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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  $\nu_r$  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  $\nu_s$ 's.  $\nu_r$  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<sup>1-7)</sup> of constituent elementary reactions (termed simply steps in what follows),  $\nu_s$ 's, and formulated the stoichiometric number  $\nu_r$  of the rate-determining step of the overall reaction of a single route<sup>\*\*)</sup> as<sup>3-7)</sup>

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

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

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<sup>\*\*)</sup> Let  $S$  be the number of steps occurring in the system and  $I$  the number of independent intermediates;  $S - I$  is shown<sup>4,5)</sup> to give the number of independent reaction route<sup>4,5)</sup>. 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)

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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

$$V_+ = v_{+r}/v_r \quad (2.1)$$

$$V_- = v_{-r}/v_r \quad (2.2)$$

and the net rate  $V$  of the overall reaction as

$$V = V_+ - V_- \quad (3)$$

MATSUDA and HORIUTI<sup>(6)</sup> 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

$$V_+ = 1 \left\{ \frac{v_1}{v_{+1}} + \frac{v_{-1}v_2}{v_{+1}v_{+2}} + \frac{v_{-1}v_{-2}v_3}{v_{+1}v_{+2}v_{+3}} + \dots + \frac{v_{-1}v_{-2} \dots v_{-(s-1)}v_s}{v_{+1}v_{+2} \dots v_{+(s-1)}v_{+s}} \right\} \quad (4.1)$$

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

hence,

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

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

$$V = V_+ - V_- = -dN_R/m_R dt = dN_P/m_P dt \quad (5.1)$$

$$-d(z_R N_R)/m_R dt = z_R V_+ - z_P V_- = d(z_P N_P)/m_P dt, \quad (5.2)$$

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)

$$V_+/V_- = 1 + (z_R - z_P) d \ln N_R / dz_R \quad (5.3)$$

or

$$V_-/V_+ = 1 + (z_P - z_R) d \ln N_P / dz_P. \quad (5.4)$$

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.<sup>9)</sup> The present paper deals with the extension of the method of determining  $\nu_r$  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<sup>9)</sup> 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<sup>10-14)</sup> 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,

$$\sum_i m_i M_i = 0 \quad (6)$$

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

$$V = dN_i / m_i dt, \quad (7)$$

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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

$$V = dN_1/m_1 dt = \{(V_{21} + V_{31}) - (V_{12} + V_{13})\} / m_1 n_1 \quad (8.1)$$

$$= dN_2/m_2 dt = \{(V_{12} + V_{32}) - (V_{21} + V_{23})\} / m_2 n_2 \quad (8.2)$$

$$= dN_3/m_3 dt = \{(V_{13} + V_{23}) - (V_{31} + V_{32})\} / m_3 n_3, \quad (8.3)$$

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

$$n_1 d(N_1 z_1)/dt = V_{21} z_2 + V_{31} z_3 - (V_{12} + V_{13}) z_1 \quad (9.1)$$

$$n_2 d(N_2 z_2)/dt = V_{12} z_1 + V_{32} z_3 - (V_{21} + V_{23}) z_2 \quad (9.2)$$

$$n_3 d(N_3 z_3)/dt = V_{13} z_1 + V_{23} z_2 - (V_{31} + V_{32}) z_3. \quad (9.3)$$

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,

$$n_1 d(N_1 z_1)/dt = V_{31} z_3 \quad \text{and} \quad n_2 d(N_2 z_2)/dt = V_{32} z_3,$$

whence  $V_{31}$  and  $V_{32}$  are extrapolated as  $(n_1/z_3) d(N_1 z_1)/dt$  and  $(n_2/z_3) d(N_2 z_2)/dt$  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<sup>8)</sup>

$$\begin{aligned} R_i &= (V_{ij} + V_{ik}) / (V_{ji} + V_{ki}) \quad i, j, k=1, 2 \text{ or } 3 \\ &= 1 + n_i(z_i - z_j) (dN_i/dt) / \{n_i N_i dz_i/dt + (z_j - z_k) V_{ki}\} \end{aligned} \quad (10.1)$$

or

$$R_i = 1 + n_i(z_i - z_k) (dN_i/dt) / \{n_i N_i dz_i/dt + (z_k - z_j) V_{ji}\}. \quad (10.2)$$

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.*

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

or

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

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.*

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

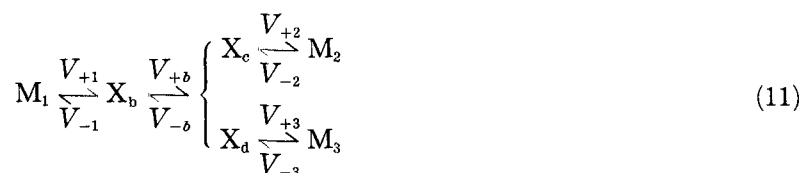
The right-hand sides of Eqs. (10') are of the similar form to that of Eq. (5.3) and are also evaluated from experimental data.

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.*



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  $\alpha + \beta = 1$ .

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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<sup>6)</sup> as

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

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

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

or

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

hence we have

$$V_{12} = V_{+1}\alpha V_{+b}V_{+2}/\left\{\alpha V_{+b}V_{+2} + V_{-1}V_{+2} + \alpha V_{-b}V_{-1} + \beta V_{+b}V_{+3}(\alpha V_{-b} + V_{+2})/(\beta V_{-b} + V_{+3})\right\}. \quad (13)$$

$V_{21}$  is given similarly as

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

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

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

or

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

since atoms A transferred from  $X_c$  to  $X_b$  by the reverse step of  $b$  with  $\alpha V_{-b}$  are distributed from  $X_b$  to  $M_1$ ,  $X_c$  and  $M_3$  with rates  $V_{-1}$ ,  $\alpha V_{+b}$  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

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

or

$$V_{12}/V_{21} = V_{+1}V_{+b}V_{+2}/V_{-1}V_{-b}V_{-2}. \quad (16)$$

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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  $b$ .

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Similarly we have

$$V_{13} = V_{+1}\beta V_{+b}V_{+3}/\{\beta V_{+b}V_{+3} + V_{-1}V_{+3} + \beta V_{-b}V_{-1} + \alpha V_{+b}V_{+2}(\beta V_{-b} + V_{+3})/(\alpha V_{-b} + V_{+2})\} \quad (17)$$

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

or

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

and

$$V_{23} = V_{-2}\alpha V_{-b}\beta V_{+b}V_{+3}/\{\alpha V_{-b}\beta V_{+b}V_{+3} + V_{+2}\beta V_{+b}V_{+3} + V_{+2}\alpha V_{+b}V_{+3} + V_{+2}\alpha V_{+b}\beta V_{-b} + V_{-1}(\beta V_{-b} + V_{+3})(\alpha V_{-b} + V_{+3})\} \quad (20)$$

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

or

$$V_{23}/V_{32} = V_{-2}V_{+3}/V_{+2}V_{-3}. \quad (22)$$

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

$$V_{12}/V_{21} = V_{13}/V_{31} = v_{+r}/v_{-r} \text{ and } V_{23}/V_{32} = 1 \quad (24.1)$$

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

$$V_{12}/V_{21} = v_{+r}/v_{-r}, \quad V_{13}/V_{31} = 1 \text{ and } V_{23}/V_{32} = v_{-r}/v_{+r} \quad (24.2)$$

or

$$V_{12}/V_{21} = 1 \text{ and } V_{13}/V_{31} = V_{23}/V_{32} = v_{+r}/v_{-r}, \quad (24.3)$$

respectively.

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

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

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  $\nu_r$  can be determined, and if the overall reaction is controlled not by a unique



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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,  $\nu_r$  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	$\left\{ \begin{array}{l} \text{path I} \\ \text{path II} \\ \text{path III} \end{array} \right.$	$\begin{array}{c} 1 \\ V_{-2}/V_{+2} \\ 1 \end{array}$	$\begin{array}{c} 1 \\ 1 \\ V_{-3}/V_{+3} \end{array}$
step <i>b</i>	$V_{+b}/V_{-b}$	$V_{-b}/V_{+b}$	$V_{-b}/V_{+b}$

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)

\*) 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.

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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



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

$$V = dN_2/m_2 dt = (V_{12} - V_{21})/m_2 n_2 \quad (27.1)$$

$$= dN_3/m_3 dt = (V_{13} - V_{31})/m_3 n_3 \quad (27.2)$$

$$n_2 d(N_2 z_2)/dt = V_{12} z_1 - V_{21} z_2 \quad (28.1)$$

and

$$n_3 d(N_3 z_3)/dt = V_{13} z_1 - V_{31} z_3, \quad (28.2)$$

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

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$$V_{12}/V_{21} = 1/\left\{1 + (z_2 - z_1) d \ln N_2/dz_2\right\} \quad (29.1)$$

$$V_{13}/V_{31} = 1/\left\{1 + (z_3 - z_1) d \ln N_3/dz_3\right\}. \quad (29.2)$$

$V_{ij}/V_{ji}$ '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<sup>6)</sup> as

$$V_{12}/V_{21} = V_{+b}V_{+2}/V_{-b}V_{-2} \quad (30.1)$$

$$V_{13}/V_{31} = V_{+b}V_{+3}/V_{-b}V_{-3}, \quad (30.2)$$

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<sup>6)</sup>. 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<sup>6)</sup> to

$$V_{12}/V_{21} = V_{+1}V_{+b}/V_{-1}V_{-b} \quad (31.1)$$

$$V_{13}/V_{31} = V_{+1}V_{+b}V_{+3}/V_{-1}V_{-b}V_{-3} \quad (31.2)$$

and

$$V_{23}/V_{32} = V_{+3}/V_{-3}, \quad (31.3)$$

*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<sup>9,10)</sup> 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

$$V_+ = 1/\left\{\frac{\nu_1}{\nu_{+1}} + \frac{\nu_{-1}\nu_2}{\nu_{+1}\nu_{+2}} + \dots + \frac{\nu_{-1}\nu_{-2}\dots\nu_{-(s-1)}\nu_s}{\nu_{+1}\nu_{+2}\dots\nu_{+(s-1)}\nu_{+s}}\right\} \quad (32.1)$$

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

where  $v_{+s}$  or  $v_{-s}$  ( $s=1, 2, \dots, S$ ) is the forward or backward unidirectional rate of the constituent  $s$ -th step of the overall reaction and  $\nu_s$  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

$$V = \frac{v_{+1} - v_{-1}}{\nu_1} = \frac{v_{+2} - v_{-2}}{\nu_2} = \dots = \frac{v_{+S} - v_{-S}}{\nu_S}. \quad (33)$$

These equations are written as

$$\begin{aligned} V &= \frac{1 - v_{-1}/v_{+1}}{\nu_1/v_{+1}} = \frac{(v_{-1}/v_{+1})(1 - v_{-2}/v_{+2})}{(v_{-1}/v_{+1})(\nu_2/v_{+2})} = \dots \\ &= \frac{(v_{-1}/v_{+1})(v_{-2}/v_{+2}) \cdots (v_{-(s-1)}/v_{+(s-1)})(1 - v_{-s}/v_{+s})}{(v_{-1}/v_{+1})(v_{-2}/v_{+2}) \cdots (v_{-(s-1)}/v_{+(s-1)})(\nu_s/v_{+s})}, \end{aligned} \quad (34)$$

hence we have

$$V = \frac{1 - \prod_{s=1}^S v_{-s}/v_{+s}}{\frac{\nu_1}{v_{+1}} + \frac{v_{-1}\nu_2}{v_{+1}v_{+2}} + \dots + \frac{v_{-1}v_{-2} \cdots v_{-(s-1)}\nu_s}{v_{+1}v_{+2} \cdots v_{+(s-1)}v_{+s}}}. \quad (35)$$

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

$$V = V_+ - V_- \quad (36.1)$$

and

$$V_+/V_- = \prod_{s=1}^S v_{+s}/v_{-s}. \quad (36.2)$$

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.*

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

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$$-\left(\prod_{s'}^{s'} v_{-s'}/v_{+s'}\right) / (\nu_a/v_{+a} + v_{-a}\nu_b/v_{+a}v_{+b} + \dots + v_{-a}v_{-b}\dots\nu_{s'}/v_{+a}v_{+b}\dots v_{+s'}), \quad (37.1)$$

where  $v_{+s'}$  or  $v_{-s'}$  ( $s'=a, b, \dots, S'$ ) is the forward or backward unidirectional rate of step  $s'$  which belongs to the member of Eq. (33) picked up arbitrarily 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

$$V = V'_+ - V'_- \quad (37.2)$$

and

$$V'_+/V'_- = \prod_{s'}^{s'} v_{+s'}/v_{-s'}, \quad (37.3)$$

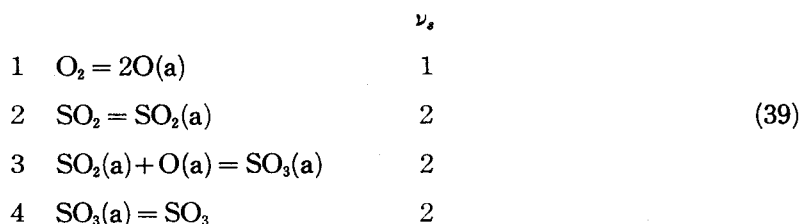
formally similar to Eqs. (36), although  $V'_+$  or  $V'_-$  thus framed is not shown to correspond to any forward or backward unidirectional rate respectively through a single path as those given by Eqs. (4). Eqs. (37) are referred to in the following section.

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

HAPPEL and CSUHA<sup>11)</sup> discussed an isotopic exchange between three species with reference to the catalytic oxidation of sulfur dioxide,



on the basis of the mechanism,



where (a) denotes the adsorbed state. They defined two paths of transfer of oxygen atoms between  $\text{O}_2$  and  $\text{SO}_3$  and between  $\text{SO}_2$  and  $\text{SO}_3$  (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 unidirectional rates of each paths,  $V_+^{(p)}$  and  $V_-^{(p)}$  ( $p=1$  and 2), to satisfy the equations,

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

and

$$t_0^{O_2} = z_{O_2} V_+^{(1)} - z_{SO_2} V_-^{(1)} \quad (41.1)$$

or

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

where  $V$  is the net rate of reaction (38),  $z_i$  the atomic fraction of  $^{18}\text{O}$  used as a tracer in species  $i$  and  $t_0^i$  the net rate of transfer of  $^{18}\text{O}$  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.*

$$t_0^{O_2} = t_0^{SO_2} = t_0^{SO_3}, \quad (42)$$

hence given  $V_+^{(p)}$  and  $V_-^{(p)}$  as<sup>\*</sup>

$$V_+^{(1)} = 1 \left/ \left\{ \frac{\nu_1}{\nu_{+1}} + \frac{\nu_{-1}\nu_3}{\nu_{+1}\nu_{+3}} + \frac{\nu_{-1}\nu_{-3}\nu_4}{\nu_{+1}\nu_{+3}\nu_{+4}} \right\} \right. \quad (43.1)$$

$$V_-^{(1)} = 1 \left/ \left\{ \frac{\nu_4}{\nu_{-4}} + \frac{\nu_{+4}\nu_3}{\nu_{-4}\nu_{-3}} + \frac{\nu_{+4}\nu_{+3}\nu_1}{\nu_{-4}\nu_{-3}\nu_{-1}} \right\} \right. \quad (43.2)$$

$$V_+^{(2)} = 1 \left/ \left\{ \frac{\nu_2}{\nu_{+2}} + \frac{\nu_{-2}\nu_3}{\nu_{+2}\nu_{+3}} + \frac{\nu_{-2}\nu_{-3}\nu_4}{\nu_{+2}\nu_{+3}\nu_{+4}} \right\} \right. \quad (43.3)$$

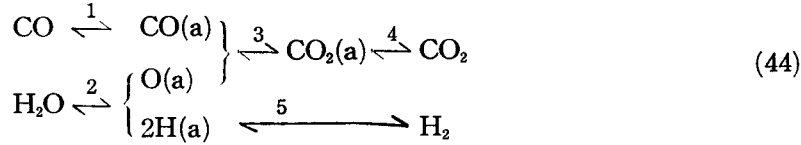
$$V_-^{(2)} = 1 \left/ \left\{ \frac{\nu_4}{\nu_{-4}} + \frac{\nu_{+4}\nu_4}{\nu_{-4}\nu_{-3}} + \frac{\nu_{+4}\nu_{+3}\nu_2}{\nu_{-4}\nu_{-3}\nu_{-2}} \right\} \right. \quad (43.4)$$

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 differential reactor as Eq. (42) requires, but presumably with considerable difficulty.

OKI, MEZAKI and HAPPEL<sup>13,14)</sup> have discussed the isotopic exchange among three species on the mechanism of water-gas shift reaction catalyzed by iron oxide,  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ , using oxygen-18 as a tracer. They analyzed the exchange of  $^{18}\text{O}$  between  $\text{CO}$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  on the basis of a scheme,

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

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and derived

$$\frac{v_{+1}v_{+3}v_{+4}}{v_{-1}v_{-3}v_{-4}} = \frac{1}{t_0^{\text{CO}} - Vz_{\text{CO}}} \left\{ (t_0^{\text{CO}} - Vz_{\text{CO}_2}) + \left( \frac{v_{+4}}{v_{-4}} - 1 \right) (t_0^{\text{CO}} - t_0^{\text{CO}_2}) \right\} \quad (45)$$

from the steady state conditions\*)

$$V = -dn_{\text{CO}}/dt = v_{+s} - v_{-s} \quad (s=1, 2, 3, 4 \text{ and } 5) \quad (46)$$

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

$$t_0^{\text{CO}} = -d(n_{\text{CO}}z_{\text{CO}})/dt = z_{\text{CO}}v_{+1} - z_{\text{CO(a)}}v_{-1} \quad (47.1)$$

$$= z_{\text{CO(a)}}v_{+3} - z_{\text{CO}_2\text{(a)}}v_{-3} \quad (47.2)$$

$$t_0^{\text{CO}_2} = d(n_{\text{CO}_2}z_{\text{CO}_2})/dt = z_{\text{CO}_2\text{(a)}}v_{+4} - z_{\text{CO}_2}v_{-4}, \quad (47.3)$$

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

$$\frac{v_{+1}v_{+3}}{v_{-1}v_{-3}} = \frac{t_0^{\text{CO}} - Vz_{\text{CO}_2}}{t_0^{\text{CO}} - Vz_{\text{CO}}} = 1 - (z_{\text{CO}_2} - z_{\text{CO}}) \left( \frac{dn_{\text{CO}}}{dt} / n_{\text{CO}} \frac{dz_{\text{CO}}}{dt} \right) \quad (48.1)$$

$$= 1 + (z_{\text{CO}} - z_{\text{CO}_2}) d \ln n_{\text{CO}} / dz_{\text{CO}}. \quad (48.2)$$

The condition  $v_{+4}/v_{-4}=1$  may lead to  $z_{\text{CO}_2\text{(a)}}=z_{\text{CO}_2}$ ; Eqs. (48) are derived from Eqs. (46), (47.1) and (47.2) with the latter condition. Therefore, if  $v_{+4}/v_{-4}=1$  or  $z_{\text{CO}_2\text{(a)}}=z_{\text{CO}_2}$  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

\*) They described<sup>14)</sup> that for the derivation of Eq. (45) they used Eqs. (47) and "CSUHA's definition"<sup>12)</sup>

$$V = V_{\pm}^{1.3.4} - V_{\mp}^{1.3.4}$$

where  $V_{\pm}^{1.3.4}$  and  $V_{\mp}^{1.3.4}$  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,  $t_0^{\text{CO}} = t_0^{\text{H}_2\text{O}} = t_0^{\text{CO}_2}$ .

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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,

$$R_i - R_{ij} = \frac{-n_i(z_i - z_j)(dN_i/dt)(z_j - z_k)V_{ki}}{n_i N_i dz_i/dt + (z_j - z_k)V_{ki}} \quad (\text{I. i})$$

or

$$R_i - R_{ik} = \frac{n_i(z_i - z_k)(dN_i/dt)(z_j - z_k)V_{ji}}{n_i N_i dz_i/dt + (z_k - z_j)V_{ji}}, \quad (\text{I. ii})$$

hence we have

$$\frac{R_i - R_{ij}}{R_i - R_{ik}} = \frac{-(z_i - z_j)V_{ki}}{(z_i - z_k)V_{ji}} \times \frac{n_i N_i dz_i/dt + (z_k - z_i)V_{ji}}{n_i N_i dz_i/dt + (z_j - z_k)V_{ki}}. \quad (\text{I. iii})$$

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,

$$n_i N_i dz_i/dt = (z_k - z_i)V_{ki} + (z_j - z_i)V_{ji}. \quad (\text{I. iv})$$

Substituting  $n_i N_i dz_i/dt$  from Eq. (I.iv) into (I.iii), we have

$$\frac{R_i - R_{ij}}{R_i - R_{ik}} = -\frac{V_{ki}}{V_{ji}}, \quad z_j \neq z_i \neq z_k. \quad (\text{I. v})$$

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  $t_0^{0_2}$  and  $t_0^{SO_3}$  in terms of the unidirectional rates of the constituent steps of path 1 as

$$t_0^{0_2} = (z_{0_2}v_{+1} - z_{0(a)}v_{-1})/v_1 \quad (\text{II. i. i})$$

$$= (z_{0(a)}v_{+3} - z_{SO_3(a)}v_{-3})/v_3 \quad (\text{II. i. ii})$$

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$$= (z_{\text{SO}_2(\text{a})} v_{+4} - z_{\text{SO}_2(\text{a})} v_{-4}) / \nu_4 = t_0^{\text{SO}_2} \quad (\text{II. i. iii})$$

and  $t_0^{\text{SO}_2}$  and  $t_0^{\text{SO}_3}$  in terms of those of path 2 as

$$t_0^{\text{SO}_2} = (z_{\text{SO}_2} v_{+2} - z_{\text{SO}_2(\text{a})} v_{-2}) / \nu_2 \quad (\text{II. ii. i})$$

$$= (z_{\text{SO}_2(\text{a})} v_{+3} - z_{\text{SO}_2(\text{a})} v_{-3}) / \nu_3 \quad (\text{II. ii. ii})$$

$$= (z_{\text{SO}_3(\text{a})} v_{+4} - z_{\text{SO}_3(\text{a})} v_{-4}) / \nu_4 = t_0^{\text{SO}_3} \quad (\text{II. ii. iii})$$

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

$$t_0^{\text{SO}_2} = t_0^{\text{SO}_3^*} \quad \text{or} \quad t_0^{\text{SO}_2} = t_0^{\text{SO}_3^*}, \quad (\text{II. iii. i}), (\text{II. iii. ii})$$

respectively. Eqs. (II.i.ii), (II.ii.ii) and (II.iii) lead to  $z_{\text{O(a)}} = z_{\text{SO}_2(\text{a})}$ ; we see that Eq. (42) is the special restriction imposed upon the isotopic concentrations of intermediates.

Eliminating  $z_{\text{O(a)}}$  and  $z_{\text{SO}_3(\text{a})}$  from Eqs. (II.i), we have

$$t_0^{\text{SO}_2} = \frac{z_{\text{O}_2} - z_{\text{SO}_3} (v_{-1} v_{-3} v_{-4} / v_{+1} v_{+3} v_{+4})}{\nu_1 / v_{+1} + v_{-1} \nu_3 / v_{+1} v_{+3} + v_{-1} v_{-3} \nu_4 / v_{+1} v_{+3} v_{+4}} \quad (\text{II. iv})$$

Similarly we have from Eqs. (II.ii)

$$t_0^{\text{SO}_2} = \frac{z_{\text{SO}_2} - z_{\text{SO}_3} (v_{-2} v_{-3} v_{-4} / v_{+2} v_{+3} v_{+4})}{\nu_2 / v_{+2} + v_{-2} \nu_3 / v_{+2} v_{+3} + v_{-2} v_{-3} \nu_4 / v_{+2} v_{+3} v_{+4}} \quad (\text{II. v})$$

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

\* ) Note that either  $t_0^{\text{SO}_2} = t_0^{\text{SO}_3}$  or  $t_0^{\text{SO}_2} = t_0^{\text{SO}_3^*}$  leads to the other on account of the material balance of the isotope in the steady state.