

Page 182, equation (4.177) and the two affinities

First, let us note that vector \vec{B} was proposed to be called the (vector of) *constitutive affinity*¹. We will stick to this nomenclature here.

Substitution of (4.174) into $\mu_\alpha = \vec{\mu} \cdot \vec{e}^\alpha$ gives

$$\mu_\alpha = (-\vec{A} + \vec{B}) \cdot \vec{e}^\alpha \quad \alpha = 1, \dots, n. \quad (1)$$

From (4.175) it follows:

$$-\vec{A} \cdot \vec{e}^\alpha = - \sum_{p=1}^{n-h} A^p \vec{g}_p \cdot \vec{e}^\alpha.$$

The vector \vec{g}_p will be now transformed to the vector \vec{g}^q as shown in (A.86) and the latter will be expressed in terms of the basis \vec{e}_α as given by (4.40):

$$\begin{aligned} -\vec{A} \cdot \vec{e}^\alpha &= - \sum_{p=1}^{n-h} \sum_{q=1}^{n-h} A^p g_{pq} \vec{g}^q \cdot \vec{e}^\alpha = - \sum_{p=1}^{n-h} \sum_{q=1}^{n-h} A^p g_{pq} \left(\sum_{\gamma=1}^n P^{q\gamma} \vec{e}_\gamma \right) \cdot \vec{e}^\alpha \\ &= - \sum_{p=1}^{n-h} \sum_{q=1}^{n-h} A^p g_{pq} P^{q\alpha} \end{aligned} \quad (2)$$

The constitutive affinity vector is located in subspace \mathcal{W} ; in the basis \vec{f}_σ of this subspace (see p. 152) it is expressed as $\vec{B} = \sum_{\sigma=1}^h B^\sigma \vec{f}_\sigma$. Upon substitution from (4.34) we get:

$$\vec{B} \cdot \vec{e}^\alpha = \sum_{\sigma=1}^h B^\sigma \left(\sum_{\gamma=1}^n S_{\sigma\gamma} \vec{e}^\gamma \right) \cdot \vec{e}^\alpha = \sum_{\sigma=1}^h B^\sigma S_{\sigma\alpha}. \quad (3)$$

Equations (1)-(3) give (4.177).

Components of constitutive affinity vector can be expressed explicitly in terms of molar chemical potentials, similarly as in (4.176). Covariant components can be expressed substituting from (4.173) and (4.34) as follows:

$$B_\sigma = \vec{\mu} \cdot \vec{f}_\sigma = \left(\sum_{\alpha=1}^n \mu_\alpha \vec{e}^\alpha \right) \cdot \left(\sum_{\alpha=1}^n S_{\sigma\alpha} \vec{e}^\alpha \right) = \sum_{\alpha=1}^n \mu_\alpha S_{\sigma\alpha} \quad \sigma = 1, \dots, h. \quad (4)$$

¹Pekař M. Thermodynamics and foundations of mass-action kinetics. *Prog. React. Kinet. Mechan.*, 2005, vol. 30, no. 1/2, p. 3-113. ISSN 1468-6783.

The relationship between contravariant and covariant components is given by (A.89); in our case:

$$B^\sigma = \sum_{\tau=1}^h f^{\sigma\tau} B_\tau = \sum_{\alpha=1}^n \sum_{\tau=1}^h \mu_\alpha S_{\tau\alpha} f^{\sigma\tau} \quad \sigma = 1, \dots, h \quad (5)$$

where (4) was introduced in the second equality. Herein, $f^{\sigma\tau}$ is the contravariant metric tensor (of the subspace \mathcal{W}) which is obtained by inverting the covariant metric tensor $f_{\sigma\tau} = \vec{f}_\sigma \cdot \vec{f}_\tau$ which follows from (4.34).

Note. Given the stoichiometric matrix $\|P^{p\alpha}\|$ the vector \vec{g}^p is obtained from (4.40) and from it the contravariant metric tensor $g^{pq} = \vec{g}^p \cdot \vec{g}^q$, cf. (A.85). The covariant metric tensor g_{pq} is then obtained by the inversion of the latter, see (A.83).