

17.14: Cell Potentials and the Gibbs Free Energy

In Section 17.11, we see that the electrical potential drop across the standard cell $Pt^0 | H_2 | H^+ || Ag^+ | Ag^0$ is 0.7992 volts. We measure this potential under conditions in which no current is flowing. That is, we find the counter-potential at which no current flows through the cell in either direction. An arbitrarily small change in the counter-potential away from this value, in either direction, is sufficient to initiate current flow. This means that the standard potential is measured when the cell is operating reversibly. By the definition of a standard cell, all of the reactants are at the standard condition of unit activity. If any finite current is drawn from a cell of finite size, the concentrations of the reagents will no longer be exactly the correct values for a standard cell. Nevertheless, we can calculate the energy that would be dissipated in the surroundings if the cell were to pass one mole of electrons (corresponding to consuming one mole of silver ions and one-half mole of hydrogen gas) through the external circuit while the cell conditions remain exactly those of the standard cell. This energy is

$$96,485 \text{ C mol}^{-1} \times 0.7992 \text{ V} = 77,110 \text{ J mol}^{-1}$$

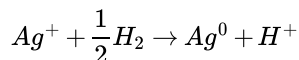
The form in which this energy appears in the surroundings depends on the details of the external circuit. However, we know that this energy represents the reversible work done on electrons in the external circuit as they traverse the path from the anode to the cathode. We call this the electrical work. Above we describe this as the energy change for a hypothetical reversible process in which the composition of the cell does not change. We can also view it as the energy change per electron for one electron-worth of real process, multiplied by the number of electrons in a mole. Finally, we can also describe it as the reversible work done on electrons during the reaction of one mole of silver ions in an infinitely large standard cell.

The Gibbs free energy change for an incremental reversible process is $dG = VdP + SdT + dw_{NPV}$, where dw_{NPV} is the increment of non-pressure-volume work. In the case of an electrochemical cell, the electrical work is non-pressure-volume work. In the particular case of an electrochemical cell operated at constant temperature and pressure, $dP = dT = 0$, and $dG = dw_{NPV} = dw_{\text{elect}}$.

The electrical work is just the charge times the potential drop. Letting n be the number of moles of electrons that pass through the external circuit for one unit of reaction, the total charge is $Q = -n\mathcal{F}$, where \mathcal{F} is one faraday. For a standard cell, the potential drop is \mathcal{E}^0 , so the work done on the electrons is $Q\mathcal{E}^0 = -n\mathcal{F}\mathcal{E}^0$. Since the standard conditions for Gibbs free energies are the same as those for electrical cell potentials, we have

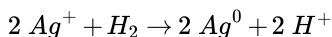
$$w_{\text{elect}}^{\text{rev}} = \Delta_r G^o = -n\mathcal{F}\mathcal{E}^o$$

If the reaction occurs spontaneously when all of the reagents are in their standard states, we have $\mathcal{E}^o > 0$. For a spontaneous process, the work done on the system is less than zero, $w_{\text{elect}}^{\text{rev}} < 0$; the work done on the surroundings is $\hat{w}_{\text{elect}}^{\text{rev}} = -w_{\text{elect}}^{\text{rev}} > 0$; and the energy of the surroundings increases as the cell reaction proceeds. The standard potential is an intensive property; it is independent of the size of the cell and of the way we write the equation for the chemical reaction. However, the work and the Gibbs free energy change depend on the number of electrons that pass through the external circuit. We usually specify the number of electrons by specifying the chemical equation to which the Gibbs free energy change applies. That is, if the associated reaction is written as



we understand that one mole of silver ions are reduced and one mole of electrons are transferred; $n = 1$ and

$\Delta_r G^o = -\mathcal{F}\mathcal{E}^o$. If the reaction is written



we understand that two moles of silver ions are reduced and two moles of electrons are transferred, so that $n = 2$ and $\Delta_r G^o = -2\mathcal{F}\mathcal{E}^o$.

The same considerations apply to measurement of the potential of electrochemical cells whose component are not at the standard condition of unit activity. If the cell is not a standard cell, we can still measure its potential. We use the same symbol to denote the potential, but we omit the superscript zero that denotes standard conditions. These are, of course, just the conventions we have been using to distinguish the changes in other thermodynamic functions that occur at standard conditions from those that do not. We have therefore, for the Gibbs free energy change for the reaction occurring in an electrochemical cell that is not at standard conditions,

$$w_{elect}^{rev} = \Delta_r G = -n\mathcal{F}\mathcal{E}$$

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