Page 187, equations (4.208) and (4.209)

From the definition (4.165) of coefficients $\omega_{\beta\gamma}$ it follows:

$$\sum_{\gamma=1}^{n} \omega_{\beta\gamma} \mathrm{d}\rho_\gamma = \sum_{\gamma=1}^{n} \left(g_\gamma \delta_{\beta\gamma} - \rho_\beta \frac{\partial \hat{f}_\beta}{\partial \rho_\gamma} - f_\beta \delta_{\beta\gamma} \right) \mathrm{d}\rho_\gamma$$

$$= g_\beta \mathrm{d}\rho_\beta - \rho_\beta \sum_{\gamma=1}^{n} \frac{\partial \hat{f}_\beta}{\partial \rho_\gamma} \mathrm{d}\rho_\gamma - f_\beta \mathrm{d}\rho_\beta;\ \beta = 1, ..., n-1. \tag{1}$$

The differential of partial free energy reads:

$$\mathrm{d}f_\beta = \frac{\partial \hat{f}_\beta}{\partial T} \mathrm{d}T + \sum_{\gamma=1}^{n} \frac{\partial \hat{f}_\beta}{\partial \rho_\gamma} \mathrm{d}\rho_\gamma$$

and from this then follows:

$$-\rho_\beta \sum_{\gamma=1}^{n} \frac{\partial \hat{f}_\beta}{\partial \rho_\gamma} \mathrm{d}\rho_\gamma = \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T} - \rho_\beta \mathrm{d}f_\beta. \tag{2}$$

Additional relationships among differential can be obtained from the relationship (4.193) for partial thermodynamic pressure:

$$\mathrm{d}P_\beta = \rho_\beta \mathrm{d}g_\beta + g_\beta \mathrm{d}\rho_\beta - \rho_\beta \mathrm{d}f_\beta - f_\beta \mathrm{d}\rho_\beta,$$

$$g_\beta \mathrm{d}\rho_\beta - \rho_\beta \mathrm{d}f_\beta - f_\beta \mathrm{d}\rho_\beta = \mathrm{d}P_\beta - \rho_\beta \mathrm{d}g_\beta. \tag{3}$$

Substituting from (2) and (3) into (1) we obtain:

$$\sum_{\gamma=1}^{n} \omega_{\beta\gamma} \mathrm{d}\rho_\gamma = g_\beta \mathrm{d}\rho_\beta + \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T} \mathrm{d}T - \rho_\beta \mathrm{d}f_\beta - f_\beta \mathrm{d}\rho_\beta$$

$$= \mathrm{d}P_\beta - \rho_\beta \mathrm{d}g_\beta + \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T} \mathrm{d}T \tag{4}$$

and this is equation (4.208).

Summing (4) from $\beta = 1$ to $\beta = n-1$ we get:

$$\sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} \omega_{\beta\gamma} \mathrm{d}\rho_\gamma = \sum_{\beta=1}^{n-1} \mathrm{d}P_\beta - \sum_{\beta=1}^{n-1} \rho_\beta \mathrm{d}g_\beta + \sum_{\beta=1}^{n-1} \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T} \mathrm{d}T. \tag{5}$$

From eq. (4.187) we have

$$\mathrm{d}P = \sum_{\alpha=1}^{n} \mathrm{d}P_\alpha = \sum_{\beta=1}^{n-1} \mathrm{d}P_\beta + \mathrm{d}P_n. \tag{6}$$

From Gibbs-Duhem equation (4.207), taking into account the definitions of mass fraction, (4.22), and volume, (4.195), it further follows:

$$\begin{aligned} -\rho s\,\mathrm{d}T + \rho v\,\mathrm{d}P - \sum_{\alpha=1}^{n} \rho_\alpha \mathrm{d}g_\alpha &= -\rho s\,\mathrm{d}T + \mathrm{d}P - \sum_{\beta=1}^{n-1} \rho_\beta \mathrm{d}g_\beta - \rho_n \mathrm{d}g_n \\ &= 0. \end{aligned} \tag{7}$$

Substitution from (6) and (7) into (5) results in following expression:

$$\sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} \omega_{\beta\gamma} \mathrm{d}\rho_\gamma = \mathrm{d}P - \mathrm{d}P_n + \rho_n \mathrm{d}g_n + \rho s\,\mathrm{d}T - \mathrm{d}P + \sum_{\beta=1}^{n-1} \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T} \mathrm{d}T. \tag{8}$$

From equation (4.164), taking into account (4.92) and the definition of mass fraction, (4.22), we derive:

$$\begin{aligned} \rho s\,\mathrm{d}T = -\rho \frac{\partial \hat{f}}{\partial T} \mathrm{d}T = -\rho \frac{\partial}{\partial T} \left(\sum_{\alpha=1}^{n} w_\alpha \hat{f}_\alpha \right) \mathrm{d}T = -\rho \left(\sum_{\alpha=1}^{n} w_\alpha \frac{\partial \hat{f}_\alpha}{\partial T} \right) \mathrm{d}T \\ = -\sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial T}\,\mathrm{d}T. \end{aligned} \tag{9}$$

Substituting (9) into (8), eq. (4.209) follows:

$$\begin{aligned} \sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} \omega_{\beta\gamma} \mathrm{d}\rho_\gamma &= -\mathrm{d}P_n + \rho_n \mathrm{d}g_n - \sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial T}\,\mathrm{d}T + \sum_{\beta=1}^{n-1} \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T}\,\mathrm{d}T \\ &= -\mathrm{d}P_n + \rho_n \mathrm{d}g_n - \rho_n \frac{\partial \hat{f}_n}{\partial T}\,\mathrm{d}T. \end{aligned}$$