2.F.5. Grand Potential

The grand potential Ω is defined by the Legendre transform

$$\Omega = U - S\,T - \sum_j \mu_j{}'\,N_j$$

$$= \boldsymbol{X}\cdot\boldsymbol{Y} \qquad \text{[(2.61) used.]} \tag{2.122}$$

so that

$$\Omega = \Omega(\boldsymbol{\xi}_\Omega) \qquad \text{with} \qquad \boldsymbol{\xi}_\Omega = (\,T, \boldsymbol{X}, \{\,\mu_j{}'\,\}\,) \tag{2.122a}$$

Following closely the procedure described in §2.F.2, we have

$$d\,\Omega = -S\,d\,T + \boldsymbol{Y}\cdot d\,\boldsymbol{X} - \sum_j N_j\,d\,\mu_j{}' \tag{2.123}$$

$$= \boldsymbol{\Psi}_\Omega\cdot d\,\boldsymbol{\xi}_\Omega \qquad \text{with} \qquad \boldsymbol{\Psi}_\Omega = (\,-S, \boldsymbol{Y}, \{\,-N_j\,\}\,)$$

$$= \frac{\partial\,\Omega}{\partial\,\boldsymbol{\xi}_\Omega}\cdot d\,\boldsymbol{\xi}_\Omega$$

Thus,

$$\boldsymbol{\Psi}_\Omega = \frac{\partial\,\Omega}{\partial\,\boldsymbol{\xi}_\Omega} \tag{2.122b}$$

or, more specifically,

$$-S = \left(\frac{\partial\,\Omega}{\partial\,T}\right)_{\boldsymbol{X},\{\,\mu_j{}'\,\}} \tag{2.124}$$

$$\boldsymbol{Y} = \left(\frac{\partial\,\Omega}{\partial\,\boldsymbol{X}}\right)_{T,\,\{\,\mu_j{}'\,\}} \qquad \text{or} \qquad Y_k = \left(\frac{\partial\,\Omega}{\partial\,X_k}\right)_{T,\{X_{i\neq k}\},\,\{\,\mu_j{}'\,\}} \tag{2.125}$$

$$N_j = -\left(\frac{\partial\,\Omega}{\partial\,\mu_j{}'}\right)_{T,\boldsymbol{X},\{\,\mu_{k\neq j}{}'\,\}} \tag{2.126}$$

The Maxwell equations are

$$\frac{\partial\,\Psi_{\Omega\,k}}{\partial\,\xi_{\Omega\,j}} = \frac{\partial\,\Psi_{\Omega\,j}}{\partial\,\xi_{\Omega\,k}} \tag{2.126a}$$

or

$$\frac{\partial}{\partial\,\boldsymbol{X}}\left(\frac{\partial\,\Omega}{\partial\,T}\right) = \frac{\partial}{\partial\,T}\left(\frac{\partial\,\Omega}{\partial\,\boldsymbol{X}}\right)$$

$$\rightarrow \quad -\left(\frac{\partial\,S}{\partial\,X_k}\right)_{T,\{X_{i\neq k}\},\{\,\mu_j{}'\,\}} = \left(\frac{\partial\,Y_k}{\partial\,T}\right)_{\boldsymbol{X},\{\,\mu_j{}'\,\}} \tag{2.127}$$

$$\frac{\partial}{\partial\,\mu_k{}'}\left(\frac{\partial\,\Omega}{\partial\,T}\right) = \frac{\partial}{\partial\,T}\left(\frac{\partial\,\Omega}{\partial\,\mu_k{}'}\right)$$

$$\rightarrow \quad -\left(\frac{\partial\,S}{\partial\,\mu_k{}'}\right)_{T,\boldsymbol{X},\{\mu_{j\neq k}{}'\}} = -\left(\frac{\partial\,N_k}{\partial\,T}\right)_{\boldsymbol{X},\,\{\mu_j{}'\}} \tag{2.128}$$

$$\frac{\partial}{\partial\,\mu_k{}'}\left(\frac{\partial\,\Omega}{\partial\,X_i}\right) = \frac{\partial}{\partial\,X_i}\left(\frac{\partial\,\Omega}{\partial\,\mu_k{}'}\right)$$

$$\rightarrow \quad \left(\frac{\partial\,Y_i}{\partial\,\mu_k{}'}\right)_{T,\boldsymbol{X},\{\,\mu_{j\neq k}{}'\,\}} = -\left(\frac{\partial\,N_k}{\partial\,X_i}\right)_{T,\,\{X_{n\neq i}\},\{\,\mu_j{}'\,\}} \tag{2.129}$$

$$\frac{\partial}{\partial \mu_k'}\left(\frac{\partial \Omega}{\partial \mu_i'}\right) = \frac{\partial}{\partial \mu_i'}\left(\frac{\partial \Omega}{\partial \mu_k'}\right)$$

$$\rightarrow \quad -\left(\frac{\partial N_i}{\partial \mu_k'}\right)_{T,\boldsymbol{X},\{\mu_{j\neq k}'\}} = -\left(\frac{\partial N_k}{\partial \mu_i'}\right)_{T,\boldsymbol{X},\{\mu_{j\neq i}'\}} \qquad (2.130)$$

(2.83d) becomes

$$d\Omega = -\bar{d}W_{\text{free}}\Big|_{(T,\boldsymbol{X},\{\mu_j'\})=\text{const}} \quad \rightarrow \quad \Delta\Omega = -W_{\text{free}}\Big|_{(T,\boldsymbol{X},\{\mu_j'\})=\text{const}} \qquad (2.132)$$

so that at constant $(T, \boldsymbol{X}, \{\mu_j'\})$, the reversible work $-W_{\text{free}}$ done on the system is converted entirely to $\Delta\Omega$. Hence [c.f. (2.83e)],

$$\Delta\Omega < 0 \qquad \text{for all spontaneous processes at constant } (T, \boldsymbol{X}, \{\mu_j'\}) \qquad (2.133)$$

which means the equilibrium state for processes at constant $(T, \boldsymbol{X}, \{\mu_j'\})$ has the minimal grand potential.