$$dS = \frac{dU - đW^{i}_{rev}}{T}$$

Exercise B5. Differentiate eqn. IIIB-B6 at fixed N and simplify to obtain the Gibbs equation. (This development is sufficiently similar to Exmp. B5 and it can be used as a guide and no solution is given.)

Ans. B3. In preparation for substitution we rearrange eqn. III-B4

$$\frac{n^{BE}_{j,mp}}{g_j} = \frac{1}{e^{\alpha+\beta\varepsilon_j(V)}-1} \quad ; \quad 1 + \frac{n^{BE}_{j,mp}}{g_j} = \frac{e^{\alpha+\beta\varepsilon_j(V)}}{e^{\alpha+\beta\varepsilon_j(V)}-1} = \frac{1}{1-e^{-\alpha-\beta\varepsilon_j(V)}}$$

So
$$\ln\left(\frac{g_j+n_{j,i}}{g_j}\right) = \ln\left[1-e^{-\alpha-\beta\varepsilon_j(V)}\right]$$

Then
$$\frac{g_j}{n^{BE}_{j,mp}} = e^{\alpha+\beta\varepsilon_j(V)}-1 \quad \text{so} \quad \ln\left(\frac{g_j+n^{BE}_{j,mp}}{n^{BE}_{j,mp}}\right) = \alpha + \beta\varepsilon_j(V)$$

Since
$$S^{BE}_{eq} = -k\sum_j g_j \ln\left[1-e^{-\alpha-\beta\varepsilon_j(V)}\right] + k\sum_j n_{j,i}[\alpha+\beta\varepsilon_j(V)]$$

This is recognized as eqn. IIIB-B6 with $\beta = 1/kT$ and $\sum n_{j,i} = N$, $\sum n_{j,i}\varepsilon_j(V) = U$.

Ans. B4.

$$\left(\frac{\partial S^{BE}_{eq}}{\partial U}\right)_{N,V} = \frac{1}{T} - \frac{U}{T^2}\left(\frac{\partial T}{\partial U}\right)_{N,v} + Nk\left(\frac{\partial\alpha}{\partial U}\right)_{N,V} - k\sum_j \frac{g_j e^{-\alpha-\beta\varepsilon_j(V)}}{\left[1-e^{-\alpha-\varepsilon_j(V)/kT}\right]} + \left(\frac{\partial\alpha}{\partial U}\right)_{N,V} - \frac{\varepsilon_j(V)}{kT^2}\left(\frac{\partial T}{\partial U}\right)_{N,V}$$

$$= \frac{1}{T} - \left(\frac{U}{T^2} - \frac{\sum n^{BE}_{j,mp}\varepsilon_j(V)}{T^2}\right)\left(\frac{\partial T}{\partial U}\right)_{N,V} + \left(Nk - k\sum n^{BE}_{j,mp}\right)\left(\frac{\partial\alpha}{\partial U}\right)_{N,V}$$