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

1. Nernst Equation

The Nernst equation relates the potential difference between a material in intimate electrical contact with a solution at equilibrium. It is defined as the potential at standard conditions and an activity-dependent term and is historically defined in terms of the forward reduction reaction. For these questions, reference the Standard Electrode Potential tables.

A. Assume you have a rod of iron that you want to use as 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 $Fe^{2+} + 2e \rightleftharpoons Fe(s)$. You measure the equilibrium voltage between it and the hydrogen reference electrode to be -0.629V. Find the concentration of dissolved Fe^{2+}

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,

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

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.

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?

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.

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 are no dissolved gasses.

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 would 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?

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.

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 SiO_2. 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.)

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 35 mV for the hydrogen evolution reaction. What is the rate of reduction of the hydrogen evolution reaction at an applied overpotential of 250 mV? How many liters of hydrogen per cm^2 per hour do we evolve?

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 equilibrium potential. Assume that the pH is 4 and the dissolved ions of iron(II) is 1e-6 M/l.

c. Now, how much overpotential is needed to be applied to produce a current density of 10 mA/cm^2 ? Assume the Tafel slope 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

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

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).