Example 5. Differentiate the equilibrium entropy for a closed system of Boltzons and substitute eqn. IIIB-19 to derive the Gibbs equation.

The equilibrium entropy of a system of Boltzons is given by eqn. IIIB-13. Its differential in a closed system (N = const) is

$$d(S^{MB})\Big|_N = d\left(\frac{U}{T} + Nk\,\ell n\,Z(T,V)\right)\Big|_N = \frac{dU}{T} - \frac{UdT}{T^2} + \frac{Nk}{Z}\left[\left(\frac{\partial Z(T,V)}{\partial T}\right)_V dT + \left(\frac{\partial Z(T,V)}{\partial V}\right)_T dV\right]$$

Now by the definition of Z, eqn. IIIB-12

$$\frac{Nk}{Z}\left(\frac{\partial Z(T,V)}{\partial T}\right)_V = \frac{Nk}{Z}\left[\frac{\partial}{\partial T}\left(\sum_j g_j e^{-\varepsilon_j(V)/kT}\right)\right]_V = \frac{Nk}{ZkT^2}\left(\sum_j \varepsilon_j g_j e^{-\varepsilon_j(V)/kT}\right)$$

Substituting the distribution function $n_j^{MB} = [Ng_j \exp(-\varepsilon_j(V)/kT)]/Z$, we obtain

$$\frac{Nk}{Z}\left(\frac{\partial Z}{\partial T}\right)_V = \frac{-1}{T}\sum_j n_j^{MB}\,\varepsilon_j = -\frac{U}{T^2}$$

Similarly

$$\frac{Nk}{Z}\left(\frac{\partial Z(T,V)}{\partial V}\right)_T = \frac{Nk}{Z}\left[\frac{\partial}{\partial V}\left(\sum_j g_j e^{-\varepsilon_j(V)/kT}\right)\right]_T = -\frac{Nk}{ZkT}\sum_j \frac{d\varepsilon_j(V)}{dV}\,g_j e^{-\varepsilon_j(V)/KT}$$

and again substituting n_j^{MB}, we have

$$\frac{Nk}{Z}\left(\frac{\partial Z}{\partial V}\right)_T = -\frac{1}{T}\sum_j n_j^{MB}\frac{d\varepsilon_j(V)}{dV}$$

Thus the differential entropy is

$$d(S^{MB})\Big|_N = \frac{dU}{T} - \frac{UdT}{T^2} + \frac{U}{T^2}dT - \frac{1}{T}\sum_j n_j^{MB}\frac{d\varepsilon_j(V)}{dV}\,dV = \frac{dU}{T} - \frac{đW^i_{rev}}{T} \qquad \text{QED.}$$

IV. DETERMINING ENTROPY PRODUCTION

Eqn. IIIB-5 is the most general form of the second law. But its use requires the determination of entropy change. The Gibbs equation is the origin of all macroscopic determinations of entropy change. For general complex, simple, and simple compressible media it is, respectively

$$dS = \frac{dU - đW^i_{rev}}{T} = \frac{dU - \sum_{k=1}^{K}\bar{F}_k\cdot d\bar{X}_k}{T} \qquad \text{(IIIB-20a)}$$

$$dS = \frac{dU - \bar{F}\cdot d\bar{X}}{T}\,; \qquad dS = \frac{dU + p\,dV}{T} \qquad \text{(IIIB-20b,c)}$$

The Gibbs equation is valid for any process between equilibrium states; it is independent of the path.