

## F: Maxwell's Relations

For a well-behaved function,  $\mathfrak{F}$ , the order of derivatives is permutable

$$\left[ \frac{\partial}{\partial y} \left( \frac{\partial \mathfrak{F}}{\partial x} \right)_{y,z} \right]_{x,z} = \left[ \frac{\partial}{\partial x} \left( \frac{\partial \mathfrak{F}}{\partial y} \right)_{x,z} \right]_{y,z}$$

Corresponding relationships from the second derivatives of  $E$  are

$$\begin{aligned} \left( \frac{\partial T}{\partial V} \right)_{S,\{n_i\}} &= - \left( \frac{\partial P}{\partial S} \right)_{V,\{n_i\}} \\ \left( \frac{\partial \tilde{\mu}_i}{\partial V} \right)_{S,\{n_i\}} &= - \left( \frac{\partial P}{\partial n_i} \right)_{S,V,\{n_{j \neq i}\}} \\ \left( \frac{\partial \tilde{\mu}_i}{\partial S} \right)_{V,\{n_i\}} &= \left( \frac{\partial T}{\partial n_i} \right)_{S,V,\{n_{j \neq i}\}} \\ \left( \frac{\partial \tilde{\mu}_k}{\partial n_j} \right)_{S,V,\{n_{i \neq j}\}} &= \left( \frac{\partial \tilde{\mu}_j}{\partial n_k} \right)_{S,V,\{n_{i \neq k}\}} \end{aligned}$$

from the second derivatives of  $H$  are

$$\begin{aligned} \left( \frac{\partial T}{\partial P} \right)_{S,\{n_i\}} &= \left( \frac{\partial V}{\partial S} \right)_{P,\{n_i\}} \\ \left( \frac{\partial \tilde{\mu}_i}{\partial P} \right)_{S,\{n_i\}} &= \left( \frac{\partial V}{\partial n_i} \right)_{S,P,\{n_{j \neq i}\}} \\ \left( \frac{\partial \tilde{\mu}_i}{\partial S} \right)_{P,\{n_i\}} &= \left( \frac{\partial T}{\partial n_i} \right)_{S,P,\{n_{j \neq i}\}} \\ \left( \frac{\partial \tilde{\mu}_k}{\partial n_j} \right)_{S,P,\{n_{i \neq j}\}} &= \left( \frac{\partial \tilde{\mu}_j}{\partial n_k} \right)_{S,P,\{n_{i \neq k}\}} \end{aligned}$$

from the second derivatives of  $F$  are

$$\begin{aligned} - \left( \frac{\partial S}{\partial V} \right)_{T,\{n_i\}} &= - \left( \frac{\partial P}{\partial T} \right)_{V,\{n_i\}} \\ \left( \frac{\partial \tilde{\mu}_i}{\partial V} \right)_{T,\{n_i\}} &= - \left( \frac{\partial P}{\partial n_i} \right)_{T,V,\{n_{j \neq i}\}} \\ \left( \frac{\partial \tilde{\mu}_i}{\partial T} \right)_{V,\{n_i\}} &= - \left( \frac{\partial S}{\partial n_i} \right)_{T,V,\{n_{j \neq i}\}} \\ \left( \frac{\partial \tilde{\mu}_k}{\partial n_j} \right)_{T,V,\{n_{i \neq j}\}} &= \left( \frac{\partial \tilde{\mu}_j}{\partial n_k} \right)_{T,V,\{n_{i \neq k}\}} \end{aligned}$$

and from the second derivatives of  $G$  are

$$\begin{aligned}-\left(\frac{\partial S}{\partial P}\right)_{T,\{n_i\}} &= \left(\frac{\partial V}{\partial T}\right)_{P,\{n_i\}} \\ \left(\frac{\partial \tilde{\mu}_i}{\partial P}\right)_{T,\{n_i\}} &= \left(\frac{\partial V}{\partial n_i}\right)_{T,P,\{n_{j \neq i}\}} \\ \left(\frac{\partial \tilde{\mu}_i}{\partial T}\right)_{P,\{n_i\}} &= -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,\{n_{j \neq i}\}} \\ \left(\frac{\partial \tilde{\mu}_k}{\partial n_j}\right)_{T,P,\{n_{i \neq j}\}} &= \left(\frac{\partial \tilde{\mu}_j}{\partial n_k}\right)_{T,P,\{n_{i \neq k}\}}\end{aligned}$$

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