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NOTE ON CHEMICAL KINETICS IN THE NEIGHBOURHOOD OF EQUILIBRIUM

By

Takashi Nakamura*)

(Received June 4, 1958)

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 \(^2\), of classical chemical kinetics \(^2\)\(^-\)\(^4\), or of the theory of absolute reaction rate \(^3\)\(^4\); the relation is expressed as

\[
v = -\lambda \Delta \mu
\]

with the positive constant coefficient,

\[
\lambda = \frac{\bar{v}(e)}{RT},
\]

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 \(^2\)-\(^4\) of the relation indicate, the expression (1) with (1\(\lambda\)) is appropriate only for an elementary reaction (ER), but not for a complex reaction \(^1\)-\(^4\), i.e., an overall reaction (OR) composed

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\(^2\) Cf. Prigogine, Ref. 9, p. 57, in which the Guldberg-Waage law of mass action is used.


\(^4\) (a) Horiuti, Proc. Japan Acad. 29, 160 (1953); (b) Horiuti, this Journal 5, 1 (1957).
of a set of ER's. In this connection Horiiuti has pointed out\(^5\) that the linear relation (1) with (Li) can be extended to the case of the rate \(V\) and the affinity \(-\Delta^0\mu\) of an OR close to equilibrium, provided that the constituent ER's provide a single reaction route\(^{1(b)}\) and there exists a rate-determining step; his expression\(^*)\) is

\[
V = -\lambda^0\Delta^0\mu \tag{2}
\]

with

\[
\lambda^0 = \bar{V}^0/\nu_rRT \] and \(\bar{V}^0 = \bar{v}_r^0/\nu_r\), \(\tag{2i}\)

where \(\nu_r\) and \(\bar{v}_r\) are the stoichiometric number\(^{4(b)}\) and the forward rate, respectively, of the rate-determining step, and \(\bar{V} = \bar{v}_r/\nu_r\) may be interpreted as "the forward rate of the OR"\(^{4(b)}\). 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\(^{6,7}\), which will be referred to as HN\(^7\) and NY\(^7\) 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 \((s=1,\ldots,S)\) will be expressed as

\[
v_s = \sum_{p=1}^{P} V_p v_s^{(p)}, \tag{3}\]

where \(P\) is the number of the reaction routes appropriate to the \(S\) ER's \((P \leq S)\), \(V_p\) is the rate\(^{**}\) 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 \((p=1,\ldots,P)\).

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 \(-\Delta\mu\) of each ER:

\[
v_s = -\lambda_s\Delta\mu, \quad s = 1,\ldots,S, \tag{1'}\]

or

\[-\Delta\mu = v_s v_s, \quad s = 1,\ldots,S, \tag{1**}\]

with

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

\(^{**}\) Cf. Appendix I.


8) Nakamura and Yamazaki this Journal 5, 98 (1957).
where \( v_s, \bar{v}_s \) and \( -\Delta_f \mu \) are the rate, the forward rate and the affinity, respectively, of the \( s \)-th ER. Substituting (3) into (1*) we have
\[
\sum_{q=1}^{P} \kappa_s V_p v_s^{(q)} = -\Delta_f \mu,
\]
and further, remembering that \( -\sum_{s=1}^{S} v_s^{(p)} \Delta_f \mu \) equals\(^\text{***)} \) the affinity \( -\Delta_f \mu \) of the \( p \)-th OR, we obtain
\[
\sum_{s=1}^{S} \nu_s^{(p)} \sum_{q=1}^{Q} \kappa_s V_q v_s^{(q)} = -\Delta_f \mu.
\]
The rearrangement of the latter expression yields the linear relation between the rates \( V_p \) and the affinities \( -\Delta_f \mu \) of the \( P \) OR's,
\[
\begin{bmatrix}
-\Delta_f \mu = \sum_{q=1}^{Q} \kappa_{pq} V_q,
\end{bmatrix}
\]
with the constant coefficients,
\[
\kappa_{pq} = \sum_{s=1}^{S} \nu_s^{(p)} v_s^{(q)} = RT \sum_{s=1}^{S} \nu_s^{(p)} v_s^{(q)} / \bar{v}_s^{(q)},
\]
Inasmuch as \( \kappa_s = RT / \bar{v}_s^{(q)} > 0 \) \((s=1, \ldots, S)\) in (4\(\text{v}\)), it can readily be shown\(^{**\text{v}}\) that the determinant \( \det (\kappa_{pq}) \) of the matrix \((\kappa_{pq})\) is non-zero, and hence we can invert the relation (4) as
\[
\begin{bmatrix}
V_p = -\sum_{s=1}^{S} \lambda_{pq} \Delta_f \mu,
\end{bmatrix}
\]
where the matrix \((\lambda_{pq})\) is the reciprocal of the matrix \((\kappa_{pq})\). The linear relation (4\(\text{v}\)) 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\(\text{v}\)).

The relation (1\(\text{i}\)) or (1\(\text{v}\)) for the \( S \) ER's is, in the terminology of thermodynamics of irreversible processes\(^{9,10}\), the phenomenological relation between \( S \) forces and \( S \) fluxes \((-\Delta_f \mu \) and \( v_s, s=1, \ldots, S)\). Now we see that in the steady state this relation can be reduced\(^{**\text{v}}\) to the

---

\(^*\) Cf. Appendix I.

\(^{**}\) Cf. Appendix III.

\(^{**\text{v}}\) Extending the treatment of NY we can show an interesting connection between the expressions (1\(\text{v}\)) and (4), or (1\(\text{i}\)) and (4\(\text{v}\)); cf. Appendix II.


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,

\[
i_s = \lambda_s e_s \quad \text{or} \quad e_s = \kappa_s i_s, \quad (\lambda_s = 1/\kappa_s)
\]

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*):

\[
E_p = \sum_{q=1}^{P} \kappa_{pq} I_q, \quad p = 1, \ldots, P
\]

\[
I_p = \sum_{q=1}^{P} \lambda_{pq} E_q, \quad \text{where} \quad \kappa_{pq} \quad \text{and} \quad \lambda_{pq} \quad \text{are the impedance and admittance matrices respectively, and} \quad E_p \quad \text{and} \quad I_p \quad \text{are the EMF and the current, respectively, at the} \ p \text{-th terminal pair.}
\]

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

\[
-A^{(1)} \mu = \kappa V_1 \quad \text{and} \quad \kappa = \sum_{i=1}^{S} \kappa_i \langle \nu_1^{(1)} \rangle^2.
\]

Furthermore, if the \( r \)-th ER is a very "slow" one compared with other \( S-1 \) ER's, i.e., \( \lambda_i \ll \lambda_r \) 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

\[
V_1 = -A^{(1)} \mu / \kappa
\]

with

\[
\kappa = \kappa_r \langle \nu_1^{(r)} \rangle^2 = \langle \nu_1^{(r)} \rangle^2 RT / \theta_r^{(r)}.
\]

This is nothing but the linear relation for the single OR, (2) with (2*) previously obtained by Horiiuti in a different way.*

*= 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-Herzfeld mechanism)\(^\text{\textsuperscript{11}}\):

1. \( \ce{C2H4 -> 2CH2} \),
2. \( \ce{CH3 + C2H4 -> CH4 + C2H6} \),
3. \( \ce{C2H4 -> C2H2 + H} \),
4. \( \ce{H + C2H6 -> H2 + C2H2} \),
5. \( \ce{H + C2H2 -> C2H4} \),

in which three independent intermediates\(^\text{\textsuperscript{10,17}}\), \( \ce{CH3} \), \( \ce{C2H3} \) and \( \ce{H} \) are involved. For the above set with \( S=5 \) and \( P=2 \) we may choose the two reaction routes as follows\(^\text{\textsuperscript{\textbullet}}\):

<table>
<thead>
<tr>
<th>Route</th>
<th>Stoichiometric no. ((v_1^{(p)}, v_2^{(p)}, \ldots, v_s^{(p)}))</th>
<th>The ( p ) th OR</th>
<th>Rate and affinity of OR</th>
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<tr>
<td>I</td>
<td>((0, 0, 1, 1, 0))</td>
<td>( \ce{C2H4 = C2H2 + H2} )</td>
<td>( V_1, -\Delta^{(I)}\mu )</td>
</tr>
<tr>
<td>II</td>
<td>((1, 2, 1, 0, 1))</td>
<td>( 2\ce{C2H4 = 2CH2 + C2H2} )</td>
<td>( V_{11}, -\Delta^{(II)}\mu )</td>
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Then the relation (4) or (4*) becomes

\[
-\Delta^{(I)}\mu = \kappa_{11} V_1 + \kappa_{12} V_{11},
-\Delta^{(II)}\mu = \kappa_{21} V_1 + \kappa_{22} V_{11},
\]

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

\[
V_1 = -\lambda_{11} \Delta^{(I)}\mu - \lambda_{12} \Delta^{(II)}\mu,
V_{11} = -\lambda_{21} \Delta^{(I)}\mu - \lambda_{22} \Delta^{(II)}\mu,
\]

with

\[
\begin{pmatrix}
\lambda_{11} & \lambda_{12} \\
\lambda_{21} & \lambda_{22}
\end{pmatrix}
= D^{-1}
\begin{pmatrix}
\kappa_1 + 4\kappa_2 + \kappa_3 + \kappa_5 & -\kappa_3 \\
-\kappa_3 & \kappa_3 + \kappa_5
\end{pmatrix},
\]

where

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

In (8) or (8*), the coefficients \( \kappa_{12} = \kappa_{21} = \kappa_4 = RT/\bar{v}_4 \) or \( \lambda_{12} = \lambda_{21} = -\bar{v}_4 / D = \)

\(^{\text{\textsuperscript{\textbullet}}\text{\textsuperscript{\textbullet}}}\) Quoted from p. 11 of Ref. 4b.
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\[ -RT/D\delta_{i}^{(a)} \] express the coupling of the simultaneous reactions I and II which involve the third ER, \( \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H} \) 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 \( V_{II} \) of the reaction II through the coupling. Moreover the rate and the affinity, \( V_{I} \) and \( -\Delta^{(\mu)} \) (or \( V_{II} \) and \( -\Delta^{(\mu)} \)) 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\(^7\) 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

\[ R_m = \sum_{s=1}^{S} b_{ms} \sum_{p=1}^{P} V_p \delta_{s(p)} = \sum_{p=1}^{P} V_p \left( \sum_{s=1}^{S} b_{ms} \delta_{s(p)} \right) = \sum_{p=1}^{P} V_p B_m^{(p)} \]

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

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

\(^{**}\) 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 \( B_m^{(p)} \) 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 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

\[
\Delta \mu = \sum_{s} \mu_{s} b_{s} + \sum_{m} \mu_{m} b_{m} ,
\]

\[
\Delta^{(p)} \mu = \sum_{m} \mu_{m} B_{m}^{(p)} ,
\]

\[
\sum_{s=1}^{S} \nu_{s}^{(p)} b_{s} = 0 ,
\]

where \(\mu_{m}\) and \(\mu_{i}^{;}\) are respectively the chemical potentials of the \(m\)-th molecule and the \(i\)-th independent intermediate, and \(b_{s}\) 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

\[
\frac{J_{s}}{J_{t}} = \frac{X_{s}}{X_{t}} , \quad s = 1, \ldots, S ,
\]

(NY, Eq. 6)

which can be inverted as

\[
X_{t} = \sum_{s=1}^{S} K_{ts} J_{s} , \quad t = 1, \ldots, S ,
\]

(A)

where \((K_{ts})\) 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\(^{*)}\)

\[
J_{t} = V_{t} \quad \text{for} \quad t = 1, \ldots, P ,
\]

\[
J_{t} = 0 \quad \text{for} \quad t = P+1, \ldots, S ,
\]

in the steady state ,

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

\[
-\Delta^{(p)} \mu = T \sum_{s=1}^{P} K_{ts} V_{s} , \quad \text{for} \quad t = 1, \ldots, P ,
\]

(B)

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

\(^{*)\} \text{See NY, Eqs. (5), (9) and (10), and remember that } J_{t}'s \text{ with } t = P+1, \ldots, S \text{ are the rates}

\text{of increases of the independent intermediates, which vanish in the steady state.}
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\[ T K_{ts} = \sum_{\ell=1}^{S} \kappa_{\ell} \nu^{(\ell)}_{ts} \nu^{(\ell)}_{t s} = \kappa_{ts} \quad \text{for } t, s = 1, \cdots, P, \]  
\( (C) \)

as shown below.

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

\[ L_{ts} = \sum_{\ell=1}^{S} \beta_{\ell} T_{\ell} \sum_{\ell=1}^{S} \beta_{t} T_{t} , \]

\[ (\beta^{-1})_{\ell t} = \nu^{(\ell)}_{t} \quad \text{for } \ell = 1, \cdots, S \text{ and } t = 1, \cdots, P, \]  
\( (D) \)

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

\[ K_{ts} = \sum_{\ell=1}^{S} (\kappa_{\ell} T_{\ell}) (\beta^{-1})_{\ell t} (\beta^{-1})_{ts} , \]

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

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

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

\[ \sum_{s=1}^{S} \sum_{t=1}^{S} K_{ts} J_{t} J_{s} . \]  
\( (F) \)

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 \( t=P+1, \cdots, S \) (steady state), we see that the quadratic form with the \( P \times P \) matrix \( \kappa_{ts} \) [cf. the relation (C) of Appendix II],

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

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

13) E.g., HALMOS, Finite Dimensional Vector Spaces, Princeton University Press (1948), § 56.