Appendix A

Thermodynamic justification of $\Delta_{\text{reaction}}G = -zFE_{\text{reversible cell}}$

Description

Consider an electrochemical cell that is operating in a thermodynamically reversible fashion.

Let 'the system' refer to the chemical reaction inside the electrochemical cell. This system is able to do some electrical work on the load, but does not do any other non-expansion work. Let ΔG be the change in Gibbs energy of the system. Let zF be the charge passing through the load, and $E_{\text{reversible cell}}$ be the electromotive force exerted on the load. The non-expansion work done by the system on the load is $charge \times voltage$ or $+zFE_{\text{reversible cell}}$. The non-expansion work done on the system is therefore $-zFE_{\text{reversible cell}}$.

It will be shown that $\Delta G = W_{\text{non-expansion}}$. The non-expansion work term here is the electrical work done on this system by the electrical load. Hence $\Delta_{\text{reaction}}G = -zFE_{\text{reversible cell}}$.

Proof

Applying the first law of thermodynamics to the system gives us the following, where the work terms refer to work done on the system, $-zFE_{\text{reversible cell}}$ and $-p\mathrm{d}V$ respectively.

$$\mathrm{d}U = \delta q + W_{\text{non-expansion}} + W_{\text{expansion}} \quad (1)$$

The second law for a reversible process gives us

$$\mathrm{d}S = \delta q/T \quad (2)$$

From (1) and (2)

$$\mathrm{d}U = T\mathrm{d}S + W_{\text{non-expansion}} + W_{\text{expansion}} \quad (3)$$

$$\mathrm{d}U + p\mathrm{d}V - T\mathrm{d}S = W_{\text{non-expansion}} \quad (4)$$

$$\mathrm{d}G = W_{\text{non-expansion}} \quad (5)$$

In our picture of an electrochemical cell, the only process taking place inside the cell is the chemical reaction that has a Gibbs energy change $\Delta_{\text{reaction}}G$. And the only non-expansion work done by the system is the electrical $charge \times voltage$ work.

$$\int \mathrm{d}G = \Delta_{\text{reaction}}G \quad (6)$$

$$W_{\text{non-expansion}} = -zFE_{\text{reversible cell}} \quad (7)$$

And therefore

$$\Delta_{\text{reaction}}G = -zFE_{\text{reversible cell}} \quad (8)$$

This provides a more rigorous justification for Equation (2.26) than the compact argument that $\Delta G_{\text{total}} = 0$ when a suitable electrical work term is included for a reversible cell.