

UWO **CHEM 1302**

Winter 2025, Chapter 12 Notes



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12. Voltaic Cells

12.I

12.1 Galvanic Cells

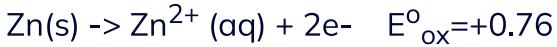
12.1.1

Galvanic/Voltaic Cells

- A galvanic cell constructed of two half cells is shown below.
- Before we take a deeper look, let's review what we already know about galvanic cells:
 - Do galvanic cells have spontaneous or non-spontaneous electron flow?
 - Is the E° positive or negative?
 - According to the equation $\Delta G^\circ = -nFE^\circ_{\text{redox}}$ then is the E°_{redox} positive or negative?
- Let's take a look at our 2 half reactions from the table again:

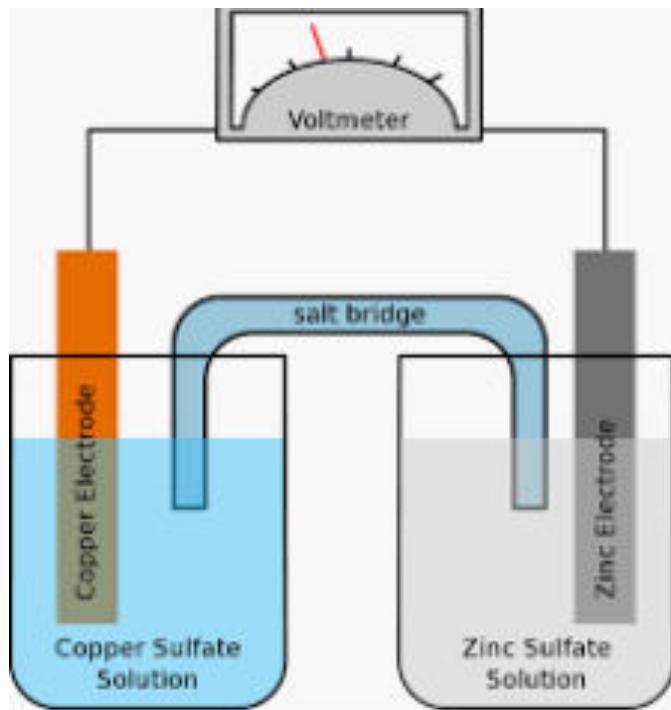


- In order to get an E°_{redox} that is positive, we needed to flip the Zn(s) equation:



$E^\circ_{\text{redox}} = 1.1\text{V}$ (you might see the E°_{cell} be referred to as the electromotive force or emf, they mean the same thing!)

Now let's label the galvanic cell...



- 1) Which is the reduction half equation and which is the oxidation half reaction?
- 2) Using the following "Wize Concept," label the anode and cathode in the above diagram.

 **WIZE CONCEPT**

The anode is always where oxidation happens.

The cathode is always where reduction happens.

There are different ways to remember this. One way is to remember that anode and oxidation both start with vowels, while cathode and reduction both start with consonants. The other way to remember this is: An Ox Red Cat! Pick your favourite way :)

3) Show where the ions are moving (into solution/onto electrode)

4) Which electrode is shrinking? Which is growing?

5) Consider the salt bridge. Let's say it's made of KCl. Which half cell would the K⁺ ions travel to? Which half cell would the Cl⁻ ions travel to?

 **WIZE CONCEPT**

Anions of the salt bridge move to the anodic solution

Cations of the salt bridge move to the cathodic solution.

This helps to complete the circuit and prevent charges from building up by keeping the solution neutral.

6) Draw the direction of electron flow.

- Analogy: Running out of your last exam! Everyone is running in the same direction and to where they want to go (outside of the school!)

 **WIZE TIP**

Since the anode is always where oxidation happens and the cathode is always where reduction happens, then electrons will always flow from the anode to the cathode!

7) Write in the charges (+ or -) for each electrode.

 **WIZE CONCEPT**

Since galvanic cells involve spontaneous electron flow, electrons will travel to where they want to go!

Electrons will always go from the anode to the cathode.

But here, since it's spontaneous flow it means that the cathode will have a positive charge (electrons want to go here) and the anode will have a negative charge (electrons want to get away from here!)

We will see how this is different for electrolytic cells...

8) Write in the spectator ions (in this case it is SO_4^{2-} , you might also see NO_3^- in other cases).

- These ions are called "spectator" ions because that's all they are doing...spectating! They don't participate in the actual reaction, but help to balance charges!

12.1.2

In a galvanic cell, oxidation occurs at the:

anode

cathode

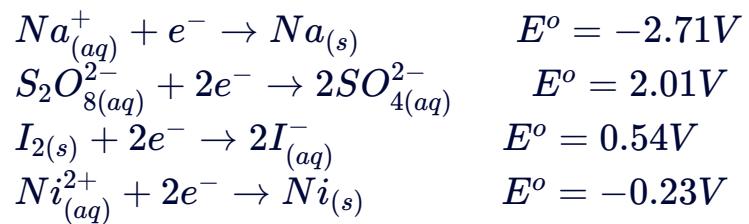
salt bridge

electrolyte

in cathodic space

12.1.3

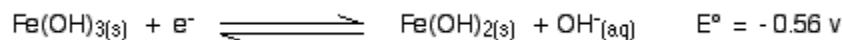
Construct a galvanic cell with the highest voltage given the following half reactions. Determine the voltage produced and express it in standard cell notation.



Will a Reaction Occur?

Will oxygen oxidise iron(II) hydroxide to iron(III) hydroxide under alkaline conditions?

The E° values are:



Will chlorine oxidise manganese(II) ions to manganate(VII) ions?

The E° values are:

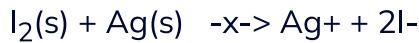


Will Zn²⁺ react with Cu(s)?



You are told that $I_2(s)$ and $Ag(s)$ do not react. Without using reduction potentials, what does this tell us about their relative reduction potentials?

Let's write out this reaction:



How could we have a reaction using the reactants and products in the above equation?



What is being oxidized and what is being reduced in our reaction?

oxidized: _____

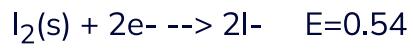
reduced: _____

What can we say about the reduction potentials?

_____ SRP > _____ SRP

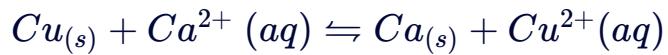
Let's check:

On SRP table it says:



12.1.5

Given the half cells below, which direction will the following reaction proceed?



12.1.6

Given the following half cells, what is the maximum voltage of a battery that could be constructed?



12.2 Cell Notation

12.2.1

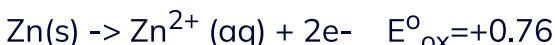
Cell Diagram

- The **cell diagram aka standard cell notation** is as follows:



If we wanted to write this notation for the galvanic cell we just drew...

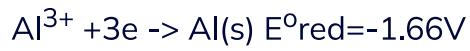
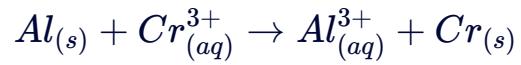
- These were the 2 half reactions that were involved:



- It can also be called **standard** cell notation because it is describing **SATP**: _____ C, _____ atm, [_____ M]
- Note that if a half cell does not contain a solid species then an inert electrode must be used. eg. $\text{Pt}_{(\text{s})}$

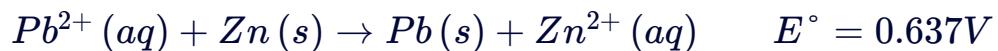
12.2.2

Write the cell notation for the voltaic (or galvanic) cell that incorporates the following redox reaction:



12.2.3

In a zinc-lead cell the reaction is:



Which of the following statements about this cell is FALSE?

The zinc electrode is the cathode

The reaction will go in the direction indicated

The shorthand notation is $Zn (s) | Zn^{2+} (aq) || Pb^{2+} (aq) | Pb (s)$

The lead electrode is positively charged

12.3 Important Equations + Nonstandard conditions (Nernst Equation)

12.3.1

Cell Potentials and Gibbs Free Energy

- Free energy (ΔG°) and cell potential (E°_{cell}) are related through the following equation:

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

ΔG° = Free energy difference between products and reactants in their standard states

n = # moles of electrons

F = Faraday constant = $96485 \frac{\text{C}}{\text{mol e}^-}$

E°_{cell} = Standard electrochemical reduction potential

** If E°_{cell} is positive, the process is spontaneous **

- Remember that ΔG° and E° are for the cell at standard conditions (1 atm for gases and 1M for solutions)

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K$$

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K$$

$$K = e^{\frac{nFE^\circ}{RT}}$$

- Under non-standard conditions we have:

$$\Delta G = \Delta G^\circ + RT \ln Q = -nFE_{\text{cell}}$$

- We can correct the E° to reflect the non-standard conditions by using the Nernst equation

$$E_{\text{cell}} = E_{\text{cell}}^0 \frac{-RT}{nF} \ln Q \text{ or } E_{\text{cell}} = E_{\text{cell}}^0 \frac{-0.05916V}{n} \log Q$$

$$R = \text{gas constant } \left(\frac{8.314J}{\text{mol K}} \right)$$

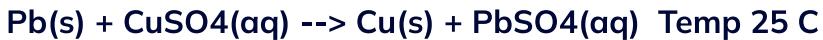
$$T = \text{temperature}$$

$n = \# \text{of electrons}$

$F = \text{Faradays Constant}$

12.3.2

Calculate the ΔG° and K_{eq} for following electrochemical cells: $\Delta G^\circ = -nFE^\circ_{cell}$ & $K_{eq} = e^{nFE^\circ/RT}$



1) From a standard reduction potential table we can find the following:



2) Let's try to solve for ΔG° first:

$$\Delta G^\circ = -nFE^\circ_{cell}$$

We know n =moles of electrons involved

Here, $n =$ _____

F is just a constant (Faraday's constant): 96500C/mole-

E°_{cell} we can calculate by using the 2 half reactions, reversing a reaction based on the overall chemical reaction, and then adding up the E° values for oxidation and reduction:

In our overall equation, when we look at the reactants, which is being oxidized and which is being reduced?

Based on this info, which equation should we reverse from the table? _____

What is the E°_{cell} (redox)=?

Now we can plug these values in and solve for ΔG° :

$\Delta G^\circ = -nFE^\circ_{\text{cell}}$

If we wanted our ΔG° to be in kJ/mol what would our answer be? _____

3) Now let's solve for K_{eq} :

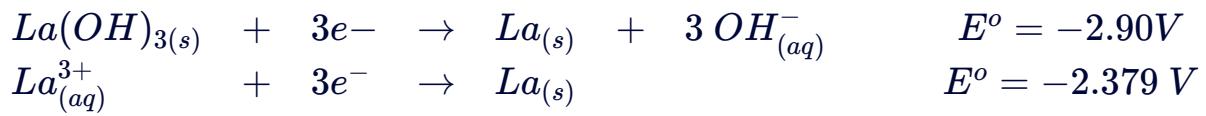
$$K_{\text{eq}} = e^{nFE^\circ/\text{RT}}$$

We already found n and E° , we know F (96500C/mole-), we know R (8.314J/molK) and the temperature is given in the question (25C=298K!) Note: These equations are used for standard conditions, so the temperature would have to be 25C or 298K!

$$K_{\text{eq}} = e^{nFE^\circ/\text{RT}}$$

12.3.3

Use the following reduction potentials to calculate the K_{sp} of $\text{La(OH)}_{3(s)}$



3.64×10^{-27}

3.56×10^{-27}

3.67×10^{-27}

3.54×10^{-27}

Cells Operating at Non-Standard Conditions: The Nernst Equation

- If we want to operate a cell at non-standard conditions (not 1 M solutions) we need to use the Nernst equation to find new electromotive force

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln Q$$

R: The ideal gas constant (8.314 J/molK)

T: Temperature (K)

n: # of electrons involved

F: The Faraday Constant (96500 C/mol e-)

E_{cell}^o : standard electromotive force

12.3.5

Determine the voltage produced in a galvanic cell at room temperature made up of the following half reactions at a pH of 3.5 and the following concentrations. $[MnO_4^-] = 0.5 \text{ M}$, $[Mn^{2+}] = 0.4 \text{ M}$, $[Sn^{4+}] = 2.0 \text{ M}$ and $[Sn^{2+}] = 0.8 \text{ M}$ $R=8.314\text{J/molK}$



Using the Nernst Equation:

$$E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln Q$$

12.3.6

At 25C, what is the potential of the following cell and what is the K_{eq} ?



1) Is the reaction occurring in standard or non-standard conditions?

If it is occurring in standard conditions --> it is asking us to solve for E_{cell}°

If it is occurring in nonstandard conditions --> it is asking us to solve for E_{cell}

2) Which equation will we use to solve this problem?

Nernst equation for non-standard conditions!

$$E = E^\circ - \frac{(RT/nF)}{\ln(Q)}$$

E is what the question is asking us to solve

E° we can calculate by using the SRP from a table

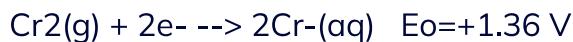
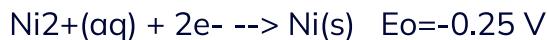
R=8.314J/molK

n=# of electrons involved in the overall reaction

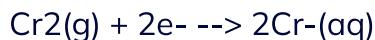
F=faraday's constant (96500C/mole-)

Q=[products]/[reactants]

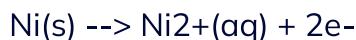
3) Solve for E_{ocell} using SRP tables:



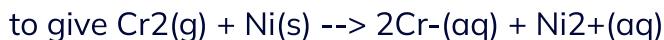
From this the standard cell reaction would be:



$E^\circ =$



$E^\circ =$



$E^\circ =$

4) Now we can determine E at non-standard conditions via the NERNST Equation:

$$E = E^\circ - \frac{(RT/nF)}{\ln(Q)}$$

Bonus: Is this reaction spontaneous or not?

5) What is K_{eq} at 298 K?

$$K_{eq} = e^{nFE_o/RT}$$