NOTE ON CHEMICAL KINETICS IN THE NEIGHBOURHOOD OF EQUILIBRIUM

By

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This paper examines the linear relation between the rate and the affinity of a complex reaction, i.e., an overall reaction composed of a set of elementary reactions. The linear relation is derived for $P$ simultaneous overall reactions in the steady state. The expression so obtained involves terms expressing the coupling (interference) of the overall reactions when $P \geq 2$, or is shown to reduce to the expressions by Horiuti or Hollingsworth when $P = 1$.

The linear relation between the rate and the affinity of a chemical reaction close to equilibrium has been discussed by a number of authors on the basis of a thermodynamical consideration, or of classical chemical kinetics; the relation is expressed as

$$v = -\lambda \Delta \mu$$

with the positive constant coefficient,

$$\lambda = \bar{v}^{(e)}/RT,$$

where $v$, $\bar{v}$ and $-\Delta \mu$ are, respectively, the rate, the forward rate and the affinity, $R$ is the gas constant, and the superscript $(e)$ designates the value at equilibrium.

However, as the derivations of the relation indicate, the expression (1) with (1$\lambda$) is appropriate only for an elementary reaction (ER), but not for a complex reaction, i.e., an overall reaction (OR) composed

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2) Research Institute for Catalysis, Hokkaido University.
1) (a) PRIGOGINE, OUTER and HEREO, J. Phys. Colloid Chem. 52, 321 (1948); (b) MANES, HOFER and WELLER, J. Chem. Phys. 18, 1355 (1950).
2) Cf. PRIGOGINE, Ref. 9, p. 57, in which the GULD BERG-WAAGE law of mass action is used.
4) (a) HORIUTI, Proc. Japan Acad. 29, 160 (1953); (b) HORIUTI, this Journal 5, 1 (1957).
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of a set of ER's. In this connection Horiuti has pointed out\textsuperscript{5} that the linear relation (1) with (1\textsuperscript{1}) can be extended to the case of the rate \( V \) and the affinity \( -A_0^\mu \) of an OR close to equilibrium, provided that the constituent ER's provide a single reaction route\textsuperscript{4b,7} and there exists a rate-determining step; his expression\textsuperscript{8} is

\[ V = -\lambda^OR A_0^\mu \]  

(2)

with

\[ \lambda^OR = \bar{v}_{\ell} / \nu_{\ell} \text{ and } \bar{v}_{\ell} = \bar{v}_{\ell} / \nu_{\ell}, \]  

(2\textsuperscript{1})

where \( \nu_{\ell} \) and \( \bar{v}_{\ell} \) are the stoichiometric number\textsuperscript{4b,7} and the forward rate, respectively, of the rate-determining step, and \( \bar{v}_{\ell} = \bar{v}_{\ell} / \nu_{\ell} \) may be interpreted as "the forward rate of the OR"\textsuperscript{4b,7}. In the present note we will examine a more general characteristic of an OR composed of ER's close to equilibrium, basing our discussion on the two recent papers by us\textsuperscript{7}, which will be referred to as HN\textsuperscript{7} and NY\textsuperscript{8} in what follows.

In HN we have discussed the steady state of \( S \) concurrent ER's, and shown that in the steady state, \( P \) OR's will in general result from the ER's and the rate \( v_s \) of the \( s \)-th ER \((s=1,\cdots,S)\) will be expressed as

\[ v_s = \sum_{p=1}^{S} V_s V_{s}^{(p)}, \]  

(3)

where \( P \) is the number of the reaction routes appropriate to the \( S \) ER's \((P \leq S)\), \( V_p \) is the rate\textsuperscript{9} of the OR of the \( p \)-th reaction route (or the \( p \)-th OR, for short), and \( v_{s}^{(p)} \) is the stoichiometric number of the \( s \)-th ER for the \( p \)-th reaction route \((p=1,\cdots,P)\).

Now we will assume that the \( S \) ER's are close to equilibrium and hence the relation (1) holds for the rate \( v_s \) and the affinity \( -A_0^\mu \) of each ER:

\[ v_s = -\lambda_s A_0^\mu, \quad s = 1,\cdots,S, \]  

\(1'\)

or

\[ -A_0^\mu = v_s v_s, \quad s = 1,\cdots,S, \]  

\(1'^{\ast}\)

with

\textsuperscript{*) Cf. Section III of Ref. 4a, or Eq. (67) of Ref. 4b.

\textsuperscript{**) Cf. Appendix I.


8) NAKAMURA and YAMAZAKI this Journal 5, 98 (1957).
\[ \lambda_s = \bar{v}_s^{(q)}/RT \quad \text{and} \quad \kappa_s = 1/\lambda_s, \]

where \( v_s, \bar{v}_s \) and \( -\Delta_{s\mu} \) are the rate, the forward rate and the affinity, respectively, of the \( s \)-th ER. Substituting (3) into (1*) we have

\[ \sum_{q=1}^{P} \kappa_s V_q \nu_s^{(q)} = -\Delta_{s\mu}, \]

and further, remembering that \( -\sum_{s=1}^{S} \nu_s^{(p)} \Delta_{s\mu} \) equals** the affinity \( -\Delta_{s\mu} \) of the \( p \)-th OR, we obtain

\[ \sum_{s=1}^{S} \nu_s^{(p)} \sum_{q=1}^{P} \kappa_s V_q \nu_s^{(q)} = -\Delta_{s\mu}. \]

The rearrangement of the latter expression yields the linear relation between the rates \( V_p \) and the affinities \( -\Delta_{s\mu} \) of the \( P \) OR's,

\[ -\Delta_{s\mu} = \frac{\sum_{q=1}^{P} \kappa_{pq} V_q}{\prod_{q=1}^{P}} \quad p = 1, \ldots, P, \quad (4) \]

with the constant coefficients,

\[ \kappa_{pq} = \sum_{s=1}^{S} \nu_s^{(p)} \nu_s^{(q)} = RT \sum_{s=1}^{S} \nu_s^{(p)} \nu_s^{(q)} \bar{v}_s^{(e)}. \quad (4\*) \]

Inasmuch as \( \kappa_s = RT/\bar{v}_s^{(e)} > 0 \) \( (s = 1, \ldots, S) \) in (4\*), it can readily be shown** that the determinant \( \det (\kappa_{pq}) \) of the matrix \( (\kappa_{pq}) \) is non-zero, and hence we can invert the relation (4) as

\[ V_p = -\sum_{s=1}^{P} \lambda_{pq} \Delta_{s\mu}, \quad p = 1, \ldots, P, \quad (4\*) \]

where the matrix \( (\lambda_{pq}) \) is the reciprocal of the matrix \( (\kappa_{pq}) \). The linear relation \( (4\*) \) is, in its form, closer to (1) or (2) than (4), but the relation between the coefficients \( \lambda_{pq} \) and the stoichiometric numbers is in general more complicated than (4\*).

The relation (1') or (1\#) for the \( S \) ER's is, in the terminology of thermodynamics of irreversible processes***, the phenomenological relation between \( S \) forces and \( S \) fluxes \( (\Delta_{s\mu} \text{ and } v_s, s = 1, \ldots, S) \). Now we see that in the steady state this relation can be reduced**** to the

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** Cf. Appendix I.

*** Cf. Appendix III.

**** Extending the treatment of NY we can show an interesting connection between the expressions (1\#) and (4), or (1') and (4\#); cf. Appendix II.


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expression (4) or \((4^*)\), which involves \(P\) pairs of forces and fluxes \((-\Delta^{(p)}\mu\) and \(V_p, p = 1, \ldots, P\)). An analogous situation is found in the theory of electric network circuits. Consider a \(2P\)-terminal \((P\)-terminal pair\) network consisting of circuit elements which obey the linear relation between current \(i\) and EMF (electromotive force) \(e\), i.e., for the \(s\)-th element,

\[
\begin{align*}
\lambda_s e_s & \quad \text{or} \quad e_s = \kappa_s j_s, \quad (\lambda_s = 1/\kappa_s)
\end{align*}
\]

where \(\lambda_s\) and \(\kappa_s\) are the admittance (conductance) and the impedance (resistance) of the \(s\)-th element. Then, as is well-known, the current-EMF relation for the network is quite similar to the expression (4) or \((4^*)\):

\[
\begin{align*}
E_p &= \sum_{q=1}^{P} \kappa_{pq} I_q, \\
I_p &= \sum_{q=1}^{P} \lambda_{pq} E_q,
\end{align*}
\]

where \(\kappa_{pq}\) and \(\lambda_{pq}\) are the impedance and admittance matrices respectively, and \(E_p\) and \(I_p\) are the EMF and the current, respectively, at the \(p\)-th terminal pair.

In the relation (4) for the steady state, the coefficients \(\kappa_{pq}\) with \(p \neq q\), satisfying the reciprocity relation \(\kappa_{pq} = \kappa_{qp}\), describe the coupling (or interference) between the \(p\)-th and \(q\)-th OR's. As one can readily see from the expression \((4^*)\) for \(\kappa_{pq}\) as well as the definition of the stoichiometric number, it is necessary for the non-vanishing coupling that the two OR's possess at least one ER in common.

In the special case of a single reaction route, i.e., \(P = 1^*\), Eqs. (4) and \((4^*)\) reduce to

\[
\text{Eq. (5)}: \quad V_i = -\Delta^{(1)}\mu/\kappa
\]

Furthermore, if the \(r\)-th ER is a very "slow" one compared with other \(S - 1\) ER's, i.e., \(\lambda_r \ll \lambda_i\) or \(\kappa_r \gg \kappa_i\) \((i=1, \ldots, r-1, r+1, \ldots, S)\), then we may call the \(r\)-th ER the rate-determining step and simplify (5) and \((5^*)\) into

\[
\text{Eq. (6)}: \quad V_i = -\Delta^{(1)}\mu/\kappa
\]

with

\[
\kappa = \kappa_r (\nu_i^{(r)})^2 = (\nu_i^{(r)})^2 RT/\bar{\nu}_i^{(r)}, \quad (6^*)
\]

This is nothing but the linear relation for the single OR, (2) with \((2^*)\) previously obtained by Horiuti in a different way\(^\text{(*)}\).

\(^{(*)}\) Recently Hollingsworth (Ref. 6) also treated this case and obtained the same result as our (5) and \((5^*)\) (cf. his Eq. (15)). (Cf. also Prigogine et al., Ref. a, Eq. 23.)
As an example we will now apply the linear relation (4) or (4*) to the following set of ER's put forward for the thermal decomposition reaction of ethane (the Rice-Hertzfeld mechanism)\textsuperscript{11};

1. \( \text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3 \),
2. \( \text{CH}_3 + \text{C}_2\text{H}_6 \rightarrow \text{CH}_4 + \text{C}_2\text{H}_5 \),
3. \( \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H} \),
4. \( \text{H} + \text{C}_2\text{H}_6 \rightarrow \text{H}_2 + \text{C}_2\text{H}_5 \),
5. \( \text{H} + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6 \),

in which three independent intermediates, \( \text{CH}_3 \), \( \text{C}_2\text{HS} \), and \( \text{H} \) are involved.

For the above set with \( S = 5 \) and \( P = 2 \) we may choose the two reaction routes as follows:\textsuperscript{8}:

<table>
<thead>
<tr>
<th>Route</th>
<th>Stoichiometric no.</th>
<th>The ( p ) th OR</th>
<th>Rate and affinity of OR</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>((0, 0, 1, 1, 0))</td>
<td>( \text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2 )</td>
<td>( V_I, , -\mathcal{J}_I^I \mu )</td>
</tr>
<tr>
<td>II</td>
<td>((1, 2, 1, 0, 1))</td>
<td>( 2\text{C}_2\text{H}_6 = 2\text{CH}_4 + 2\text{C}_2\text{H}_4 )</td>
<td>( V_{II}, , -\mathcal{J}_I^I \mu )</td>
</tr>
</tbody>
</table>

Then the relation (4) or (4*) becomes

\[
-\mathcal{J}_I^I \mu = \kappa_{11} V_1 + \kappa_{12} V_{II},
-\mathcal{J}_I^I \mu = \kappa_{21} V_1 + \kappa_{22} V_{II},
\]

with

\[
\begin{pmatrix}
\kappa_{11} & \kappa_{12} \\
\kappa_{21} & \kappa_{22}
\end{pmatrix}
= \begin{pmatrix}
\kappa_3 + \kappa_4 & \kappa_3 \\
\kappa_3 & \kappa_3 + 4 \kappa_2 + \kappa_3 + \kappa_5
\end{pmatrix},
\]

or

\[
V_1 = -\lambda_{11} \mathcal{J}_I^I \mu - \lambda_{12} \mathcal{J}_I^I \mu,
V_{II} = -\lambda_{21} \mathcal{J}_I^I \mu - \lambda_{22} \mathcal{J}_I^I \mu,
\]

with

\[
\begin{pmatrix}
\lambda_{11} & \lambda_{12} \\
\lambda_{21} & \lambda_{22}
\end{pmatrix}
= \mathcal{D}^{-1}\begin{pmatrix}
\kappa_3 + 4 \kappa_2 + \kappa_3 + \kappa_5 & -\kappa_3 \\
-\kappa_3 & \kappa_3 + \kappa_5
\end{pmatrix},
\]

where

\[
\mathcal{D} = \det (\kappa_{pq}) = (\kappa_1 + 4 \kappa_2) (\kappa_3 + \kappa_4) + \kappa_5 (\kappa_3 + \kappa_5) + \kappa_1 \kappa_3.
\]

In (8) or (8\textsuperscript{*}), the coefficients \( \kappa_{12} = \kappa_{21} = \kappa_4 = RT/\mathcal{T}_c \) or \( \lambda_{12} = \lambda_{21} = -\mathcal{T}_c/\mathcal{D} = \)

\textsuperscript{8} Quoted from p. 11 of Ref. 4b.

\textsuperscript{11} Rice and Hertzfeld, J. Am. Chem. Soc. 56, 284 (1934).
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$-RT/\Delta G^\circ$ express the coupling of the simultaneous reactions I and II which involve the third ER, $\text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}$ of (7) in common. Thus, for instance, by varying the chemical potential (concentration) of the chemical species $\text{H}_2$ involved in the reaction I but not in II, we can control the rate $V_\text{II}$ of the reaction II through the coupling. Moreover the rate and the affinity, $V_\text{I}$ and $-\Delta G^\circ$ (or $V_\text{II}$ and $-\Delta G^\circ$) are not necessarily of the same sign\(^9\) contrary to the case of the relation (1) or (2), i.e., the case of ER or $P=1$. It has been pointed out\(^9\) that the coupling of chemical reactions is of great importance in biological processes, and one may find some useful applications of the relation (4) or (4\*) also in such problems.

Finally the author wishes to express his sincere thanks to Professor J. Horiuti and Mr. H. Yamazaki for kind advices.

Appendix I

First we will show that the quantity $V_p$ in (3), which has originally been introduced as the coefficients of the linear combination in HN [cf. Eqs. (10) and (12) of HN], is the rate of the $p$-th OR. The rate of production $R_m$ of the $m$-th molecule\(^7\) by the $S$ ER's is

$$\sum_{s=1}^{S} b_{ms} v_s,$$

where $b_{ms}$ is the stoichiometric coefficient\(^7\) of the $m$-th molecule in the $s$-th ER. Thus, by virtue of (3) and HN's Eq. (5'), we have

$$R_m = \sum_{s=1}^{S} b_{ms} \sum_{p=1}^{P} V_p B_{mp} = \sum_{p=1}^{P} V_p \left( \sum_{s=1}^{S} b_{ms} B_{mp} \right) = \sum_{p=1}^{P} V_p B_{mp}',$$

where $B_{ms}$ is the stoichiometric coefficient\(^7\) of the $m$-th molecule in the $P$ OR. The last expression, representing the rate $R_m$ as the sum of the contributions $V_p B_{mp}$ from the respective OR's, indicates\(^7\) that $V_p$ is nothing but the rate of the $p$-th OR\(\ast\).

\(^9\) Cf. e.g., Ref. 9, p. 25, and Ref. 12, p. 42

\(^\ast\) The above argument needs a few modifications in the case when all the $P$ OR's are not independent (Ref. 12, p. 468), i.e., the rank of the matrix $B_{ms}$ is smaller than $P$. An example of this case is the set of ER's for the hydrogen electrode reaction, given in Ref. 8, Eq. (11). The set provides two reaction routes 1 and 2 (Ref. 8), which lead to the same OR, $2\text{H}^+ + 2\text{e} = \text{H}_2$. We can easily see that the rate of this OR is the sum of $V_1$ (the rate through the catalytic mechanism) and $V_2$ (the rate through the electrochemical mechanism) rather than either of them.

Similarly, the quantity $-\sum_{s=1}^{S} \nu_s^{(p)} \Delta \mu$ is shown to be equal to the affinity $-\Delta^{(p)} \mu$ of the $p$-th OR, since it follows from the definitions of the affinities and the stoichiometric number that

$$\Delta \mu = \sum \mu_i b_i + \sum \mu_m b_m$$

$$\Delta^{(p)} \mu = \sum \mu_m b_m^{(p)}$$

$$\sum_{s=1}^{S} \nu_s^{(p)} b_s^{(p)} = 0,$$

where $\mu_m$ and $\mu_i$ are respectively the chemical potentials of the $m$-th molecule and the $i$-th independent intermediate, and $b_s^{(p)}$ is the stoichiometric coefficient of the $i$-th independent intermediate in the $s$-th ER.

**Appendix II**

Another derivation of (4), which is more closely related with the treatment of NY, will be given here.

In NY the phenomenological relation (1') for the $S$ ER's was transformed into

$$J_s = \sum_{t=1}^{S} \bar{L}_{st} X_t , \quad s = 1, \ldots, S,$$

(NY, Eq. 6)

which can be inverted as

$$X_t = \sum_{s=1}^{S} \bar{K}_{ts} J_s , \quad t = 1, \ldots, S,$$

(A)

where $(\bar{K}_{ts})$ is the reciprocal matrix of the matrix $(\bar{L}_{st})$. The forces $X_t$ and the fluxes $J_t$ in the above expressions had the properties that\(^{*)}

$$J_t = V_t \quad \text{for} \quad t = 1, \ldots, P,$$

$$J_t = 0 \quad \text{for} \quad t = P+1, \ldots, S,$$

and

$$X_t = -\Delta^{(p)} \mu / T \quad \text{for} \quad t = 1, \ldots, P,$$

where $T$ is temperature. Thus the new phenomenological relation (A) will, in the steady state, reduce to

$$-\Delta^{(p)} \mu = T \sum_{t=1}^{P} \bar{K}_{ts} V_s , \quad \text{for} \quad t = 1, \ldots, P,$$

(B)

which is the same as the relation (4) in the text, since

\(^{*)}\quad \text{See NY, Eqs. (5), (9) and (10), and remember that } J_t \text{'s with } t = P+1, \ldots, S \text{, are the rates of increases of the independent intermediates, which vanish in the steady state.}
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\[ T \bar{K}_{ts} = \sum_{t=1}^{S} \kappa_{t} v_{t}^{(t)} v_{s}^{(t)} = \kappa_{ts} \quad \text{for } t, s = 1, \ldots, P, \quad (C) \]

as shown below.

**Proof of (C).** We quote the following relations from NY:

\[ \bar{L}_{st} = \sum_{t=1}^{S} \beta_{st} \beta_{ts} \bar{L}_{tt} = \sum_{t=1}^{S} \beta_{st} \beta_{ts} \bar{L}_{tt} \quad \text{for } i=1, \ldots, S \text{ and } t=1, \ldots, P, \quad (D) \]

where \( \beta \) and \( \beta^{-1} \) were the transformation matrix and its reciprocal respectively. Calculating the reciprocal of the matrix \( \bar{L}_{st} \), we have

\[ \bar{K}_{ts} = \sum_{t=1}^{S} (\kappa_{t}/T) (\beta^{-1})_{st} (\beta^{-1})_{ts} \]

which, together with (D), leads to the expression (C).

**Appendix III**

It follows from the definitions of \( J_{t} \) in NY and \( K_{ts} \) in Appendix II that the transformation of the quadratic form

\[ \sum_{s=1}^{S} (\kappa_{s}/T) v_{s}^{2} \quad , \quad (E) \]

by the non-singular matrix \( \beta \) leads to the quadratic form with the \( S \times S \) matrix \( \bar{K}_{ts} \),

\[ \sum_{t=1}^{S} \sum_{s=1}^{S} \bar{K}_{ts} J_{t} J_{s} \quad . \quad (F) \]

Since \( \kappa_{s} > 0 \), the quadratic form (E) and hence (F) are positive definite; this is in accord with the fact that the expression (E) or (F) is the entropy production. Considering the case \( J_{t}=0 \) for \( t=P+1, \ldots, S \) (steady state), we see that the quadratic form with the \( P \times P \) matrix \( \kappa_{ts} \) [cf. the relation (C) of Appendix II],

\[ T^{-1} \sum_{t=1}^{P} \sum_{s=1}^{P} \kappa_{ts} J_{t} J_{s} = \sum_{t=1}^{P} \sum_{s=1}^{P} \bar{K}_{ts} J_{t} J_{s} \]

also is positive definite, and hence the matrix \( \kappa_{ts} \) is non-singular, i.e., \( \det (\kappa_{ts}) \neq 0 \).