, but can we calculate the concentration from the E?

Let's write out a problem.

### **Primary Voltaic Cells**

The Redox reactions we have studied so far in this chapter have resulted in the reactants being consumed and eventually the reaction stopping. This type of cell is called a primary voltaic cell and we are familiar with the everyday application of batteries.

#### **Dry cells**

Let's draw a common battery

### **Secondary Voltaic Cells**

The secondary voltaic cell is reversible and the reactants can be regenerated. This is usually achieved by passing a current in the opposite direction of the reaction current flow. This is “recharging” the battery. This is commonly seen in automobile batteries and rechargeable batteries.

**The lead storage battery**

**The nickel/cadmium cell**

**The hydrogen/oxygen fuel cell**