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# Instructions for use
APPLICATION OF STOICHIOMETRIC NUMBER
TO THEOREM OF
MINIMUM ENTROPY PRODUCTION

By

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The concept of the stoichiometric number [HORIUTI and NAKAMURA, Z. phys. Chem. (Neue Folge) 11, 358 (1957)] is applied to the derivation of PRIGOGINE's theorem on the relation between the minimum entropy production and the steady (stationary) state of an overall reaction consisting of elementary reactions. It is shown that the number of reaction routes \(P\) [loc. cit.] is equal to DE GROOT's order of this steady state.

As demonstrated by HORIUTI et al.,\(^1\)\(^-\)\(^3\) the concept of the stoichiometric number is useful for treating the steady (stationary) state of an overall reaction (OR) consisting of elementary reactions (ER's). In this note it will be shown that the concept is applicable to the generalization of the proof of PRIGOGINE's theorem\(^1\) on the relation between the minimum entropy production and the steady state of the OR.

The theorem states that as long as the linear relations are valid, the steady state of an OR resulting from a set of ER's corresponds to the minimum of the entropy production \(\sigma = (dS/dt)_{\text{eq}}\), for given constant values of the chemical potentials of the molecules\(^**\) and hence for constant values of the affinities (isotaffine\(^**\)) of the OR's synthesized from the above set.\(^3\) The proof goes as follows. When use is made of the linear relation

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\(^**\) Molecules in the sense of Ref. 1, i.e. chemical species other than intermediates. Terminologies and notations of Refs. 1 and 3 will be used in what follows.

3) J. HORIUTI, this Journal 5, 1 (1957).
Application of Stoichiometric Number to Theorem of Minimum Entropy Production

\begin{equation}
v_s = L_{ss} \left( -\Delta \mu / T \right), \quad (1)
\end{equation}

the entropy production by the ER's is given by\textsuperscript{\textasteriskcentered}

\begin{equation}
\sigma = (dS/dt)_{\text{ess}} = \sum_{s=1}^{S} v_s \left( -\Delta \mu / T \right) = \sum_{s=1}^{S} L_{ss} \left( -\Delta \mu / T \right)^2, \quad (2)
\end{equation}

where ER's are numbered by \( s=1, \ldots, S \), and \( v_s, -\Delta \mu \) and \( L_{ss} \) are the rate, the affinity and the phenomenological coefficient\textsuperscript{\textasteriskcentered}, respectively, of the \( s \)-th ER. Now suppose that these ER's allow \( P \) reaction routes\textsuperscript{o} (\( P \leq S \)) specified by sets of stoichiometric numbers \( (\nu_{s}^{(p)}, \ldots, \nu_{s}^{(p)}) \), \( p=1, \ldots, P \). Some routes may result in real OR's and other in null OR's\textsuperscript{**}; anyway we have the relations,

\begin{equation}
\sum_{s=1}^{S} \left( -\Delta \mu \right) \nu_{s}^{(p)} = \text{const.}, \quad p=1, \ldots, P, \quad (3)
\end{equation}

since the left hand side is the affinity of the resultant OR, which is kept constant for a real OR (vide supra) or equal to zero for a null OR. The minimum of (2) under the auxiliary conditions (3) can be determined as the extremum of the function

\[
\Phi = \sum_{s=1}^{S} L_{ss} \left( -\Delta \mu / T \right)^2 - \sum_{p=1}^{P} 2V^{(p)} \sum_{s=1}^{S} \left( -\Delta \mu / T \right) \nu_{s}^{(p)} ,
\]

where \(-2V^{(p)}/T\) is the Lagrange multiplier. From

\[
\frac{\partial \Phi}{\partial \left( -\Delta \mu / T \right)} = 2L_{ss} \left( -\Delta \mu / T \right) - \sum_{p=1}^{P} 2V^{(p)} \nu_{s}^{(p)} = 0
\]

as well as the linear relation (1), we have

\begin{equation}
v_s = \sum_{p=1}^{P} V^{(p)} \nu_{s}^{(p)}, \quad s=1, \ldots, S \quad (4)
\end{equation}

for the rates of the ER's at \( \sigma = \text{minimum} \). As shown by Horiiuti et al.,\textsuperscript{1}(4) is the necessary and sufficient condition for the steady state, i.e., that the abundances of intermediates do not vary with time, and the constant \( V^{(p)} \) may now be interpreted as the rate of the OR through the \( p \)-th reaction route. Hence we see that (4) is a generalization of

\textsuperscript{\textasteriskcentered} As shown in Refs. 3 and 4, kinetical consideration gives the content of the constant \( L_{ss} \) as

\[ L_{ss} = \bar{v}_{s}^{e}/R, \]

where \( \bar{v}_{s}^{e} \) is the forward rate of the \( s \)-th ER at equilibrium and \( R \) the gas constant.

\textsuperscript{**} A null or real OR is Nullreaktion or Realreaktion, respectively, of Ref. 3 (cf. §1 of Ref. 3); the former is an OR expressed by the trivial chemical reaction equation \( 0 = 0 \), and the latter an OR expressed by a usual chemical reaction equation.
the results obtained by PRIGOINE for some special examples\(^{*}\), for which the number of the reaction routes \(P\) was one.

It may be interesting to view the above derivation of (4) from another angle. We will consider the transformation of the force-flux pairs\(^{\text{v}}\) by a non-singular matrix \(\beta\) and its reciprocal \(\beta^{-1}\),

\[
J_p = \sum_{s=1}^{S} \beta_{ps} v_s, \quad X_p = \sum_{s=1}^{S} (-\mathcal{A}_{ps}/T) (\beta^{-1})_{sp}.
\]

In terms of the new forces \(X_p\) and fluxes \(J_p\) \((p=1, \cdots, S)\), the linear relation (1) and the entropy production (2) become

\[
J_p = \sum_{s=1}^{S} \tilde{J}_{ps} X_q
\]

and

\[
\sigma = \sum_{p=1}^{S} J_p X_p = \sum_{p=1}^{S} \sum_{q=1}^{S} \tilde{J}_{pq} X_p X_q,
\]

where

\[
\tilde{J}_{pq} = \sum_{s=1}^{S} \beta_{ps} \beta_{qs} L_{ss}
\]
satisfies ONsager's reciprocity relations. Now we will require

\[
\beta_{p+i,s} = b_{is} \text{ for } s=1, \cdots, S \text{ and } i=1, \cdots, I,
\]

\[
(\beta^{-1})_{sp} = \nu_{sp} \text{ for } s=1, \cdots, S \text{ and } p=1, \cdots, P,
\]

where \(I = S - P\) is the number of independent intermediates\(^{\text{v}}\), and \(b_{is}\) the number\(^{\text{v}}\) of the \(i\)-th independent intermediate formed by every act of the \(s\)-th ER; the requirements (8) and (9) imposed upon the matrices \(\beta\) and \(\beta^{-1}\) are compatible with the relation \(\beta \beta^{-1} = \text{unit matrix}\) (cf. Appendix). Then the auxiliary condition (3) is equivalent to fixing the values of \(P\) forces

\^*) One of PRIGOINE's examples is the set of ER's [Eq. (6.21) of Ref. 4],

\[
\begin{align*}
\text{Br}_2 & \longrightarrow 2\text{Br}, \\
\text{Br} + \text{H}_2 & \longrightarrow \text{HBr} + \text{H}, \\
\text{Br}_2 + \text{H} & \longrightarrow \text{HBr} + \text{Br},
\end{align*}
\]

for which \(P=1\) and the stoichiometric numbers \((\nu_1^{(1)}, \nu_2^{(1)}, \nu_3^{(1)})\) are \((0, 1, 1)\). Hence (4) becomes

\[
\nu_1 = 0, \quad \nu_2 = \nu_3 = V^{(1)}.
\]

\^\text{**}) This number \(b_{is}\) is called the stoichiometric coefficient of the \(i\)-th independent intermediate in the \(s\)-th ER in Ref. 4.

Application of Stoichiometric Number to Theorem of Minimum Entropy Production

\[ X_p = \sum_{s=1}^{S} (-J_s \mu_l / T) \nu^{(p)}_s, \quad p = 1, \ldots, P, \]

and it is readily shown\(^{4)}\) that the minimum of the entropy production (7) under the condition (3) leads to the stationary state of the \(P\)-th order of de Groot\(^{5)}\), in which \(I\) fluxes

\[ J_{p+1} = \sum_{s=1}^{S} b_{p} v_s \quad \text{(rate of increase of the \(i\)-th independent intermediate)}, \quad i = 1, \ldots, I, \]

vanish. It follows from (5) and (8) that

\[ v_s = \sum_{p=1}^{S} (\beta^{-1})_{p} J_{p} = \sum_{p=1}^{S} (\beta^{-1})_{p} J_{p} = \sum_{p=1}^{S} J_{p} v^{(p)}_s, \quad s = 1, \ldots, S, \]

and we have again (4) with the identities

\[ V^{(p)} = J_{p}, \quad p = 1, \ldots, P, \]

i.e., that \(V^{(p)}\) in (4) is the flux conjugate to the fixed force \(X_p\) \((p = 1, \ldots, P)\).

The above transformation\(^*\) may be illustrated by the set of ER's for the hydrogen electrode reaction quoted in Ref. 1 as an example:

\[ H^+ + e^- \rightarrow H(a), \quad 2H(a) \rightarrow H_2, \quad H(a) + H^+ + e^- \rightarrow H_2. \]

For the set (11), \(S = 3, P = 2, I = 1\), the stoichiometric numbers \((\nu_1^{(p)}, \nu_2^{(p)}, \nu_3^{(p)})\) for \(p = 1\) and \(p = 2\) are \((2, 1, 0)\) and \((1, 0, 1)\) (i.e., the catalytic and electrochemical mechanism routes\(^*\)\(^*\)) respectively, and the numbers \((b_{11}, b_{12}, b_{13})\) for the sole independent intermediate \(H(a)\) (a hydrogen atom chemisorbed on the electrode) are \((1, -2, -1)\). Hence we see that

\[ \beta = \begin{pmatrix} 0 & 1 & 0 \\ 1 & -2 & 0 \\ 1 & -2 & -1 \end{pmatrix}, \quad \beta^{-1} = \begin{pmatrix} 2 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 1 & -1 \end{pmatrix}, \]

and the linear relation (6) is

\[ \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \begin{pmatrix} L_{22} & -2L_{23} & -2L_{22} \\ -2L_{22} & L_{11} + 4L_{22} & L_{11} + 4L_{22} \\ -2L_{23} & L_{11} + 4L_{22} & L_{11} + 4L_{23} + L_{33} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \end{pmatrix}, \]

\[ \text{(*) This transformation can be considered as the generalization of the simple example described in p. 41 of Ref. 4.} \]

\[ \text{(**) Cf. Eqs. (13), (14C) and (14E) of Ref. 1; see also J. O'M. Bockris, Chem. Rev. 43, 625 (1948).} \]
In the steady state, the fluxes $J_i$ and $J_e$ are the OR rates through the catalytic and electrochemical mechanism routes respectively, and the rate of increase $J_i$ of the intermediate $H(a)$ vanishes.

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Appendix

Construction of Matrices $\beta$ and $\beta^{-1}$ Subject to Requirements (8) and (9).

One can find out a $(S \times S)$ non-singular matrix $\beta'$ subject to the requirement,

$\beta_{p+i,s} = b_{ts}$ for $i = 1, \ldots, I$ and $s = 1, \ldots, S$,  \hspace{1cm} (A.1)

since the $I$ vectors $(b_{i1}, \ldots, b_{iS})$, $i = 1, \ldots, I$ are linearly independent according to the definition of independent intermediates\(^1\). Let the matrix $a'$ be the reciprocal of $\beta'$, then

$$\sum_{s=1}^{S} \beta_{ps}' a_{qs}' = \delta_{pq}$$  \hspace{1cm} (assuming $\delta_{pq} = KRONEOVER's$ delta)

for $p, q = 1, \ldots, S$.  \hspace{1cm} (A.2)

From (A.1) and (A.2) we have

$$\sum_{s=1}^{S} b_{ts} a_{qs}' = 0$$  \hspace{1cm} for $i = 1, \ldots, I$ and $q = 1, \ldots, P$,

which implies\(^*)\) that the $P$ linearly independent vectors $(a_{1q}', \ldots, a_{Pq}')$, $q = 1, \ldots, P$ are connected with the stoichiometric numbers by linear transformations:

$$a_{iq}' = \sum_{p=1}^{P} \nu_{ip}^{(p)} f_{pq}, \hspace{1cm} q = 1, \ldots, P,$$

$$\nu_{ip}^{(p)} = \sum_{q=1}^{P} a_{iq}' (f^{-1})_{qp}, \hspace{1cm} p = 1, \ldots, P,$$

where $f$ and $f^{-1}$ are a $(P \times P)$ non-singular matrix and its reciprocal respectively.

Then the matrix $\beta$ with the elements

$$\beta_{ps} = \sum_{q=1}^{P} f_{pq} a_{qs}' \hspace{1cm} p = 1, \ldots, P\right\} \\
\beta_{p+i,s} = \beta_{p+i,s} = b_{ts} \hspace{1cm} i = 1, \ldots, I \right\}$$

\* Cf. Ref. 1, Eqs. (6) and (10).
and the matrix $a$ with the elements
\[ a_{pq} = \nu^{(q)}_t, \quad q = 1, \ldots, P \]
\[ a_{s,t+i} = a_{s+1,t+i}, \quad s = 1, \ldots, S, \quad i = 1, \ldots, I \]
are the required matrices $\beta$ and $\beta^{-1}$ respectively, since they satisfy (8) and (9) as well as the relation $a\beta = \text{unit matrix}$:
\[
\sum_{q=1}^{P} a_{pq} \beta_{qt} = \sum_{q=1}^{P} a_{pq} \beta_{qt} + \sum_{i=1}^{I} a_{s,t+i} \beta_{s+i,t} \\
= \sum_{p=1}^{P} \sum_{q=1}^{P} \sum_{r=1}^{P} a\beta_{pq} (f^{-1})_{pq} f_{qr} \beta_{rt} + \sum_{i=1}^{I} a_{s,t+i} \beta_{s+i,t} \\
= \sum_{p=1}^{P} a\beta_{pq} + \sum_{i=1}^{I} a_{s,t+i} \beta_{s+i,t} = \sum_{p=1}^{S} a\beta_{pq} \\
= \delta_{st}.
\]