Alternative derivations of restrictions on kinetics

Chapter 4.7 presents some thermodynamic restrictions on kinetics (reaction rates), see especially p. 211. They can be derived in alternative ways which are described below[1] and can serve also as an exercise for interested and inquiring readers.

Procedure A

First, we remind that the derivation in the book begins with the definition of "strong" equilibrium as given by (4.311) and explored in footnote 22 on page 211. This starting point is retained here.

As explained in footnote 22 on page 211, the function $\tilde{\Pi}_0(T, B^\sigma, A^r)$ has in the equilibrium defined by (4.311) zero and minimum value (at any equilibrium values of T and B^σ which are denoted by the superscript ^{o} as in the book). Consequently, the function and its first and second derivatives with respect to (chemical) affinities must have the following properties (in equilibrium):

$$\tilde{\Pi}_0(T^o, B^{\sigma o}, 0) = 0, \tag{1}$$

$$\frac{\partial \tilde{\Pi}_0(T^o, B^{\sigma o}, 0)}{\partial A^r} = 0; \quad r = 1, \ldots, n-h \tag{2}$$

and the matrix

$$\frac{\partial^2 \tilde{\Pi}_0(T^o, B^{\sigma o}, 0)}{\partial A^r \partial A^p} \quad (r, p = 1, \ldots, n-h) \tag{3}$$

must be positive semidefinite. Condition (1) is fulfilled trivially:

$$\tilde{\Pi}_0(T^o, B^{\sigma o}, 0) = \sum_{p=1}^{n-h} 0\, \tilde{J}_p(T^o, B^{\sigma o}, 0) = 0. \tag{4}$$

The derivative in condition (2) is (for some superscript s; $s = 1, \ldots, n-h$):

$$\begin{aligned} \frac{\partial \tilde{\Pi}_0}{\partial A^s} &= \sum_{p=1}^{n-h} \left(\frac{\partial A^p}{\partial A^s} \tilde{J}_p + A^p \sum_{r=1}^{n-h} \frac{\partial \tilde{J}_p}{\partial A^r} \frac{\partial A^r}{\partial A^s} \right) \\ &= \tilde{J}_s(T, B^\sigma, A^r) + \sum_{p=1}^{n-h} A^p \frac{\partial \tilde{J}_p(T, B^\sigma, A^r)}{\partial A^s}. \end{aligned} \tag{5}$$

[1] This text is based on notes by I. Samohýl which he had never published.

As stated above, all affinities vanish in equilibrium and (2) with (5) give

$$\tilde{J}_s(T^o, B^{\sigma o}, 0) = 0; \quad s = 1, \ldots, n-h, \tag{6}$$

i.e., in the equilibrium defined by the vanishing affinities of all independent reactions also all rates of these reactions are zero.

To get some results from the condition around (3) the second derivatives should be calculated starting from (5):

$$\begin{aligned}\frac{\partial^2 \tilde{\Pi}_0}{\partial A^s \partial A^t} &= \frac{\partial \tilde{J}_s}{\partial A^t} + \sum_{p=1}^{n-h} \frac{\partial A^p}{\partial A^t}\frac{\partial \tilde{J}_p}{\partial A^s} + A^p \sum_{r=1}^{n-h} \frac{\partial^2 \tilde{J}_p}{\partial A^s \partial A^r}\frac{\partial A^r}{\partial A^t} \\ &= \frac{\partial \tilde{J}_s(T, B^\sigma, A^r)}{\partial A^t} + \frac{\partial \tilde{J}_t(T, B^\sigma, A^r)}{\partial A^s} + \sum_{p=1}^{n-h} A^p \frac{\partial^2 \tilde{J}_p(T, B^\sigma, A^r)}{\partial A^s \partial A^t}. \end{aligned} \tag{7}$$

Using (7) in the condition (3) we obtain that in the equilibrium defined by the vanishing affinities the matrix with the elements

$$\frac{\partial \tilde{J}_s(T^o, B^{\sigma o}, 0)}{\partial A^t} + \frac{\partial \tilde{J}_t(T^o, B^{\sigma o}, 0)}{\partial A^s}; \quad s, t, \ldots, n-h \tag{8}$$

must be positive semidefinite. In other words, the symmetrized matrix with the elements

$$\frac{\partial \tilde{J}_{(s}}{\partial A^{t)}} = \frac{1}{2}\left(\frac{\partial \tilde{J}_s}{\partial A^t} + \frac{\partial \tilde{J}_t}{\partial A^s}\right); \quad s, t, \ldots, n-h \tag{9}$$

must be positive semidefinite in the equilibrium

$$\frac{\partial \tilde{J}_{(s}(T^o, B^{\sigma o}, 0)}{\partial A^{t)}}; \quad s, t, \ldots, n-h. \tag{10}$$

This is the same result as that which follows from equation (e) in footnote 22 on page 211 in the book – the quadratic form in this equation is positive semidefinite, consequently, also its symmetrized matrix is positive semidefinite (see also note on matrices at the end of this text). Results (6) and (10) are valid for any values of T, B^σ at $A^r = 0$ $(T^o, B^{\sigma o})$, $r = 1, \ldots, n-h$, generally.

Procedure B

Let us define Π_0 as a function[2] of a real parameter λ as follows:

$$\bar{\Pi}_0(\lambda) \equiv \bar{\Pi}_0(T, B^\sigma, \lambda A^p) = \sum_{r=1}^{n-h} \lambda A^r \bar{J}_r(T, B^\sigma, \lambda A^p) \tag{11}$$

[2]Cf. also equation (a) in footnote 22 on page 211 in the book.

for any $T > 0$ and any real B^σ and A^p.

Equilibrium (4.311) may be now expressed in terms of the parameter λ as

$$\lambda = 0 \tag{12}$$

at any values of T, B^σ, A^p (the superscript symbol ^{o} is superfluous in this part). The condition of zero and minimum value of $\bar{\Pi}_0$ at equilibrium can be expressed as

$$\bar{\Pi}_0(T, B^\sigma, \lambda A^p)|_{\lambda=0} = 0 \tag{13}$$

$$\frac{\mathrm{d}\bar{\Pi}_0(T, B^\sigma, \lambda A^p)}{\mathrm{d}\lambda}\Big|_{\lambda=0} = 0 \tag{14}$$

$$\frac{\mathrm{d}^2\bar{\Pi}_0(T, B^\sigma, \lambda A^p)}{\mathrm{d}\lambda^2}\Big|_{\lambda=0} \geq 0 \tag{15}$$

which are valid for any values of T and B^σ, and fixed but arbitrary A^p.

Upon inserting definition (11) into (13) it is seen that (13) is fulfilled trivially:

$$\bar{\Pi}_0(T, B^\sigma, \lambda A^p)|_{\lambda=0} = \sum_{r=1}^{n-h} \lambda A^r \bar{J}_r(T, B^\sigma, \lambda A^p)|_{\lambda=0} = 0. \tag{16}$$

The first derivative of the function (11) is:

$$\frac{\mathrm{d}\bar{\Pi}_0}{\mathrm{d}\lambda} = \sum_{r=1}^{n-h} \Big(A^r \bar{J}_r(T, B^\sigma, \lambda A^p) + \lambda A^r \sum_{p=1}^{n-h} A^p \frac{\partial \bar{J}_r(T, B^\sigma, \lambda A^p)}{\partial A^p} \Big) \tag{17}$$

and from it we obtain the necessary condition for minimum (14) in the form:

$$\frac{\mathrm{d}\bar{\Pi}_0}{\mathrm{d}\lambda}\Big|_{\lambda=0} = \sum_{r=1}^{n-h} A^r \bar{J}_r(T, B^\sigma, 0) = 0. \tag{18}$$

Equality (18) should be valid for any A^r, consequently, rates of all independent reactions should vanish in equilibrium:

$$\bar{J}_r(T, B^\sigma, 0) = 0; \qquad r = 1, \ldots, n-h, \tag{19}$$

which is equivalent to the result (6).

The second derivative of the function (11) is obtained by differentiation of (17):

$$\frac{\mathrm{d}^2\bar{\Pi}_0}{\mathrm{d}\lambda^2} = \sum_{r=1}^{n-h} \Big(A^r \sum_{p=1}^{n-h} A^p \frac{\partial \bar{J}_r(T, B^\sigma, \lambda A^p)}{\partial A^p} + A^r \sum_{p=1}^{n-h} A^p \frac{\partial \bar{J}_r(T, B^\sigma, \lambda A^p)}{\partial A^p} + \\ + \lambda A^r \sum_{p=1}^{n-h} A^p \sum_{s=1}^{n-h} A^s \frac{\partial^2 \bar{J}_r(T, B^\sigma, \lambda A^s)}{\partial A^p A^s} \Big). \tag{20}$$

Thus, the sufficient condition of the minimum (15) is:

$$\frac{\mathrm{d}^2\bar{\Pi}_0}{\mathrm{d}\lambda^2}\bigg|_{\lambda=0} = 2\sum_{r=1}^{n-h}\sum_{p=1}^{n-h} A^r A^p \frac{\partial \bar{J}_r(T, B^\sigma, 0)}{\partial A^p} \geq 0. \tag{21}$$

Therefore, the following quadratic form is positive semidefinite in equilibrium defined by (12) (or (4.311)):

$$\sum_{r=1}^{n-h}\sum_{p=1}^{n-h} A^r A^p \frac{\partial \bar{J}_r(T, B^\sigma, 0)}{\partial A^p} \geq 0. \tag{22}$$

Equation (22) is equivalent to equation (e) in footnote 22 on page 211 in the book.

Note on derivatives of reaction rates

Results (6) or (19) are valid at any T, B^σ (values in equilibrium). In other words, regardless the values of T, B^σ in equilibrium, the reaction rates have the same (zero) value in equilibrium. That is the rates are independent of T, B^σ in equilibrium:

$$\frac{\partial \tilde{J}_r(T^o, B^{\sigma o}, 0)}{\partial T} = 0, \qquad \frac{\partial \tilde{J}_r(T^o, B^{\sigma o}, 0)}{\partial B^\sigma} = 0, \qquad r = 1, \ldots, n-h.$$

Note on matrices

Matrix of quadratic form (22), of course, taken in equilibrium $A^p = 0$ at any T, B^σ, can be decomposed to symmetric and skew-symmetric parts as follows:

$$\frac{\partial \bar{J}_r}{\partial A^p} = \frac{\partial \bar{J}_{(r}}{\partial A^{p)}} + \frac{\partial \bar{J}_{[r}}{\partial A^{p]}} \tag{23}$$

where the skew-symmetric part is defined by (cf. (9))

$$\frac{\partial \bar{J}_{[r}}{\partial A^{p]}} \equiv \frac{1}{2}\Big(\frac{\partial \bar{J}_r}{\partial A^p} - \frac{\partial \bar{J}_p}{\partial A^r}\Big); \qquad r, p = 1, \ldots, n-h. \tag{24}$$

Inserting the decomposition into (22) we obtain:

$$\sum_{r=1}^{n-h}\sum_{p=1}^{n-h} A^r A^p \frac{\partial \bar{J}_{(r}(T, B^\sigma, 0)}{\partial A^{p)}} \geq 0 \tag{25}$$

because the skew-symmetric parts cancel. Therefore, the symmetrized matrix of the positive semidefinite form (22) is positive semidefinite in equilibrium defined by $A^p = 0$ at any T, B^σ; this is the same result as (10).