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Because $f = \hat{f}(T, \rho_\alpha), \alpha = 1, ..., n$, cf. (4.160), we have $\rho f = \rho \hat{f}(T, \rho_\alpha)$ and then:

$$\mathrm{d}(\rho f) = \frac{\partial \rho \hat{f}}{\partial T}\mathrm{d}T + \sum_{\alpha=1}^{n} \frac{\partial \rho \hat{f}}{\partial \rho_\alpha}\mathrm{d}\rho_\alpha \equiv \rho \frac{\partial \hat{f}}{\partial T}\mathrm{d}T + \sum_{\alpha=1}^{n} \frac{\partial \rho \hat{f}}{\partial \rho_\alpha}\mathrm{d}\rho_\alpha. \tag{1}$$

Substituting from (4.164) and (4.161) into (1), **equation (4.201)** follows.

Capitalizing upon (1), **equation (4.202)** can be derived as follows:

$$\mathrm{d}(\rho u) = \mathrm{d}[\rho(f + Ts)] = \mathrm{d}(\rho f) + \mathrm{d}(\rho T s) = -\rho s\, \mathrm{d}(T) + \sum_{\alpha=1}^{n} g_\alpha \mathrm{d}\rho_\alpha +$$

$$\rho s\, \mathrm{d}T + T\, \mathrm{d}(\rho s) = T\, \mathrm{d}(\rho s) + \sum_{\alpha=1}^{n} g_\alpha \mathrm{d}\rho_\alpha.$$

The remaining equations require some preliminary considerations. Note, that, cf. (4.195):

$$\mathrm{d}v \equiv \mathrm{d}(1/\rho) = -(1/\rho^2)\, \mathrm{d}\rho. \tag{2}$$

From the definition of the mass fraction w_α, (4.22), and its property (4.23) two equations follow:

$$\mathrm{d}w_\alpha \equiv \mathrm{d}(\rho_\alpha/\rho) = (\rho\, \mathrm{d}\rho_\alpha - \rho_\alpha \mathrm{d}\rho)/\rho^2 \quad \Rightarrow \quad \mathrm{d}\rho_\alpha/\rho = \mathrm{d}w_\alpha + \rho_\alpha \mathrm{d}\rho/\rho^2. \tag{3}$$

$$\sum_{\alpha=1}^{n} w_\alpha = 1 \quad \Rightarrow \quad \sum_{\alpha=1}^{n} \mathrm{d}w_\alpha = 0. \tag{4}$$

Substitution of (4.193) and the mass fraction definition (4.22) into the definition (4.187) of the thermodynamic pressure result in following equation:

$$P = \sum_{\alpha=1}^{n} \rho_\alpha g_\alpha - \sum_{\alpha=1}^{n} \rho_\alpha f_\alpha = \rho \sum_{\alpha=1}^{n} w_\alpha g_\alpha - \rho \sum_{\alpha=1}^{n} w_\alpha f_\alpha = \rho(g - f) \tag{5}$$

where also (4.192) and (4.92) were used.

Now we are ready to derive **equation (4.204)** starting with (4.201):

$$\rho\, \mathrm{d}f + f \mathrm{d}\rho = -\rho s\, \mathrm{d}T + \sum_{\alpha=1}^{n} g_\alpha \mathrm{d}\rho_\alpha. \tag{6}$$

The free energy differential is expressed from (6)

$$\mathrm{d}f = -(f/\rho)\,\mathrm{d}\rho - s\,\mathrm{d}T + (1/\rho)\sum_{\alpha=1}^{n} g_\alpha \mathrm{d}\rho_\alpha. \tag{7}$$

The density derivatives in (7) are substituted from (2) and (3):

$$\mathrm{d}f = \rho f \mathrm{d}v - s\,\mathrm{d}T + \sum_{\alpha=1}^{n} g_\alpha \mathrm{d}w_\alpha + (\mathrm{d}\rho/\rho^2)\sum_{\alpha=1}^{n} \rho_\alpha g_\alpha. \tag{8}$$

Definitions (4.22) and (4.192) are introduced into (8) giving:

$$\mathrm{d}f = \rho f \mathrm{d}v - s\,\mathrm{d}T + \sum_{\alpha=1}^{n} g_\alpha \mathrm{d}w_\alpha + (g/\rho)\mathrm{d}\rho. \tag{9}$$

The last term in (9) is modified using (2):

$$\mathrm{d}f = \rho f \mathrm{d}v - s\mathrm{d}T + \sum_{\alpha=1}^{n} g_\alpha \mathrm{d}w_\alpha - \rho g\,\mathrm{d}v. \tag{10}$$

Rearrangement of (10) and substitution from (5) end in:

$$\mathrm{d}f = -s\,\mathrm{d}T - \rho(g-f)\mathrm{d}v + \sum_{\alpha=1}^{n} g_\alpha \mathrm{d}w_\alpha = -s\,\mathrm{d}T - P\mathrm{d}v + \sum_{\alpha=1}^{n} g_\alpha \mathrm{d}w_\alpha. \tag{11}$$

The last term in (11) can be modified, taking into account (4), as follows:

$$\begin{aligned}\sum_{\alpha=1}^{n} g_\alpha \mathrm{d}w_\alpha = &\sum_{\beta=1}^{n-1} g_\beta \mathrm{d}w_\beta + g_n \mathrm{d}w_n = \sum_{\beta=1}^{n-1} g_\beta \mathrm{d}w_\beta + g_n\left(-\sum_{\beta=1}^{n-1}\mathrm{d}w_\beta\right) = \\ &\sum_{\beta=1}^{n-1}(g_\beta - g_n)\,\mathrm{d}w_\beta.\end{aligned} \tag{12}$$

After substitution from (12) into (11), equation (4.204) results.

Derivation of the **remaining Gibbs equations** is now straightforward. For example, it follows from (4.197) that $\mathrm{d}u = \mathrm{d}f + T\mathrm{d}s + s\,\mathrm{d}T$ and substitution for $\mathrm{d}f$ from (4.204) gives the **equation (4.203)**.