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

By

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In connection with the irreversible thermodynamical treatment of chemical reactions, this paper deals with kinetics of a complex kinetic system consisting of elementary reactions whose rates vary linearly with their affinities. First, the establishment of a steady state in an open system is examined. Second, the treatment is extended to the case of a quasi-steady (pseudo-stationary) state in a closed system, and the results so obtained are compared with HIRSCHFELDER's discussion of the steady state approximation in chemical kinetics [J. Chem. Phys., **26**, 271 (1957)]. This paper also supplements the treatment of a preceding paper (Part I) by the present author [This Journal, **7**, 224 (1959)].

Introduction

The application of irreversible thermodynamics¹⁾²⁾ to chemical reaction has been described by a number of authors. In this connection the relation between chemical kinetics and the thermodynamical theory of chemical reactions has also been discussed. We shall recall some of the results. First, the *force* X of a chemical reaction is its affinity divided by temperature and the *flux* v is its reaction rate¹⁾²⁾. On the other hand, the theory of absolute reaction rates provides the relation between the reaction rates and thermodynamical quantities³⁾, *i. e.*, free energy, affinity, *etc.*; thus it can be shown⁴⁾⁻⁶⁾ that in the neighborhood of equilibrium the flux (rate) of an *elementary reaction* is expressed in the linear form^{**)},

$$v = LX, \quad (1)$$

and the constant coefficient L in (1) is written as

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^{***)} The expressions (1) and (2) have first been obtained by PRIGOGINE *et al.*⁴⁾, whose derivation is based on the naive, empirical rate equations for elementary reactions (*cf.* §3 of Part I⁷⁾). Essentially the same expressions have been derived from the theory of absolute reaction rates, by several authors⁵⁾⁶⁾.

$$L = v_f^{(e)}/R, \quad (2)$$

where R is the gas constant, v_f is the forward rate and the superscript (e) designates the value at equilibrium. Now suppose that S elementary reactions are simultaneously taking place in a system, and that each of them obeys the linear relation of the form (1). Then we can write as

$$v_s = L_s X_s, \quad s = 1, 2, \dots, S, \quad (3)$$

where v_s and X_s are the flux and the force of the s -th elementary reaction.

The expression (3) is a special case of the linear phenomenological relation in irreversible thermodynamics, which is usually expressed as¹⁾²⁾

$$v_s = \sum_{t=1}^S L_{st} X_t, \quad s = 1, 2, \dots, S. \quad (4)$$

Namely, the off-diagonal coefficients L_{st} ($s \neq t$) of (4) do not occur in (3), which implies that the S reactions are *kinetically* independent. In irreversible thermodynamics the linear transformation of the form,

$$v_s = \sum_{t=1}^S \alpha_{st} v'_t, \quad X'_t = \sum_{s=1}^S X_s \alpha_{st} \quad (\det(\alpha_{st}) \neq 0), \quad (5)$$

is often considered for forces and fluxes³⁾. When expressed in terms of the new set of forces X'_s and fluxes v'_s , the linear relation (3) takes the form (4), in which the matrix (coefficients) L_{st} obeys the ONSAGER reciprocity relation, $L_{st} = L_{ts}$, because the congruence transformation³⁾ of the diagonal matrix L_s of (3) yields a symmetry matrix⁴⁾.

An interesting example is the system of the monomolecular triangular reactions, $B \rightleftharpoons C$, $C \rightleftharpoons A$ and $A \rightleftharpoons B$, which has been considered by ONSAGER⁵⁾ or DE GROOT¹⁾, in order to elucidate the relation between the principle of detailed balance and the ONSAGER reciprocal relation. Suppose that the fluxes, v_i and the forces X_i ($i=1, 2, 3$) of the three monomolecular reactions are transformed into the new fluxes, $v'_1 = v_1 - v_3$, $v'_2 = v_2 - v_3$, $v'_3 = v_3$, and the new forces, $X'_1 = X_1$, $X'_2 = X_2$, $X'_3 = X_1 + X_2 + X_3$. Obviously this transformation is an example of (5). Then we obtain Eqs. (49) and (50) of DE GROOT's Chapter IX^{**1)}, which satisfy the ONSAGER reciprocity relation.

The expression (4) together with the ONSAGER relation is usually the basis of thermodynamical theories¹⁾²⁾; e.g., MEIXNER¹⁰⁾, and KIRKWOOD and CRAWFORD¹²⁾, starting from (4), discussed the relaxation of chemical reactions.

*) Cf. also Eq. (44) of Part I.

***) Note that the third force, $X'_3 (= X_1 + X_2 + X_3)$ is identically equal to zero in this example, and that DE GROOT's J_i and A_i/T are the same as v_i and X_i , respectively, of this paper. Also, there are a few misprints of signs in DE GROOT's Eqs. (49) and (50).

In the present case of chemical reactions, the transformation (5) is accompanied⁷⁾¹⁰⁾¹¹⁾ by a transformation of the reaction equations, and *vice versa*. This is of considerable interest, because chemists often consider such a transformation of reaction equations and use different *representations* to describe a macroscopic chemical change due to simultaneous chemical reactions; the preceding paper, Part I⁷⁾ has been concerned with transformations between different representations. Suppose, for instance, that two reactions¹³⁾,



are taking place in a system. Macroscopically, the chemical changes due to the simultaneous reactions (a) and (b) can be equally well described by



where the reaction (b') is a linear combination¹³⁾ of (a) and (b); *i. e.*, the latter representation, (a') and (b') can be obtained by a linear transformation, from the former representation, (a) and (b). In other words, these two representations are *equivalent*⁷⁾¹¹⁾.

In chemical kinetics, on the other hand, the treatment of a *complex kinetic system*¹⁴⁾ (*i. e.*, a system of simultaneous reactions) has been a subject of a number of discussions¹⁵⁾. When all the reactions in the system are first-order, the mathematical treatment is rather simple and a general theory can be developed¹⁵⁾¹⁶⁾. The system which involves higher-order reactions defies such a simple, general treatment. Even in that case, provided that the reactions are elementary reactions in the neighbourhood of equilibrium, their "rate equations" reduce to the linear form (3) irrespective of their orders, so that the system is capable of general, exact mathematical solutions¹⁰⁾. Among various irreversible processes, chemical reactions are a notorious example which, in many practical cases, does not obey the linear relation such as (3) or (4)²⁾¹⁷⁾; in other words, a chemical reaction "in the neighbourhood of equilibrium" is considered a rather exceptional case. Recently, however, several authors have been concerned with chemical reactions close to equilibrium, and interesting result, experimental and theoretical, have been obtained^{2)4)10)12), 18)-21)}.

In Part I, §2⁷⁾ we have briefly discussed the concepts of the *steady state* in an open system and the *quasi-steady state* ("approximately" steady state) in a closed system. In the present paper, we shall deal with the establishment of a steady or quasi-steady state in a kinetic system of simultaneous elementary reactions whose rates are given by (3). Thus we shall further elucidate the

relation between chemical kinetics and the thermodynamical theory of chemical reactions. On the other hand it will be shown that this kinetic system also serves as a "model" which illustrates the general features of a steady or quasi-steady state¹⁴⁾ of chemical reactions. The treatment of such a model has the advantage that simple solutions can be readily obtained whereas the mathematical solutions of complex kinetic systems far from equilibrium are, in general, too complicated to be visualized easily.

§ 1. Fundamental Equations

We shall consider S simultaneous elementary reactions which obey the linear relation (3) and take place in a closed system of *constant temperature and volume*. In the case of reactions close to equilibrium, we can assume the linear relation between the forces X_s and the deviation from the equilibrium¹⁰⁾, as

$$X_s = \sum_{t=1}^S X_{st}(\xi_t - \xi_t^{(e)}), \quad (8)$$

where the variable ξ_t is the "extent of reaction" of the t -th reaction²⁾²²⁾, the superscript (e) designates the value at equilibrium, and X_{st} is a constant coefficient (see below). Combining (3) with (8) and using the relation²⁾²²⁾,

$$v_s = d\xi_s/dt,$$

we have a set of simultaneous equations,

$$(1/L_s)d\xi_s/dt = \sum_{t=1}^S X_{st}(\xi_t - \xi_t^{(e)}), \quad s=1, 2, \dots, S. \quad (9)$$

Since the transformation property of ξ_s is the same as that of the fluxes v_s , Eq. (9) becomes, after the transformation of variables (5),

$$\sum_{t=1}^S H_{st}d\zeta_t/dt = \sum_{t=1}^S Y_{st}\zeta_t, \quad s=1, 2, \dots, S, \quad (10)$$

where

$$\begin{aligned} \xi_s - \xi_s^{(e)} &= \sum_{t=1}^S \alpha_{st}\zeta_t, & H_{st} &= \sum_{u=1}^S (1/L_u)\alpha_{us}\alpha_{ut}, \\ Y_{st} &= \sum_{u=1}^S \sum_{v=1}^S X_{uv}\alpha_{us}\alpha_{vt}. \end{aligned} \quad (11)$$

If the matrix α_{st} in (11) is so chosen²³⁾ that H_{st} and Y_{st} are unit and diagonal matrices, respectively, then the variables ζ_s defined by (11) are the "normal coordinates"²³⁾, and the set of equations (10) take the simplest form,

$$d\zeta_s/dt = \lambda_s\zeta_s, \quad s=1, 2, \dots, S, \quad (12)$$

where λ_s is the s -th diagonal elements of the above diagonal matrix, *i.e.*, the s -th *eigenvalue*. As pointed out by MEIXNER¹⁰⁾, the eigenvalues λ_s are always negative, and the solution of the simultaneous equations (9) is readily obtained from (11) and (12):

$$\hat{\xi}_s - \xi_s^{(e)} = \sum_{u=1}^S \alpha_{s,u} \zeta_u^{(0)} \exp(-t/\tau_u), \quad (13)$$

where $\zeta_u^{(0)}$ is the initial value of ζ_u , and τ_u is the relaxation time defined by

$$\tau_u = -\lambda_u^{-1} > 0. \quad (13 \text{ a})$$

In the above treatment we have tacitly assumed that the S elementary reactions of (3) are (stoichiometrically) *independent*. In the case of a kinetic system with (stoichiometrically) dependent reactions^{*}), there is a certain difficulty with the definition of the variables $\hat{\xi}_s$. The definition of $\hat{\xi}_s$ in such a case will be discussed in §2.

Suppose that the above S reactions involve N chemical species. To the same approximation as (8), the change of the chemical potential μ_i of the i -th chemical species is given by

$$\mu_i = \mu_i^{(e)} + \sum_{s=1}^S M_{is} (\hat{\xi}_s - \xi_s^{(e)}), \quad i=1, 2, \dots, N, \quad (14)$$

where

$$M_{is} = (\partial \mu_i / \partial \xi_s)^{(e)}.$$

By virtue of the relation,

$$X_s = - \sum_{i=1}^N \mu_i b_{is} / T = - \sum_{i=1}^N (\mu_i - \mu_i^{(e)}) b_{is} / T, \quad (15)$$

we have

$$X_{st} = - \sum_{i=1}^N M_{it} b_{is} / T, \quad (16)$$

where b_{is} is the stoichiometric coefficient²²⁾ of the i -th chemical species in the s -th reaction. For the simplicity of discussion, we assume the system under consideration to be an ideal system;^{**)} thus μ_i , M_{is} and X_{st} are written as²²⁾

$$\begin{aligned} \mu_i &= \mu_i^* + RT \ln(N_i/V), \\ M_{is} &= RT b_{is} / N_i^{(e)}, \quad X_{st} = -R \sum_{i=1}^N b_{is} b_{it} / N_i^{(e)}, \end{aligned} \quad (17)$$

where μ_i^* is a function only of temperature, N_i the number of moles of the

^{*}) Cf. DE GROOT, Ref. 1, p. 180. The definition of (stoichiometrical) *independence* of simultaneous reactions is described in p. 468 of PRIGOGINE and DEFAY, Ref. 22.

^{**}) A more general treatment is possible, but will be more cumbersome.

i -th chemical species, and V the volume of the system.

§ 2. Steady State

According to the thermodynamical theory of irreversible processes¹⁾²⁾, external *constraints* (dis-equilibrium forces²⁴⁾) need to be applied to a system for a steady state to be established in it. In the case of the kinetic system considered in §1, the chemical potentials of *some* of the N chemical species involved in the reactions (say, the species with the index numbers $i=1, 2, \dots, M$, where $M < N$) need to be kept constant by the constraints. In accordance with HIRSCHFELDER³¹⁾ and Part I⁷⁾, the M chemical species whose chemical potentials are fixed, will be called *principal chemical species*, and the other chemical species will be called *intermediates*.

In §1 we have assumed that the change of the chemical potentials in the system obeys the expression (14). Suppose, however, that at a certain time (say $t=0$) the system is brought into contact with an "infinite" *reservoir*²⁵⁾²⁶⁾ which contains the M principal chemical species and exchanges them with the system, so that the chemical potentials (concentrations) of the principal chemical species in the system are fixed^{*)}. Thus after $t=0$ we can write as

$$\mu_i = \mu_i^0, \quad i=1, 2, \dots, M, \quad (18a)$$

$$\mu_i = \mu_i^{(e)} + \sum_{s=1}^S M_{is} (\xi_s - \xi_s^{(e)}), \quad i=M+1, M+2, \dots, N, \quad (18b)$$

where μ_i^0 is the value of the i -th chemical potential in the reservoir, which is constant. After $t=0$, the system becomes an open system. It is no longer possible to define the variables ξ_s as *quantities of state*, in the case of an open system^{**)}. However, the rates v_s of elementary reactions, rather than macroscopic reaction rates, are always unambiguously defined quantities, and after $t=0$ we define ξ_s by

$$\xi_s = \xi_s^{(0)} + \int_0^t v_s dt \quad (t > 0), \quad (19)$$

where $\xi_s^{(0)}$ is the value of ξ_s at $t=0$.

*) Cf. Part I, §2. Similar cases have been considered by DE GROOT¹⁾ PRIGOGINE²⁾, DENBIGH²⁷⁾²⁸⁾, JOST¹⁶⁾, BAK²⁹⁾ and others. Since, in this paper, we are not interested in transport processes, we shall neglect the affinities of the transport processes between the system and the reservoir³⁰⁾.

***) Cf. DE GROOT, Ref. 1, p. 180. As was pointed out in §1, a similar difficulty arises in the case of (stoichiometrically) dependent reactions in a closed system. In that case also, we can unambiguously define ξ_s of *elementary* reactions by using an expression similar to (19), i.e., by defining ξ_s as the integral of v_s over t .

According to (18), the forces (15) are written as the sum of the contribution from the intermediates and that from the principal chemical species :

$$X_s = \sum_{t=1}^S X_{st}^* (\hat{\xi}_t - \hat{\xi}_t^{(e)}) + X_s^0, \quad (20 \text{ a})$$

where X_{st}^* and X_s^0 are constants defined by

$$X_{st}^* = - \left(\sum_{i=M+1}^N M_{it} b_{is} \right) / T = - R \sum_{i=M+1}^N b_{is} b_{it} / N_i^{(e)}, \quad (20 \text{ b})$$

$$X_s^0 = - \sum_{i=1}^M (\mu_i^0 - \mu_i^{(e)}) b_{is} / T. \quad (20 \text{ c})$$

Combining the fundamental equations (3) with (20), and introducing the "normal coordinates" η_s defined by the relations²³⁾,

$$\begin{aligned} \hat{\xi}_s - \hat{\xi}_s^{(e)} &= \sum_{t=1}^S \gamma_{st} \eta_t, & \delta_{st} &= \sum_{u=1}^S (1/L_u) \gamma_{us} \gamma_{ut}, \\ \lambda_s^* \delta_{st} &= \sum_{u=1}^S \sum_{v=1}^S X_{uv}^* \gamma_{us} \gamma_{vt}, & \det(\gamma_{st}) &\neq 0, \end{aligned} \quad (21)$$

we have, instead of (12), a set of simultaneous equations,

$$d\eta_s/dt = \lambda_s^* \eta_s + Y_s^0, \quad s=1, 2, \dots, S, \quad (22)$$

In (21) and (22), δ_{st} is KRONECKER's delta and Y_s^0 is a constant defined by

$$Y_s^0 = \sum_{t=1}^S X_{ts}^0 \gamma_{ts}. \quad (23)$$

Of particular interest, in connection with the solution of (22), is the rank I of the matrix^{*)},

$$\left\| \begin{array}{cccc} b_{M+1,1} & b_{M+1,2} & \cdots & b_{M+1,S} \\ b_{M+2,1} & b_{M+2,2} & \cdots & b_{M+2,S} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ b_{N,1} & b_{N,2} & \cdots & b_{N,S} \end{array} \right\|, \quad (24)$$

which consists of the stoichiometric coefficients b_{is} of the intermediates ($M < i \leq N$ and $1 \leq s \leq S$). It can now be shown (cf. Appendix) that P of the eigenvalues λ_s^* are zero, and that the remaining ones are negative^{**) :} say,

*) HORIUTI and the present author³³⁾ have previously considered the physical meaning of the rank I , and called the quantity "the number of independent intermediates".

**) The relation (25) implies that the quadratic form $\sum_s \sum_t X_{st}^* x_s x_t$ is negative semidefinite, and the rank³⁶⁾ of the quadratic form is I . Similar quadratic form are discussed in the theory of *stability* of thermodynamical systems^{2)22)22a)}.

$$\lambda_s^* = 0 \text{ for } s=1, 2, \dots, P; \quad \lambda_s^* < 0 \text{ for } s = P+1, P+2, \dots, S, \quad (25)$$

where

$$P = S - I. \quad (26)$$

Hence the solutions of (22) is*)

$$\eta_s = \eta_s^{(0)} + Y_s^0 t, \quad \text{for } s=1, 2, \dots, P, \quad (27 \text{ a})$$

$$\eta_s = \eta_s^{(\infty)} + (\eta_s^{(0)} - \eta_s^{(\infty)}) \exp(-t/\tau_s), \\ \text{for } s = P+1, P+2, \dots, S, \quad (27 \text{ b})$$

where $\eta_s^{(0)}$ is the initial value of η_s , $\eta_s^{(\infty)}$ the steady state value of η_s , and τ_s the relaxation time:

$$\eta_s^{(\infty)} = -Y_s^0/\lambda_s^*, \quad \tau_s = -1/\lambda_s^* > 0, \quad s = P+1, P+2, \dots, S.$$

As mentioned in Introduction, the transformation (5), (11) or (21) is accompanied by a transformation of the reaction equations, and the new set of S reactions associated with⁷⁾¹⁰⁾ the normal coordinates η_s ($s=1, 2, \dots, S$), have the stoichiometric coefficients,⁷⁾

$$b'_{is} = \sum_{i=1}^S b_{ii} \gamma_{is}. \quad (28)$$

The force of the reaction associated with η_s is given by

$$X'_s = - \sum_{i=1}^N \mu_i b'_{is} / T, \quad s = 1, 2, \dots, S, \quad (29)$$

which, in turn, is equal to the right hand side of (22), as one can easily prove it. Let us now describe the chemical change in the system in terms of this new *representation*, *i. e.*, this new set of reactions. The solutions (27) imply that in the course of time the rates, $d\eta_s/dt$ of the $S-P$ reactions with the index number $s=P+1, P+2, \dots, S$ approach exponentially to zero, whereas the P reactions with $s=1, 2, \dots, P$ take place with the constant rates,

$$d\eta_s/dt = Y_s^0, \quad s = 1, 2, \dots, P. \quad (30)$$

In the following the former $S-P$ reactions will be called the *transient reactions*, and the latter P reactions the *steady reactions*. Namely, the $S-P$ transient reactions decline with the relaxation times τ_s , so that the system approaches to a *steady state*, in which only the P steady reactions exist.

In Appendix we shall further prove interesting relations: [A] the steady reactions involve no intermediates, *i. e.*,

*) Compare this solution with Eq. (23) of Part I.

$$b'_{is} = \sum_{i=1}^S b_{ii} \tilde{\eta}_{is} = 0 \quad \text{for } i > M \text{ and } s = 1, 2, \dots, P; \quad (31)$$

[B] each transient reaction involves at least one intermediate. It follows from (18), (29) and (31) that the forces X'_s of the steady reactions are kept constant^{*)}, *i. e.*,

$$X'_s = - \sum_{i=1}^M \mu_i^0 b'_{is} / T = \text{const.}, \quad s = 1, 2, \dots, P.$$

Thus the result (27) is quite understandable; in the course of time the concentrations of the intermediates vary, approaching constant values (the *steady state concentrations*)⁷⁾²⁾³¹⁾, so that the rates of the transient reactions change with time until the steady state is reached, whereas the steady reactions, which involve no intermediate, proceed with constant rates. In this connection it is interesting to see that the rate of irreversible entropy production in the system $(dS/dt)_{\text{irr}}$ is given by¹⁾²⁾

$$\left(\frac{dS}{dt} \right)_{\text{irr}} = \sum_{s=1}^S \left(\frac{d\eta_s}{dt} \right) X'_s = \sum_{s=1}^P (Y_s^0)^2 + \sum_{s=P+1}^S \left(\frac{\eta_s^{(0)} - \eta_s^{(\infty)}}{\tau_s} \right)^2 \exp(-2t/\tau_s),$$

which takes its minimum value $\sum_{s=1}^S (Y_s^0)^2$ at the steady state, in accordance with the theorem of minimum entropy production¹⁾²⁾⁷⁾²⁴⁾.

Example^{**) :} Two monomolecular reactions $A \rightleftharpoons M$ and $M \rightleftharpoons B$ are taking place in a system, and the concentrations of A and B are kept constant. The concentration of M will vary until the steady state concentration is reached⁷⁾²⁷⁾. In the steady state the rates of the two reactions become equal, so that the net rate of production of M is zero; then the macroscopic chemical change in the system is expressed by the single *overall reaction* $A \rightleftharpoons B$ ⁷⁾, which is the sum of $A \rightleftharpoons M$ and $M \rightleftharpoons B$ and does not involve the *intermediate* M. A simple calculation shows that the steady reaction in this case is $\alpha A \rightleftharpoons \alpha B$, where the constant coefficient α is expressed, in terms of L_s of (3), as $\alpha = [L_1 L_2 / (L_1 + L_2)]^{1/2}$; in other words, the steady reaction is essentially the same as the overall reaction $A \rightleftharpoons B$, as might be expected beforehand.

In general, the macroscopic chemical change in the steady state of a complex kinetic system is expressed in terms of a few, simple overall reactions, which involve no intermediates, *i. e.*, satisfy the relation (31). This point has been the subject of Part I. It can be readily shown^{***)} that the set of these overall reactions are *equivalent*⁷⁾¹¹⁾ to the set of the P steady reactions, *i. e.*,

*) Such a situation is called *isozaffine* (cf. DE GROOT, Ref. 1, p. 174).

**) Cf. also the calculation in Part I, §2.

***) Cf. §4 of this paper.

the reactions which correspond to the zero eigenvalues. In the above example, in which case $P=1$, the steady reaction and the overall reaction $A \rightleftharpoons B$ differ only by a constant factor α .

§ 3. Quasi-steady State

The system considered in §2 is an open system, since the exchange of matter with the external reservoir is allowed. Removing the reservoir we now return to the case of the closed system, which is again described by the set of simultaneous equations (9). Although a steady state is established only in an open system, the concept of a *quasi-steady state*²⁵⁾³¹⁾ is often very useful in chemical kinetics of a closed system. In the following we are concerned with the establishment of a *quasi-steady state* in the above closed system.

In the present case *principal chemical species* and *intermediates* are defined by their relative stabilities; intermediates are unstable species, so that their concentrations are at all times much less than the concentrations of principal chemical species³²⁾. Supposing that the chemical species with the index numbers $i=1, 2, \dots, M$ are principal chemical species and those with $j=M+1, M+2, \dots, N$ are intermediates, we have the relation,

$$N_i^{(e)} \gg N_j^{(e)}, \quad \text{if } i \leq M \text{ and } j > M. \quad (32)$$

The solution of the simultaneous equations (9) is (13), but for our purpose it is convenient to rewrite it in terms of the variables η_s defined in §2:

$$\eta_s = \sum_{u=1}^S \beta_{su} \zeta_u^{(0)} \exp(-t/\tau_u), \quad (33)$$

where β_{su} is the transformation matrix which connects η_s with ζ_u , *i.e.*,

$$\eta_s = \sum_{u=1}^S \beta_{su} \zeta_u. \quad (34)$$

A situation of great interest arises under the condition (32). Namely, [1] $\tau_u \gg \tau_v$ if $u \leq P$ and $v > P$, *i.e.* the first P of the S relaxation times τ_s ($s=1, 2, \dots, S$) in (33) are quite *long* compared with the remaining ones, where P is defined by (26); [2] $|\beta_{su}| \gg |\beta_{sv}|$ in (33) if $s \leq P$, $u \leq P$, and $v > P$, *i.e.* the contribution of the exponential terms with the *short* relaxation times, to η_s with the index number $s=1, 2, \dots, P$ is negligibly small; [3] $|\beta_{su}| \ll |\beta_{sv}|$ in (33) if $s > P$, $u \leq P$ and $v > P$, *i.e.* the contribution of the exponential terms with the *long* relaxation times, to η_s with $s=P+1, P+2, \dots, S$ is negligibly small. The mathematical derivation of these results will be described later in this Section.

We shall hence suppose*) that the "negligibly small" terms in (33) are

*) In other words, we shall assume the relation (41).

omitted; then (33) will be called the *solution of the steady-state approximation*. The physical significance of this approximate solution is clear when the macroscopic chemical change in the system is again described in terms of the S reactions associated with the variables (extents of reaction) η_s , $s=1, 2, \dots, S$ (cf. §2). Then the first P reactions are *slow reactions*, *i. e.*, characterized by the *long* relaxation times, whereas the remaining $S-P$ reactions are *transient reactions* with the short relaxation times and will quickly decay. After the transient reactions have died away, *i. e.*, after the *induction period*⁽¹⁴⁾⁽³¹⁾, a *quasi-steady state* will be attained; then the change in the system is described by the above P slow reactions, which *do not involve the intermediates* according to (31) of §2.

We shall now consider the relation between the condition (32) and the above statements [1]-[3]. For this purpose, the fundamental equations (9) will be rewritten in terms of the variables η_s . The right hand side of (9) splits into two parts:

$$X_s = \sum_{t=1}^S X_{st}(\xi_t - \xi_t^{(e)}) = \sum_{t=1}^S (X_{st}^* + X_{st}^0)(\xi_t - \xi_t^{(e)}), \quad (35)$$

where the relations (17) and (20 b) have been used, and X_{st}^0 is defined by

$$X_{st}^0 = -R \sum_{i=1}^M b_{is} b_{it} / N_i^{(e)}. \quad (36)$$

Using the transformation properties (21) we obtain from (9),

$$d\eta_s/dt = \sum_{t=1}^S (\lambda_s^* \delta_{st} + Y_{st}^0) \eta_t, \quad (37)$$

where λ_s^* and Y_{st}^0 is written, by virtue of (21), (28) and (36), as

$$\lambda_s^* = -R \sum_{i=M+1}^N (b_{is}^2 / N_i^{(e)}), \quad Y_{st}^0 = \sum_{u=1}^S \sum_{v=1}^S X_{uv}^0 \gamma_{us} \gamma_{vt} = -R \sum_{i=1}^M b_{is} b_{it} / N_i^{(e)}. \quad (38)$$

The equations (35) and (37) correspond to (20 a) and (22), respectively, in the case of an open system. In handling the fundamental equations (37), the properties of the matrix $[\lambda_s^* \delta_{st} + Y_{st}^0]$ are important. Suppose that the matrix is divided into the four submatrices **A**, **B**, **C** and **D** as shown in Fig. 1 a. Taking (25) of §2 into account, we observe that actually the eigenvalues λ_s^* occur only on the principal diagonal of **B**. If, as expressed by (32), the concentrations of the intermediates are sufficiently low, it follows from (38) that the absolute values of the non-zero eigenvalues λ_s^* are much larger than the absolute values of Y_{st}^0 , because λ_s^* and Y_{st}^0 contain the “large” factor $1/N_i^{(e)}$ ($i > M$) and the “small” factor $1/N_i^{(e)}$ ($i \leq M$), respectively:

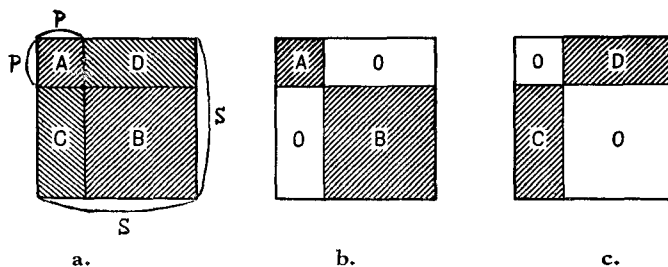


Fig. 1. a. Matrix $[\lambda_s^* \delta_{st} + Y_{st}^0] (= \mathbf{F}_0 + \mathbf{F}')$;
 b. Zero-order approximation matrix \mathbf{F}_0 ;
 c. Perturbation matrix \mathbf{F}' .

$$\lambda_u^* < 0 \text{ and } |\lambda_u^*| \gg |Y_{st}^0|, \text{ if } u > P. \quad (39)$$

Let us now tentatively assume that the submatrices **C** and **D** in the matrix $[\lambda_s^* \delta_{st} + Y_{st}^0]$ (Fig. 1 a) are negligible. If the matrix elements in **C** and **D** are set equal to zero, then the matrix takes the form of Fig. 1 b, so that the fundamental equations (37) splits into the two sets,

$$d\eta_{js}/dt = \sum_{t=1}^P Y_{st}^0 \eta_t, \quad s = 1, 2, \dots, P, \quad (40 \text{ a})$$

and

$$d\eta_{js}/dt = \sum_{t=P+1}^S (\lambda_s^* \delta_{st} + Y_{st}^0) \eta_t, \quad s = P+1, P+2, \dots, S, \quad (40 \text{ b})$$

where we have used (25). Thus the sets (40a) and (40b) are solved *independently*; the solution of (40a) and that of (40b) take the form of (33), but there are obviously no "cross terms" between them, *i. e.*,

$$\beta_{su} = 0, \quad \text{if } s \leq P \text{ and } u > P, \text{ or if } s > P \text{ and } u \leq P. \quad (41)$$

In terms of the normal coordinates ζ_s which diagonalize the matrices $[Y_{st}]$ of (40a) and $[\lambda_s^* \delta_{st} + Y_{st}^0]$ of (40b), *i. e.*, **A** and **B** of Fig. 1 b, the equations (40a) and (40b) take the forms

$$d\zeta_s/dt = \lambda_s \zeta_s, \quad s = 1, 2, \dots, P, \quad (42 \text{ a})$$

and

$$d\zeta_s/dt = \lambda_s \zeta_s, \quad s = P+1, P+2, \dots, S, \quad (42 \text{ b})$$

respectively. Comparing (42) and (40) with (39), we observe* that the absolute value of λ_s in (42a) is of the order of $|Y_{st}^0|$, whereas that of λ_s in (42b) is of

* It follows from (25) and (39) that the submatrix **A** consists of the "small" elements Y_{st}^0 , whereas the submatrix **B** consists of the "large" negative diagonal elements $\lambda_s^* + Y_{ss}^0$ and the "small" off-diagonal elements Y_{st}^0 .

the order of $|\lambda_u^*|$ ($u > P$). Since the relaxation time τ_u in (33) is given by $\tau_u = -1/\lambda_u$, we thus find

$$\tau_s = -1/\lambda_s \gg -1/\lambda_t = \tau_t, \quad \text{if } s \leq P \text{ and } t > P, \quad (43)$$

which is the above statement [1]. Combining the results (41) and (43), we see that when the submatrices **C** and **D** are neglected in solving (37), the solution of the *steady state approximation* (see above) is obtained.

The effect of the neglected submatrices **C** and **D** upon the results can be calculated by the perturbation theory frequently used in quantum mechanics; the solution of the equations (40) is considered the zero-order approximation, and **C** and **D** are treated as a perturbation. Since the difference $|\lambda_s - \lambda_t|$ ($s \leq P$ and $t > P$) between the zero-order approximation eigenvalues in (42a) and (42b) is "large" (see above) and since the matrix elements Y_{st}^0 in **C** and **D** are "small" the effect of **C** and **D** is, according to the perturbation theory, expected to be small [cf. (51) below]. When **C** and **D** are not neglected in solving (37), those coefficients β_{su} which have been considered in (41) (*i.e.* the coefficients of the "cross terms") will no longer be zero, but still their absolute values will be quite small. Thus we arrive at the results [2] and [3] mentioned above.

We shall now turn to the perturbation theoretical calculation of the correction terms due to **C** and **D**, which represent the "interaction" between the slow reactions and the transient reactions. For this purpose we shall use the formula devised by MONTROLL³⁰) and matrix notations. The fundamental equations (37) are rewritten in a matrix form as

$$d\mathbf{x}(t)/dt = (\mathbf{F}_0 + \mathbf{F}') \cdot \mathbf{x}(t). \quad (44)$$

In (44), $\mathbf{x}(t)$ is a vector whose s -th component is γ_{ss} , and the matrix $[\lambda_s^* \delta_{st} + Y_{st}^0]$ of (37) has been split into the two terms \mathbf{F}_0 and \mathbf{F}' ; \mathbf{F}_0 is the matrix of Fig. 1b, and hence \mathbf{F}' is the perturbation matrix consisting of the submatrices **C** and **D** (Fig. 1c). The vector $\mathbf{x}(t)$ is expressed as

$$\mathbf{x}(t) = \mathbf{K}(t) \cdot \mathbf{x}(0), \quad (45)$$

where $\mathbf{x}(0)$ is the initial value of $\mathbf{x}(t)$, and $\mathbf{K}(t)$ is the transition probability matrix³¹⁾. Let $\mathbf{K}_0(t)$ represent the transition probability matrix $\mathbf{K}(t)$ calculated in the zero-order approximation, so that $\mathbf{K}_0(t) \cdot \mathbf{x}(0)$ is the zero-order solution, *i.e.* the solution of the steady-state approximation (see above). According to MONTROLL³⁰) the solution $\mathbf{x}(t)$ in the first-order approximation is calculated by

$$\mathbf{x}(t) = \mathbf{K}_0(t) \cdot \mathbf{x}(0) + \left[\int_0^t \mathbf{K}_0(t-\tau) \cdot \mathbf{F}' \cdot \mathbf{K}_0(\tau) d\tau \right] \mathbf{x}(0), \quad (46)$$

where the second term of the right-hand side represents the first-order correction

due to \mathbf{F}' (i. e. \mathbf{C} and \mathbf{D}).

The equation (33) is also written in a matrix form as

$$\mathbf{x}(t) = \mathbf{S} \cdot \mathbf{T}(t) \cdot \mathbf{y}(0) = \mathbf{S} \cdot \mathbf{T}(t) \cdot \mathbf{S}^{-1} \cdot \mathbf{x}(0), \quad (47)$$

where \mathbf{S} represents the matrix $[\beta_{su}]$, \mathbf{S}^{-1} is the reciprocal matrix of \mathbf{S} , $\mathbf{T}(t)$ is the diagonal matrix $[\delta_{st} \exp(-t/\tau_s)] = [\delta_{st} \exp(\lambda_s t)]$, and $\mathbf{y}(0)$ is a vector whose s -th component is $\zeta_s^{(0)}$. We shall suppose that β_{us} , λ_s and τ_s in the zero-order approximation are known and have been used for the matrices \mathbf{S} and $\mathbf{T}(t)$ of (47); then the expression (47) is the zero-order solution, and we have

$$\mathbf{K}_0(t) \cdot \mathbf{x}(0) = \mathbf{S} \cdot \mathbf{T}(t) \cdot \mathbf{S}^{-1} \cdot \mathbf{x}(0), \quad \text{i. e. } \mathbf{K}_0(t) = \mathbf{S} \cdot \mathbf{T}(t) \cdot \mathbf{S}^{-1}. \quad (48)$$

Hence (46) is rewritten as

$$\mathbf{x}(t) = \mathbf{S} \cdot \left[\mathbf{T}(t) + \mathbf{T}(t) \cdot \int_0^t \mathbf{T}(-\tau) \cdot (\mathbf{S}^{-1} \cdot \mathbf{F}' \cdot \mathbf{S}) \cdot \mathbf{T}(\tau) d\tau \right] \cdot \mathbf{y}(0). \quad (49)$$

The integral on the right-hand side of (49) is easily calculated, and the following expression is obtained:

$$\begin{aligned} \eta_s = \sum_{u=1}^S \beta_{su} \left[\exp(-t/\tau_u) \zeta_u^{(0)} + \exp(-t/\tau_u) \sum_{v=1}^S G_{uv} (\lambda_u - \lambda_v)^{-1} \zeta_v^{(0)} \right. \\ \left. - \sum_{v=1}^S \exp(-t/\tau_v) G_{uv} (\lambda_u - \lambda_v)^{-1} \zeta_v^{(0)} \right], \end{aligned} \quad (50)$$

where G_{uv} is the (u, v) -element of the matrix $\mathbf{S}^{-1} \cdot \mathbf{F}' \cdot \mathbf{S}$. The second and the third terms on the right-hand side of (50) are the correction terms in the first-order approximation. Since the matrix $\mathbf{S} = [\beta_{su}]$ in (49) is of the zero-order approximation and hence satisfies the condition (41), it can be readily shown*) that

$$\begin{aligned} G_{uv} = G_{vu} = 0, \quad \text{if } u \leq P \text{ and } v \leq P, \text{ or if } u > P \text{ and } v > P, \\ G_{uv} = G_{vu} = \sum_{s=1}^P \sum_{t=P+1}^S Y_{st}^0 \beta_{su} \beta_{tv}, \quad \text{if } u \leq P \text{ and } v > P. \end{aligned}$$

Therefore we observe that the correction terms on the right-hand side of (50) contain the factors

$$\sum_{s=1}^P \sum_{t=P+1}^S \left[Y_{st}^0 / (\lambda_u - \lambda_v) \right] \beta_{su} \beta_{tv}, \quad (51)$$

where $u \leq P$ and $v > P$, or $u > P$ and $v \leq P$. As was pointed out above, the factor $Y_{st}^0 / (\lambda_u - \lambda_v)$ in (51) insures the smallness of the correction terms. Also, the expression (50) is rewritten as

*) Here it is to be noted that $[\beta_{su}]$ is an orthogonal matrix and $[Y_{st}^0]$ a symmetrical matrix.

$$\eta_s = \sum_{u=1}^P \beta_{su} \left\{ \exp(-t/\tau_u) \left[\zeta_u^{(0)} + \sum_{v=P+1}^S G_{uv} (\lambda_u - \lambda_v)^{-1} \zeta_v^{(0)} \right] - \sum_{v=P+1}^S \exp(-t/\tau_v) G_{uv} (\lambda_u - \lambda_v)^{-1} \zeta_v^{(0)} \right\}, \quad \text{for } s \leq P, \quad (52 \text{ a})$$

and

$$\eta_s = \sum_{u=P+1}^S \beta_{su} \left\{ \exp(-t/\tau_u) \left[\zeta_u^{(0)} + \sum_{v=1}^P G_{uv} (\lambda_u - \lambda_v)^{-1} \zeta_v^{(0)} \right] - \sum_{v=1}^P \exp(-t/\tau_v) G_{uv} (\lambda_u - \lambda_v)^{-1} \zeta_v^{(0)} \right\}, \quad \text{for } s > P. \quad (52 \text{ b})$$

These results will be discussed in § 4.

§ 4. Discussion

Under the condition of a steady state, as many chemists realize, the mathematical treatment of complex kinetic systems^{14,31)} as well as the stoichiometric equations describing the macroscopic chemical change^{*}) is much simplified, because the concentrations of the intermediates are supposed to be kept constant.

We shall return to the case of the open system considered in § 2. The macroscopic chemical change has been described by the S variables η_s and the S reactions associated with η_s 's, where S is the number of the elementary reactions in the system. A few of these reactions, which have been called *steady reactions*, involve no intermediates and take place with constant rates, $d\eta_s/dt = Y_s^0$ [cf. (30)]; the other reactions called *transient reactions* produce (or consume) the intermediates and exponentially die down during the induction period. Therefore, when a steady state is established, the system is described in terms of a few steady reactions or a few variables (η_s with $s \leq P$). These steady reactions are not quite the same as the "overall reactions" usually considered by chemists and discussed in Part I. However they are *equivalent*^{**)} to the overall reactions. Also the "rate equations" (30) of the steady reactions are equivalent to the linear relations of the overall reactions, Eq. (39) of Part I. In other words, the solution of (30) is the same as that of Part I, Eq. (39). Further details will be described in Appendix.

The same variables η_s and the same reactions have been used in the treatment of the closed system in § 3. We have, to a good approximation

^{*}) Cf. Part I. § 1.

^{***)} The definition of the word, *equivalent* (PRIGOGINE¹¹⁾) has been described in Part I. In other words, the steady reactions and the overall reactions are connected by a linear transformation. Cf. also (6) and (7) of Introduction, and the simple example at the end of § 2.

(*steady-state approximation*), demonstrated that the transient reactions (involving unstable intermediates) rapidly die away, whereas the steady reactions (called *slow reactions* in §3) decay quite slowly as compared with the transient reactions. The "rate equation" of these steady (slow) reactions is, in the steady state approximation, given by (40a). In Appendix we shall show that Eqs. (47) and (48) of Part I are equivalent to (40a) of the present paper. In other words Eqs. (47) and (48) of Part I, on which the treatment of Part I, §5 is based, are the relations in the steady state approximation. In §3 of the present paper, starting from the relation (32), we have also examined the validity of the steady state approximation. In this connection, it is to be noted that in the limiting case of *infinitely* large amounts $N_i^{(e)}$ ($1 \leq i \leq M$) of the principal chemical species in (32), the results of the closed system of §3 coincide with those of the open system of §2*).

In Part I, we have not been concerned with the transient reactions, because our discussions there have been based on the assumption of a steady state or an approximate steady state (quasi-steady state). In order to *eliminate* the transient reactions we have used the "principal set transformation" defined by Eqs. (9) and (14) of Part I; in this way Eqs. (39), (47), (48), *etc.* of Part I have been derived.

The expressions (52a) and (52b) of §3 include the first-order correction to the steady state approximation. For example we shall consider (52b); as a result of the perturbation, the exponential terms with the long relaxation times as well as the terms with the short relaxation times occur in (52b). It follows therefore that the transient reactions do not completely die down after the induction period. This corresponds to the fact that in a closed system the concentrations of the principal chemical species gradually change with time, and so do the concentrations of the intermediates even after the induction period.

It is to be noted that the results of §3 have various points of contact with the theories of BENSON¹⁵⁾, BAUER^{3,7)}, and especially HIRSCHFELDER³¹⁾. The exact solution of the fundamental equations (37) or (44) of §3 is written in the form of (45). Substituting (45) into (44), we have

$$d\mathbf{K}(t)/dt = (\mathbf{F}_0 + \mathbf{F}') \cdot \mathbf{K}(t), \quad (53)$$

from which we obtain³⁴⁾

$$\mathbf{K}(t) = \mathbf{K}_0(t) + \int_0^t \mathbf{K}_0(t-\tau) \cdot \mathbf{F}' \cdot \mathbf{K}(\tau) d\tau, \quad (54)$$

*) Remember that we have considered an "infinite" reservoir attached to the closed system in §2.

where $\mathbf{K}_0(t)$ satisfies

$$d\mathbf{K}_0(t)/dt = \mathbf{F}_0 \cdot \mathbf{K}_0(t), \quad \mathbf{K}_0(0) = \text{unit matrix.}$$

When the zero-order solution $\mathbf{K}_0(t)$ is known, the right-hand side of (54) can be calculated by the iteration procedure; the expression (46) is the first approximation solution in the iterative calculation³⁴⁾. On the other hand, HIRSCHFELDER'S discussion³¹⁾ on the steady state approximation has been based on a similar iterative solutions of rate equations*).

As was pointed out in the Introduction, the treatment in the present paper is restricted to kinetic systems in the neighborhood of equilibrium, but otherwise considerably general (*i.e.* independent of the "orders" of the elementary reactions, *etc.*). Also many of the features of a steady (or quasi-steady) state observed for reactions close to equilibrium are, at least qualitatively, of more general validity.

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Appendix

We shall first examine some algebraic properties of the matrix $[X_{st}^*]$ defined by (20b):

$$X_{st}^* = - \sum_{i=M+1}^N (R/N_i^{(e)}) b_{is} b_{it}, \quad (R/N_i^{(e)} > 0). \quad (\text{A. 1})$$

As shown in (21) and (38), the matrix $[X_{st}^*]$ is transformed into the diagonal matrix $[\lambda_s^* \delta_{st}]$, where

$$\lambda_s^* = \sum_{u=1}^S \sum_{v=1}^S X_{uv}^* \gamma_{us} \gamma_{vs} = - \sum_{i=M+1}^N (R/N_i^{(e)}) (b'_{is})^2 \leq 0. \quad (\text{A. 2})$$

Thus one sees that the eigenvalues λ_s^* are negative or zero. Let P be the number of the zero eigenvalues, and let us suppose that $\lambda_s^* = 0$ for $s=1, 2, \dots, P$. Since $R/N_i^{(e)}$ in (A.2) is positive, $\lambda_s^* = 0$ implies $b'_{is} = 0$ for $i=M+1, M+2, \dots, N$; *i.e.*,

$$b'_{is} = \sum_{t=1}^S b_{it} \gamma_{ts} = 0 \quad \text{for } i=M+1, M+2, \dots, N, \quad (\text{A. 3})$$

which is the expression (31) of §2. Similarly we can show that if $s > P$, then $\lambda_s^* \neq 0$ and at least one of b'_{is} 's ($i=M+1, M+2, \dots, N$) is non-zero.

*) Cf. also Part I, §2.

We shall now prove the relation (26). Consider the two sets of simultaneous linear equations^{*)},

$$\sum_{t=1}^S b_{it}\nu_t = 0, \quad i=M+1, M+2, \dots, N, \quad (\text{A. 4})$$

and

$$\sum_{t=1}^S X_{st}^*\nu_t = 0, \quad s=1, 2, \dots, S, \quad (\text{A. 5})$$

where b_{it} and X_{st}^* are considered constant coefficients. With the help of the relation (A.1), we can readily prove^{**)} that the set of equations (A.4) is equivalent to the set (A.5), *i.e.*, the solution of (A.4) is the same as that of (A.5). Since the rank of the coefficient matrix of (A.4) is I (*cf.* §2), the number of independent solutions of (A.4) and therefore that of (A.5) are $S-I$ ³⁶⁾. On the other hand, a solution of (A.5) is an eigenvector belonging to the zero eigenvalue of the matrix $[X_{st}^*]$ ²³⁾, so that the number of the independent eigenvectors for the zero eigenvalue is also $S-I$. It follows that the multiplicity (degeneracy)²³⁾ of the zero eigenvalue is $S-I$; *i.e.* we obtain the relation $P=S-I$.

The $P(=S-I)$ independent solutions of (A.4) or (A.5) are not unique³⁶⁾. Previous papers³³⁾⁷⁾ by HORIUTI and the present author have discussed this point and led to the concept of the *stoichiometric number*. Now we shall consider a set of P independent solutions of (A.4) or (A.5), *i.e.* a set of P independent eigenvectors belonging to the zero eigenvalues of $[X_{st}^*]$. These solutions or eigenvectors will be denoted by $(\nu_1^{(p)}, \nu_2^{(p)}, \dots, \nu_S^{(p)})$, $p=1, 2, \dots, P$ ^{***)}. On the other hand, it follows from (21) and (25) that the first P columns of the transformation matrix $[\gamma_{st}]$ are also P independent eigenvectors belonging to the zero eigenvalues²³⁾, so that we can write as

$$\gamma_{st} = \sum_{u=1}^P \nu_s^{(u)} C_{ut}, \quad s=1, 2, \dots, S \text{ and } t=1, 2, \dots, P, \quad (\text{A. 6})$$

where $[C_{ut}]$ is a $(P \times P)$ transformation matrix which connects the two sets of the eigenvectors, and

$$\det(C_{ut}) \neq 0.$$

*) *Cf.* Eq. (15) of Part I.

**) Note that we have, from (A.5) and (A.1),

$$0 = \sum_s \sum_t X_{st}^* \nu_s \nu_t = \sum_{t=M+1}^N (-R/N_t^{(e)}) \left(\sum_{t=1}^S b_{it} \nu_t \right)^2,$$

which implies

$$\sum_{t=1}^S b_{it} \nu_t = 0, \quad i = M+1, M+2, \dots, N. \quad (\text{A. 4})$$

***) *Cf.* Part I, §1 or Ref. 33.

Now Eq. (39) of Part I is rewritten as

$$\sum_{t=1}^P (K_{st}/T)(d\Xi_t/dt) = A_s/T, \quad s=1, 2, \dots, P. \quad (\text{A. 7})$$

Similarly, Eqs. (47) and (48) of Part I are combined as follows :

$$\sum_{t=1}^P (K_{st}/T)(d\Xi_t/dt) = \sum_{t=1}^P (A_{st}/T)(\Xi_t - \Xi_t^{(e)}), \quad s=1, 2, \dots, P, \quad (\text{A. 8})$$

on which equation the calculation of Part I, §5 has been based. The various quantities in (A.7) and (A.8) are expressed as

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

$$A_{st}/T = -R \sum_{u=1}^S \sum_{v=1}^S \left(\sum_{\ell=1}^M b_{iu}b_{iv}/N_i^{(e)} \right) \nu_u^{(s)}\nu_v^{(t)} = \sum_{u=1}^S \sum_{v=1}^S X_{uv}^0 \nu_u^{(s)}\nu_v^{(t)},$$

where Eqs. (9), (14), (17), (36), (40) and (57) of Part I, and (36) of the present paper have been used. If, therefore, the both hand sides of (A.7) and (A.8) are multiplied by $C_{r,s}$ and summed over $s=1, 2, \dots, P$ and if we make the substitution,

$$\Xi_t - \Xi_t^{(e)} = \sum_{s=1}^P C_{ts}\eta_s, \quad (\text{A. 9})$$

then we obtain the equations (30) and (40a), respectively, of the present paper. Hence we can conclude that equations (A.7) and (A.8) are equivalent to (30) and (40a), respectively, of the present paper.

Similarly, the relation between the steady reactions in §2 and §3 and the overall reactions of Part I is calculated as

$$b'_{is} = \sum_{t=1}^S \sum_{u=1}^P b_{it}\nu_t^{(u)} C_{us} = \sum_{u=1}^P B_{iu}C_{us}, \quad s \leq P$$

where (28) and (A.6) of the present paper, and (17) of Part I have been used.

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