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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 theorem¹⁾ 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 $\sigma = (dS/dt)_{i,r,r}$ for given constant values of the chemical potentials of the *molecules*^{***)} and hence for constant values of the affinities (*isoeffine*⁵⁾) of the OR's synthesized from the above set.¹⁾ 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.

1) J. HORIUTI and T. NAKAMURA, *Z. phys. Chem. (Neue Folge)* **11**, 358 (1957).

2) J. HORIUTI, *Z. phys. Chem. (Neue Folge)* **12**, 321 (1957).

3) J. HORIUTI, *this Journal* **5**, 1 (1957).

4) I. PRIGOGINE, *Introduction to Thermodynamics of Irreversible Processes*, p. 74 *et seq.*, C. C. THOMAS, Illinois (1955).

$$v_s = L_{ss}(-\Delta_s\mu/T), \quad (1)$$

the entropy production by the ER's is given by¹⁾

$$\sigma = (dS/dt)_{irr} = \sum_{s=1}^S v_s(-\Delta_s\mu/T) = \sum_{s=1}^S L_{ss}(-\Delta_s\mu/T)^2, \quad (2)$$

where ER's are numbered by $s=1, \dots, S$, and v_s , $-\Delta_s\mu$ and L_{ss} are the rate, the affinity and the phenomenological coefficient^{*)}, respectively, of the s -th ER. Now suppose that these ER's allow P reaction routes¹⁾ ($P \leq S$) specified by sets of stoichiometric numbers $(\nu_s^{(p)}, \dots, \nu_s^{(p)})$, $p=1, \dots, P$. Some routes may result in *real* OR's and other in *null* OR's^{**)}; anyway we have the relations,

$$\sum_{s=1}^S (-\Delta_s\mu)\nu_s^{(p)} = \text{const.}, \quad p = 1, \dots, P, \quad (3)$$

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

$$\Phi = \sum_{s=1}^S L_{ss}(-\Delta_s\mu/T)^2 - \sum_{p=1}^P 2V^{(p)} \sum_{s=1}^S (-\Delta_s\mu/T) \nu_s^{(p)},$$

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

$$\frac{\partial\Phi}{\partial(-\Delta_s\mu/T)} = 2L_{ss}(-\Delta_s\mu/T) - \sum_{p=1}^P 2V^{(p)}\nu_s^{(p)} = 0$$

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

$$v_s = \sum_{p=1}^P V^{(p)}\nu_s^{(p)}, \quad s = 1, \dots, S \quad (4)$$

for the rates of the ER's at σ =minimum. As shown by HORIUTI *et al.*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

*) 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.

***) 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 PRIGOGINE 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 pairs⁵⁾ by a non-singular matrix β and its reciprocal β^{-1} ,

$$J_p = \sum_{s=1}^S \beta_{ps} v_s, \quad X_p = \sum_{s=1}^S (-\Delta_s \mu / T) (\beta^{-1})_{sp}. \quad (5)$$

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

$$J_p = \sum_{q=1}^S \bar{L}_{pq} X_q \quad (6)$$

and

$$\sigma = \sum_{p=1}^S J_p X_p = \sum_{p=1}^S \sum_{q=1}^S \bar{L}_{pq} X_p X_q, \quad (7)$$

where

$$\bar{L}_{pq} = \sum_{s=1}^S \beta_{ps} \beta_{qs} L_{ss}$$

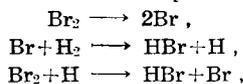
satisfies ONSAGER's reciprocity relations. Now we will require

$$\beta_{p+i,s} = b_{is} \quad \text{for } s=1, \dots, S \text{ and } i=1, \dots, I, \quad (8)$$

$$(\beta^{-1})_{sp} = \nu_s^{(p)} \quad \text{for } s=1, \dots, S \text{ and } p=1, \dots, P, \quad (9)$$

where $I=S-P$ is the number of *independent intermediates*¹⁾, and b_{is} the number^{**)} of the i -th independent intermediate formed by every act of the s -th ER; the requirements (8) and (9) imposed upon the matrices β and β^{-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 PRIGOGINE's examples is the set of ER's [Eq. (6.21) of Ref. 4],



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

$$v_1 = 0, \quad v_2 = v_3 = V^{(1)}.$$

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

5) S. R. DE GROOT, *Thermodynamics of Irreversible Processes*, Chapters I, X and XI, North-Holland Publishing Co., Amsterdam (1952).

$$X_p = \sum_{s=1}^S (-\Delta_s \mu / T) \nu_s^{(p)}, \quad p = 1, \dots, P,$$

and it is readily shown^{4b)} that the minimum of the entropy production (7) under the condition (3) leads to the *stationary state of the P-th order* of DE GROOT⁵⁾, in which *I* fluxes

$$J_{r+i} = \sum_{s=1}^S b_{is} v_s = \left(\begin{array}{c} \text{rate of increase of the } i\text{-th} \\ \text{independent intermediate} \end{array} \right), \quad i = 1, \dots, I,$$

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

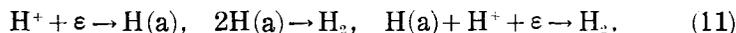
$$v_s = \sum_{p=1}^P (\beta^{-1})_{sp} J_p = \sum_{p=1}^P (\beta^{-1})_{sp} J_p = \sum_{p=1}^P J_p \nu_s^{(p)}, \quad s = 1, \dots, S,$$

and we have again (4) with the identities

$$V^{(p)} = J_p \quad p = 1, \dots, P, \quad (10)$$

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

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



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

$$\begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \begin{pmatrix} L_{22} & -2L_{22} & -2L_{22} \\ -2L_{22} & L_{11} + 4L_{22} & L_{11} + 4L_{22} \\ -2L_{22} & L_{11} + 4L_{22} & L_{11} + 4L_{22} + L_{33} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \end{pmatrix}. \quad (12)$$

*) This transformation can be considered as the generalization of the simple example described in p. 41 of Ref. 4.

**) Cf. Eqs. (13), (14C) and (14E) of Ref. 1; see also J. O'M. BOCKRIS, Chem. Rev. **43**, 525 (1948).

In the steady state, the fluxes J_1 and J_2 are the OR rates through the catalytic and electrochemical mechanism routes respectively, and the rate of increase J_3 of the intermediate H(a) vanishes.

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Appendix

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

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

$$\beta'_{P+\ell, s} = b_{\ell s} \quad \text{for } i=1, \dots, I \text{ and } s=1, \dots, S, \quad (\text{A. 1})$$

since the I vectors (b_{i1}, \dots, b_{iS}) , $i=1, \dots, I$ are linearly independent according to the definition of independent intermediates¹⁾. Let the matrix α' be the reciprocal of β' , then

$$\sum_{s=1}^S \beta'_{ps} \alpha'_{sq} = \delta_{pq} \quad (\delta_{pq} = \text{Kronecker's delta})$$

$$\text{for } p, q = 1, \dots, S. \quad (\text{A. 2})$$

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

$$\sum_{s=1}^S b_{\ell s} \alpha'_{sq} = 0 \quad \text{for } i=1, \dots, I \text{ and } q=1, \dots, P,$$

which implies^{*)} that the P linearly independent vectors $(\alpha'_{i1}, \dots, \alpha'_{iS})$, $q=1, \dots, P$ are connected with the stoichiometric numbers by linear transformations:

$$\alpha'_{sq} = \sum_{p=1}^P \nu_s^{(p)} f_{pq}, \quad q = 1, \dots, P,$$

$$\nu_s^{(p)} = \sum_{q=1}^P \alpha'_{sq} (f^{-1})_{qp}, \quad p = 1, \dots, P,$$

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

Then the matrix β with the elements

$$\left. \begin{aligned} \beta_{ps} &= \sum_{q=1}^P f_{pq} \beta'_{qs}, & p &= 1, \dots, P \\ \beta_{P+\ell, s} &= \beta'_{P+\ell, s} = b_{\ell s}, & i &= 1, \dots, I \end{aligned} \right\} \quad s = 1, \dots, S,$$

*) Cf. Ref. 1, Eqs. (6) and (10).

and the matrix α with the elements

$$\left. \begin{aligned} \alpha_{sq} &= \nu_s^{(q)}, & q &= 1, \dots, P \\ \alpha_{s, P+i} &= \alpha'_{s, P+i}, & i &= 1, \dots, I \end{aligned} \right\} \quad s = 1, \dots, S,$$

are the required matrices β and β^{-1} respectively, since they satisfies (8) and (9) as well as the relation $\alpha\beta = \text{unit matrix}$:

$$\begin{aligned} \sum_{q=1}^S \alpha_{sq} \beta_{qt} &= \sum_{q=1}^P \alpha_{sq} \beta_{qt} + \sum_{i=1}^I \alpha_{s, P+i} \beta_{P+i, t} \\ &= \sum_{p=1}^P \sum_{q=1}^P \sum_{r=1}^P \alpha'_{sp} (f^{-1})_{pq} f_{qr} \beta'_{rt} + \sum_{i=1}^I \alpha'_{s, P+i} \beta'_{P+i, t} \\ &= \sum_{p=1}^P \alpha'_{sp} \beta'_{pt} + \sum_{i=1}^I \alpha'_{s, P+i} \beta'_{P+i, t} = \sum_{p=1}^S \alpha'_{sp} \beta'_{pt} \\ &= \delta_{st}. \end{aligned}$$