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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 consideration¹⁾, of classical chemical kinetics²⁾, or of the theory of absolute reaction rate³⁾⁴⁾; the relation is expressed as

$$v = -\lambda \Delta\mu \quad (1)$$

with the positive constant coefficient,

$$\lambda = \bar{v}^{(e)}/RT, \quad (1\lambda)$$

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 derivations²⁾⁻⁴⁾ of the relation indicate, the expression (1) with (1 λ) is appropriate only for an *elementary reaction* (ER), but not for a *complex reaction*¹⁾⁻⁶⁾, i. e., an *overall reaction* (OR) composed

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1) (a) PRIGOGINE, OUTER and HEROU, 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 GULDBERG-WAAGE law of mass action is used.

3) GILKERSON, JONES and GALLUP, J. Chem. Phys. **20**, 1182 (1952); ZWOLINSKI and MARCUS, J. Chem. Phys. **21**, 2235 (1953); VAN RYSSELBERGHE, J. Chem. Phys. **22**, 761 (1954).

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 HORIUTI has pointed out¹⁾ that the linear relation (1) with (1λ) can be extended to the case of the rate V and the affinity $-\Delta^{\text{OR}}\mu$ of an OR close to equilibrium, provided that the constituent ER's provide a single *reaction route*^{4b)7)} and there exists a rate-determining step; his expression^{*)} is

$$V = -\lambda^{\text{OR}}\Delta^{\text{OR}}\mu \quad (2)$$

with

$$\lambda^{\text{OR}} = \bar{V}^{(e)}/\nu_r RT \quad \text{and} \quad \bar{V}^{(e)} = \bar{v}_r^{(e)}/\nu_r, \quad (2\lambda)$$

where ν_r and \bar{v}_r are the *stoichiometric number*^{4b)7)} 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"^{4b)6)}. 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 us⁷⁾⁸⁾, which will be referred to as HN⁷⁾ and NY⁸⁾ 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 ($s=1, \dots, S$) will be expressed as

$$v_s = \sum_{p=1}^P V_p \nu_s^{(p)}, \quad (3)$$

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 $\nu_s^{(p)}$ is the stoichiometric number of the s -th ER for the p -th reaction route ($p=1, \dots, P$).

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 $-\Delta_s\mu$ of each ER:

$$v_s = -\lambda_s \Delta_s \mu, \quad s = 1, \dots, S, \quad (1')$$

or

$$-\Delta_s \mu = \kappa_s v_s, \quad s = 1, \dots, S, \quad (1'')$$

with

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

**) Cf. Appendix I.

5) BAUER, J. Chem. Phys. **21**, 1888 (1953).

6) HOLLINGSWORTH, J. Chem. Phys. **27**, 1346 (1957).

7) HORIUTI and NAKAMURA, Z. f. phys. Chem. (Neue Folge) **11**, 358 (1957).

8) NAKAMURA and YAMAZAKI this Journal **5**, 98 (1957).

$$\lambda_s = \bar{v}_s^{(e)}/RT \quad \text{and} \quad \kappa_s = 1/\lambda_s,$$

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 $-\Delta^{(p)}\mu$ of the p -th OR, we obtain

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

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

$$-\Delta^{(p)}\mu = \sum_{q=1}^P \kappa_{pq} V_q, \quad p = 1, \dots, P, \quad (4)$$

with the constant coefficients,

$$\kappa_{pq} = \sum_{s=1}^S \kappa_s \nu_s^{(p)} \nu_s^{(q)} = RT \sum_{s=1}^S \nu_s^{(p)} \nu_s^{(q)} / \bar{v}_s^{(e)}. \quad (4\kappa)$$

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

$$V_p = -\sum_{q=1}^P \lambda_{pq} \Delta^{(q)}\mu, \quad p = 1, \dots, P, \quad (4^*)$$

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

The relation (1') or (1*) for the S ER's is, in the terminology of thermodynamics of irreversible processes⁹⁾¹⁰⁾, the phenomenological relation between S forces and S fluxes ($-\Delta_s\mu$ and v_s , $s=1, \dots, S$). Now we see that in the steady state this relation can be reduced***) to the

*) 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.

9) PRIGOGINE, *Introduction to Thermodynamics of Irreversible Processes*, C. C. THOMAS, Illinois. (1955).

10) DE GROOT, *Thermodynamics of Irreversible Processes*, North-Holland Publishing Co., Amsterdam (1952).

expression (4) or (4*), which involves P pairs of forces and fluxes ($-\Delta^{(p)}\mu$ and V_p , $p=1, \dots, P$). 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 λ_s and κ_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*):

$$\left. \begin{aligned} E_p &= \sum_{q=1}^P \kappa_{pq} I_q, \\ I_p &= \sum_{q=1}^P \lambda_{pq} E_q, \end{aligned} \right\} \quad p = 1, \dots, P$$

where κ_{pq} and λ_{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 κ_{pq} with $p \neq q$, satisfying the reciprocity relation^{9,10)} $\kappa_{pq} = \kappa_{qp}$, describe the *coupling* (or *interference*) between the p -th and q -th OR's. As one can readily see from the expression (4 κ) for κ_{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 κ) reduce to

$$-\Delta^{(1)}\mu = \kappa V_1 \quad \text{and} \quad \kappa = \sum_{s=1}^S \kappa_s (\nu_s^{(1)})^2. \quad (5), (5\kappa)$$

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 $\kappa_r \gg \kappa_i$ ($i=1, \dots, r-1, r+1, \dots, S$), then we may call the r -th ER the *rate-determining step* and simplify (5) and (5 κ) into

$$V_1 = -\Delta^{(1)}\mu/\kappa \quad (6)$$

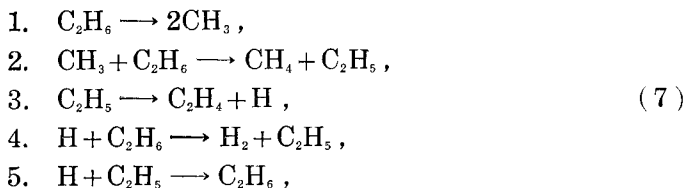
with

$$\kappa = \kappa_r (\nu_r^{(1)})^2 = (\nu_r^{(1)})^2 RT/\bar{v}_r^{(e)}. \quad (6\kappa)$$

This is nothing but the linear relation for the single OR, (2) with (2 λ) previously obtained by HORIUTI in a different way¹⁾.

*) Recently HOLLINGSWORTH (Ref. 6) also treated this case and obtained the same result as our (5) and (5 κ) (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*¹⁾ put forward for the thermal decomposition reaction of ethane (the RICE-HERZFELD mechanism)¹¹⁾;



in which three *independent intermediates*^(b)7), CH_3 , C_2H_5 and H are involved. For the above set with $S=5$ and $P=2$ we may choose the two reaction routes as follows*³⁾:

Route p	Stoichiometric no. $(\nu_1^{(p)}, \nu_2^{(p)}, \dots, \nu_5^{(p)})$	The p th OR	Rate and affinity of OR
I	(0, 0, 1, 1, 0)	$C_2H_6 = C_2H_4 + H_2$	$V_I, -\Delta^{(I)}\mu$
II	(1, 2, 1, 0, 1)	$2C_2H_6 = 2CH_4 + C_2H_4$	$V_{II}, -\Delta^{(II)}\mu$

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

$$\begin{aligned} -\Delta^{(I)}\mu &= \kappa_{11}V_I + \kappa_{12}V_{II}, \\ -\Delta^{(II)}\mu &= \kappa_{21}V_I + \kappa_{22}V_{II}, \end{aligned} \quad (8)$$

with

$$\begin{pmatrix} \kappa_{11} & \kappa_{12} \\ \kappa_{21} & \kappa_{22} \end{pmatrix} = \begin{pmatrix} \kappa_3 + \kappa_4 & \kappa_3 \\ \kappa_3 & \kappa_1 + 4\kappa_2 + \kappa_3 + \kappa_5 \end{pmatrix}, \quad (8\kappa)$$

or

$$\begin{aligned} V_I &= -\lambda_{11}\Delta^{(I)}\mu - \lambda_{12}\Delta^{(II)}\mu, \\ V_{II} &= -\lambda_{21}\Delta^{(I)}\mu - \lambda_{22}\Delta^{(II)}\mu, \end{aligned} \quad (8^*)$$

with

$$\begin{pmatrix} \lambda_{11} & \lambda_{12} \\ \lambda_{21} & \lambda_{22} \end{pmatrix} = D^{-1} \begin{pmatrix} \kappa_1 + 4\kappa_2 + \kappa_3 + \kappa_5 & -\kappa_3 \\ -\kappa_3 & \kappa_3 + \kappa_4 \end{pmatrix}, \quad (8^*\lambda)$$

where

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

In (8) or (8*), the coefficients $\kappa_{12} = \kappa_{21} = \kappa_3 = RT/\bar{v}_3^{(e)}$ or $\lambda_{12} = \lambda_{21} = -\kappa_3/D =$

*) Quoted from p. 11 of Ref. 4b.

11) RICE and HERZFELD, J. Am. Chem. Soc. **56**, 284 (1934).

$-RT/D\ddot{v}_3^{(e)}$ express the coupling of the simultaneous reactions I and II which involve the third ER, $C_2H_5 \rightarrow C_2H_4 + H$ of (7) in common. Thus, for instance, by varying the chemical potential (concentration) of the chemical species 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 $-A^{(I)}\mu$ (or V_{II} and $-A^{(II)}\mu$) are not necessarily of the same sign^{*)} contrary to the case of the relation (1) or (2), i.e., the case of ER or $P=1$. It has been pointed out^{*)} 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*¹²⁾ of the m -th molecule in the s -th ER. Thus, by virtue of (3) and HN's Eq. (5'), we have

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

where $B_m^{(p)}$ is the stoichiometric coefficient¹²⁾ 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, indicates¹²⁾ that V_p is nothing but the rate of the p -th OR^{**)}.

*) 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, $2H^+ + 2e = H_2$. 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.

12) PRIGOGINE and DEFAY (translated by EVERETT), *Chemical Thermodynamics*, Longmans Green Co., London (1950, 1954), p. 14.

Similarly, the quantity $-\sum_{s=1}^S \nu_s^{(p)} \Delta_s \mu$ 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

$$\begin{aligned} \Delta_s \mu &= \sum_i \mu_i' b_{is}' + \sum_m \mu_m b_{ms}, \\ \Delta^{(p)} \mu &= \sum_m \mu_m B_m^{(p)}, \\ \sum_{s=1}^S \nu_s^{(p)} b_{is}' &= 0, \end{aligned}$$

where μ_m and μ_i' are respectively the chemical potentials of the m -th molecule and the i -th independent intermediate, and b_{is}' 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

$$J_s = \sum_{t=1}^S \bar{L}_{st} X_t, \quad s = 1, \dots, S, \quad (\text{NY, Eq. 6})$$

which can be inverted as

$$X_t = \sum_{s=1}^S \bar{K}_{ts} J_s, \quad t = 1, \dots, S, \quad (\text{A})$$

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^{*}

$$\left. \begin{aligned} J_t &= V_t \quad \text{for } t = 1, \dots, P, \\ J_t &= 0 \quad \text{for } t = P+1, \dots, S, \end{aligned} \right\} \text{ in the steady state,}$$

and

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

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

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

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

^{*}) See NY, Eqs. (5), (9) and (10), and remember that J_t 's with $t = P+1, \dots, S$, are the rates of increases of the independent intermediates, which vanish in the steady state.

$$T\bar{K}_{ts} = \sum_{i=1}^S \kappa_i \nu_i^{(t)} \nu_i^{(s)} = \kappa_{ts} \quad \text{for } t, s = 1, \dots, P, \quad (\text{C})$$

as shown below.

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

$$\begin{aligned} \bar{L}_{st} &= \sum_{i=1}^S \beta_{si} \beta_{ti} L_{ii} = \sum_{i=1}^S \beta_{si} \beta_{ti} \lambda_i T, \\ (\beta^{-1})_{it} &= \nu_i^{(t)} \quad \text{for } i=1, \dots, S \text{ and } t=1, \dots, P, \end{aligned} \quad (\text{D})$$

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

$$\bar{K}_{ts} = \sum_{i=1}^S (\kappa_i/T) (\beta^{-1})_{it} (\beta^{-1})_{is},$$

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

Appendix III

It follows from the definitions of J_t in NY and \bar{K}_{ts} in Appendix II that the transformation of the quadratic form

$$\sum_{s=1}^S (\kappa_s/T) v_s^2, \quad (\text{E})$$

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

$$\sum_{t=1}^S \sum_{s=1}^S \bar{K}_{ts} J_t J_s. \quad (\text{F})$$

Since $\kappa_s > 0$, the quadratic form (E) and hence (F) are positive definite; this is in accord with the fact⁽⁸⁾⁻⁽¹⁰⁾ that the expression (E) or (F) is the entropy production. Considering the case $J_t = 0$ for $t = P+1, \dots, S$ (steady state), we see that the quadratic form with the $P \times P$ matrix κ_{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⁽¹³⁾ the matrix κ_{ts} is non-singular, i. e., $\det(\kappa_{ts}) \neq 0$.

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