

10.2: The connection to ΔG

Recall that in addition to being used as a criterion for spontaneity, ΔG also indicated the maximum amount of non p-V work a system could produce at constant temperature and pressure. And since w_e is non p-V work, it seems like a natural fit that

$$\Delta G = -nFE$$

If all of the reactants and products in the electrochemical cell are in their standard states, it follows that

$$\Delta G^\circ = -nFE^\circ$$

where E° is the **standard cell potential**. Noting that the molar Gibbs function change can be expressed in terms of the reaction quotient Q by

$$\Delta G = \Delta G^\circ + RT \ln Q$$

it follows that

$$-nFE = -nFE^\circ + RT \ln Q$$

Dividing by $-nF$ yields

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

which is the **Nernst equation**. This relationship allows one to calculate the cell potential of a electrochemical cell as a function of the specific activities of the reactants and products. In the Nernst equation, n is the number of electrons transferred per reaction equivalent. For the specific reaction harnessed by Volta in his original battery, $E^\circ = 0.763 \text{ V}$ (at 25°C) and $n = 2$. So if the Zn^{2+} and H^+ ions are at a concentration that gives them unit activity, and the H_2 gas is at a partial pressure that gives it unit fugacity:

$$E = 0.763 \text{ V} - \frac{RT}{nF} \ln(1) = 0.763$$

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