6

6.1 (a) By Eqn. (6.2-3)

$$\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_{j\neq i}} = \overline{G}_i\ ;$$

but $\overline{G}_i = \overline{H}_i - T\overline{S}_i$. Thus

$$\left(\frac{\partial H}{\partial N_i}\right)_{P,S,N_{j\neq i}} = \overline{H}_i - T\overline{S}_i$$

(b) Since $U = U(S,V,\underline{N})$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,\underline{N}} dS + \left(\frac{\partial U}{\partial V}\right)_{S,\underline{N}} dV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} dN_i$$

$$= TdS - PdV + \sum_i \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}} dN_i \qquad (1)$$

However, we also have $U = H - PV$; $dU = dH - PdV - VdP$, and, by Eqn. (6.2-3)

$$dU = VdP + TdS + \sum \overline{G}_i dN_i - PdV - VdP = TdS - PdV + \sum \overline{G}_i dN_i \qquad (2)$$

Equating (1) and (2) shows that $\overline{G}_i = \left(\frac{\partial U}{\partial N_i}\right)_{S,V,N_{j\neq i}}$. Next we start from

$$A = A(T,V,\underline{N})$$

$$\Rightarrow dA = \left(\frac{\partial A}{\partial T}\right)_{V,\underline{N}} dT + \left(\frac{\partial A}{\partial V}\right)_{T,\underline{N}} dV + \sum_i \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}} dN_i$$

or

$$dA = -SdT - PdV + \sum_i \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}} dN_i \qquad (3)$$

However, we also have that $A = U - TS$;

$$dA = dU - TdS - SdT = TdS - PdV + \sum \overline{G}_i dN_i - TdS - SdT$$

or

$$dA = -SdT - PdV + \sum \overline{G}_i dN_i \qquad (4)$$

Comparing (3) and (4) yields

$$\overline{G}_i = \left(\frac{\partial A}{\partial N_i} \right)_{T,V,N_{j \neq i}}$$