

THERMODYNAMICS AND ELECTROCHEMISTRY

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Electrochemistry, that is, the chemistry of electricity-generating cells and reactions, is handled similarly by several branches of science (chemistry, physics, etc.). This paper will only address them from a thermodynamic standpoint, including finding the voltage under various temperature and pressure conditions, but will be limited to situations where the pressure and temperature are held constant.

Equations and Concepts:

Initially we need to know the full-cell reaction, which is usually either given, or trivially found. This will be explained in the example. We can start with the general Gibbs energy equation for a chemical reaction.

$$\Delta G = \Delta G^\circ + RT \ln(J_a) \quad (1)$$

The 'zero exponent' notation is used to relate the value is at standard state, which can be created by knowing the ΔG of formation (or, similarly, the ΔH_{form} and ΔS_{form} . J_a is the reaction quotient, which will be explored next. It is of note that if we are looking at an equilibrium situation ($\Delta G = 0$), this quantity becomes K_a , the equilibrium constant. Regardless of the situation, the J_a or K_a can be constructed as follows. Consider a generalized chemical reaction wherein the lowercase characters are stoichiometric coefficients, and the uppercase letters denote chemical species:



$$J_a = \frac{a_D^d + a_E^e}{a_B^b + a_C^c} \quad (3)$$

It is the quotient of the product of the activities of the products over the product of the activities of the reactants, with each term raised to the power of it's stoichiometric coefficient. It is of note that condensed phases (solids and liquids) can often be approximated to have activity of 1, this assume that they are absolutely pure. The activities of gases are given by it's partial pressure normalized to either 1 bar or 1 atmosphere. Now we can link this expression for the Gibbs energy to the figure of merit for the cell, the electromotive force (in volts).

$$\Delta G = -\mathcal{E}z\mathcal{F} \quad (4)$$

Similarly

$$\Delta G^\circ = -\mathcal{E}^\circ z\mathcal{F} \quad (5)$$

In these equations z denotes the number of electrons transferred in the reaction, while \mathcal{F} is Faraday's constant, 96480 Coulombs per mole. We can substitute these expressions into the earlier expression for ΔG and simplify a bit.

$$-\mathcal{E}z\mathcal{F} = -\mathcal{E}^\circ z\mathcal{F} + RT\ln(J_a) \quad (6)$$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{z\mathcal{F}}\ln(J_a) \quad (7)$$

If ΔG is negative (and similarly if \mathcal{E} is positive) then the reaction will occur spontaneously, if it were positive (and E negative) the reaction would prefer to run the opposite direction, and a voltage would need to be applied to the cell in order to run the reaction the way it is written.

Example 1

Find the open circuit voltage of the following electrochemical cell at 1000K:



Given: $\Delta G_f^\circ = -92000 + 11T(cal/mol)$

$$z = 1 \quad (2)$$

$$\Delta G^\circ = -92000 + 11 * 1000 = -81,000(cal/mol) \quad (3)$$

$$J_a = \frac{a_{LiCl}}{a_{Li}a_{Cl_2}^{1/2}} \quad (4)$$

Here we assume that the lithium and lithium chloride are entirely pure. This isn't a bad assumption, as lithium is metallic while LiCl is ionic, and they would not easily mix. As such, the activities of the condensed components become one, and we use the partial pressure of chlorine gas for it's activity.

$$J_a = \frac{1}{1 * \sqrt{1}} = 1 \quad (5)$$

We can return to the equation for electromotive force.

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{z\mathcal{F}}\ln(J_a) \quad (6)$$

$$\mathcal{E} = \mathcal{E}^\circ - \frac{1000R}{96480}\ln(1) \quad (7)$$

We recognize that the natural logarithm of one is zero, and thus the entire term disappears, and the voltage is simply the standard voltage. This can be found from the original definition of standard state voltage in terms of standard state Gibbs energy.

$$\mathcal{E} = \mathcal{E}^\circ = \frac{\Delta G^\circ}{-z\mathcal{F}} \quad (8)$$

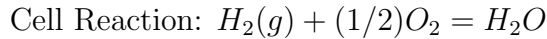
Before we can use ΔG° we need to convert it from calories per mole into joules per mole, as joules per coulomb directly yields volts, which is what we're after.

$$\mathcal{E} = \frac{-81,000 * 4.187}{-1 * 96480} = 3.515V \quad (9)$$

While this is a very powerful battery, however both the lithium and LiCl need to be in a liquid phase for it to function, requiring very high temperatures, making this an impractical battery.

Example 2

A standard among electrochemical cells is the oxygen-hydrogen cell, which uses water as its electrolyte. Given an open circuit voltage of 1.229V at 298K (pure water as the electrolyte and both gases at one atmosphere), what voltage could it provide if both gases were pressurized to 20 atmospheres? What voltage would it attain if, in addition to pressurizing the gases, salt were added to the water, making its activity .80? What if it were operated with both gases at 20 atmospheres, pure water, but at 370K, near the boiling point of water?



We can extract from the reaction the number of electrons being transferred (z), as oxygen is typically -2, and hydrogen can only form +1, we see that $z = 2$.

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{z\mathcal{F}} \ln \left(\frac{a_{H_2O}}{P_{H_2} P_{O_2}^{1/2}} \right) \quad (10)$$

$$\mathcal{E} = 1.229 - \frac{2477.69}{192960} \ln \left(\frac{1}{20\sqrt{20}} \right) \quad (11)$$

$$\mathcal{E} = 1.229 - (-0.0577) = 1.287V \quad (12)$$

If we add salt, we repeat the same steps, with the new value for the activity of the water.

$$\mathcal{E} = 1.229 - \frac{2477.69}{192960} \ln \left(\frac{0.8}{20\sqrt{20}} \right) \quad (13)$$

$$\mathcal{E} = 1.229 - (-0.0605) = 1.289V \quad (14)$$

For the final set of conditions, we again simply use the same form.

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{z\mathcal{F}} \ln \left(\frac{a_{H_2O}}{P_{H_2} P_{O_2}^{1/2}} \right) \quad (15)$$

$$\mathcal{E} = 1.229 - \frac{8.3144 \times 380}{2 \times 96480} \ln \left(\frac{1}{20\sqrt{20}} \right) \quad (16)$$

$$\mathcal{E} = 1.303V \quad (17)$$

It becomes obvious that a significantly higher voltage cannot be obtained with this cell, illustrating that the cell reaction (and thusly \mathcal{E}°) has the highest degree of functionality upon the voltage.