

Summary of Potentials and References

Instead of beginning with a full cell and then splitting into half-cell reactions, we can derive everything beginning with the half-cell reactions.

System Definition

In our system, we have two half-cells, defined arbitrarily as follows:

Half Reaction 1 (anode): $aA \rightarrow cC + ne^-$

Half Reaction 2 (cathode): $bB + ne^- \rightarrow dD$

Overall Reaction: $aA + bB \rightarrow cC + dD$

This can easily be generalized to any reactions.

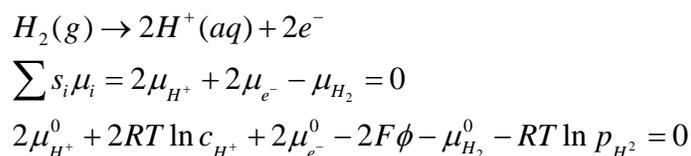
Chemical Equilibrium and SHE

We will start with a definition of chemical equilibrium from thermodynamics (this is derived in most thermodynamics textbooks and probably online somewhere as well):

$$\sum_i s_i \mu_i = 0$$

We will also define: $\mu_i = \mu_i^0 + RT \ln a_i$. For our purposes, any molecule will have $\mu_i^0 = \Delta G_i^f$ (defined relative to the standard state such that pure elements have $\Delta G^f = 0$). Additionally, gases and solvated species have activities defined as: $a_i^{gas} = p_i$ and $a_i^{solvated} = c_i$. This should all be familiar from our class and previous thermodynamics classes.

The only new part that electrochemistry adds that is different from your previous thermodynamics courses is the definition that $\mu_{e^-} = \mu_{e^-}^0 - F\phi$. Essentially, we are stating that the chemical potential of the electron is the voltage, with Faraday's constant accounting for units. Let's take a look at the hydrogen electrode:



Following standard thermodynamic conventions, $\mu_{H^+}^0 = \mu_{H_2}^0 = 0$. But what is $\mu_{e^-}^0$? As mentioned in class, if we were a physicist, we would define the standard chemical potential of an electron as zero in a vacuum. However, this is rather inconvenient for us. Accordingly, we will define it as whatever value is required to make ϕ of the hydrogen reaction equal to zero at standard state for the molecules involved.

At standard state, we have 1 bar of hydrogen gas and 1M protons in solution. Our equation thus becomes:

$$2(0) + 2RT \ln(1) + 2\mu_{e^-}^0 - 2F\phi - (0) - RT \ln(1) = 0$$

$$2\mu_{e^-}^0 = 2F\phi = 0$$

$$\mu_{e^-}^0 = 0$$

That was convenient! We have now defined the *Standard Hydrogen Electrode*. From now on, when we are deriving our half-reaction potentials and say they are “vs SHE”, we are really saying that we are using $\mu_{e^-}^0$ such that the hydrogen reaction has $\phi = 0$. It is certainly not a coincidence that this results in $\mu_{e^-}^0 = 0$, a direct consequence of defining $\Delta G_{H_2}^f = \Delta G_{H^+}^f = 0$. When we refer to other reference reactions, we are really just defining $\mu_{e^-}^0$ such that those reactions have $\phi = 0$.

In practice, we can just subtract the potential of another reaction to use it as a reference, a corollary that can be derived with a similar logic as shown above:

$$\phi \text{ vs } RXN \ Z = \phi \text{ vs } SHE - \phi_{RXN \ Z} \text{ vs } SHE$$

Half-Reaction Potentials, ϕ_0 , and the Nernst Equation

Let's return to our system defined at the beginning and derive the half reaction potentials:



$$\sum s_i \mu_i = c\mu_C + n\mu_{e^-} - a\mu_A = 0$$

$$c\mu_C^0 + cRT \ln a_C + n\mu_{e^-}^0 - nF\phi_1 - a\mu_A^0 - aRT \ln a_A = 0$$

With some rearrangement we get:

$$(c\mu_C^0 - a\mu_A^0) + RT \ln \frac{(a_C)^c}{(a_A)^a} = nF\phi_1$$

Let's define:

$$\phi_1^0 = \frac{1}{nF} (c\mu_C^0 - a\mu_A^0) = \frac{1}{nF} \sum_{i \in rxn, i \neq e^-} s_i \mu_i^0 = \frac{1}{nF} \sum_{i \in rxn, i \neq e^-} s_i \Delta G_i^f$$

$$\phi_1 = \phi_1^0 + RT \ln \frac{(a_C)^c}{(a_A)^a} = \phi_1^0 + \frac{RT}{nF} \ln \prod_{i \in rxn, i \neq e^-} a_i^{s_i}$$

This should be looking familiar to what we did in class. I denoted the potentials with the subscript "1" to indicate that this is the first half reaction. In particular, note that ϕ_0 is defined as the potential of the half reaction when all reactants are at standard state, and ϕ is the standard half reaction potential adjusted by a Nernstian shift. All of the above derivations are written as ϕ vs SHE because we set $\mu_e^- = 0$, but the same derivation holds with other reference reactions and ϕ vs RXN Z = ϕ vs SHE - $\phi_{RXN Z}$ vs SHE is still true.

The Full Cell

Following a similar derivation (note the signs because of how we define our products and reactants and where the electron is located in the chemical equation),

$$\phi_2 = \phi_2^0 + RT \ln \frac{(a_B)^b}{(a_D)^d} = \phi_2^0 - \frac{RT}{nF} \ln \prod_{i \in rxn 2, i \neq e^-} a_i^{s_i}$$

$$\phi_1^0 = \frac{1}{nF} (b\mu_B^0 - d\mu_D^0) = \frac{-1}{nF} \sum_{i \in rxn 2, i \neq e^-} s_i \mu_i^0 = \frac{-1}{nF} \sum_{i \in rxn 2, i \neq e^-} s_i \Delta G_i^f$$

Our full cell open circuit potential is going to be:

$$U = \phi_2 - \phi_1 = \phi_2^0 - \frac{RT}{nF} \ln \prod_{i \in rxn 2, i \neq e^-} a_i^{s_i} - \phi_1^0 - \frac{RT}{nF} \ln \prod_{i \in rxn 1, i \neq e^-} a_i^{s_i}$$

$$U = \phi_2^0 - \phi_1^0 - \frac{RT}{nF} \ln \prod_{i \in full rxn} a_i^{s_i}$$

$$U = U^0 - \frac{RT}{nF} \ln \prod_{i \in full rxn} a_i^{s_i}$$

Note that we have used the definition of OCV as the cathode (reduction reaction) minus the anode (oxidation reaction). This should look very familiar, as we now have the OCV with a Nernstian shift depending on the reactants and products. If we look a little deeper:

$$U^0 = \phi_2^0 - \phi_1^0 = \frac{1}{nF} (b\mu_B^0 - d\mu_D^0) - \frac{1}{nF} (c\mu_C^0 - a\mu_A^0)$$

$$U^0 = \frac{-1}{nF} (c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0) = \frac{-1}{nF} \sum_{i \in full rxn} s_i \mu_i^0 = \frac{-1}{nF} \sum_{i \in full rxn} s_i \Delta G_i^f$$

Note that we have simply derived the definition of voltage given in class for a full reaction:

$$-nFU^0 = \Delta G_{rxn}$$