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

By

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This paper deals with some general features of the steady state of chemical reactions. The description of macroscopic chemical change in the steady state, by reaction equations (stoichiometric equations) is discussed, and in this connection the concept of the *principal set* of reaction equations is introduced (§ 1). The application of the concept to the treatments of chemical reactions by thermodynamics of irreversible processes and by chemical kinetics is considered (§ 3-§ 5). The connection with the previous papers by PRIGOGINE *et al.*, MEIXNER, HORIUTI, HOLLINGSWORTH, the present author, *etc.* is also described. Further discussions are left to the subsequent paper (Part II).

Introduction

It is characteristic of most chemical reactions that they are described by more or less simple reaction equations (stoichiometric equations) such as $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$, $\text{H}_2 + \text{Br}_2 = 2\text{HBr}$, $3\text{H}_2 + \text{N}_2 = 2\text{NH}_3$, *etc.* However, the molecular processes underlying these reactions are not always so simple as the above equations look. For instance, the second of the above examples, *i.e.*, the gas phase reaction,



is a *complex reaction*¹⁾ and has the mechanism consisting of the monomolecular decomposition process,



the binary rearrangement collision process,



and so on¹⁾. Elementary processes or *elementary reactions* such as (2) or (3) can be theoretically treated, at least in principle, by the classical collision theory²⁾, the theories³⁾ of monomolecular reaction rate, the transition state method⁴⁾, the quantum mechanical collision theory⁵⁾, and the like⁶⁾. In this way we can

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understand the properties of the elementary reactions and derive laws for them, *i. e.*, the rate law, the dependence of the rate on temperature, *etc.*

How are the properties of an observed macroscopic chemical reaction (*overall reaction*) connected with those of the constituent elementary reactions? This is now one of important problems of chemical kinetics. If, for example, the gas phase reaction,



took place^{*)} by the triple collision process,



and by its reverse process, the relation between the overall reaction (4) and the elementary reaction (5) would be trivial, *e. g.*, the rate law of the former would be the same as that of the latter, and the relation between the rate constants and the equilibrium constant (or between the heats of reaction and the activation energies) of the reaction (4) could be most simply stated⁷⁾. In reality, the reaction (4) is known to consist of several elementary reactions, and accordingly its behaviour is by no means simple¹⁰⁾. However, even in the case of such a complex reaction, if one of the constituent elementary reactions can be taken to be the *rate-determining step*, then the other elementary reactions are practically in equilibrium, and under such a condition the properties of the overall reaction are closely related with those of the rate-determining step. HORIUTI, using the concept of the *stoichiometric number*^{**)} introduced by himself, has discussed the general properties of an overall reaction with a rate-determining step, and obtained a number of interesting results¹¹⁾. For example, he has proved the relation¹¹⁾,

$$\bar{k}/\bar{k} = K^{1/\nu},$$

where ν is the stoichiometric number of the rate-determining step, and \bar{k} , \bar{k} , and K are the forward and the backward rate constants and the equilibrium constant, respectively, of the overall reaction.

In connection with the treatment of such complex reactions in general, the

*) SLATER, in his celebrated textbook (Ref. 7), assumed this to be the case, in order to illustrate kinetics and equilibrium of chemical reactions. This is, of course, an oversimplification and far from reality. The proof of the mass action law described in the above book is based on such an assumption, and is not valid for complex reactions in general. More correct proof has been given by FROST (Ref. 8) or by HORIUTI (§7 of Ref. 11b). On the other hand, the reaction between hydrogen H_2 and iodine I_2 is known to consist solely of the binary collision process, $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ (cf., however, Ref. 9).

***) Cf. §1 of this paper.

concept of the *steady (stationary) state* of a chemical reaction is very important, and has been the subject of many discussions. A classic example is the famous work of CHRISTIANSEN, HERZFELD and POLANYI who explained the hydrogen-bromine reaction (1) in terms of the mechanism (2), (3), *etc.* and on the assumption of steady state. The purpose of the present paper is to examine some general features of chemical reactions in the steady state. We shall be interested especially in the behaviour of the chemical reactions in the neighbourhood of equilibrium (§3 and the following), where rather simple and general theory can be developed by virtue of the simple linear rate law (§3) of constituent elementary reactions. In recent years thermodynamical theory of the steady (stationary) state of irreversible phenomena has been investigated by a number of authors¹²⁾⁻¹⁶⁾. Among them PRIGOGINE¹⁷⁾ and others have discussed also the steady state of chemical reactions. The thermodynamical theory of irreversible processes deals almost exclusively with linear processes, and makes use of the linear relations between the fluxes and affinities, such as the above linear rate law. Consequently, our treatments of reactions in the neighbourhood of equilibrium have close connection with the thermodynamical theory. This point will also be discussed in the following.

§ 1. Overall Reactions in Steady State^{*)}

We shall begin with the simplest example. Consider the elementary reactions,



taking place in a system. The macroscopic chemical changes resulting from the set of simultaneous reactions (6) can be equally well described by another set of reaction equations which are linear combinations of (6); for instance, by



which are the sum and the difference of the two reactions of (6). Thus the sets (6) and (7) are *equivalent systems* (PRIGOGINE¹⁸⁾) or *equivalent sets*.

Mathematically, the relation between two equivalent sets of reaction equations is a linear transformation by a non-singular matrix, *i. e.*, a matrix whose determinant is not zero. Let b_{is} and B_{it} be the stoichiometric coefficients^{**)} of the i -th chemical species, in the s -th reaction of one set and in the t -th reaction of

^{*)} Cf. Ref. 22.

^{**)} Here we shall employ PRIGOGINE and DEFAY's definition of stoichiometric coefficient (cf. p. 14 of Ref. 19). The stoichiometric *coefficients* should not be confused with the stoichiometric *number* introduced by HORIUTI and discussed also in the present paper.

the other set respectively, then the relation is

$$\sum_{s=1}^S b_{is} \alpha_{st} = B_{it}, \quad \begin{cases} i = 1, 2, \dots, N \\ t = 1, 2, \dots, S \end{cases} \quad (8)$$

where α_{st} is an $(S \times S)$ non-singular matrix, and S and N are respectively the number of reactions in each set and the number of the chemical species involved in these reactions. Corresponding to the linear transformation (8), the rates, the extents of reaction (DE DONDER²⁰) and the affinities are similarly transformed:

$$\left. \begin{aligned} \sum_{t=1}^S \alpha_{st} V_t &= v_s, \\ \sum_{t=1}^S \alpha_{st} \mathcal{E}_t &= \hat{\xi}_s, \\ \sum_{s=1}^S \alpha_s \alpha_{st} &= A_t, \end{aligned} \right\} \quad (t, s = 1, 2, \dots, S), \quad (9)$$

where v_s , $\hat{\xi}_s$ and a_s are the rate, the extent of reaction and the affinity, respectively, of the s -th reaction of the first set; V_t , \mathcal{E}_t , A_t are similar quantities of the t -th reaction of the second set. The relations (9) follow¹⁸) from the equalities,

$$\sum_{s=1}^S \sum_{t=1}^S b_{is} \alpha_{st} V_t = \sum_{t=1}^S B_{it} V_t = \dot{N}_i = \sum_{s=1}^S b_{is} v_s, \quad (9a)$$

$$v_s = \hat{\xi}_s, \quad V_t = \mathcal{E}_t, \quad (9b)$$

$$a_s = -\sum_i \mu_i b_{is}, \quad A_t = -\sum_i \mu_i B_{it}, \quad (9c)$$

where \dot{N}_i and μ_i are the net rate of production (the rate of the change of the mole number²⁰) and the chemical potential, respectively, of the i -th chemical species.

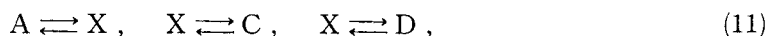
Now suppose that the set of elementary reactions (6) are in the steady state, *i. e.*, the rate of production of the *intermediate* X is balanced by the rate of its consumption. Thus the net rate of production \dot{N}_X of the intermediate X vanishes; hence the rate of the second reaction of (7) is evidently zero. Accordingly the macroscopic chemical change is expressed by the single reaction $A=B$ of (7), which does not involve the intermediate X. In the usual chemists' language the set of elementary reactions (6) is the "mechanism" of the observed steady *overall reaction* $A=B$, and A and B are the reactant and the product of the overall reaction. In the above transformation, (6)→(7), the transformation matrix $[\alpha_{st}]$ is evidently

$$\begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}, \quad (10)$$

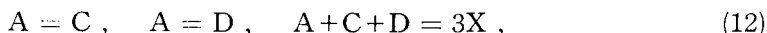
and, according to (9), the rates, V_1 and V_2 of the reactions of (7) satisfy the relation

$$\left. \begin{aligned} V_1 + V_2 &= v_1, \\ V_1 - V_2 &= v_2, \end{aligned} \right\} \quad (10 a)$$

where v_1 and v_2 are the rates of the elementary reactions of (6). Another simple example is a set of the simultaneous elementary reactions,



where X is an intermediate. The set of reactions,



is equivalent to the set (11), but in the steady state the rate V_3 of the third reaction of (12) similarly becomes zero and the macroscopic chemical change is described by the two simultaneous overall reactions $A=C$ and $A=D$. The matrix $[\alpha_{st}]$ of the transformation (11)→(12) is now

$$\begin{pmatrix} 1 & 1 & 1 \\ 1 & 0 & -1 \\ 0 & 1 & -1 \end{pmatrix}. \quad (13)$$

We see that by virtue of the transformation by (10) or (13) the intermediate X has been eliminated from the first reaction of (7) or from the first and the second of (12), and the new set (7) or (12) is suitable for the description of the macroscopic chemical change in the steady state. In the following we shall call such a set and such a transformation the *principal set* and the *principal set transformation*, respectively.

The general form of the principal set transformation matrix has been studied by the present author and YAMAZAKI²¹⁾, who have shown that the matrix $[\alpha_{st}]$ of the principal set transformation must satisfy the condition

$$\alpha_{st} = \nu_s^{(t)} \quad \text{for } s=1, 2, \dots, S \text{ and } t=1, 2, \dots, P, \quad (14)$$

where $\nu_s^{(t)}$ is the *stoichiometric numbers* defined by HORIUTI and the present author^{22)11b)}.

We shall consider a set of S simultaneous elementary reactions, and suppose that I chemical species among the N chemical species involved in these reactions are the intermediates, so that, when the steady state is established, the remaining M chemical species ($M=N-I$) are the reactants (or the products) of the overall reactions (cf. the above examples and below). The latter M species are called "molecules" by HORIUTI^{11b) 22)}, or *principal chemical components* by

HIRSCHFELDER³¹⁾. Let b_{is} be the stoichiometric coefficients in the s -th elementary reaction ($s = 1, 2, \dots, S$), and let the suffices $i = 1, 2, \dots, M$ and $i = M+1, M+2, \dots, N$ designate respectively the M "molecules" and the I' intermediates. Now the stoichiometric numbers^{*} are a set of S numbers ($\nu_1, \nu_2, \dots, \nu_s$) which satisfy the I' simultaneous linear equations,

$$\sum_{s=1}^S b_{is} \nu_s = 0, \quad i = M+1, M+2, \dots, N. \quad (15)$$

More specifically, if the rank²³⁾ of the $(I' \times S)$ matrix $[b_{is}]$ ($i = M+1, M+2, \dots, N$ and $s = 1, 2, \dots, S$) is I , we have P linearly independent solutions of (15), *i. e.*, P sets of stoichiometric numbers denoted by $(\nu_1^{(p)}, \nu_2^{(p)}, \dots, \nu_s^{(p)})$, $p = 1, 2, \dots, P$, where^{**)} $P = S - I$.

In the case of the above examples, simple calculation leads to the results: $S = 2$, $M = 2$, $I' = I = 1$, $P = 1$ and $(\nu_1^{(1)}, \nu_2^{(1)}) = (1, 1)$ for the example (6); $S = 3$, $M = 3$, $I' = I = 1$, $P = 2$, $(\nu_1^{(1)}, \nu_2^{(1)}, \nu_3^{(1)}) = (1, 1, 0)$ and $(\nu_1^{(2)}, \nu_2^{(2)}, \nu_3^{(2)}) = (1, 0, 1)$ for the example (11). Now one sees that the first column, $(1, 1)$ of the matrix (10), and the first and the second columns, $(1, 1, 0)$ and $(1, 0, 1)$ of the matrix (13) are respectively the stoichiometric numbers for the sets of elementary reactions (6) and (11), *i. e.*, these matrices satisfy the condition (14).

In general cases, the transformation of the above set of S elementary reactions by the matrix $[\alpha_{st}]$ subject to the condition (14), leads to the S reactions of the principal set, whose stoichiometric coefficients B_{it} , rates V_t , extents of reaction Ξ_t and affinities A_t ($t = 1, 2, \dots, S$) are expressed by (8) and (9), in terms of the corresponding quantities, b_{is} , ν_s , ξ_s and a_s ($s = 1, 2, \dots, S$) of the elementary reactions. As shown in Appendix, *in a steady state* in which the numbers of moles of the intermediates do not vary with time, *i. e.*,

$$\dot{N}_i = 0 \quad \text{for} \quad i = M+1, M+2, \dots, N,$$

*) The concept of the stoichiometric number has originated from HORIUTI and IKUSHIMA's paper [Proc. Imp. Acad. Japan **15**, 39 (1939)]. FROST (Ref. 8) has used similar numbers for his kinetic proof of the mass action law; his numbers n_p, n_q, \dots in p. 177 of Ref. 1 are the same as our ν_1, ν_2, \dots . BORESKOV [J. Phys. Chem. USSR **19**, 92 (1945); Dokl. Akad. Nauk SSSR **129**, 607 (1959)], in his discussion of the relation between the activation energy and the heat of reaction, has used a number (called "molekular nosti" by him) which is closely related to HORIUTI's stoichiometric number of the rate determining step.

***) In Refs. 11 b and 22, M , I' , I and P are called the numbers of "molecules", of intermediates, of independent intermediates and of reaction routes, respectively, and $(\nu_1^{(p)}, \nu_2^{(p)}, \dots, \nu_s^{(p)})$ or $\nu_s^{(p)}$ are called the stoichiometric numbers of the p -th reaction route or the stoichiometric number of the s -th elementary reaction in the p -th reaction route, respectively. For further details and examples of the stoichiometric numbers, see Ref. 11 b and Ref. 22.

the rates of the $(P+1)$ -th, $(P+2)$ -th, \dots and S -th reactions of this principal set vanish, *i. e.*,

$$V_t = 0 \quad \text{for} \quad t > P. \quad (16)$$

Consequently, in the steady state of the above S elementary reactions, the macroscopic chemical change is described by the 1st, 2nd, \dots , P -th reactions of the principal set, *i. e.*, macroscopically, one observes P simultaneous overall reactions, in which the reactants (or the products) have the stoichiometric coefficients,

$$B_{it} = \sum_{s=1}^S b_{is} \alpha_{st} = \sum_{s=1}^S b_{is} \nu_s^{(t)}, \quad i=1, 2, \dots, M \text{ and } t=1, 2, \dots, P, \quad (17)$$

but none of the intermediates ($i=M+1, M+2, \dots, N$) is involved as shown in Appendix, *i. e.*,

$$B_{it} = 0, \quad i=M+1, M+2, \dots, N \text{ and } t=1, 2, \dots, P. \quad (18)$$

The applications of such a transformation and the principal set will be discussed in the following Sections.

Algebraically, the linearly independent solutions of the homogeneous linear equations (14), having the properties of vectors, are not unique and neither are the stoichiometric numbers. However, it is usually convenient²²⁾ to choose such a set of P linearly independent solutions that make the resultant P overall reactions simplest. For instance, in the case of the example (11), $(\nu_1, \nu_2, \nu_3) = (2, 1, 1)$ and $(0, 1, -1)$ too are a set of linearly independent solutions of the equations (15), *i. e.*, the stoichiometric numbers of (11). If we replace the first and the second columns of the matrix (13) by $(2, 1, 1)$ and $(0, 1, -1)$ respectively, the resultant overall reactions in the steady state will be $2A=C+D$ and $D=C$, which are *equivalent*¹⁸⁾ to the overall reactions, $A=C$ and $A=D$ of (12), but slightly more complicated.

The relation (14) determines only the first P columns of the matrix $[\alpha_{st}]$; the $(P+1)$ -th, $(P+2)$ -th, \dots , S -th columns are arbitrary in so far as the matrix is non-singular. This can be seen from the proofs of (16) and (18) presented in Appendix.

Taking into account (9) and (14), we have

$$v_s = \sum_{t=1}^S \alpha_{st} V_t = \sum_{t=1}^P \nu_s^{(t)} V_t + \sum_{t=P+1}^S \alpha_{st} V_t, \quad (19)$$

which, in a steady state, leads to

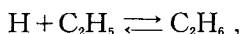
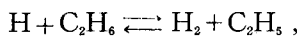
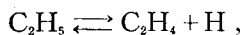
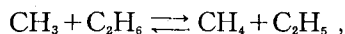
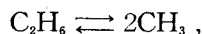
$$v_s = \sum_{t=1}^P V_t \nu_s^{(t)}, \quad (20)$$

by virtue of (16). This relation, which connects the rates v_s of the S elementary reactions with those V_t of the P overall reactions in a steady state, has been

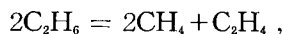
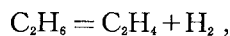
obtained by HORIUTI and the present author in a different way²²⁾.

In general, the P simultaneous overall reactions determined by (17) are not necessarily *independent*^{*)}.

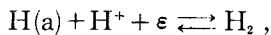
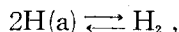
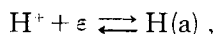
The set of elementary reactions^{**)},



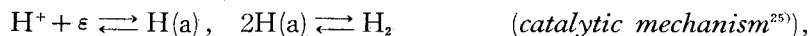
is the RICE-HERZFELD mechanism of the thermal decomposition of ethane²⁴⁾. For the above set with $S=5$, $I=I=3$ and $P=2$, the sets of numbers, (0, 0, 1, 1, 0) and (1, 2, 1, 0, 1) are two sets of the stoichiometric numbers, and the resultant overall reactions in the steady state are, according to (17),



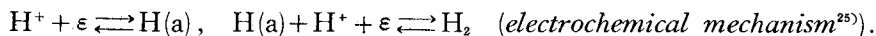
which are, of course, independent. Next, we shall consider the set of elementary reactions^{***)},



which were assumed^{****)} to take place on a hydrogen electrode (cathode) by some authors²⁵⁾ (the "dual theory" of the hydrogen electrode process). In this example involving one intermediate H(a), the stoichiometric numbers are^{****)} taken to be (2, 1, 0) and (1, 0, 1), which however lead to the same overall reaction, $2\text{H}^+ + 2\varepsilon = \text{H}_2$. Thus we have one independent overall reaction, which takes place simultaneously by two mechanisms,



and



*) Cf. p. 468 of PRIGOGINE and DEFAY (Ref. 19), for the definition of the *independence* of chemical reactions. Let R be the rank of the $(M \times P)$ matrix $[B_{it}]$ ($i=1, 2, \dots, M$ and $t=1, 2, \dots, P$), then R reactions among the P overall reactions are independent.

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

****) Here H(a), H^+ and ε denote respectively a hydrogen atom adsorbed on the electrode metal, a hydrogen ion in the electrolyte and a metal electron.

*****) Cf. also § 4 of Ref. 22.

§ 2. Establishment of Steady State: Simple Examples

In § 1, we have discussed the relation between the rates of overall reactions in a steady state and those of the constituent elementary reactions. Of great interest in this connection is how such a steady state is established. We shall first treat some simple examples^{*}) in order to illustrate some underlying principles.

As remarked by DENBIGH^{15)26a)}, PRIGOGINE^{12) 14)} and others, an "ideal" steady state, *i. e.*, a steady state in which the net rates of production of the intermediates are *exactly* equal to zero, is established only in an open system. As an example we shall consider the elementary reactions (6), which will be assumed to be first order. Thus the net rate of production \dot{n}_X of the intermediate X is expressed as

$$\dot{n}_X = -(\bar{k}_1 + \bar{k}_2)n_X + \bar{k}_1 n_A + \bar{k}_2 n_B, \quad (21)$$

where n_A , n_B and n_X are the concentrations (number of moles per unit volume^{**}), and \bar{k}_s and \bar{k}_s are the forward and the backward rate constants of the s -th elementary reactions ($s=1, 2$). Suppose that the reactions are taking place in an open system, where the "molecules" (principal chemical components³⁴⁾, A and B are exchanged with the external environment which acts as a *reservoir*²⁷⁾ of the "molecules", so that the concentrations n_A and n_B are kept constant^{***)}, *i. e.*, $n_A = n_A^0$ and $n_B = n_B^0$ where n_A^0 and n_B^0 are the concentrations of A and B in the reservoir (the environment). Thus Eq. (21) becomes

$$\dot{n}_X = -(\bar{k}_1 + \bar{k}_2)n_X + \bar{k}_1 n_A^0 + \bar{k}_2 n_B^0, \quad (22)$$

from which we have at once

$$n_X = n_X^s + (n_X^0 - n_X^s)e^{-t/\tau}, \quad (23)$$

where n_X^0 is the initial value of n_X , and τ and n_X^s are given by

$$n_X^s = (\bar{k}_1 n_A^0 + \bar{k}_2 n_B^0) / (\bar{k}_1 + \bar{k}_2), \quad (24)$$

^{*}) To illustrate the steady state of a chemical reaction, the water-tank model has been used by DENBIGH *et al.* (Ref. 26 a) and especially by HORIUTI ["Shokubai Kwagaku", Asakura Book Co., Tokyo (1953) (in Japanese)].

^{**}) Of course $n_X = N_X/V$, $n_A = N_A/V$, *etc.*, where V is the volume of the system, and N_X , N_A , *etc.* are the numbers of moles. In this Section we consider reaction rates *per unit volume*.

^{***}) Since in the present paper we are not interested in transport processes, we shall assume that the transport of A and B, between the environment and the system, is rapid enough, so that the concentrations n_A and n_B in the system are always equal to the concentrations n_A^0 and n_B^0 in the environment, in spite of the chemical reactions (6). In other words, we shall neglect the affinities of the transport processes (cf. p. 79 of Ref. 14).

and

$$1/\tau = \bar{k}_1 + \bar{k}_2 . \quad (25)$$

Eq. (23) implies that in the course of time, \dot{n}_X and n_X exponentially approach to zero and to the steady state concentration^{26a)} n_X^s , respectively, the latter being such a value of n_X that makes the right hand side of (21) zero for the fixed values, n_A^0 and n_B^0 , of the concentrations of the molecules A and B [cf. (24) and (25)]. In other words, for $t \gg \tau$ the exponential term in the right hand side of (23) becomes negligibly small, and a steady state ($\dot{n}_X = 0$) is attained, the relaxation time τ in (23) giving the measure of the *induction period*. A similar calculation can be carried out for the simultaneous elementary reactions (11). In this case also, the change of n_X is given by (23), but the steady state concentration n_X^s and the relaxation time τ therein are now expressed as

$$n_X^s = (\bar{k}_1 n_A^0 + \bar{k}_2 n_B^0 + \bar{k}_3 n_C^0) \tau , \quad (26)$$

and

$$1/\tau = \bar{k}_1 + \bar{k}_2 + \bar{k}_3 . \quad (27)$$

The above calculations may be extended to the case of a more complicated set of first-order reactions by the general theory of coupled first-order reactions developed by a number of authors²⁸⁾⁻³²⁾.

In the case of reactions in a closed system, the concentrations of "molecules" can not remain constant. Let us again consider the reactions (6) taking place in a closed system. Instead of (22) we must then consider the differential equation (21) together with the rate equations for \dot{n}_A and \dot{n}_B ,

$$\left. \begin{aligned} \dot{n}_A &= -\bar{k}_1 n_A + \bar{k}_1 n_X , \\ \dot{n}_B &= -\bar{k}_2 n_B + \bar{k}_2 n_X . \end{aligned} \right\} \quad (28)$$

The formal solution of (21) is written as

$$n_X = C \exp(-t/\tau) + \exp(-t/\tau) \int_0^t (\bar{k}_1 n_A + \bar{k}_2 n_B) \exp(t'/\tau) dt' , \quad (29)$$

where C is the integration constant. If the rate constants \bar{k}_1 and/or \bar{k}_2 are large (*i. e.*, the chemical species X is very reactive), τ is small according to (25), so that in the course of time, the first term on the right hand side of (29) rapidly approaches to zero. After this initial induction period, the change of n_X is expressed by the second term, *i. e.*, the principal solution³⁴⁾ of (21). Only when n_A and n_B are constant and equal to n_A^0 and n_B^0 , this term reduces to n_X^s of (24), *i. e.*,

$$n_X = n_X^s \quad (\text{constant}), \quad \dot{n}_X = 0 . \quad (30)$$

However, when the changes of the concentrations, n_A and n_B of "molecules" are small in the time interval under consideration, we can, to a good approximation, neglect the deviation from the condition of the steady state (30). Such a situation has been discussed by a number of authors³³⁾⁻³⁴⁾ for various special examples. Also, HIRSCHFELDER has shown that starting from an expression like (29), one can calculate the small deviation from the steady state values (30), in a closed system. We shall examine this problem more closely in the succeeding paper (Part II).

§ 3. Linear Relations in the Neighbourhood of Equilibrium^{*)}

Consider an elementary reaction such as the binary collision process in an ideal gas,



The assumption of the reaction rate proportional to the collision frequency leads to⁷⁾ the rate equations for the forward and backward rates, \bar{v} and \bar{v} of the process (31):

$$\bar{v} = \bar{k}[\text{I}_2][\text{H}_2], \quad \bar{v} = \bar{k}[\text{HI}]^2, \quad (32)$$

where \bar{k} and \bar{k} are the rate constants, and $[\text{I}_2]$ etc. mean the concentration of I_2 etc. Starting from such rate equations, PRIGOGINE, OUTER and HERBO have derived³⁵⁾³⁶⁾ the relation⁴⁰⁾

$$\bar{v}/\bar{v} = \exp(a/RT), \quad (33)$$

i. e.,

$$v = \bar{v} - \bar{v} = \bar{v} [1 - \exp(-a/RT)], \quad (34)$$

where a and v are the affinity and the rate, respectively, of the elementary reaction, and R and T are the gas constant and temperature. Although the above derivation of (33) or (34) is simple and elementary, the use of rate equations like (32) (*i. e.*, the rate expression such that each reactant has an order equal to the absolute value of its stoichiometric coefficient in the "microscopic" reaction equation^{**)}) is unwarranted for elementary reactions other than homogeneous elementary reactions in an ideal gas mixture. More

^{*)} Cf. Ref. 38.

^{**)} Ref. 1, p. 176. Note that reaction equations (stoichiometric equations) such as (1), (4) and (7) give only the stoichiometric relationship between the amounts of the chemical species produced (or consumed) by these reactions, whereas "microscopic" reaction equations such as (2), (3), (6) and (31) represent microscopic elementary processes themselves.

elaborate and general proof of (33), based on the theory of absolute reaction rate, has been given by HORIUTI^{37,40)}.

For a reaction close to equilibrium, we can suppose that $|a|/RT \ll 1$, so that the expression (34) reduces to

$$a = \kappa v \quad \text{with} \quad \kappa = RT/\bar{v}^{(e)}, \quad (35)$$

where $\bar{v}^{(e)}$ is the value of the forward rate at the equilibrium, and the constant coefficient κ is called "reaction resistance" (PRIGOGINE *et al.*³⁵⁾.

The expression (35) is the linear rate law or the *linear relation*^{13,14)} between the affinity and the rate of elementary reactions in the neighbourhood of equilibrium. The linear relations for S simultaneous *elementary* reactions are

$$a_s = \kappa_s v_s, \quad \kappa_s = RT/\bar{v}_s^{(e)}, \quad s=1, 2, \dots, S, \quad (36)$$

where a_s , *etc.* denote the affinity *etc.* of the s -th elementary reaction.

Multiplying the both sides of the first expression of (36) by α_{st} (cf. §1) and summing over $s=1, 2, \dots, S$, we obtain, by virtue of (9),

$$A_t = \sum_{u=1}^S K_{tu} V_u, \quad t=1, 2, \dots, S, \quad (37)$$

where

$$K_{tu} = \sum_{s=1}^S \kappa_s \alpha_{st} \alpha_{su} = RT \sum_{s=1}^S \alpha_{st} \alpha_{su} / \bar{v}_s^{(e)}. \quad (38)$$

Now we see that corresponding to the transformation (8) of the reaction equations the linear relation (36) is transformed* into (37); the equation (37) is the linear relation expressed in terms of the rates V_t and the affinities A_t given by (9), and the expression (38) gives the transformation properties of the coefficients κ_s .

Now let us suppose that the matrix $[\alpha_{st}]$ of the transformations in (8) and (38) satisfies the condition (14); then the equations (37) are the linear relation for the reactions of the principal set and, as we have seen in §1,

$$V_u = 0 \quad \text{for} \quad u > P,$$

in the steady state. Consequently, the first P equations of (37) are written as

$$A_t = \sum_{u=1}^P K_{tu} V_u \quad t=1, 2, \dots, P. \quad (39)$$

Since $t \leq P$, $u \leq P$ in (39), the coefficients** K_{tu} in (39) are expressed, according to (14) and (38), as

$$K_{tu} = \sum_{s=1}^S \kappa_s \nu_s^{(t)} \nu_s^{(u)} = RT \sum_{s=1}^S \nu_s^{(t)} \nu_s^{(u)} / \bar{v}_s^{(e)}. \quad (40)$$

*) The transformation properties of linear relations in general are frequently discussed in thermodynamics of irreversible processes (cf. Ref. 13, Chapter XI).

**) Note that the coefficients K_{tu} in (37) form an $(S \times S)$ matrix, whereas those in (39) form a $(P \times P)$ matrix.

According to §1, the relation (39) with (40) is now the linear relation between the rates and the affinities of the P macroscopically observed overall reactions³⁸⁾ in the steady state of the S simultaneous elementary reactions ($P < S$). In the special case of $P=1$, the relations (39) and (40) reduce to the formulae,

$$A_1 = K_{11} V_1 \quad \text{and} \quad K_{11} = \sum_{s=1}^S \kappa_s (\nu_s^{(1)})^2, = RT \sum_{s=1}^S (\nu_s^{(1)})^2 / \bar{v}_s^{(e)}, \quad (41)$$

which have been obtained independently by HOLLINGSWORTH^{39)*}.

The linear relations (37) and (39) are also written as

$$V_u = \sum_{t=1}^S A_{ut} A_t, \quad u=1, 2, \dots, S, \quad (42)$$

$$V_u = \sum_{t=1}^P L_{ut} A_t, \quad u=1, 2, \dots, P, \quad (43)$$

where $[A_{ut}]$ and $[L_{ut}]$ are respectively the reciprocal matrices of the $(S \times S)$ matrix $[K_{tu}]$ of (37) and of the $(P \times P)$ matrix $[K_{tu}]$ of (39)**).

§ 4. Theorem of Minimum Entropy Production***)

As is well-known, the thermodynamical theory of irreversible processes is usually based on the linear relation of the form (37), (39), (42) or (43) between the rates (fluxes) and the affinities (forces). The constant coefficients, K_{tu} , L_{ut} and A_{ut} in these expressions are the *phenomenological coefficients* in the thermodynamical theory, and satisfy the Onsager reciprocal relation,

$$K_{tu} = K_{ut}, \quad A_{tu} = A_{ut}, \quad L_{tu} = L_{ut}, \quad (44)$$

as verified by the expression (38) or (40) as well as the relation between K_{tu} and L_{tu} , or K_{tu} and A_{tu} .

One of interesting theorems of thermodynamics of irreversible processes is PRIGOGINE and DE GROOT's *theorem of minimum entropy production*^{13, 14)}. The theorem states: "When a system, characterized by S independent forces X_1, X_2, \dots, X_S , is kept in a state with fixed X_1, X_2, \dots, X_p ($P < S$) and minimum entropy production $(dS/dt)_{i,r,r}$, the fluxes J_t with the index numbers

*) If $\nu_1^{(1)} = \nu_2^{(1)} = \dots = \nu_S^{(1)} = 1$, the relations (41) further reduce to the expression,

$$A_1 = (\sum_s \kappa_s) V_1.$$

PRIGOGINE *et al.* have considered a special example, and obtained this expression [cf. Eq. (23) of Ref. 35]. They called K_{11} in (41) or $(\sum_s \kappa_s)$ in the above expression the "total reaction resistance".

***) It can readily be shown that these two matrices $[K_{tu}]$ of (37) and (39) are non-singular [cf. Ref. 38].

****) Cf. Ref. 21.

$t = P+1, P+2, \dots, S$ vanish*)." The present author and YAMAZAKI²¹⁾ have pointed out that this theorem can be applied to the case of chemical reactions by using the concept of the principal set** discussed in § 1. In this case the affinities and the rates of the reactions of the principal set are essentially the forces and the fluxes, respectively, in the above theorem, *i. e.*,

$$X_t = A_t/T = - \sum_{i=1}^N \mu_i B_{it}/T, \quad J_t = V_t \quad (t=1, 2, \dots, S), \quad (45)$$

where A_t and V_t obey the linear relation (37) or (42), and the entropy production $(dS/dt)_{irr}$ is given by^{13, 14, 21)}

$$(dS/dt)_{irr} = \sum_{s=1}^S v_s a_s/T = \sum_{t=1}^S V_t A_t/T = T^{-1} \sum_{t=1}^S \sum_{u=1}^S A_{ut} A_u A_t = T \sum_{t=1}^S \sum_{u=1}^S A_{ut} X_u X_t,$$

according to (42) and (45). Suppose that the concentrations or the chemical potentials of the "molecules" are kept constant (cf. § 2), and those of the intermediates are allowed to vary. According to (45) this amounts to fixing the P forces X_t ($t=1, 2, \dots, P$), since the 1st, 2nd, ..., P -th reactions of the principal set involve only the "molecules" ($i \leq M$) [cf. Eq. (18)], whereas the remaining $S-P$ reactions involve the intermediates ($i > M$) too. Then it follows from the above theorem that the minimum of the entropy production $(dS/dt)_{irr}$ corresponds to

$$\dot{X}_t = V_t = J_t = 0, \quad \text{for } t > P, \quad (46)$$

which implies that the chemical reactions are in the steady state (cf. Appendix). In DE GROOT's terminology,¹³⁾ the *order* of this steady state is P , where P has been the number of the reaction routes*** defined by HORIUTI and the present author²²⁾

§ 5. Exponential Decay of Overall Reactions

We have seen in § 1 that macroscopically we observe P overall reactions in a steady state of S elementary reactions ($P < S$ in general), and in § 3 that if the constituent elementary reactions are close to equilibrium, these overall reactions obey the linear relation (39) or (43) between the rates and the affinities. In the case of reactions in a *closed system*, we can further assume the linear relation between the affinities and the deviation from the equilibrium, as

$$A_t = \sum_{u=1}^P A_{tu} (\mathcal{E}_u - \mathcal{E}_u^{(e)}), \quad t=1, 2, \dots, P, \quad (47)$$

so far as the deviation is small and the condition of the steady state, $\mathcal{E}_t = \text{const.}$

*) Quoted from § 71 of Ref. 13, with slight modification of the notations.

***) Another method which does not make use of the principal set, has been devised by PRIGOGINE (Ref. 14) and generalized by the present author and YAMAZAKI (Ref. 21).

****) Cf. the footnote on p. 228 of this paper.

for $t > P$ [cf. (46)] is maintained. In (47), A_{tu} 's are constant coefficients, Ξ_u is the extent of reaction of the u -th overall reaction (cf. §1), and the superscript (e) designates the value at the equilibrium. On the other hand the linear relation (39) is rewritten as

$$A_t = \sum_{u=1}^P K_{tu} (d\Xi_u/dt), \quad t=1, 2, \dots, P. \quad (48)$$

The system of the simultaneous equations (47) and (48) can be solved⁽¹⁸⁾ as shown below, and consequently the approach to equilibrium (relaxation), of the P overall reactions may be calculated. However, we must remember that the use of the linear relations (48) [or (39)] and (47) rests on the assumption that the deviation from the steady state is negligible during the relaxation process (cf. §3 and the above). This point will be more closely examined in the subsequent paper (Part II).

In his paper⁽¹¹⁾ on the thermodynamical theory of relaxation phenomena, MEIXNER already treated equations of the same form as the above system of the linear equations (47) and (48). Since the matrices $[A_{tu}]$ and $[K_{tu}]$ are symmetric and the quadratic forms $\sum_t \sum_u (-A_{tu})x_t x_u$ and $\sum_t \sum_u K_{tu}x_t x_u$ are positive definite⁽¹¹⁾, they are simultaneously diagonalized by a non-singular matrix $[T_{tp}]$ as,

$$\sum_{t=1}^P \sum_{u=1}^P K_{tu} T_{tp} T_{uq} = \tau_p \delta_{pq}, \quad \sum_{t=1}^P \sum_{u=1}^P A_{tu} T_{tp} T_{uq} = -\delta_{pq},$$

where δ_{pq} is the Kronecker delta, and τ_p 's ($p=1, 2, \dots, P$) are positive and the roots of the secular equation,

$$\det (K_{tu} + \tau A_{tu}) = 0.$$

Thus Eqs. (48) and (47) become

$$A'_p = \tau_p (d\Xi'_p/dt), \quad p=1, 2, \dots, P, \quad (49)$$

$$A'_p = -(\Xi'_p - \Xi_p^{(e)}), \quad p=1, 2, \dots, P, \quad (50)$$

where the quantities with a prime are related to the original ones by

$$A'_p = \sum_{u=1}^P A_u T_{up}, \quad \Xi_u = \sum_{p=1}^P T_{up} \Xi'_p. \quad (51)$$

The solutions of (49) and (50) are now,

$$\Xi'_p - \Xi_p^{(e)} = C_p e^{-t/\tau_p}, \quad p=1, 2, \dots, P, \quad (52)$$

where C_p 's are the integration constants to be determined from the initial condition. This is MEIXNER's result⁽¹⁸⁾.

Corresponding to the above transformation by the matrix $[T_{up}]$, the set of the P overall reactions is transformed into a new set, *i. e.*, an equivalent system

(cf. § 1); the relation between the both sets is given by

$$B'_{ip} = \sum_{u=1}^P B_{iu} T_{up}, \quad (53)$$

where B_{ip} and B'_{ip} are the stoichiometric coefficients of the i -th chemical species in the p -th reactions of the old and the new sets, respectively. The expression (52) means that the P overall reactions of the new set are "normal modes", and approach exponentially to the equilibrium, τ_p 's being the relaxation times of this exponential decay. When expressed in terms of the old set of overall reactions, the decay is expressed as

$$\bar{E}_u - \bar{E}_u^{(e)} = \sum_{p=1}^P T_{up} C_p e^{-t/\tau_p}, \quad u=1, 2, \dots, P, \quad (54)$$

i. e., a superposition of exponentials, with a spectrum of P relaxation times.

Now we suppose that the above reactions take place *at constant temperature and volume*. Then it follows from the definition of A_t , A_{tu} and \bar{E}_u that

$$A_t = - \sum_{i=1}^M \mu_i B_{it}, \quad A_{tu} = \left(\frac{\partial A_t}{\partial \bar{E}_u} \right)^{(e)}, \quad N_i - N_i^{(e)} = \sum_{u=1}^P B_{iu} (\bar{E}_u - \bar{E}_u^{(e)}), \quad (55)$$

where μ_i , N_i and B_{it} are the chemical potential, the number of moles and the stoichiometric coefficients in the t -th overall reaction, respectively, of the i -th chemical species, and in the differentiation with respect to \bar{E}_u , temperature, volume and the remaining \bar{E}_s 's ($s \neq u$) are kept constant. Now assume that the system is a mixture of perfect gases and hence the chemical potential μ_i is expressed as¹⁹⁾

$$\mu_i = \mu_i^* + RT \ln (N_i/V), \quad (56)$$

where μ_i^* is a function only of temperature and V is the volume of the "reaction vessel". Then it follows from (55) and (56) that

$$\frac{\partial A_t}{\partial \bar{E}_u} = - \sum_{i=1}^M B_{it} \frac{\partial}{\partial \bar{E}_u} RT \ln N_i = -RT \sum_{i=1}^M B_{it} B_{iu} / N_i,$$

i. e.,

$$A_{tu} = -RT \sum_{i=1}^M B_{it} B_{iu} / N_i^{(e)}. \quad (57)$$

It may be of interest to note the formal resemblance between the expressions (40) for K_{tu} and (57) for A_{tu} .

A corresponding expression of A_{tu} for reactions *at constant temperature and pressure* can readily be obtained. Eq. (56) is rewritten as

$$\mu_i = \mu_i^* + RT \ln (pN_i/NRT), \quad (56')$$

where p is pressure and

$$N = \sum_{i=1}^M N_i.$$

Accordingly we have the differential at constant temperature and pressure:

$$\frac{\partial A_i}{\partial \bar{E}_u} = -RT \sum_{i=1}^M \sum_{j=1}^M B_{ii} B_{ju} \left(\frac{\delta_{ij}}{N_i} - \frac{1}{N} \right)$$

Then the expression of A_{iu} become

$$A_{iu} = -RT \sum_{i=1}^M \sum_{j=1}^M B_{ii} B_{ju} \left(\frac{\delta_{ij}}{N_i^{(e)}} - \frac{1}{N^{(e)}} \right) \quad (57')$$

instead of (57).

In the rather trivial case of a single overall reaction, *i.e.*, $P=1$, Eqs. (40) and (57) reduce to

$$K_{11} = RT \sum_{s=1}^S (\nu_s^{(1)})^2 / \bar{\nu}_s^{(e)}, \quad (58)$$

and

$$A_{11} = -RT \sum_{i=1}^M (B_{ii})^2 / N_i^{(e)}. \quad (59)$$

Furthermore, if the r -th elementary reaction is rate-determining step, *i.e.*, $\bar{\nu}_r^{(e)} \ll \bar{\nu}_s^{(e)}$ ($s=1, \dots, r-1, r+1, \dots, S$), then the expression (58) becomes

$$K_{11} = RT (\nu_r^{(1)})^2 / \bar{\nu}_r^{(e)}. \quad (60)$$

In this special case, the expressions (52) and (54) become

$$\bar{E}_1 - \bar{E}_1^{(e)} = \bar{E}'_1 - \bar{E}_1^{(e)} = C_1 e^{-t/\tau_1}, \quad (61)$$

and the relaxation time τ_1 is given by

$$\tau_1 = -\frac{K_{11}}{A_{11}} = \frac{(\nu_r^{(1)})^2 / \bar{\nu}_r^{(e)}}{\sum_{i=1}^M (B_{ii})^2 / N_i^{(e)}} \quad (62)$$

The expressions essentially same as (61) and (62) are first obtained by HORIUTI⁴²⁾ in a different way, and applied to the experimental determination of the mechanism of the catalyzed ammonia synthetic reaction,



by ENOMOTO and HORIUTI⁴³⁾, and more recently by BOKHOVEN, GORGELS and MARS⁴⁴⁾. ENOMOTO and HORIUTI observed exponential decay of the overall reaction (63), and measured the relaxation time and the "forward rate"³⁹⁾ $\bar{V}^{(e)} \equiv \bar{\nu}_r^{(e)} / \nu_r^{(1)}$, of the overall reaction (63) at the equilibrium, in order to determine the stoichiometric number $\nu_r^{(1)}$ of the rate-determining step: In this particular case of (63), Eq. (62) becomes

$$\tau_1 = \frac{\nu_r^{(1)}}{\bar{V}^{(e)}} \left(\frac{1}{N_{N_2}^{(e)}} + \frac{9}{N_{H_2}^{(e)}} + \frac{4}{N_{NH_3}^{(e)}} \right)^{-1}. \quad (64)$$

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Appendix

According to (9 a), (8) and (14), the net rate of production \dot{N}_i of an intermediate ($i=M+1, M+2, \dots, N$) is given by²⁰⁾

$$\begin{aligned} \dot{N}_i &= \sum_{t=1}^S B_{it} V_t = \sum_{s=1}^S \sum_{t=1}^S b_{is} \alpha_{st} V_t = \sum_{s=1}^S \sum_{t=1}^P b_{is} \nu_s^{(t)} V_t + \sum_{s=1}^S \sum_{t=P+1}^S b_{is} \alpha_{st} V_t \\ &= \sum_{t=1}^P \left(\sum_{s=1}^S b_{is} \nu_s^{(t)} \right) V_t + \sum_{s=1}^S b_{is} \left(\sum_{t=P+1}^S \alpha_{st} V_t \right). \end{aligned}$$

Thus, by virtue of (15), we have

$$\dot{N}_i = \sum_{s=1}^S b_{is} \left(\sum_{t=P+1}^S \alpha_{st} V_t \right), \quad i=M+1, M+2, \dots, N. \quad (A)$$

In the steady state, $\dot{N}_i=0$ for $i>M$, so that the equations (A) become

$$\sum_{s=1}^S b_{is} \left(\sum_{t=P+1}^S \alpha_{st} V_t \right) = 0, \quad i=M+1, M+2, \dots, N,$$

which implies that

$$\sum_{t=P+1}^S \alpha_{st} V_t, \quad s=1, 2, \dots, S \quad (B)$$

is a solution of (15), *i. e.*, (B) is expressed as a linear combination of the stoichiometric numbers;

$$\sum_{t=P+1}^S \alpha_{st} V_t = \sum_{t=1}^P C_t \nu_s^{(t)}, \quad (C)$$

where C_t 's are the coefficients of the linear combination. By virtue of (14), (C) is now rewritten as

$$0 = \sum_{t=1}^P \alpha_{st} C_t - \sum_{t=P+1}^S \alpha_{st} V_t, \quad s=1, 2, \dots, S. \quad (D)$$

In so far as the matrix $[\alpha_{st}]$ is non-singular, the S columns of $[\alpha_{st}]$ are linearly independent²³⁾. Hence it follows from (D) that

$$C_1 = C_2 = \dots = C_P = V_{P+1} = V_{P+2} = \dots = V_S = 0.$$

On the other hand, according to (8), (14) and (15), we obtain

$$B_{it} = \sum_{s=1}^S b_{is} \alpha_{st} = \sum_{s=1}^S b_{is} \nu_s^{(t)} = 0, \quad \text{for } i>M \text{ and } t \leq P.$$

Thus we finish the proofs of (16) and (18).

Next we shall show that each of the $(P+1)$ -th, $(P+2)$ -th, \dots , S -th reactions of the principal set involves at least one intermediate. The number of the independent solutions of the simultaneous equations (15) is P (§ 1), and according to (14), the 1st, 2nd, \dots , P -th columns of the matrix $[\alpha_{st}]$ are a set of P independent solutions of (15). Since all the columns of $[\alpha_{st}]$ are independent (see above), any of the $(P+1)$ -th, $(P+2)$ -th, \dots , S -th columns of $[\alpha_{st}]$ can not be a solutions of (15). Consequently, for $t > P$, at least one of B_{it} 's ($i = M+1, M+2, \dots, N$) is not zero, since otherwise it would follow that

$$\sum_{s=1}^N b_{is} \alpha_{st} = B_{it} = 0, \quad \text{for } i = M+1, M+2, \dots, N,$$

i. e., the t -th column would be a solution of (15), contrary to the above fact.

According to (8), Eq. (A) is rewritten as

$$\dot{N}_i = \sum_{t=P+1}^N B_{it} V_t \quad \text{for } i > M.$$

Thus the condition (46) of § 4 necessarily implies that

$$\dot{N}_i = 0 \quad \text{for } i > M,$$

i. e., the steady state.

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