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RELATIONS BETWEEN UNIDIRECTIONAL RATES OF OVERALL REACTION AND ISOTOPIC EXCHANGE AMONG THREE SPECIES INVOLVED IN THE REACTION

By

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Abstract

The method of determining the stoichiometric number ν_r of the rate-determining step developed by HORIUTI *et al.* was extended to the case where the isotopic exchange occurs among three species. The forward and backward unidirectional rates of the exchange between species i and j (i, j=1, 2 and 3), V_{ij} and V_{ji}, were expressed in terms of the forward and backward unidirectional rates of constituent steps, v_{+s} and v_{-s}, of the reaction and their stoichiometric numbers ν_s's. ν_r is conversely determinable, as exemplified, from their functions, V_{ij}/V_{ji}'s and the ratio of the total forward rate from a species *e.g.* i toward the other two to its reverse total rate, *i.e.* $(V_{ij}+V_{ik})/(V_{ji}+V_{ki})$; in the presence of the rate-determining step both functions give v_{+r}/v_{-r} (or v_{-r}/v_{+r}) of the rate-determining step and are experimentally determinable by the formulas similar to that in the case of exchange between two species. The treatments of other authors were discussed in comparison with the present one.

Introduction

Isotopic exchanges accompanied by an overall reaction are utilized to trace the reaction mechanism. HORIUTI has introduced the concept of the stoichiometric numbers$^{1\sim7)}$ of constituent elementary reactions (termed simply steps in what follows), ν_s's, and formulated the stoichiometric number ν_r of the rate-determining step of the overall reaction of a single route**) as$^{3\sim7)}$

$$\nu_r = -\Delta G/RT \ln (V_+/V_-), \tag{1}$$

where $-\Delta G$ is the affinity of the reaction, R the gas constant, T the

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**) Let S be the number of steps occurring in the system and I the number of independent intermediates; $S-I$ is shown$^{4,5)}$ to give the number of independent reaction route$^{4,5)}$. If $S-I$ is unity, the reaction is called to be of a single route, which is expressed by a unique set of stoichiometric numbers of the steps. (Cf. Ref. 7) absolute temperature, and V_+ and V_- the forward and backward unidirectional rates of the reaction at the steady state, which are traceable by means of isotope in the presence of the rate-determining step, *i.e.* in case where all other constituent steps except the latter are in partial equilibria; V_+ and V_- are then shown to be given by the forward and backward unidirectional rates of the rate-determining step, v_{+r} and v_{-r}, as

$$V_+ = v_{+r}/\nu_r \tag{2.1}$$

$$V_- = v_{-r}/\nu_r \tag{2.2}$$

and the net rate V of the overall reaction as

$$V = V_+ - V_- . \tag{3}$$

MATSUDA and HORIUTI[6] have shown that V_+ and V_- can be given by the forward and backward unidirectional rates of transfer of a kind of atoms, which are exclusively comprised in one R of reactants and another P of products, provided that the atoms of the latter kind are handed over from R to P through a single line of steps, termed a single ***path of exchange*** as traced by an appropriate isotope of the atom. V_+ and V_- are shown to be expressed by the forward and backward unidirectional rates, v_{+s}'s and v_{-s}'s, of constituent steps of the single path of the exchange as

$$V_+ = 1\Bigg/\left\{\frac{\nu_1}{v_{+1}} + \frac{v_{-1}\nu_2}{v_{+1}v_{+2}} + \frac{v_{-1}v_{-2}\nu_3}{v_{+1}v_{+2}v_{+3}} + \cdots + \frac{v_{-1}v_{-2}\cdots v_{-(S-1)}\nu_S}{v_{+1}v_{+2}\cdots v_{+(S-1)}v_{+S}}\right\} \tag{4.1}$$

$$V_- = V_+ \prod_{s=1}^{S} v_{-s}/v_{+s} \tag{4.2}$$

hence,

$$V_+/V_- = \prod_{s=1}^{S} v_{+s}/v_{-s} , \tag{4.3}$$

where steps $1, 2, \cdots S$ are the constituent steps of the single path. V_+ and V_- can be determined experimentally by

$$V = V_+ - V_- = -\mathrm{d}N_R/m_R\mathrm{d}t = \mathrm{d}N_P/m_P\mathrm{d}t \tag{5.1}$$

$$-\mathrm{d}(z_R N_R)/m_R\mathrm{d}t = z_R V_+ - z_P V_- = \mathrm{d}(z_P N_P)/m_P\mathrm{d}t , \tag{5.2}$$

where N_i ($i=R$ and P) is the number of molecules of i in the system, m_i the coefficient of i in the chemical equation and z_i the atomic fraction of the isotope in i. We have from Eqs. (5.1) and (5.2)

$$V_+/V_- = 1 + (z_R - z_P)\,\mathrm{d}\ln N_R/\mathrm{d}z_R \tag{5.3}$$

or

$$V_-/V_+ = 1+(z_P-z_R)\,\mathrm{d}\ln N_P/\mathrm{d}z_P\,. \tag{5.4}$$

Eqs. (5) cannot, however, be applied to the case of tracer comprised in three species involved in the overall reaction as shown in a previous paper.[8] The present paper deals with the extension of the method of determining ν_r to the case of the isotopic transfer among three species accompanied by an overall reaction of a single route. The net rate V of the overall reaction and the transfer of atoms A traced by its isotope A′ are expressed in terms of six unidirectional rates, V_{ij}'s, of transfer of atoms A from a species M_i to another M_j ($i, j=1, 2$ or 3). V_{ij}'s are formulated in terms of the forward and backward unidirectional rates, v_{+s}'s and v_{-s}'s, of the constituent steps. It is shown that in the presence of the rate-determining step its rate ratio v_{+r}/v_{-r} (or v_{-r}/v_{+r}) is given by $(V_{ij}+V_{ik})/(V_{ji}+V_{ki})$ which is determinable experimentally by an expression similar to Eq. (5.3) under particular conditions of isotope contents in the respective species (Cf. §1). The cases of the absence of the rate-determining step are also discussed. Isotopic difference of rates is ignored throughout the present discussion.

TEMKIN[9] has tentatively put forward identical expressions of V_+ and V_- of the overall reaction with Eqs. (4.1) and (4.2) without exact proof. Happel and his coworkers[10~14] have developed the method to determine the unidirectional rates among three species but under restricted experimental conditions. TEMKIN's expressions of unidirectional rates and the treatment developed by HAPPEL *et al.* are discussed in comparison with the present treatment.

§ 1. Phenomenological description of isotopic transfer among three species and the net rate of overall reaction

Consider a unique overall reaction,

$$\sum_i m_i \mathrm{M}_i = 0 \tag{6}$$

where M_1, M_2 and M_3 are three species in which element A involved in the reaction is exclusively comprised and m_i's are coefficients of M_i's in the chemical equation (6) with negative or positive sign for reactants or products respectively; the movement of element A in course of the reaction is traceable by means of isotope A′ of A. The net rate V of the reaction at the steady state is given as

$$V = \mathrm{d}N_i/m_i\mathrm{d}t\,, \tag{7}$$

where N_i is the number of molecules of M_i in the system.

The unidirectional rate V_{ij} or V_{ik} of transfer of atoms A from M_i to M_j or M_k ($i, j, k=1$, 2 or 3) is expressed by the rate of increase of the number of atoms A′ in M_j or M_k respectively for $z_i=1$ and $z_j=z_k=0$, where z_i's are the atomic fractions of A′ in M_i's.

The net rate V is given as

$$V=\mathrm{d}N_1/m_1\mathrm{d}t=\left\{(V_{21}+V_{31})-(V_{12}+V_{13})\right\}\Big/m_1n_1 \tag{8.1}$$

$$=\mathrm{d}N_2/m_2\mathrm{d}t=\left\{(V_{12}+V_{32})-(V_{21}+V_{23})\right\}\Big/m_2n_2 \tag{8.2}$$

$$=\mathrm{d}N_3/m_3\mathrm{d}t=\left\{(V_{13}+V_{23})-(V_{31}+V_{32})\right\}\Big/m_3n_3\,, \tag{8.3}$$

where n_i is the number of atoms A in molecule M_i. Rates of increase of atoms A′ in the respective species are given as

$$n_1\mathrm{d}(N_1z_1)/\mathrm{d}t=V_{21}z_2+V_{31}z_3-(V_{12}+V_{13})z_1 \tag{9.1}$$

$$n_2\mathrm{d}(N_2z_2)/\mathrm{d}t=V_{12}z_1+V_{32}z_3-(V_{21}+V_{23})z_2 \tag{9.2}$$

$$n_3\mathrm{d}(N_3z_3)/\mathrm{d}t=V_{13}z_1+V_{23}z_2-(V_{31}+V_{32})z_3\,. \tag{9.3}$$

These six equations are not independent but any one of Eqs. (8) or Eqs. (9) is derived identically from the other two of Eqs. (8) or Eqs. (9) respectively, so that six V_{ij}'s are not evaluated from experimental data in general except in the following special cases.

In the case where $z_1=z_2=0$, Eqs. (9.1) and (9.2) assume the forms,

$$n_1\mathrm{d}(N_1z_1)/\mathrm{d}t=V_{31}z_3 \text{ and } n_2\mathrm{d}(N_2z_2)/\mathrm{d}t=V_{32}z_3\,,$$

whence V_{31} and V_{32} are extrapolated as $(n_1/z_3)\,\mathrm{d}(N_1z_1)/\mathrm{d}t$ and $(n_2/z_3)\,\mathrm{d}(N_2z_2)/\mathrm{d}t$ respectively at $z_1=z_2=0$. V_{12}, V_{21}, V_{13} and V_{23} are similarly evaluated.

We now introduce the functions $R_i=(V_{ij}+V_{ik})/(V_{ji}+V_{ki})$, $(i, j, k=1, 2$ or 3) of V_{ij}'s, each of which is given according to Eqs. (8.1) and (9.1), Eqs. (8.2) and (9.2), or Eqs. (8.3) and (9.3), respectively, as[8)]

$$R_i=(V_{ij}+V_{ik})/(V_{ji}+V_{ki}) \qquad i, j, k=1, 2 \text{ or } 3$$

$$=1+n_i(z_i-z_j)(\mathrm{d}N_i/\mathrm{d}t)\Big/\left\{n_iN_i\mathrm{d}z_i/\mathrm{d}t+(z_j-z_k)\,V_{ki}\right\} \tag{10.1}$$

or

$$R_i=1+n_i(z_i-z_k)(\mathrm{d}N_i/\mathrm{d}t)\Big/\left\{n_iN_i\mathrm{d}z_i/\mathrm{d}t+(z_k-z_j)\,V_{ji}\right\}. \tag{10.2}$$

In the special case where $(z_j-z_k)\,V_{ki}=0$ or $(z_k-z_j)\,V_{ji}=0$, R_i assumes the particular value R_{ij} or R_{ik}, *i.e.*

$$R_{ij} = 1 + (z_i - z_j)\,\mathrm{d}\ln N_i/\mathrm{d}z_i \tag{10$'$.1}$$

or

$$R_{ik} = 1 + (z_i - z_k)\,\mathrm{d}\ln N_i/\mathrm{d}z_i\,, \tag{10$'$.2}$$

respectively. In the further special case where $z_j = z_k$, both R_{ij} and R_{ik} give $\{R_i\}_{z_j=z_k}$, *i. e.*

$$R_{ij} = R_{ik} = \left\{(V_{ij} + V_{ik})/(V_{ji} + V_{ki})\right\}_{z_j=z_k} = \{R_i\}_{z_j=z_k}\,.$$

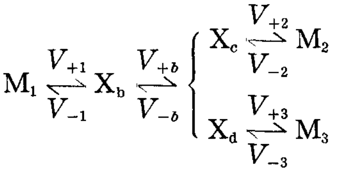
The right-hand sides of Eqs. (10′) are of the similar form to that of Eq. (5.3) and are also evaluated from experimental data.

It may be noted that one of the conditions, $z_2 = z_3$, $z_3 = z_1$ and $z_1 = z_2$ may be realized without difficulty, if one of the ratios, V_{12}/V_{21}, V_{13}/V_{31} and V_{23}/V_{32} is close to unity as discussed later. Even if all of these conditions are not satisfied, either R_{ij} or R_{ik} gives the upper limit of R_i and the other its lower limit as shown in Appendix I.

§ 2. Formulation of V_{ij}'s, V_{ij}/V_{ji}'s and R_i's

V_{ij}'s, V_{ij}/V_{ji}'s and R_i's are expressed in terms of unidirectional rates of constituent steps of the overall reaction of a single route in several simplified cases and their interrelations discussed.

2.1 Consider an isotopic exchange among molecules M_1, M_2 and M_3 through a branching scheme of steps which accompanies the overall reaction (6), *i. e.*



$$\mathrm{M}_1 \underset{V_{-1}}{\overset{V_{+1}}{\rightleftharpoons}} \mathrm{X}_b \underset{V_{-b}}{\overset{V_{+b}}{\rightleftharpoons}} \left\{ \begin{array}{l} \mathrm{X}_c \underset{V_{-2}}{\overset{V_{+2}}{\rightleftharpoons}} \mathrm{M}_2 \\ \mathrm{X}_d \underset{V_{-3}}{\overset{V_{+3}}{\rightleftharpoons}} \mathrm{M}_3 \end{array} \right. \tag{11}$$

where X_b, X_c and X_d are intermediates which comprise atoms A traced by its isotope A′. In this scheme both molecules and intermediates not comprising atoms A are not expressed if any. The flow of atoms A from M_1 to X_b, from X_c to M_2 and from X_d to M_3 are assumed to be effected through respective single paths (termed path I, II and III respectively), hence in accordance with Eqs. (4). V_{+i} and V_{-i} ($i = 1$, 2 and 3) are defined as the unidirectional rates of atoms A transferred from or to M_i respectively. X_b is supposed to branch off to yield intermediates X_c and X_d with forward and backward unidirectional rates, V_{+b} and V_{-b}, of step b distributing atoms A from X_b between X_c and X_d at a fixed ratio $\alpha : \beta$, where $\alpha + \beta = 1$.

The rate V_{ij} of transfer of atoms A from one of the species M_i to the other M_j, where $i, j=1$, 2 or 3, is now expressed in terms of V_{+i}'s and V_{-i}'s. The unidirectional rate V_{12} of transfer of atoms A from M_1 to M_2 is thus expressed after the method developed by MATSUDA and HORIUTI[6] as

$$V_{12} = V_{+1} V_{b2}/(V_{-1} + V_{b2} + V_{b3}) \tag{12.1}$$

where V_{b2} or V_{b3} is the unidirectional rate of atoms A transferred from X_b to M_2 or M_3 respectively, which is expressed respectively as

$$V_{b2} = \alpha V_{+b} V_{+2}/(\alpha V_{-b} + V_{+2})^{*)} \tag{12.2}$$

or

$$V_{b3} = \beta V_{+b} V_{+3}/(\beta V_{-b} + V_{+3})^{*)}\,, \tag{12.3}$$

hence we have

$$\begin{aligned} V_{12} = {} & V_{+1} \alpha V_{+b} V_{+2}\Big/\Big\{\alpha V_{+b} V_{+2} + V_{-1} V_{+2} + \alpha V_{-b} V_{-1} \\ & + \beta V_{+b} V_{+3}(\alpha V_{-b} + V_{+2})/(\beta V_{-b} + V_{+3})\Big\}\,. \end{aligned} \tag{13}$$

V_{21} is given similarly as

$$V_{21} = V_{-2} V_{c1}/(V_{+2} + V_{c1} + V_{c3}) \tag{14.1}$$

where V_{c1} or V_{c3} is the unidirectional rate of atoms A transferred from X_c to M_1 or M_3 respectively, which is expressed as

$$V_{c1} = \alpha V_{-b} V_{-1}/(V_{-1} + \alpha V_{+b} + V_{b3}) \tag{14.2}$$

or

$$V_{c3} = \alpha V_{-b} V_{b3}/(V_{-1} + \alpha V_{+b} + V_{b3})\,, \tag{14.3}$$

since atoms A transferred from X_c to X_b by the reverse step of b with αV_{-b} are distributed from X_b to M_1, X_c and M_3 with rates V_{-1}, αV_{+b} and V_{b3} respectively. Substituting V_{c1} and V_{c3} into Eq. (14.1) from Eqs. (14.2) and (14.3) and V_{b3} implied in the latter from Eq. (12.3), we have

$$V_{21} = (V_{-1} \alpha V_{-b} V_{-2} / V_{+1} \alpha V_{+b} V_{+2})\, V_{12} \tag{15}$$

or

$$V_{12}/V_{21} = V_{+1} V_{+b} V_{+2} / V_{-1} V_{-b} V_{-2}\,. \tag{16}$$

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*) The probability ratio $\alpha : \beta$ is conserved in the reverse step in the absence of isotopic difference of rate on account of one-to-one correspondence of X_c and X_d to be combined in the reverse step of b.

Similarly we have

$$V_{13} = V_{+1}\beta V_{+b}V_{+3}\Big/\Big\{\beta V_{+b}V_{+3} + V_{-1}V_{+3} + \beta V_{-b}V_{-1}$$

$$+\alpha V_{+b}V_{+2}(\beta V_{-b} + V_{+3})/(\alpha V_{-b} + V_{+2})\Big\} \tag{17}$$

$$V_{31} = (V_{-1}\beta V_{-b}V_{-3}/V_{+1}\beta V_{+b}V_{+3})\, V_{13} \tag{18}$$

or

$$V_{13}/V_{31} = V_{+1}V_{+b}V_{+3}/V_{-1}V_{-b}V_{-3}\,, \tag{19}$$

and

$$V_{23} = V_{-2}\alpha V_{-b}\beta V_{+b}V_{+3}\Big/\Big\{\alpha V_{-b}\beta V_{+b}V_{+3} + V_{+2}\beta V_{+b}V_{+3} + V_{+2}\alpha V_{+b}V_{+3}$$

$$+ V_{+2}\alpha V_{+b}\beta V_{-b} + V_{-1}(\beta V_{-b} + V_{+3})(\alpha V_{-b} + V_{+3})\Big\} \tag{20}$$

$$V_{32} = (V_{-3}\beta V_{-b}\alpha V_{+b}V_{+2}/V_{-2}\alpha V_{-b}\beta V_{+b}V_{+3})\, V_{23} \tag{21}$$

or

$$V_{23}/V_{32} = V_{-2}V_{+3}/V_{+2}V_{-3}\,. \tag{22}$$

If one of the steps of path I or step *b* is rate-determining, Eqs. (16), (19) and (22) are reduced to

$$V_{12}/V_{21} = V_{13}/V_{31} = v_{+r}/v_{-r} \text{ and } V_{23}/V_{32} = 1 \tag{24. 1}$$

and if one of the steps of path II or III is rate-determining, we have

$$V_{12}/V_{21} = v_{+r}/v_{-r}\,, \qquad V_{13}/V_{31} = 1 \text{ and } V_{23}/V_{32} = v_{-r}/v_{+r} \tag{24. 2}$$

or

$$V_{12}/V_{21} = 1 \text{ and } V_{13}/V_{31} = V_{23}/V_{32} = v_{+r}/v_{-r}\,, \tag{24. 3}$$

respectively.

From Eqs. (16), (19) and (22) we have

$$V_{23}/V_{32} = (V_{13}/V_{31})/(V_{12}/V_{21})\,. \tag{25}$$

If either V_{12}/V_{21} or V_{13}/V_{31} is determined by simultaneous use of another isotope which is exchanged exclusively between M_1 and M_2, or between M_1 and M_3 through paths I, II and step *b*, or paths I, III and step b, respectively, all the V_{ij}'s can be determined by solving Eqs. (8), (9) and (25) with the observed value of V_{12}/V_{21} or V_{13}/V_{31}, noting only two of Eqs. (8) or of Eqs. (9) are independent. If, in this case, the rate-determining step is one of the constituent steps of the exchange, its stoichiometric number ν_r can be determined, and if the overall reaction is controlled not by a unique rate-determining step but by two constituent steps cooperatively, *i.e.* these alone are not in partial equilibria (termed the rate-controlling steps), each of the two rate-controlling steps may be on different paths of I, II and III, or consist in step b which can be determined by comparing V_{12}/V_{21}, V_{13}/V_{31} and V_{23}/V_{32} thus determined each other on the basis of Eqs. (16), (19) and (22).

R_i's are expressed in terms of V_{+i}'s and V_{-i}'s by Eqs. (13), (15), (17), (18), (20) and (21), and reduced to simple forms, *i.e.* rate ratios, as shown in Table 1 in the presence of the rate-determining step. R_1, R_2 or R_3 may be determined uniquely by Eqs. (10) respectively in the special case where $z_2=z_3$, $z_3=z_1$ or $z_1=z_2$, which is realized if the rate-determining step is one of constituent steps of the path of exchange*). Table 1 indicates that R_1, $1/R_2$ or $1/R_3$ gives v_{+r}/v_{-r} if one of the steps of path I, II or III, respectively, is rate-determining and that if step b is rate-determining, all of R_1, $1/R_2$ and $1/R_3$ give v_{+r}/v_{-r}. Therefore, ν_r can be determined, in this case, by substituting V_+/V_- in Eq. (1) by R_1, $1/R_2$ or $1/R_3$.

TABLE 1. The relations between R_i's and the rate-determining step

rate-determining step		R_1	R_2	R_3
one of the steps of	path I	V_{+1}/V_{-1}	1	1
	path II	1	V_{-2}/V_{+2}	1
	path III	1	1	V_{-3}/V_{+3}
step b		V_{+b}/V_{-b}	V_{-b}/V_{+b}	V_{-b}/V_{+b}

If the overall reaction is controlled by two steps (*i. e.* the rate-controlling steps) on any two of paths I, II, III or one of them and step b, R_i's are expressed approximately by rate ratios shown in Table 2, taking into account that both V_{+i}'s and V_{-i}'s of the two paths or of the path and step b are small enough to be ignored as compared with the other V_{+i}'s and V_{-i}'s; their upper limits or lower limits, R_{ij} or R_{ik} of R_i, may be determined experimentally by Eq. (10'.1) or (10'.2). (Cf. Appendix I)

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*) For example, if one of the steps of path I is rate-determining, the exchange between M_2 and M_3 must be much faster than the exchanges between M_1 and M_2 and between M_1 and M_3, *viz.*, $V_{23}/V_{32}=1$, hence the condition, $z_2=z_3$, may readily be fulfilled. In the case where step b is rate-determining, the condition is met, if $z_2=z_3$ initially and no isotopic difference of rate exists.

TABLE 2. The relations between R_i's and two rate-controlling steps

two rate-controlling steps		R_1	R_2	R_3
consist in a step of	path I & step b	$\frac{V_{+1}V_{+b}}{V_{-1}V_{-b}}$	—	—
	path II & step b	—	$\frac{V_{-2}V_{-b}}{V_{+2}V_{+b}}$	$\frac{V_{-b}}{V_{+b}}$
	path III & step b	—	$\frac{V_{-b}}{V_{+b}}$	$\frac{V_{-3}V_{-b}}{V_{+3}V_{+b}}$
	path I & path II	$\frac{V_{+1}}{V_{-1}}$	$\frac{V_{-2}}{V_{+2}}$	—
	path I & path III	$\frac{V_{+1}}{V_{-1}}$	—	$\frac{V_{-3}}{V_{+3}}$
	path II & path III	—	$\frac{V_{-2}}{V_{+2}}$	$\frac{V_{-3}}{V_{+3}}$

Blanks mean that R_i's are not reduced to simple rate ratio.

2.2 Several simplified cases of scheme (11)

Consider a variant of scheme (11), where the path with rates V_{+1} and V_{-1} lacks as

$$M_1 \overset{b}{\rightleftarrows} \begin{cases} X_c \overset{\text{II}}{\rightleftarrows} M_2 \\ \qquad \text{III} \\ X_d \rightleftarrows M_3 \end{cases} \tag{26}$$

Step b stands for that with rates V_{+b} and V_{-b}, path II with rates V_{+2} and V_{-2} and III with rates V_{+3} and V_{-3}; M_1 is thus supposed to branch off in intermediates X_c and X_d through a single step b. Atoms A are thus transferable from M_2 to M_3 or reversely only through M_1, so that the net rate V and the exchange are described in terms of four unidirectional rates, V_{12}, V_{21}, V_{13} and V_{31} as

$$V = dN_2/m_2dt = (V_{12} - V_{21})/m_2n_2 \tag{27.1}$$

$$= dN_3/m_3dt = (V_{13} - V_{31})/m_3n_3 \tag{27.2}$$

$$n_2d(N_2z_2)/dt = V_{12}z_1 - V_{21}z_2 \tag{28.1}$$

and

$$n_3d(N_3z_3)/dt = V_{13}z_1 - V_{31}z_3\,, \tag{28.2}$$

which are special cases of Eqs. (8.2), (8.3), (9.2) and (9.3) respectively where $V_{23} = V_{32} = 0$. We can solve these equations similarly to the exchange between two species as

$$V_{12}/V_{21}=1\Big/\left\{1+(z_2-z_1)\,\mathrm{d}\ln N_2/\mathrm{d}z_2\right\} \tag{29.1}$$

$$V_{13}/V_{31}=1\Big/\left\{1+(z_3-z_1)\,\mathrm{d}\ln N_3/\mathrm{d}z_3\right\}. \tag{29.2}$$

V_{ij}/V_{ji}'s are expressed similarly to Eq. (16), (19) or (22) in terms of V_{+i} and V_{-i} ($i=b$, 2 and 3) after the method developed by MATSUDA and HORIUTI$^{6)}$ as

$$V_{12}/V_{21}=V_{+b}V_{+2}/V_{-b}V_{-2} \tag{30.1}$$

$$V_{13}/V_{31}=V_{+b}V_{+3}/V_{-b}V_{-3}, \tag{30.2}$$

which are equivalent to Eqs. (16) and (19) respectively in case of $V_{+1}/V_{-1}=1$. R_i's assume the forms, in this case, $R_1=(V_{12}+V_{13})/(V_{21}+V_{31})$, $R_2=V_{21}/V_{12}$ and $R_3=V_{31}/V_{13}$. R_1 is expressed in terms of V_{+i} and V_{-i} ($i=b$, 2 and 3) as well similarly to the formulation in the previous section after the method developed by MATSUDA and HORIUTI$^{6)}$. Tables 1 and 2 hold by excluding the rows of path I.

Let us next consider the case where path II in scheme (11) lacks or M_2 replaces X_c; V_{ij}/V_{ji}'s are now developed after the method presented by MATSUDA and HORIUTI$^{6)}$ to

$$V_{12}/V_{21}=V_{+1}V_{+b}/V_{-1}V_{-b} \tag{31.1}$$

$$V_{13}/V_{31}=V_{+1}V_{+b}V_{+3}/V_{-1}V_{-b}V_{-3} \tag{31.2}$$

and

$$V_{23}/V_{32}=V_{+3}/V_{-3}, \tag{31.3}$$

i.e. Eqs. (16), (19) and (22) with $V_{+2}/V_{-2}=1$. Tables 1 and 2 hold by excluding the rows of path II.

Another case where path III in scheme (11) lacks is formally equivalent to the above case where path II and M_2 respectively replaces path III and M_2.

§ 3. Discussion of other treatments in comparison with the present ones

3.1 Temkin's expression of the unidirectional rates

TEMKIN$^{9,10)}$ has tentatively proposed expressions of the forward and backward unidirectional rates, V_+ and V_-, of an overall reaction of a single route, irrespective of the presence of the rate-determining step as

$$V_+=1\Big/\left\{\frac{\nu_1}{v_{+1}}+\frac{v_{-1}\nu_2}{v_{+1}v_{+2}}+\cdots+\frac{v_{-1}v_{-2}\cdots v_{-(S-1)}\nu_S}{v_{+1}v_{+2}\cdots v_{+(S-1)}v_{+S}}\right\} \tag{32.1}$$

$$V_- = V_+ \prod_{s=1}^{S} v_{-s}/v_{+s}\,, \tag{32.2}$$

where v_{+s} or v_{-s} ($s=1, 2, \cdots, S$) is the forward or backward unidirectional rate of the constituent s-th step of the overall reaction and ν_s the stoichiometric number of s-th step. We now discuss his expressions to elucidate whether V_+ and V_- are in general determinable by an isotopic tracer or not.

The net rate V of the reaction at a steady state is expressed as

$$V = \frac{v_{+1}-v_{-1}}{\nu_1} = \frac{v_{+2}-v_{-2}}{\nu_2} = \cdots = \frac{v_{+S}-v_{-S}}{\nu_S}\,. \tag{33}$$

These equations are written as

$$\begin{aligned} V &= \frac{1-v_{-1}/v_{+1}}{\nu_1/v_{+1}} = \frac{(v_{-1}/v_{+1})(1-v_{-2}/v_{+2})}{(v_{-1}/v_{+1})(\nu_2/v_{+2})} = \cdots \\ &= \frac{(v_{-1}/v_{+1})(v_{-2}/v_{+2})\cdots(v_{-(S-1)}/v_{+(S-1)})(1-v_{-S}/v_{+S})}{(v_{-1}/v_{+1})(v_{-2}/v_{+2})\cdots(v_{-(S-1)}/v_{+(S-1)})(\nu_S/v_{+S})}\,, \end{aligned} \tag{34}$$

hence we have

$$V = \frac{1-\prod_{s=1}^{S} v_{-s}/v_{+s}}{\dfrac{\nu_1}{v_{+1}} + \dfrac{v_{-1}\nu_2}{v_{+1}v_{+2}} + \cdots + \dfrac{v_{-1}v_{-2}\cdots v_{-(S-1)}\nu_S}{v_{+1}v_{+2}\cdots v_{+(S-1)}v_{+S}}}\,. \tag{35}$$

Supposing that the forward and backward unidirectional rates, V_+ and V_-, are given by Eqs. (32), we have from Eqs. (32) and (35)

$$V = V_+ - V_- \tag{36.1}$$

and

$$V_+/V_- = \prod_{s=1}^{S} v_{+s}/v_{-s}\,. \tag{36.2}$$

Temkin's expressions of unidirectional rates, Eqs. (32) and of their interrelations, Eqs. (36), coincide with those of MATSUDA and HORIUTI, Eqs. (4) and Eq. (5.1), if the overall reaction of a single route consists only of a single path, so that the former is, in this case, verified to be the unidirectional rates of transfer of a kind of atoms traced by its isotope between two species by the latter; Temkin's expression is not in general verified to provide the unidirectional rates since the overall reaction may not consist only of a single path.

However, it should be noted that we can also set up an equation similar to Eq. (35) with several members of Eq. (33) picked up arbitrarily, *i.e.*

$$V = 1/(\nu_a/v_{+a} + v_{-a}\nu_b/v_{+a}v_{+b} + \cdots + v_{-a}v_{-b}\cdots\nu_{S'}/v_{+a}v_{+b}\cdots v_{+S'})$$

$$-\left(\prod_{s'}^{S'} v_{-s'}/v_{+s'}\right)\Big/\left(\nu_a/v_{+a}+v_{-a}\nu_b/v_{+a}v_{+b}+\cdots+v_{-a}v_{-b}\cdots\nu_{S'}/v_{+a}v_{+b}\cdots v_{+S'}\right), \tag{37.1}$$

where $v_{+s'}$ or $v_{-s'}$ ($s'=a, b, \cdots S'$) is the forward or backward unidirectional rate of step s' which belongs to the member of Eq. (33) picked up arbitrarity and $\nu_{s'}$ the stoichiometric number of step s'. Denoting the first term of Eq. (37.1) by V'_+ and the second one by V'_-, we have

$$V = V'_+ - V'_- \tag{37.2}$$

and

$$V'_+/V'_- = \prod_{s'}^{S'} v_{+s'}/v_{-s'}\,, \tag{37.3}$$

formally similar to Eqs. (36), although V'_+ or V'_- thus framed is not shown to correspond to any forward or backward unidirectional rate respectively through a single path as those given by Eqs. (4). Eqs. (37) are referred to in the following section.

3.2 The treatment of the exchange between three species by HAPPEL *et al.*

HAPPEL and CSUHA[11] discussed an isotopic exchange between three species with reference to the catalytic oxidation of sulfur dioxide,

$$2SO_2+O_2=2SO_3 \tag{38}$$

on the basis of the mechanism,

		ν_s	
1	$O_2=2O(a)$	1	
2	$SO_2=SO_2(a)$	2	(39)
3	$SO_2(a)+O(a)=SO_3(a)$	2	
4	$SO_3(a)=SO_3$	2	

where (a) denotes the adsorbed state. They defined two paths of transfer of oxygen atoms between O_2 and SO_3 and between SO_2 and SO_3 (termed $p=1$ and $p=2$ respectively), each of which consists of steps 1, 3 and 4 or of steps 2, 3 and 4, respectively. They presupposed the forward and backward unidiredtional rates of each paths, $V_+^{(p)}$ and $V_-^{(p)}$ ($p=1$ and 2), to satisfy the equations,

$$V = V_+^{(p)} - V_-^{(p)} \tag{40}$$

and

$$t_0^{O_2} = z_{O_2} V_+^{(1)} - z_{SO_3} V_-^{(1)} \tag{41.1}$$

or

$$t_0^{SO_2} = z_{SO_2} V_+^{(2)} - z_{SO_3} V_-^{(2)}, \tag{41.2}$$

where V is the net rate of reaction (38), z_i the atomic fraction of ^{18}O used as a tracer in species i and t_0^i the net rate of transfer of ^{18}O from species i to the others which equals $d(N_i z_i)/m_i dt$. They presupposed under the particular experimental conditions, *i.e.*

$$t_0^{O_2} = t_0^{SO_2} = t_0^{SO_3}, \tag{42}$$

hence given $V_+^{(p)}$ and $V_-^{(p)}$ as*)

$$V_+^{(1)} = 1 \Big/ \left\{ \frac{\nu_1}{v_{+1}} + \frac{v_{-1}\nu_3}{v_{+1}v_{+3}} + \frac{v_{-1}v_{-3}\nu_4}{v_{+1}v_{+3}v_{+4}} \right\} \tag{43.1}$$

$$V_-^{(1)} = 1 \Big/ \left\{ \frac{\nu_4}{v_{-4}} + \frac{v_{+4}\nu_3}{v_{-4}v_{-3}} + \frac{v_{+4}v_{+3}\nu_1}{v_{-4}v_{-3}v_{-1}} \right\} \tag{43.2}$$

$$V_+^{(2)} = 1 \Big/ \left\{ \frac{\nu_2}{v_{+2}} + \frac{v_{-2}\nu_3}{v_{+2}v_{+3}} + \frac{v_{-2}v_{-3}\nu_4}{v_{+2}v_{+3}v_{+4}} \right\} \tag{43.3}$$

$$V_-^{(2)} = 1 \Big/ \left\{ \frac{\nu_4}{v_{-4}} + \frac{v_{+4}\nu_4}{v_{-4}v_{-3}} + \frac{v_{+4}v_{+3}\nu_2}{v_{-4}v_{-3}v_{-2}} \right\}, \tag{43.4}$$

which are expressions framed similarly to Eqs. (37) by picking up some members of Eq. (33) with the steady state conditions of reaction (38) imposed upon steps 1, 3 and 4, or steps 2, 3 and 4, respectively. These conditions Eq. (42) are not defined uniquely by the chemical equation (38) irrespective of the mechanism, but realized only under the special restriction that $z_{O(a)} = z_{SO_2(a)}$, as shown in Appendix II. The expressions (43) are concluded to be applicable only under the conditions, $t_0^{O_2} = t_0^{SO_2} = t_0^{SO_3}$. These conditions may be implemented by adjusting the isotopic concentrations in a differencial reactor as Eq. (42) requires, but presumably with considerable difficulty.

OKI, MEZAKI and HAPPEL[13,14] have discussed the isotopic exchange among three species on the mechanism of water-gas shift reaction catalyzed by iron oxide, $CO + H_2O = CO_2 + H_2$, using oxygen-18 as a tracer. They analyzed the exchange of ^{18}O between CO, H_2O and CO_2 on the basis of a scheme,

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*) Happel had proposed[10] in general the expression of unidirectional rates of respective two paths, which is similar to that of Eqs. (43), but without proof.

$$\begin{array}{lll} \mathrm{CO} \overset{1}{\rightleftarrows} \mathrm{CO(a)} & \multirow{2}{*}{$\left.\begin{array}{l} \\ \\ \end{array}\right\} \overset{3}{\rightleftarrows} \mathrm{CO_2(a)} \overset{4}{\rightleftarrows} \mathrm{CO_2}$} & \\ \mathrm{H_2O} \overset{2}{\rightleftarrows} \left\{\begin{array}{l} \mathrm{O(a)} \\ \mathrm{2H(a)} \end{array}\right. & & \\ & \xleftrightarrow{\quad 5 \quad} \mathrm{H_2} & \end{array} \tag{44}$$

and derived

$$\frac{v_{+1}v_{+3}v_{+4}}{v_{-1}v_{-3}v_{-4}} = \frac{1}{t_0^{\mathrm{CO}} - Vz_{\mathrm{CO}}}\left\{(t_0^{\mathrm{CO}} - Vz_{\mathrm{CO_2}}) + \left(\frac{v_{+4}}{v_{-4}} - 1\right)(t_0^{\mathrm{CO}} - t_0^{\mathrm{CO_2}})\right\} \tag{45}$$

from the steady state conditions*)

$$V = -\,\mathrm{d}n_{\mathrm{CO}}/\mathrm{d}t = v_{+s} - v_{-s} \qquad (s = 1, 2, 3, 4 \text{ and } 5) \tag{46}$$

and the relations of ^{18}O-exchange,

$$t_0^{\mathrm{CO}} = -\,\mathrm{d}(n_{\mathrm{CO}}z_{\mathrm{CO}})/\mathrm{d}t = z_{\mathrm{CO}}v_{+1} - z_{\mathrm{CO(a)}}v_{-1} \tag{47.1}$$

$$= z_{\mathrm{CO(a)}}v_{+3} - z_{\mathrm{CO_2(a)}}v_{-3} \tag{47.2}$$

$$t_0^{\mathrm{CO_2}} = \mathrm{d}(n_{\mathrm{CO_2}}z_{\mathrm{CO_2}})/\mathrm{d}t = z_{\mathrm{CO_2(a)}}v_{+4} - z_{\mathrm{CO_2}}v_{-4}\,, \tag{47.3}$$

where n_i is the number of moles of species i in the system. Taking into account their experimental results, $v_{+4}/v_{-4} = 1$, Eq. (45) is written as

$$\frac{v_{+1}v_{+3}}{v_{-1}v_{-3}} = \frac{t_0^{\mathrm{CO}} - Vz_{\mathrm{CO_2}}}{t_0^{\mathrm{CO}} - Vz_{\mathrm{CO}}} = 1 - (z_{\mathrm{CO_2}} - z_{\mathrm{CO}})\left(\frac{\mathrm{d}n_{\mathrm{CO}}}{\mathrm{d}t}\Big/ n_{\mathrm{CO}}\frac{\mathrm{d}z_{\mathrm{CO}}}{\mathrm{d}t}\right) \tag{48.1}$$

$$= 1 + (z_{\mathrm{CO}} - z_{\mathrm{CO_2}})\,\mathrm{d}\ln n_{\mathrm{CO}}/\mathrm{d}z_{\mathrm{CO}}\,. \tag{48.2}$$

The condition $v_{+4}/v_{-4} = 1$ may lead to $z_{\mathrm{CO_2(a)}} = z_{\mathrm{CO_2}}$; Eqs. (48) are derived from Eqs. (46), (47.1) and (47.2) with the latter condition. Therefore, if $v_{+4}/v_{-4} = 1$ or $z_{\mathrm{CO_2(a)}} = z_{\mathrm{CO_2}}$ is fulfilled, the transfer of oxygen atoms by scheme (44) is attributed to that by scheme (26).

Conclusive Remarks

So far we have investigated the isotopic exchange among three species, which accompanies an overall reaction of a single route at the steady state and then the relations between the unidirectional rates of a particular

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*) They described14) that for the derivation of Eq. (45) they used Eqs. (47) and "CSUHA's definition"12)

$$V = V_{+}^{1,3,4} - V_{-}^{1,3,4}$$

where $V_{+}^{1,3,4}$ and $V_{-}^{1,3,4}$ are the forward and backward rates of the oxygen exchange path, which are given by the equations similar to Eqs. (43). However, Eq. (45) is derived directly from Eqs. (46) and (47) without "CHUHA's definition", which is inapplicable on account of the insecurity of the conditions, $t_0^{\mathrm{CO}} = t_0^{\mathrm{H_2O}} = t_0^{\mathrm{CO_2}}$.

exchange between three species, V_{ij}'s, their functions, *i.e.* V_{ij}/V_{ji}'s, R_i's $(=(V_{ij}+V_{ik})/(V_{ji}+V_{ki}))$, and the unidirectional rates of the constituent steps of the exchange. In the case where one of the constituent steps of the exchange is the rate-determining step of the overall reaction, it is possible experimentally to determine V_{ij}/V_{ji} or R_i (or $1/R_i$) which gives v_{+r}/v_{-r} of the rate-determining step. In some cases where the rate of the overall reaction is controlled by two of these steps, we may determine the product of the rate ratios v_{+s}/v_{-s}'s of these two steps or separately each of these rate ratios from V_{ij}/V_{ji}'s or R_i's.

The above treatment was now discussed in comparison with those of other authors. The expression of the unidirectional rates of the overall reaction proposed by TEMKIN is not verified to provide any forward or backward unidirectional rates except in the case where the overall reaction consists only of a single path. The treatment developed by HAPPEL and CSUHA is so far verified only in the special case where $z_{O(a)}=z_{SO_2(a)}$. The relation obtained by OKI, MEZAKI and HAPPEL on the water-gas shift reaction catalyzed by iron oxide is shown to be a simplified case of the present treatment.

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Appendix I

It is verified that either R_{ij} or R_{ik} gives the upper limit of R_i and the other its lower limit as follows.

We have from Eqs. (10.1) and (10′.1), or Eqs. (10.2) and (10′.2), respectively,

$$R_i - R_{ij} = \frac{-n_i(z_i - z_j)(\mathrm{d}N_i/\mathrm{d}t)(z_j - z_k)\,V_{ki}}{n_i N_i \mathrm{d}z_i/\mathrm{d}t + (z_j - z_k)\,V_{ki}} \tag{I. i}$$

or

$$R_i - R_{ik} = \frac{n_i(z_i - z_k)(\mathrm{d}N_i/\mathrm{d}t)(z_j - z_k)\,V_{ji}}{n_i N_i \mathrm{d}z_i/\mathrm{d}t + (z_k - z_j)\,V_{ji}}, \tag{I. ii}$$

hence we have

$$\frac{R_i - R_{ij}}{R_i - R_{ik}} = \frac{-(z_i - z_j)\,V_{ki}}{(z_i - z_k)\,V_{ji}} \times \frac{n_i N_i \mathrm{d}z_i/\mathrm{d}t + (z_k - z_j)\,V_{ji}}{n_i N_i \mathrm{d}z_i/\mathrm{d}t + (z_j - z_k)\,V_{ki}}. \tag{I. iii}$$

We have from Eqs. (8.1) and (9.1), from Eqs. (8.2) and (9.2) or from Eqs. (8.3) and (9.3) by eliminating $(V_{12} + V_{13})$, $(V_{21} + V_{23})$ or $(V_{31} + V_{32})$ respectively,

$$n_i N_i \mathrm{d}z_i/\mathrm{d}t = (z_k - z_i)\,V_{ki} + (z_j - z_i)\,V_{ji}\,. \tag{I. iv}$$

Substituting $n_i N_i \mathrm{d}z_i/\mathrm{d}t$ from Eq. (I.iv) into (I.iii), we have

$$\frac{R_i - R_{ij}}{R_i - R_{ik}} = -\frac{V_{ki}}{V_{ji}}, \qquad z_j \neq z_i \neq z_k\,. \tag{I. v}$$

Eq. (I.v) states that either $R_i - R_{ij}$ or $R_i - R_{ik}$ is negative value and the other positive, *i.e.* either R_{ij} or R_{ik} gives the upper limit of R_i and the other its lower limit.

Appendix II

HAPPEL and CSUHA derived Eqs. (43) on the basis of the experimental conditions, Eq. (42) as follows. They expressed $t_0^{O_2}$ and $t_0^{SO_3}$ in terms of the unidirectional rates of the constituent steps of path 1 as

$$t_0^{O_2} = (z_{O_2} v_{+1} - z_{O(a)} v_{-1})/\nu_1 \tag{II. i. i}$$

$$= (z_{O(a)} v_{+3} - z_{SO_3(a)} v_{-3})/\nu_3 \tag{II. i. ii}$$

$$= (z_{\mathrm{SO_3(a)}} v_{+4} - z_{\mathrm{SO_3}} v_{-4})/\nu_4 = t_0^{\mathrm{SO_3}} \tag{II. i. iii}$$

and $t_0^{\mathrm{SO_2}}$ and $t_0^{\mathrm{SO_3}}$ in terms of those of path 2 as

$$t_0^{\mathrm{SO_2}} = (z_{\mathrm{SO_2}} v_{+2} - z_{\mathrm{SO_2(a)}} v_{-2})/\nu_2 \tag{II. ii. i}$$

$$= (z_{\mathrm{SO_2(a)}} v_{+3} - z_{\mathrm{SO_3(a)}} v_{-3})/\nu_3 \tag{II. ii. ii}$$

$$= (z_{\mathrm{SO_3(a)}} v_{+4} - z_{\mathrm{SO_3}} v_{-4})/\nu_4 = t_0^{\mathrm{SO_3}}\,. \tag{II. ii. iii}$$

It may be noted that the equality between the members (II. i. ii) and (II. i. iii) or that between (II. ii. ii) and (II. ii. iii) is due to the condition where

$$t_0^{\mathrm{O_2}} = t_0^{\mathrm{SO_3}*)} \quad \text{or} \quad t_0^{\mathrm{SO_2}} = t_0^{\mathrm{SO_3}*)}, \qquad \text{(II. iii. i), (II. iii. ii)}$$

respectively. Eqs. (II. i. ii), (II. ii. ii) and (II. iii) lead to $z_{\mathrm{O(a)}} = z_{\mathrm{SO_2(a)}}$; we see that Eq. (42) is the special restriction imposed upon the isotopic concentrations of intermediates.

Eliminating $z_{\mathrm{O(a)}}$ and $z_{\mathrm{SO_3(a)}}$ from Eqs. (II. i), we have

$$t_0^{\mathrm{O_2}} = \frac{z_{\mathrm{O_2}} - z_{\mathrm{SO_3}}(v_{-1} v_{-3} v_{-4}/v_{+1} v_{+3} v_{+4})}{\nu_1/v_{+1} + v_{-1}\nu_3/v_{+1} v_{+3} + v_{-1} v_{-3} \nu_4/v_{+1} v_{+3} v_{+4}}\,. \tag{II. iv}$$

Similarly we have from Eqs. (II. ii)

$$t_0^{\mathrm{SO_2}} = \frac{z_{\mathrm{SO_2}} - z_{\mathrm{SO_3}}(v_{-2} v_{-3} v_{-4}/v_{+2} v_{+3} v_{+4})}{\nu_2/v_{+2} + v_{-2}\nu_3/v_{+2} v_{+3} + v_{-2} v_{-3} \nu_4/v_{+2} v_{+3} v_{+4}}\,. \tag{II. v}$$

Eqs. (II. iv) and (II. v) show that Eqs. (41) are satisfied by the expressions (43) of the unidirectional rates.

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*) Note that either $t_0^{\mathrm{O_2}} = t_0^{\mathrm{SO_3}}$ or $t_0^{\mathrm{SO_2}} = t_0^{\mathrm{SO_3}}$ leads to the other on account of the material balance of the isotope in the steady state.