

## SEMIGROUP-THEORETICAL STRUCTURE OF CHEMICAL REACTION SYSTEMS

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(Summary) Chemical thermodynamic systems in process of time are examined from the algebraic theoretical point of view. We consider the direction of chemical change explicitly by means of only the additive transformation of reaction equations instead of commonly used linear combinations of them. A chemically reacting system becomes a semigroup, referred to as a reaction semigroup hereafter, by use of an equivalence relation often adopted by chemists; in a state of equilibrium the system has a group-theoretical structure as its special case. It is shown that not all additive transformations of reactions keep reaction semigroups unchanged. Properties for thermodynamic variables (chemical affinity, reaction rate, entropy production, and so on) in relation to the semigroup theory are discussed; the characteristic of reaction rates under the base transformation of reactions is found, and is applied to the analysis of two reaction systems (the catalyzed synthesis of ammonia, and the synthesis of hydrobromic acid).

Introduction. Here are two examples for chemically reacting systems:

$$C_{RS} = \{q_1, q_2\} \quad \text{and} \quad C_{RS}' = \{q_1', q_2'\}$$

where  $q_1 = "A \rightarrow B"$ ,  $q_2 = "B \rightarrow C"$ ,  $q_1' = "A \rightarrow C"$ , and  $q_2' = q_2$ . Prigogine<sup>1</sup> stated that the former is equally well described by the latter from the macroscopic/thermodynamic point of view because one of them can be derived from the other in terms of linear combinations of reaction equations; he obtained the condition that the systems become equivalent in the sense that the entropy production per unit time ( $d_i S/dt$ ) is invariant under the transformations. The former  $q_1$  can certainly be given by the subtraction of  $q_2'$  from  $q_1'$ , and conversely the latter  $q_1'$  by the addition of  $q_2$  to  $q_1$ . The subtraction of  $q_2'$  implicitly suggests that the inverse reaction equation of  $q_2'$  should occur. Such imaginary inverse changes should be removed from  $C_{RS}$ , however, in cases, such as irreversible thermodynamic processes, where the direction in change is taken into account explicitly. Even when directed reactions are assumed in a chemically reacting system, only the additive transformation of reactions can be adopted. Hence, the question arises whether  $d_i S/dt$  remains unchanged or not under the assumption that only the additive transformation is possible; this requires us to examine the algebraic property of reaction rates  $v_m$  because  $d_i S/dt$  can be expressed as  $\sum A_m v_m/T$  ( $A_m$ , chemical affinities). It is necessary to investigate the mathematical structure of reaction systems in process of time.

Algebraic Structure of Reaction Systems. Let us consider a

set of reaction equations:

$$R_E = \{ q \mid \text{reaction equations with the direction of change} \\ = \text{ordered pairs of molecules} = \text{"reactants (the left-} \\ \text{hand side)} \rightarrow \text{products (the right-hand side)}" \}$$

which represents a chemically reacting system. The following rules are regarded as valid in chemists' theory. (1) The summation of two reaction equations is possible; that is to say,  $q + q' = q'' \in R_E$ . Here the sign + means that the left(right)-hand side of  $q'$  is added together the left(right)-hand side of  $q$ . (2) The associative law of addition holds; that is,  $q + (q' + q'') = (q + q') + q''$ . In other words,  $R_E$  is a semigroup<sup>2</sup> with respect to the additive operation. Note that the semigroup is abelian ( $q + q' = q' + q$ ), and that the number of the members is infinite.

(Definition of reaction semigroups) Chemists often eliminate common molecules from both sides of a chemical reaction equation in question, and regard the resulting equation as equivalent to the original one. The elimination (and/or addition) of common molecules is an equivalence relation on  $R_E$  (hereafter denoted by the symbol  $\equiv$ , e.g., " $A + C \rightarrow B + C$ "  $\equiv$  " $A \rightarrow B$ ") because it satisfies the reflexive, the symmetric, and the transitive laws: (i)  $q \equiv q$ . (ii)  $q \equiv q'$  implies  $q' \equiv q$ . (iii)  $q \equiv q'$  and  $q' \equiv q''$  imply  $q \equiv q''$ . We can classify the members of  $R_E$  using this equivalence relation, and then obtain the quotient set:

$$R_E/\equiv = \{ r, r', \dots \} = R_S$$

This  $R_S$  is also a semigroup with respect to addition because the equivalence relation is compatible with the additive operation on reaction equations; namely,  $q \equiv q'$  and  $q'' \equiv q'''$  imply  $q + q'' \equiv q' + q'''$ . We call  $R_S$  a reaction semigroup. In the set there is only the class  $r_0$  such that  $r_0 + r = r + r_0 = r$  for all of the classes  $r$  in  $R_S$ ; in other words,  $r_0$  is the subset that consists of reaction equations with equivalent sides. We call  $r_0$  the unit reaction.

Suppose that  $r_j$  is a class in  $R_S$ ; then  $mr_j$  ( $m$ , arbitrarily chosen positive integers) can be found in  $R_S$ ; namely, the set  $\{r_0, r_j, 2r_j, 3r_j, \dots\}$  exists in  $R_S$ . This infinite subset is obviously a cyclic semigroup, and is generated by  $r_j$ . We write the semigroup as  $\langle r_j \rangle$  to signify that  $r_j$  is the generating reaction. Note that  $\langle r_j \rangle \cap \langle r_k \rangle = \{r_0\}$  ( $j \neq k$ ).  $R_S$  is finitely generated by some generating reactions, so that the minimum set of generating reactions for  $R_S$  is called a base.  $R_S$  is thus expressed as a direct sum of cyclic subsemigroups with base reactions:

$$R_S = \langle r_1 \rangle \oplus \dots \oplus \langle r_n \rangle$$

The cardinal number ( $=n$ ) of the base is constant, although there may be many bases for  $R_S$  in general.<sup>2</sup> The rank  $n$  represents the least number of generating reactions that can be chosen independently from  $R_S$ . The independent reactions in  $R_S$  can also be defined by the way that the relation  $m_1 r_1 + \dots + m_n r_n = r_0$  ( $m_j$ , positive integers) implies that  $m_j r_j = r_0$  for all  $j$ .

(Reaction groups) If in  $R_S$  there is the inverse reaction of  $r_j$ , denoted by  $-r_j$ , then  $\langle r_j \rangle$  is rewritten as  $\{\dots, -3r_j, -2r_j, -r_j, r_0, r_j, 2r_j, 3r_j, \dots\}$ . To express this set we make use of the notation  $[r_j]$ . Note:  $[-r_j] = [r_j]$ , and  $r_j + (-r_j) = r_0$ . The set  $[r_j]$  is clearly an infinite cyclic group, and none of inverse reactions in  $R_S$  allow the rank  $n$  to increase/decrease. If the inverse reactions for all of the  $r$  in  $R_S$  take place, then  $R_S$  becomes the group

$$R_G = [r_1] \oplus \dots \oplus [r_n]$$

We call it a reaction group. This chemical reaction system corresponds to the state that all reactions are in equilibrium. Any  $r_{ov}$  in  $R_G$  is expressed as  $r_{ov} = \sum m_j r_j$ , where  $m_j$  are integers (positive or negative). It is a matter for regret that no satisfactory methods are known for classification of this type of group.<sup>3</sup> Further detail of the reaction group theory will be presented in a subsequent note.<sup>4</sup>

We can now describe the general form of  $R_S$  as

$$R_S = [r_1] \oplus \dots \oplus [r_{n_G}] \oplus \langle r_{n_G+1} \rangle \oplus \dots \oplus \langle r_{n_S} \rangle$$

Additive Transformation of Reactions. Let us proceed to examine the transformation of  $r_j$  and  $r_k$  into  $r_j'$  and  $r_k'$ , where  $r_j' = r_j$  and  $r_k' = r_j + r_k$  ( $j \neq k$ ). (Note:  $r_1' = r_1$ ,  $l \neq j, k$ .) It becomes clear that

$$(a) \quad [r_j] \oplus [r_k] = [r_j'] \oplus [r_k']$$

$$(b) \quad [r_j] \oplus \langle r_k \rangle = [r_j'] \oplus \langle r_k' \rangle$$

After these transformations,  $R_S$  remains unchanged ( $R_S = R_S'$ ); that is, both (a) and (b) may be called a base transformation for  $R_S$ . The base transformation hereafter involves the transformation  $[-r_j] = [r_j]$ . Every base set can be constructed from one base set by successive use of the base transformation. The final kind of additive operation is:

$$(c) \langle r_j \rangle \oplus \langle r_k \rangle \ni \langle r_j' \rangle \oplus \langle r_k' \rangle$$

In other words,  $R_S'$  for case (c) is a subsemigroup in  $R_S$  ( $R_S \ni R_S'$ ). Not all operations of addition on  $R_S$  are base transformations. Note that the type  $\langle r_j \rangle \oplus [r_k]$  must be removed from the additive transformation of reactions because no inverse change of  $r_j$  takes place in this case.

The examples in Introduction are analyzed in order to illustrate the distinction between additive transformations.

$$R_S = \langle q_1 \rangle \oplus \langle q_2 \rangle \ni R_S' = \langle q_1' \rangle \oplus \langle q_2' \rangle. \quad R_S = \langle q_1 \rangle \oplus [q_2] = R_S' = \langle q_1' \rangle \oplus [q_2'], \text{ and } R_G = [q_1] \oplus [q_2] = R_G' = [q_1'] \oplus [q_2'].$$

#### Semigroup-Theoretical Properties of Thermodynamic Variables.

It is widely known that heats of reaction  $h_{j,T,p} = (\partial H / \partial \xi_j)_{T,p}$  can be added together in the same manner as reaction equations,<sup>5</sup> so that the set of  $h_{j,T,p}$  associated with  $R_S$  also becomes a semigroup (heat-of-reaction semigroup). This result is valid for all quantities that can be written as  $(\partial X / \partial \xi_j)_{T,p}$ , such as the chemical affinity  $A_j = -(\partial G / \partial \xi_j)_{T,p}$ , the change of volume  $v_{j,T,p} = (\partial V / \partial \xi_j)_{T,p}$ , and the change of entropy  $s_{j,T,p} = (\partial S / \partial \xi_j)_{T,p}$ , where  $X$  is an extensive

quantity, and  $\xi_j$  the extent of the  $j$ -th reaction.<sup>5</sup>

The additive property of chemical affinity can be used to characterize  $R_S$ . Let  $R_A$  be the set of chemical affinities, and let  $f_A$  be the mapping from  $R_S$  to  $R_A$ . Then  $f_A(r_{k'}) = f_A(r_j + r_k) = f_A(r_j) + f_A(r_k)$  or  $A_{k'} = A_j + A_k$  for  $r_{k'} = r_j + r_k$ . The kernel of  $f_A$  is defined by  $\text{Ker } f_A = \{r_j \mid f_A(r_j) = 0, r_j \in R_S\}$ , which in general is of the form  $\text{Ker } f_A = R_G$ . If  $\text{Ker } f_A = \{r_0\}$ , then  $R_S = \langle r_1 \rangle \oplus \dots \oplus \langle r_{n_S} \rangle$ .

Horiuti<sup>6</sup> pointed out that  $K_{\text{OV}} = \prod K_j^{m_j}$  for an overall reaction  $r_{\text{OV}}$  in an equilibrium state under some assumptions, where  $K_j$  are thermodynamic equilibrium constants. This relation leads to  $\ln K_{\text{OV}} = \sum m_j \ln K_j$ , which is similar to  $r_{\text{OV}} = \sum m_j r_j$ . Thus  $K_{k'} = K_j K_k$  for case (a) of  $R_G$ .

(Reaction rates and entropy production) Let us try to examine the algebraic property of reaction rates  $v_m = d\xi_m/dt$  under the additive transformation of reactions, which is of great importance in chemical kinetics. The difference of the entropy production per unit time between  $R_S$  and  $R_S'$  is now calculated. For the base transformation,

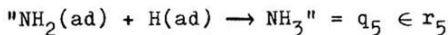
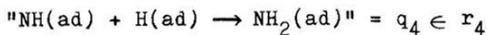
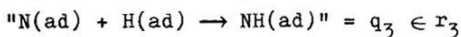
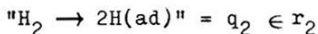
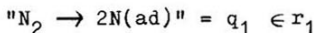
$$d_i S'/dt - d_i S/dt = \sum_m A_m (v_m' - v_m)/T$$

where the fact that  $A_j = 0$  for the base transformation was used. It is to be noted that the index  $m$  runs over only the cyclic subsemigroups in  $R_S$ . It is natural to consider thermodynamic quantities invariant under the base transformation when they can be determined as a whole for a given system of chemical reaction. The difference above must

vanish:  $\sum_m A_m (v_m' - v_m) = 0$

Assuming that  $A_m$  are independent variables, we conclude that  $v_m' = v_m$ . Note that if  $r_m' = n r_{(m)}$ , ( $n$ , a natural number), then  $v_m' = n v_{(m)}$ .

The present result is applied to the ammonia synthetic reaction:



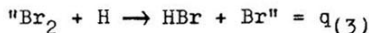
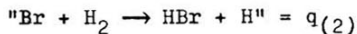
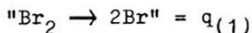
The symbol "ad" stands for "adsorption on the catalyst".

The first reaction is the rate-determining step whose reaction rate is referred to as  $v_1$ . Then

$$\begin{aligned} R_S &= \langle r_1 \rangle \otimes [r_2] \otimes \dots \otimes [r_5] = \langle r_1' \rangle \otimes [r_2] \otimes \dots \otimes [r_5] \\ &= \langle r_1'' \rangle \otimes [r_2] \otimes \dots \otimes [r_5] = \dots \end{aligned}$$

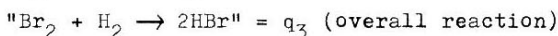
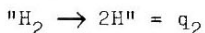
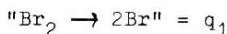
where  $r_1' = r_1 + 3r_2 \ni q_1' = \text{"N}_2 + 3\text{H}_2 \rightarrow 2\text{N(ad)} + 6\text{H(ad)}"$ , and  $r_1'' = r_1 + 3r_2 + 2r_3 + 2r_4 + 2r_5 \ni q_1'' = \text{"N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3"$  (overall reaction). Thus  $A_1(v_1' - v_1) = A_1(v_1'' - v_1) = \dots = 0$ ; namely,  $v_1 = v_1' = v_1'' = \dots$ .

The following example (the synthesis of hydrobromic acid) is a problem of special interest, which was discussed by Prigogine.<sup>7</sup>





Using the method in Reference 4, we can determine rank = 3 (the number of independent reactions) for this reaction system, so that the base reactions, for example, are adopted as follows:



$R_S$  in the steady state is of the form:  $R_S = [q_1] \oplus [q_2] \oplus \langle q_3 \rangle$ .

The base transformations are  $[q_1] \oplus [q_2] \oplus \langle q_3 \rangle = [q_1] \oplus [q_2] \oplus \langle q_3' \rangle = \dots$ . Thus we obtain  $v_3 = v_3' = v_3''$ , which give  $v_3 = 2v_{(2)} = 2v_{(3)}$ , because  $q_3' = q_3 - q_1 + q_2 = 2q_{(2)}$  and  $q_3'' = q_3 + q_1 - q_2 = 2q_{(3)}$ .

We now go back to calculation of  $d_i S/dt$ . For case (c),

$$T(d_i S'/dt - d_i S/dt) = \sum_{m(\neq j,k)} A_m(v_m' - v_m) + A_j(v_j' + v_k' - v_j) + A_k(v_k' - v_k)$$

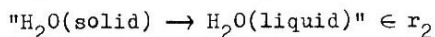
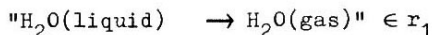
It is necessary that  $v_j' + v_k' = v_j$ ,  $v_k' = v_k$  (and  $v_m' = v_m$ ,  $m \neq j,k$ ) in order that the difference vanishes subject to the additive transformation; these conditions are just those stated by Prigogine.<sup>1</sup> Repeating the transformation  $n$  times, we have

$$T(d_i S^{(n)}/dt - d_i S/dt) = \sum_m A_m(v_m^{(n)} - v_m) + n A_j v_k^{(n)}$$

The condition that the difference vanishes for any  $n$  is given by  $|A_j v_k| \ll 1$  ( $j \neq k$ ) (and  $v_m^{(n)} = v_m$ ); in this case,  $R_S^{(n)}$  is equivalent to  $R_S$  in the sense that  $d_i S/dt$  is invariant under that transformation.

Remarks. One of the members in a class  $r_j$  is often referred to as the representative for  $r_j$ . The representatives obtained by the maximum elimination of common molecules were used to indicate classes in  $R_S$ .

The formulation described above can be applied to thermodynamic changes other than chemical reaction. An altering system in the phase for example



is shown by  $R_S = \langle r_1 \rangle \oplus \langle r_2 \rangle$ .

References.

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7. Chap. 6 in Reference 1.