



Title	KINETICS AND THERMODYNAMICS OF THE STEADY STATE OF CHEMICAL REACTIONS.
Author(s)	NAKAMURA, Takashi
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 13(1), 1-9
Issue Date	1965-07
Doc URL	http://hdl.handle.net/2115/24787
Type	bulletin (article)
File Information	13(1)_P1-9.pdf



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KINETICS AND THERMODYNAMICS OF THE STEADY STATE OF CHEMICAL REACTIONS. III

By

Takashi NAKAMURA^{*)}

(Received January 31, 1965)

Abstract

This paper clarifies some central ideas behind the calculation in a foregoing paper by the present author, This Journal, **9**, 87 (1961), which has dealt with the kinetics of a complex reaction system consisting of elementary reactions whose rates vary linearly with their affinities, special attention being paid to the condition under which a steady (or quasi-steady) state is established. An analogy with the calculation of molecular vibrations (*e. g.*, E. B. WILSON) or that of the rotational and vibrational relaxations of molecules (HERMAN and SHULER) is pointed out.

An understanding of the behavior of a complex reaction system is obtained from a set of simultaneous differential equations¹⁾²⁾, each of which is the "rate equation" of a constituent elementary step (elementary reaction) of the system. For instance, the important concept of a steady state of a complex reaction system is discussed, *i. e.*, the conditions for and the characteristics of a steady state are examined in connection with the properties of the solutions of the above simultaneous differential equations³⁾⁴⁾. It seems, however, that the difficulty with the mathematical treatment of such simultaneous differential equations prevents us from developing a sufficiently general theory. Monomolecular systems (namely, complex reaction systems consisting solely of first order reactions) are rather exceptional; the differential equations in this case can be treated by simple linear algebra and the solutions are expressed in terms of eigenvalues, eigenvectors, relaxation times, *etc.* Actually many authors²⁾ have discussed the general theory of such "linear" systems. This kind of algebra is of wide use in various problems in physics and chemistry, a well-known example familiar to chemists being the theory of molecular vibration⁵⁾. Actually MATSEN and FRANKLIN⁶⁾ have discussed an interesting analogy between the theory of monomolecular systems and the theory of molecular vibrations.

In the foregoing papers⁷⁾⁸⁾, hereafter referred to as I and II, the present author has dealt with kinetics of a complex reaction system consisting of

^{*)} The Research Institute for Catalysis, Hokkaido University, Sapporo.

elementary steps whose rates vary linearly with their affinities. Here we have another "linear system", which can be treated also by simple linear algebra. The rate law that the rate of an elementary step is proportional to the affinity of the step is a sort of limiting law, *i.e.*, it can be shown to hold in the neighborhood of equilibrium of an elementary step irrespective of its "order"*). The purpose of the present paper is to reexamine the calculations in II, and to elucidate certain central ideas contained therein. The author hopes that the present paper is helpful for reading I and II, especially the latter which is a little bit lengthy.

In II we have started with the rate equation,

$$(1/L_s)d\xi_s/dt = \sum_{t=1}^S X_{st}(\xi_t - \xi_t^{(e)}), \quad s = 1, 2, \dots, S, \quad (1)$$

which is the same as (II-9)**). PRIGOGINE⁹⁾ and MEIXNER^{10)***)} have discussed similar rate equations in their thermodynamical theory of irreversible processes. In (1) we have assumed the linear relation (II-3), *i.e.*, the rate $d\xi_s/dt$ (ξ_s =the extent⁹⁾ of the s -th reaction) is assumed to be proportional to the force X_s (=the affinity divided by temperature T), namely

$$d\xi_s/dt = L_s X_s, \quad (2)$$

while MEIXNER¹⁰⁾ has considered the more general linear relation (II-4), which is written as

$$d\xi_s/dt = \sum_{t=1}^S L_{st} X_t. \quad (3)$$

The use of (2) rather than (3) is due to the fact that the S reactions considered in (1) are elementary steps rather than macroscopic reactions****), *i.e.*, they are assumed to be "kinetically" independent. The right hand side of (1) expresses the linear relation between the force X_s and the displacement from the equilibrium, $\xi_t - \xi_t^{(e)}$. Introducing new variables q_s defined by

$$q_s = L_s^{-\frac{1}{2}}(\xi_s - \xi_s^{(e)}), \quad (4)$$

we rewrite (1) as

*) Cf. Section 3 of I.

**) Eq. (II-9), for instance, stands for Eq. (9) of II. The notations in the present paper are defined in II.

***) Cf. MEIXNER's (Ref. 10) Eq. (18). Eqs. (II-4) and (II-8) correspond to MEIXNER's Eqs. (13) and (5), respectively. See also PRIGOGINE's (Ref. 9) Chapter 6.

****) In this connection, see the discussion leading to (I-36) in Section 3 of I. In the derivation of (I-34) we can as well use the activities of reactants in place of the concentrations.

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$$dq_s/dt = \sum_{t=1}^S Z_{st} q_t, \quad s = 1, 2, \dots, S \quad (5)$$

where Z_{st} is defined by

$$Z_{st} = (L_s L_t)^{\frac{1}{2}} X_{st}. \quad (6)$$

The solution of the simultaneous equations (5) is well-known: The change of q_s with time is described in terms of S normal modes, each of which decays exponentially, *i.e.*, the change of the s -th mode is expressed as

$$\text{const.} \times e^{-t/\tau_s}.$$

The relaxation time τ_s occurring in the above expression is given by $\tau_s = -\lambda_s^{-1}$, where λ_s is the s -th eigenvalue calculated from the secular (determinantal) equation,

$$\det (Z_{st} - \lambda \delta_{st}) = 0, \quad (7)$$

where δ_{st} is KRONECKER'S delta. As pointed out by MEIXNER, the S eigenvalues obtained from (7) are all real and negative; hence $\tau_s > 0$ for $s = 1, 2, \dots, S$.

The above mathematical result implies that the chemical change in the system is expressed as a superposition of S chemical reactions, each of which corresponds to one of the S normal modes and hence decays exponentially.

The reaction system whose kinetics is expressed by (1) is a closed system in the thermodynamical sense⁹⁾. Suppose that there are N chemical species participating in the reactions and their chemical potentials are denoted by μ_i ($i = 1, 2, \dots, N$). Let us now bring the system into contact with a *reservoir* (a reservoir of "particles") which contains *some* of the N chemical species and exchanges them with the system. The system becomes an open system and we can assume that the chemical potentials of M chemical species ($M < N$) in the system are kept constant by the exchange with reservoir: thus we write as

$$\mu_i = \mu_i^0 \quad \text{for } i \leq M, \quad (8a)$$

where the constant μ_i^0 is the chemical potential of the i -th species in the reservoir. On the other hand, μ_i with $M < i \leq N$ varies with time: By virtue of (II-14) and (II-17),

$$\mu_i = \mu_i^{(e)} + \sum_t RT(b_{it}/N_i^{(e)})(\xi_t - \xi_t^{(e)}) \quad \text{for } i > M, \quad (8b)$$

where R is the gas constant, N_i the number of mole of the i -th chemical species, b_{is} the stoichiometric coefficient⁹⁾ of the i -th chemical species in the s -th elementary step, and the superscript (e) designates the value at equilibrium.

After HIRSCHFELDER the above M chemical species will be called *principal chemical species*³⁾⁸⁾. In Section 2 of I and in Section 2 of II we have noticed that the condition (8a) means an addition of an external constraint to the system and this kind of constraint is a necessary condition for a "true" steady state to be established in the system. Eventually the force X_s (= the affinity divided by temperature T) will be expressed as

$$\begin{aligned} X_s &= -\sum_i \mu_i b_{is} / T = (-\sum_i^0 \mu_i^0 b_{is} - \sum_i^* \mu_i b_{is}) / T \\ &= \left[-\sum_i^0 (\mu_i^0 - \mu_i^{(e)}) b_{is} - \sum_i^* (\mu_i - \mu_i^{(e)}) b_{is} - \sum_i \mu_i^{(e)} b_{is} \right] / T. \end{aligned} \quad (9)$$

In (9), \sum_i denotes the sum over all the chemical species, $i=1, 2, \dots, N$; \sum_i^0 is the sum over the principal chemical species, $i=1, 2, \dots, M$; \sum_i^* is the sum over $i=M+1, M+2, \dots, N$ (thus $\sum = \sum^0 + \sum^*$). The third term in the square brackets in (9), $\sum_i \mu_i^{(e)} b_{is}$ vanishes since the superscript (e) designates the equilibrium value. Using (2) and (9) we have the rate equation,

$$dq_s/dt = Z_s^0 + \sum_i Z_{st}^* q_t, \quad s=1, 2, \dots, S, \quad (10)$$

where Z_s^0 and Z_{st}^* are essentially the same as X_s^0 and X_{st}^* in (II, 20): *i.e.*, by virtue of (8) they are expressed as

$$Z_s^0 = -L_s^{\frac{1}{2}} \sum_i^0 (\mu_i^0 - \mu_i^{(e)}) b_{is} / T \quad (11a)$$

and

$$Z_{st}^* = -(L_s L_t)^{\frac{1}{2}} R \sum_i^* b_{is} b_{it} / N_i^{(e)}, \quad (11b)$$

The solution of (10) has been discussed in II. Again S normal modes need to be determined by solving the secular equation,

$$\det (Z_{st}^* - \lambda^* \delta_{st}) = 0. \quad (12)$$

The important point is that some of the S eigenvalues λ_s^* determined from (12) are zero although the rest are negative. The existence of zero eigenvalues here reminds us of a similar situation in the calculation of molecular vibrations¹¹⁾. The $3n \times 3n$ secular equation for the calculation of the normal vibrations of an n -atomic molecule takes the form,

$$\det (f_{jk} - \lambda \delta_{jk}) = 0, \quad (13)$$

provided that the potential energy matrix $[f_{jk}]$ is calculated in terms of the mass-weighted cartesian displacement coordinates¹¹⁾. In the case of a non-linear

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molecule, six of the $3n$ roots of (13) are known to be zero¹¹⁾. This is due to the fact that nuclear displacements corresponding to the translational and rotational motion of the molecule as a whole do not change the potential energy of the molecular vibration. The normal coordinates corresponding to these zero eigenvalues can readily be found by the standard method¹¹⁾. For instance, the normal coordinate corresponding to the translational motion in the x -direction is given by

$$\eta_1 = \text{const.} \times \sum_{a=1}^n m_a^{-\frac{1}{2}} q_{3a-2},$$

where m_a is the mass of the a -th nucleus and q_j is the j -th mass weighted cartesian coordinate^{*)}.

Now we ask what the normal coordinates corresponding to the zero eigenvalues of (12) are like. We will write the relation between the variables q_s in (10) and the relevant normal coordinates η_t determined from (12) as

$$q_s = \sum_{t=1}^S T_{st} \eta_t, \quad i. e., \quad \hat{\xi}_s - \hat{\xi}_s^{(e)} = \sum_{t=1}^S \gamma_{st} \eta_t. \quad (14 a)$$

In (14a) the constant coefficients T_{st} form an $S \times S$ orthogonal matrix⁵⁾, and the coefficients γ_{st} are the same as that occurs in (II-21) and are written as

$$\gamma_{st} = L_s^{-\frac{1}{2}} T_{st}.$$

Thus we have the inverse relation,

$$\eta_t = \sum_{s=1}^S q_s T_{st} = \sum_{s=1}^S q_s \gamma_{st} / L_s^{-\frac{1}{2}} = \sum_{s=1}^S (\hat{\xi}_s - \hat{\xi}_s^{(e)}) \gamma_{st} / L_s, \quad (14 b)$$

The eigenvalues λ_i^* are written as

$$\lambda_i^* \delta_{tu} = \sum_{t=1}^S \sum_{s=1}^S Z_{rs}^* T_{rt} T_{su}. \quad (15)$$

Assuming that the first P eigenvalues λ_i^* ($t=1, 2, \dots, P; P < S$) are equal to zero, we have, from (11 b) and (15), the following relation:

$$\begin{aligned} \text{For } t \leq P, \quad 0 &= -R \sum_i^* \sum_{r=1}^S \sum_{s=1}^S b_{ir} L_r^{-\frac{1}{2}} T_{rt} b_{is} L_s^{-\frac{1}{2}} T_{st} / N_i^{(e)} \\ &= -R \sum_i^* \left(\sum_{r=1}^S b_{ir} L_r^{-\frac{1}{2}} T_{rt} \right)^2 / N_i^{(e)} = -R \sum_i^* \left(\sum_{r=1}^S b_{ir} \gamma_{rt} \right)^2 / N_i^{(e)} \end{aligned} \quad (16)$$

Since $N_i^{(e)} > 0$, we have, from (16), the relation,

*) The variable q_j here is defined by Eq. (2), Section 2-2 of Ref. 5.

$$\sum_{r=1}^s b_{ir} \gamma_{rt} = 0, \quad \text{provided that } i > M \text{ and } t \leq P. \quad (17)$$

Our conclusion is that when the t -th normal coordinate η_t corresponds to a zero eigenvalue, the coefficients, $\gamma_{1t}, \gamma_{2t}, \dots, \gamma_{st}$ in (14) satisfy (17); *i.e.*, they have the property of the *stoichiometric numbers* which have been introduced by HORIUTI and the present author⁽²⁾⁷⁾ (see I) as a useful concept in dealing with a steady state of a complex reaction system. Thus the number of the zero eigenvalues P turns out to be equal to the *number of reaction routes*⁽²⁾⁷⁾ defined by these authors. The solution of the rate equations (10) is readily written down in terms of the normal coordinates η_s . For a normal mode corresponding to a zero eigenvalue, η_s takes the form,

$$\eta_s = a_s + b_s t \quad (s \leq P) \quad (18)$$

and for a normal mode corresponding to a non-zero eigenvalue, η_s takes the form,

$$\eta_s = c_s + d_s \exp(-t/\tau_s^*), \quad (s > P) \quad (19)$$

where a_s, b_s, c_s and d_s are constants, and

$$\tau_s^* = -1/\lambda_s^* > 0.$$

Thus the reaction associated⁷⁾ with a zero-eigenvalue mode has a constant rate (*steady reactions*) and survives at the steady state while that associated⁷⁾ with a non-zero eigenvalue mode dies down (*i.e.*, $d\eta_s/dt \rightarrow 0$) during the initial induction period. Also we can easily show⁸⁾ that the chemical species with index numbers greater than M [cf. Eqs. (8a) and (8b) above] are what are called intermediates in chemical kinetics. Eqs. (14 a) and (17) imply that the reactions associated with zero-eigenvalue modes do not change the concentrations of the intermediates; thus the concentrations of the intermediates change during the induction period but attains a constant value in the steady state.

We have so far considered the establishment of a steady state under a specially contrived condition, *i.e.*, by attaching the reservoir to the system. A case of more practical interest, namely, the establishment of a *quasi-steady state* in a closed system has also been considered in II. In a closed system a "true" steady state can not be established⁹⁾, but an approximately steady state, *i.e.*, a quasi-steady state is expected under a certain condition. To see this we will start with the assumption that the concentrations of the chemical species with $i=1, 2, \dots, M$ (*principal chemical species*) are much greater than those of the chemical species with $i=M+1, M+2, \dots, N$ (*intermediates*): thus

$$N_i^{(e)} \gg N_j^{(e)} \quad \text{when } i \leq M \text{ and } j > M. \quad (20)$$

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The change of all the chemical potentials is given by the same expression as (8 b):

$$\mu_i = \mu_i^{(e)} + \sum_{t=1}^S RT(b_{it}/N_i^{(e)})(\xi_t - \xi_t^{(e)}), \quad i=1, 2, \dots, N. \quad (21)$$

The rate equations of this closed system are given by (5), and, as we have seen, the chemical change in the system is described as a superposition of S reactions decaying exponentially with relaxation times τ_s ($s=1, 2, \dots, S$). The relaxation times can be calculated from the eigenvalues λ_s of the matrix $[Z_{st}]$ in (5).

The important point is that the solution of (5) under the condition (20) is closely connected with the solution of (10). To see this, we divide the matrix $[Z_{st}]$ into two parts, $[Z_{st}^0]$ and $[Z_{st}^*]$ [cf. (1), (2), (6), (9) and (21)]:

$$Z_{st} = Z_{st}^0 + Z_{st}^*, \quad (22 \text{ a})$$

$$Z_{st}^0 = -(L_s L_t)^{\frac{1}{2}} R \sum_i^0 b_{is} b_{it} / N_i^{(e)}, \quad (22 \text{ b})$$

$$Z_{st}^* = -(L_s L_t)^{\frac{1}{2}} R \sum_i^* b_{is} b_{it} / N_i^{(e)}, \quad (22 \text{ c})$$

where Z_{st}^* is the same as that occurs in (10) and (11 b). Using the normal coordinates η_s defined by (14) and (15), we rewrite (5) as

$$d\eta_s/dt = \sum_{t=1}^S (Y_{st}^0 + \lambda_s^* \delta_{st}) \eta_t, \quad s=1, 2, \dots, S \quad (23)$$

where

$$Y_{st}^0 = \sum_{u=1}^S \sum_{v=1}^S Z_{uv}^0 T_{us} T_{vt} = -R \sum_{u=1}^S \sum_{v=1}^S (\sum_i^0 b_{iu} b_{iv} / N_i^{(e)}) \gamma_{us} \gamma_{vt}. \quad (24)$$

Combining the relation (20) with (22) and remembering the definitions of \sum^0 and \sum^* , we observe that $[Z_{st}^*]$ differs only slightly from $[Z_{st}]$; *i.e.*, in the division (22 a), we may call $[Z_{st}^*]$ the dominant part. It should be noted that the dominant part $[Z_{st}^*]$ has been diagonalized in (23). Also we have seen the relation,

$$\lambda_s^* = 0 \quad \text{for } s \leq P; \quad \lambda_s^* < 0 \quad \text{for } s > P.$$

Starting with (23), the detailed discussion in II has arrived at the following conclusions. [1] The chemical change with time in the system is described as a superposition of P slowly decaying reactions (*slow reactions* with long relaxation times, $\tau_s = \lambda_s^{-1}$) and $S-P$ rapidly decaying reactions (*transient reactions* with short relaxation times). After the induction period in which the transient reactions die away, there remain the P slow reactions. [2] To a good approximation, the normal modes of the slow reactions and those of the transient

reactions can be calculated separately owing to the large difference between the relaxation times of the slow reactions and those of the transient reactions. This large difference, in turn, results from the large difference in $d\mu_i/dt$ (the rate of the change of the chemical potential μ_i) of the principal chemical species and the intermediates: From (21) we have

$$d\mu_i/dt = \sum_{t=1}^S RT(b_{it}/N_i^{(e)})(d\xi_t/dt),$$

and combining this expression with the condition (20) we find the difference in $d\mu_i/dt$ mentioned above. This is just the kind of thing HERMAN and SHULER¹³⁾ have found in their calculation of the rotational and vibrational relaxation of rotating oscillator molecules in a gas: Owing to the large order of magnitude difference in efficiency of the translational-rotational and translational-vibrational energy transfer, there is very little coupling between the vibrational and rotational relaxation. [3] Thus the chemical change in the system after the induction period is described by the equations,

$$d\eta_s/dt = \sum_{t=1}^P Y_{st}^0 \eta_t, \quad s=1, 2, \dots, P, \quad (25)$$

which are obtained from the first P equations ($s=1, 2, \dots, P$) of (23) by omitting the terms involving $\eta_{P+1}, \eta_{P+2}, \dots, \eta_S$ and making use of the fact that λ_s^* vanishes when $s \leq P$; thus in (25) the matrix $[Y_{st}^0]$ is $P \times P$ rather than $S \times S$. Of particular importance is the fact that Eq. (25) is equivalent*) to the rate equations of the *overall reactions* in the steady state¹²⁾¹⁾,

$$\sum_{t=1}^P K_{st}(d\xi_t/dt) = \sum_{t=1}^P A_{st}(\xi_t - \xi_t^{(e)}), \quad s=1, 2, \dots, P \quad (26)$$

which have been considered in I. In (26), ξ_t is the extent of the t -th overall reaction, and K_{st} and A_{st} are written as

$$K_{st}/T = \sum_{u=1}^S (1/L_u) \nu_u^{(s)} \nu_u^{(t)},$$

$$A_{st}/T = -R \sum_{u=1}^S \sum_{v=1}^S (\sum_k^0 b_{ku} b_{kv} / N_k^{(e)}) \nu_u^{(s)} \nu_v^{(t)},$$

where the stoichiometric numbers $\nu_u^{(s)}$ of HORIUTI and the present author¹²⁾⁷⁾ again occur. The significance of the rate equations (26) has been fully discussed in I, where (26) has been derived from the assumption or the approximation (*steady state approximation*¹⁾⁴⁾) that the change in the amounts of the intermediates with time is negligible [cf. (I-16)]. Our conclusion is that the use

*) Combining (I-47) and (I-48) we obtain the same equation as (26). The equivalence of (25) and (26) has been proved in Appendix of II.

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of this assumption and hence of the rate equations for the overall reactions (26) is justified to a good approximation under the condition (20). In II the possible deviation from the results of the steady state approximation has also been mathematically discussed.

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