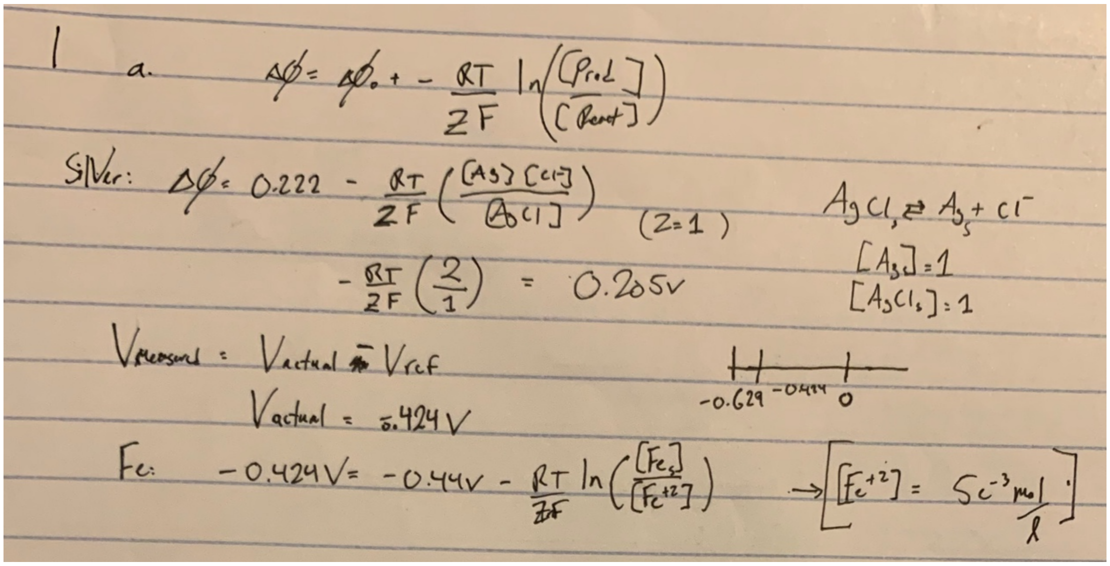
MSE 441 - Electrochemistry
Exercise Set 1
Topics regarding, Fundamental aspects and theories of electrochemistry: Electrode potential, Nernst Equation, Butler-Volmer Equation, and Pourbaix Diagrams

Question 1. Nernst Equation

The Nernst equation relates the potential difference between a material in intimate electrical contact with a solution at equilibrium. It's defined as the difference between the equilibrium potential of a material in solution at standard conditions and is historically defined in terms of the forward reduction reaction. It can be used to find the total electrochemical potential between two materials in electrical contact, such as in the case of a battery. For these questions, reference the Standard Electrode Potential tables.

A. Assume you have a nice rod of iron that you want to use a control for measuring new protective coatings. You submerge it into a 1M HCl aqueous solution and bubble in argon to remove all dissolved oxygen. Your reference electrode is a silver electrode in 2M KCl. Assume that the reaction occurring is $Fe^{2+} + e \rightleftharpoons Fe(s)$. You measure the equilibrium voltage between it and the AgCl reference electrode to be -0.629V. Find the concentration of dissolved Fe^{+2}.

A: For the silver electrode, we can set up the Nernst equation, treating the AgCl and Ag as solids with concentration as 1. We can also treat the concentration of chlorine solvated by the reference electrode as neglible compared to the concentration of chlorine from the KCl, and assume the overall concentration is 2M. Hence, we yield the Ag/AgCl potential in solution as 0.205V. Next, we subtract this potential from the measured potential and set this equal to iron's Nernst potential, -0.424V. Solving for the concentration of iron(II), you should find there to be 5e-3 mol/l Fe^{2+}, relatively high for what we assume to be the concentration of solvated species, which if unknown, is often assumed to be 1e-6 M/l.



1 a. $\Delta\phi = \Delta\phi_o + - \frac{RT}{ZF}\ln\left(\frac{[Prod]}{[React]}\right)$

Silver: $\Delta\phi = 0.222 - \frac{RT}{ZF}\left(\frac{[Ag][Cl^-]}{[AgCl]}\right)$ (Z=1)

$-\frac{RT}{ZF}\left(\frac{2}{1}\right) = 0.205v$

$AgCl_s \rightleftarrows Ag_s + Cl^-$
$[Ag_s] = 1$
$[AgCl_s] = 1$

$V_{measured} = V_{actual} - V_{ref}$

$V_{actual} = \bar{0}.424V$

-0.629 -0.424 0

Fe: $-0.424V = -0.44v - \frac{RT}{ZF}\ln\left(\frac{[Fe_s]}{[Fe^{+2}]}\right) \rightarrow \boxed{[Fe^{+2}] = 5e^{-3}\frac{mol}{l}}$

b. The first battery was the Voltaic Pile in 1794. Hence, our naming of electromotive force as voltage. Take a look at the standard electrode potential of copper (Cu) and zinc (Zn). What is the half cell, standard reduction equilibrium potential for each? Assume that the materials are in their solid forms with +2 oxidation states as per the following reaction,

$Cu^{+2} + 2e^{-} \rightleftharpoons Cu(s)$
$Zn^{+2} + 2e^{-} \rightleftharpoons Zn(s)$

A: Cu's reduction reaction is 0.34V and Zn's is -0.76V at STP.

c. You now connect them together with a wire and submerge them in solution. Assume that the concentration of both Cu^{+2} and Zn^{+2} ions to be equal. What is the equilibrium potential difference between them? What metal do you expect to be oxidized, and which one do you expect to be reduced? Compare this with the work function between the two metals.

A: First, you need to set up the overall reaction.
$Cu^{2+} + Zn \rightleftharpoons Zn^{2+} + Cu$

Next, set up the Nernst equation with the species of the products and reactants. With the concentration of all species cancelling out, you can simply take the difference between the two reduction potentials and obtain 1.1 V. Alternatively, you can infer that in connection, one of these materials will become oxidized while the other will be reduced, simply by the difference of the electronic potential. As a result, you can flip the reaction potential of one material and add the oxidation potential to the other material's reductive potential.

$V_{red} = \Delta\phi_{red,1} - \Delta\phi_{red,2}$
Or
$V_{red} = \Delta\phi_{red,1} + \Delta\phi_{oxy,2}$

We exploit the preferred oxidation of one material in connection with another all the time to prevent corrosion. In these cases, sacrificial materials called galvanic anodes are used to preferentially corrode a removable piece of metal. For instance, large boats often attach pieces of zinc, magnesium, or aluminum to prevent iron hulls from eroding. When the sacrificial material becomes fully oxidized, you can swap it out and continue to galvanically protect your system.

Comparing this with their work functions of copper and zinc, being 4.7 eV and 3.74 eV respectively, you can see that the copper is being reduced and zinc becomes oxidized and that the potential between them is 1.1eV.

D. Assume you have a platinum electrode in 1M H_2SO_4 aqueous solution and you bubble out all dissolved gasses by feeding in a stream of argon, so that only the hydrogen evolution reaction is considered. What's the amount of platinum ions that need to be solvated in order for the equilibrium potential to be equal to the solution?

A: Here, we set up our Nernst equation so that the potential difference is zero between the platinum reduction equation and hydrogen evolution reaction.
Given, $Pt^{2+} + 2e^{-} \rightarrow Pt(s)$
And $2H^{+} + 2e^{-} \rightarrow H_2\,(g)$,

First, set the platinum's Nernst equation equal to zero:

$$0 = 1.188V - RT/zF*\ln(1/[Pt^{2+}])$$

Solving for the concentration of Pt^{2+}, we find that the concentration is on the order of 10^{-44} M/liter for the highly acidic, no oxygen solution, which is in all intents and purposes basically zero. In experimental reality, there is on the order of ~thousands of solvated platinum ions needed to balance the potential.

Hence, due to how few ions become solvated to shift the electronic potential to that of its solution, this is why platinum is considered inert for most reactions! Combined with its low overpotential for evolving hydrogen gas, you can see why we use platinum in commercial electrolyzers or simply as a counter electrode.

2. Pourbaix Diagrams.
   a. Take a look at Lecture 3, slide 14. In your own words, explain the Pourbaix diagram and how to read it.

A: A Pourbaix diagram allows you to observe the stable phases of any given material as a function of pH and applied potential. It allows you to determine the stability of your material and the window of potential you can apply before you expect to chemically react with your solution.

   b. If you wanted to both evolve hydrogen and oxygen simultaneously from a two electrode system, at a basic solution of pH 12, what voltages do you need to apply on either electrode? Assume there's no dissolved gasses.

A: See Lecture 3.
Given the equations for hydrogen evolution, $E = -0.059*pH$, yielding a potential of at least -0.708V. For the oxygen evolution, $E= 1.23 – 0.059*pH$, yielding a potential of at least 0.522V.

   c. Look at $E_{rev,O2}$ line. In slide 13, we said that the equation contains a $+0.01475 \log_{10}p_{O2}$ term. We typically exclude this term because dissolved gasses are bubbled out, especially oxygen, which can induce undesirable oxidation reactions and change the equilibrium voltage we expect in our systems. Given Henry's Law, we can find the dissolution capacity of oxygen in water under STP to be 1.3×10−3 M/l*atm; what is the concentration you'd expect of oxygen in the system being exposed to the ambient atmosphere, and what is the potential needed to split water and form oxygen gas at pH 12?

A: The partial pressure of oxygen in the atmosphere is roughly 0.21 atm.

Plugging this into the Henry's Law constants table for dissolved gasses in water,
Hs = C/p

*→ 1.3e-3 (O2 mol/l*atm) * 0.21 atm O2 = 2.73e-4 M/l of O2 dissolved in water.*

$E = 1.23 – 0.059pH +0.01475 \log_{10}p_{O2} = 0.4694V$ *for the OER reaction.*

Subtracting 1.23V, the HER reaction must now reach atleast -0.7606V to form hydrogen gas.

d. Take a look at slide 15 and 16. Explain for each curve / line section why the curve either terminates or changes direction into new curve section to create the overall diagram.

A: There are three lines in the nickel diagram. The flat line corresponding to the nickel reduction reaction, and two electrolysis reactions. The first is the oxidation of nickel(s), and the other oxidizing Ni^{2+}. The first line drawn, corresponding to the dissolution of nickel is irrespective of pH and obeys only the Nernst equation. However, when the second line (green) eventually becomes more negative than this line, corresponding to the oxidation of nickel into NiO, this reaction becomes thermodynamically favored and hence forms the downward sloping line of the final diagram.

The last line drawn is the NiO / Ni(II) reaction. This line moves vertically. It uses a rate constant of 10^{12}. Because the reaction oxidizing Ni^{2+} to NiO is a 1:1 molar reaction, this equation reacts without respect to a changing ion concentration or pH. We can now solve for the pH at which this reaction occurs.

In reality, this is a simplified Pourbaix diagram. Given your solution and the presence of oxygen, there are more reactions that are possible and more possible phases that would be thermodynamically favored over what is seen here.

e. Go to the Materials Project and make an account with your EPFL email. Go to “Start Exploring Materials” and make a compound of your choice. Click on the top results and on the sidebar, navigate to “Aqueous stability.” Generate a Pourbaix and write what you see! Comment on what you see. For instance, check out SiO2. Ponder on its use as a substrate given the harsh conditions common in semiconductor fabrication processes. (Hint, H_2SO_4 and H_2O_2 form a solution called “Piranha” that is used to clean the surface of silicon wafers in between different fabrication steps. I wonder why it’s called that…)

A: Be wary of using these computational methods. While very powerful, they may be limited by their models or not be able to take in the effect of different dissolved gas concentrations. That being said, the Materials Project is a great resource if limited documentation of your system exists!

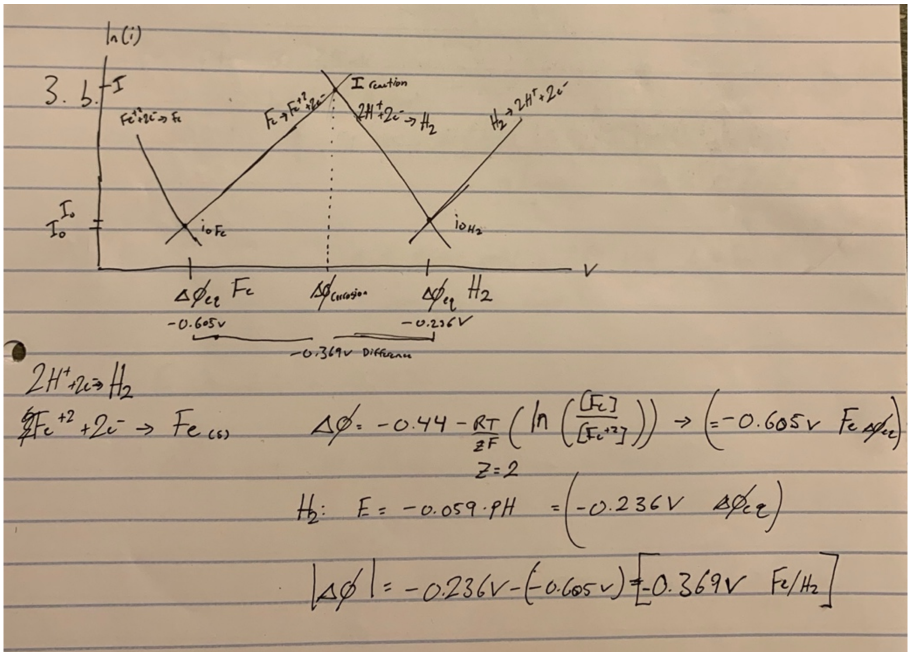
3. Butler-Volmer

a. Let’s say we have a platinum electrode and we submerge it in 1M HCl with an argon bubbler so that no oxygen is dissolved. Assume that the I_0 is 10^{-3} A/cm^2 and that the tafel slope is 35mV for the hydrogen evolution reaction. What’s the rate of reduction of the hydrogen evolution reaction at an applied overpotential of 250mV? How many liters of hydrogen per cm^2 , per hour do we evolve?

*A: the current density yields 1.26 A/cm^2. Converting amperes to electrons / second, then to mols of hydrogen formed per 2 electrons, we eventually obtain 0.0234 mol H_2 / hour * cm^2 .*

b. With the X axis as potential, and the y axis as current, draw the reduction and oxidation curves for iron and hydrogen in an oxygen free environment. Label the equilibrium potential of the solution and the equilibrium current density. Solve for the difference of equilibrium potentials. Assume that the pH is 4 and the dissolved ions of iron(II) is 1e-6 M/l.

A: given that the standard potential of iron is -0.44V, the concentration of H_2 gas produced by the reaction that can be present in the solution is 1 atm, and the pH is 4. We can set up the Nernst equation and obtain a resulting equilibrium potential difference of -0.369V.



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

$Fe^{+2} + 2e^- \rightarrow Fe_{(s)}$

$$\Delta\phi = -0.44 - \frac{RT}{zF}\left(\ln\left(\frac{[Fe]}{[Fe^{+2}]}\right)\right) \rightarrow \left(= -0.605\text{v } Fe\ \Delta\phi_{eq}\right)$$

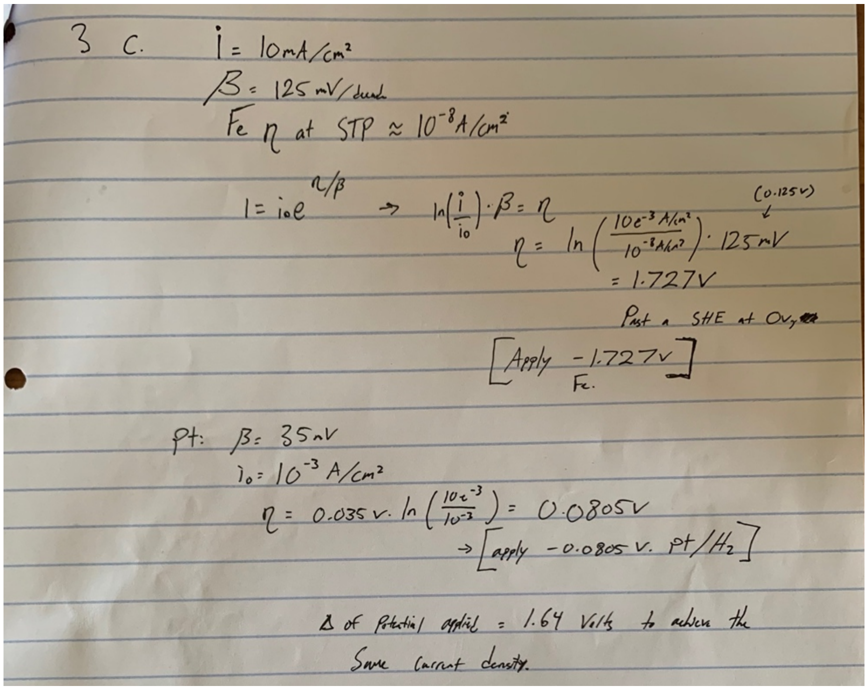
$z = 2$

$$H_2:\ E = -0.059 \cdot pH = \left(-0.236\text{V } \Delta\phi_{eq}\right)$$

$$|\Delta\phi| = -0.236\text{v} - (-0.605\text{v}) = \left[-0.369\text{v } Fe/H_2\right]$$

c. Now, how much overpotential is needed to be applied to produce a current density of 10 mA/cm^2 (of an iron electrode)? Assume the Tafel sope is 125 mV/decade. Estimate the exchange current density, I_0, from the volcano plot on slide 20 of Lecture 4. Compare this with the platinum electrode above

A: we can estimate the I_0 to be 10^{-8} A/cm^2. We can set up the Butler-Volmer equation solving for the iron's overpotential to yield -1.726V. For platinum, we find the overpotential is only -0.0806V.



3 c. $i = 10\text{mA/cm}^2$

$\beta = 125$ mV/decade

Fe η at STP $\approx 10^{-8}$ A/cm^2

$$i = i_0 e^{\eta/\beta} \rightarrow \ln\left(\frac{i}{i_0}\right)\cdot\beta = \eta$$

$$\eta = \ln\left(\frac{10e^{-3}\text{ A/cm}^2}{10^{-8}\text{ A/cm}^2}\right)\cdot \overset{(0.125\text{v})}{125\text{mV}}$$

$= 1.727\text{V}$

Past a SHE at 0v

[Apply -1.727v Fe.]

Pt: $\beta = 35$mV

$i_0 = 10^{-3}$ A/cm^2

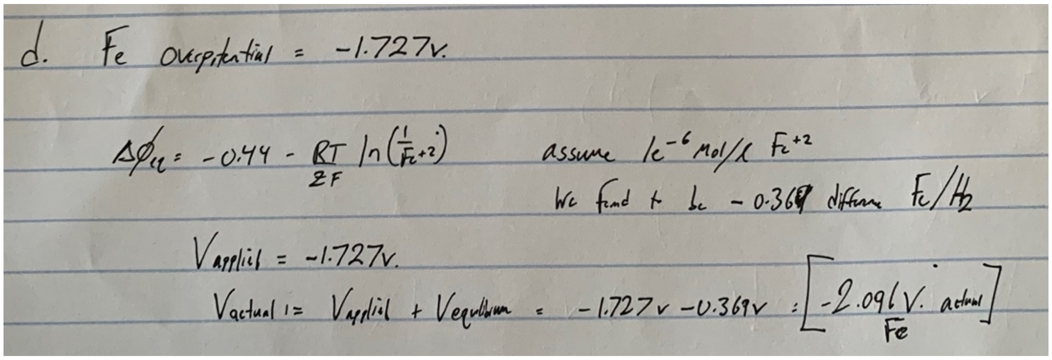
$$\eta = 0.035\text{v} \cdot \ln\left(\frac{10e^{-3}}{10^{-3}}\right) = 0.0805\text{V}$$

$\rightarrow$ [apply -0.0805 v. Pt/H_2]

Δ of Potential applied = 1.64 Volts to achieve the Same current density.

d. What is the absolute voltage of your iron electrode at this overpotential? Assume the reference electrode is a hydrogen electrode.

A: with the overpotential being $\Delta\phi_{applied} + \Delta\phi_{equilibirum}$, we find the actual potential is -2.107 V.



d. Fe overpotential = -1.727v.

$\Delta\phi_{eq} = -0.44 - \frac{RT}{zF}\ln\left(\frac{1}{Fe^{+2}}\right)$

assume $1e^{-6}$ mol/L Fe^{+2}

We find it to be -0.369 difference Fe/H_2

$V_{applied} = -1.727v.$

$V_{actual} = V_{applied} + V_{equilibrium} = -1.727v - 0.369v = \left[-2.096V.\ \text{actual}_{Fe}\right]$

e. On your diagram, add the reduction and oxidation curves for oxygen evolution reaction in water. Label on your diagram the difference of reduction curves on your platinum electrode between what you'd experience with and without oxygen. (See Lecture 6 for reference).

A: in reality, the platinum electrode will be able to completely shift its equilibrium potential to the reaction of the lowest energy. In the case with or without oxygen, that will be the hydrogen evolution potential (subject to pH). Additionally, it's worthwhile to note that at high acidic conditions, the reaction is not $\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$, but actually $2H_2O + 2e^- + \frac{1}{2}O_2 \rightarrow 2OH^-$ with an equilibrium potential of $0.401V_{SHE}$.