



HOKKAIDO UNIVERSITY

Title	THE RELATION BETWEEN STOICHIOMETRIC NUMBER AND EXCHANGE REACTION
Author(s)	MATSUDA, Akiya; HORIUTI, Juro
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 10(1), 14-23
Issue Date	1962-07
Doc URL	https://hdl.handle.net/2115/24752
Type	departmental bulletin paper
File Information	10(1)_P14-23.pdf



THE RELATION BETWEEN STOICHIOMETRIC NUMBER AND EXCHANGE REACTION^{*})

By

Akiya MATSUDA and Juro HORIUTI

(Received March 14, 1962)

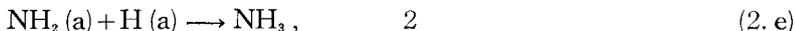
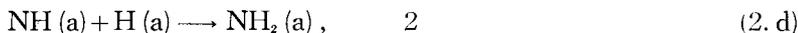
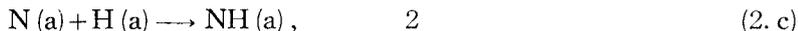
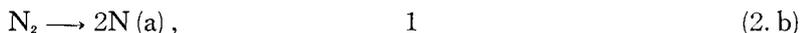
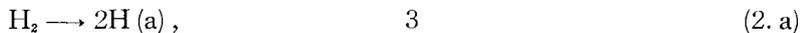
Introduction

One of the present authors has introduced the concept of stoichiometric number of elementary reactions (termed simply steps in what follows), which compose directly observed overall reactions¹⁾⁻⁵⁾.

Consider that the overall reaction



occurs as the resultant of the set of steps



where (a) denotes the adsorbed state of atom or atom group. The overall reaction (1) is completed without creating or consuming the intermediates, H(a) *etc.*, if each step occurs by the number of times of the figure annexed to the right-hand side of the appropriate scheme. These numbers are stoichiometric numbers of the respective steps; this set of stoichiometric numbers is shown⁴⁾⁵⁾ unique for such completion of (1) as mentioned above, which is termed that the set (2) of steps provides a single reaction route⁴⁾⁵⁾ of the overall reaction (1).

It has been shown in the case, where a set of steps provides a single reaction route and has a rate-determining step¹⁾³⁾⁵⁾ that

$$\vec{V} / \bar{V} = \exp(-\Delta F / \nu_r RT) \quad (3. \text{a})$$

i. e.

$$\nu_r = -\Delta F / RT \ln \vec{V} / \bar{V}, \quad (3. \text{b})$$

^{*}) This paper was presented at the Third Seminar on Electrochemistry at the Central Electrochemical Research Institute, Karaikudi, India.

where \vec{V} or \bar{V} is the forward or backward unidirectional rate of the overall reaction at the steady state, ν_r the stoichiometric number of the rate-determining step, $-\Delta F$ the affinity of the overall reaction, *i.e.* the decrease of free energy of the system, in which it occurs, per mol its occurrence and R or T the gas constant or the absolute temperature. A particular form^{6,7)}

$$\nu_r = -\frac{\vec{V}_e}{RT} \left(\frac{\partial \Delta F}{\partial V} \right)_e \quad (4. a)$$

or an alternative one

$$1/\nu_r = -RT \partial \ln \vec{V} / \partial \Delta F + RT \partial \ln \bar{V} / \partial \Delta F \quad (4. b)$$

of (3) has been applied according to circumstances, where suffix *e* signifies the quantities in equilibrium of the overall reaction and

$$V = \vec{V} - \bar{V} \quad (5)$$

is the directly observed rate of the overall reaction.

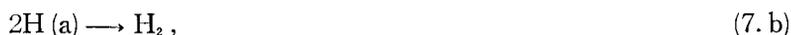
The unidirectional rate \vec{V} or \bar{V} has been determined for the practical determination of ν_r by labelling it with isotopes^{17,18)}, but this method is subject to a certain limitation, which is going to be investigated in the present paper.

We deal exclusively with the case, where there exist a single reaction route and a rate-determining step, and the isotopic tracer is transferred from a single chemical species A on the left-hand side of the chemical equation of the overall reaction to that B on its right-hand side; such tracer may be nitrogen or hydrogen isotope in the case of the overall reaction (1) and hydrogen isotope alone in the case of the hydrogen electrode reaction



where ε is metal electron.

In the case of (2) nitrogen is transferred from $\text{A} \equiv \text{N}_2$ into $\text{B} \equiv \text{NH}_3$ through the single sequence of steps (2.b), (2.c), (2.d) and (2.e) being successively handed over from one to another step. Such sequence of steps will be called a path of exchange and the single sequence, in particular, the single path of exchange. The same set provides three different sequences of steps for hydrogen transfer from $\text{A} \equiv \text{H}_2$ into $\text{B} \equiv \text{NH}_3$; such set of sequences is called a multipath, or particularly treble path, of exchange. There is a single path of hydrogen exchange between $\text{A} \equiv \text{H}^+$ and $\text{B} \equiv \text{H}_2$ for the single reaction route of (6) provided by the set,



but double path of hydrogen exchange between $A \equiv H^+$ and $B \equiv H_2$ for the alternative single reaction route provided by the set,



In what follows we first review the fundamental properties of the overall reaction of a single reaction route with a rate-determining step so far as necessary for the present application (§1), define the forward and backward exchange rates, \bar{V}_{ex} and \tilde{V}_{ex} , and the stoichiometric number ν_{ex} of the rate-determining step formally derived from \bar{V}_{ex} and \tilde{V}_{ex} (§2), develop the theory of exchange reaction through the single path (§3), treat the exchange reaction of multipath with the special example of (8) (§4) and finally draw conclusions from the results of these investigations (§5).

Isotopic difference of rates is ignored throughout the present treatment.

§ 1. Single Reaction Route with Rate-Determining Step

We have for any thermal step⁹⁾¹⁰⁾²⁾³⁾

$$\tilde{v}_s/\bar{v}_s = \exp(-\Delta F_s/RT), \quad (9)$$

where $-\Delta F_s$ is the affinity of step s or the decrease of free energy of the system, in which the step s is going on, per mol its occurrence. Let $s=1, \dots, S$ be a set of steps providing a single reaction route. The rate-determining step is defined such one among these S constituent steps as the relevant forward and the backward rates, \bar{v}_r and \tilde{v}_r , are respectively sufficiently small compared with the forward and backward rates of any other constituent step s' ($=1, \dots, r-1, r+1, \dots, S$) at the steady state of the overall reaction. In general we have⁵⁾

$$\Delta F = \sum_{s=1}^S \nu_s \Delta F_s, \quad (10)$$

where ν_s is the stoichiometric number of the s -th step referred to the chemical equation of the overall reaction^{*)}. It follows from the definition of the rate-determining step^{5)**)}, that

$$\bar{V} = \bar{v}_r/\nu_r, \quad \tilde{V} = \tilde{v}_r/\nu_r.$$

Eliminating \bar{v}_r and \tilde{v}_r from these equations and (9) written particularly for r as

*) The set of stoichiometric numbers of a single reaction route is numerically definite, when referred to the relevant chemical equation of definite coefficients as those of (2) referred to (1); cf. Refs. 4 and 5.

***) The overall reaction is completed once in forward or backward direction as soon as r occurs ν_r -times in the respective direction, since other steps are occurring back and forth sufficiently frequently according to the premise, hence the equations.

The Relation between Stoichiometric Number and Exchange Reaction

$$\bar{v}_r/\bar{v}_r = \exp(-\Delta F_r/RT),$$

we have

$$\bar{V}/\bar{V} = \exp(-\Delta F_r/RT). \quad (11)$$

We might agree for the sake of definite presentation that

$$\bar{V} > \bar{V}, \quad (12. a)$$

or according to (5) that

$$V > 0. \quad (12. b)$$

The directions of individual steps are selected properly, so that all ν_s 's are positive^{*)}. We have now at the steady state

$$V = \frac{\bar{v}_s - \bar{v}_s}{\nu_s}, \quad s = 1, \dots, S. \quad (13)$$

It follows from (13), (12.b) and (9)

$$-\Delta F_s > 0, \quad (14. a)$$

unless $\nu_s = 0$, in which case

$$\Delta F_s = 0, \quad \nu_s = 0. \quad (14. b)$$

In consequence, we have

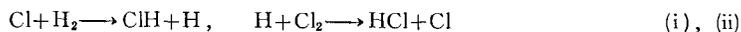
$$-\Delta F > 0 \quad (15)$$

apart from the trivial case, where all ν_s 's are zero. A step of zero stoichiometric number will be called a zero-step^{*)}.

We have besides by the definition of the rate-determining step with reference to (9) and (13)

$$-\Delta F_s \doteq 0,$$

*) It might seem at first sight that a zero-step has nothing to do with the steady reaction in question, hence ignorable. The following example might show that this is not the case. Consider the Nernst chain



and the other set which consists of the Nernst chain and the additional step



Each set has a single reaction route (Ref. 4 and 5) which is specified by the stoichiometric numbers 1 and 1 respectively of the steps (i) and (ii) for the former set and by those 1, 1 and 0 respectively of the steps (i), (ii) and (iii) for the latter set, as referred to the chemical equation $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ of the overall reaction.

There exists now the physical difference between the two sets that the population of Cl, hence of H, is maintained at any incidental value in the former set, whereas at that in equilibrium with Cl_2 in the latter set.

hence by (14) and (15)

$$-\nu_r \Delta F_r > -\sum \nu_s \Delta F_s, \quad (16)$$

or practically

$$\Delta F = \nu_r \Delta F_r.$$

Eq. (3) is obtained by substituting ΔF_r from the above equation into (11).

§ 2. Exchange Rates and ν_{ex}

Let I be the kind of atom exchanged between A and B, I' its particular isotope with which the exchange is traced, x_A or x_B the fraction of I' in I of A or that of B and m the number of I atoms comprized in either side of the relevant chemical equation*).

The forward exchange rate \vec{V}_{ex} is now defined as the rate of I' transferred from A to B for $x_A=1$ and $x_B=0$ divided by m , whereas the backward one \bar{V}_{ex} that reversely from B to A for $x_A=0$ and $x_B=1$ similarly divided by m . It follows from the definitions that

$$V = \vec{V}_{ex} - \bar{V}_{ex}, \quad (17)$$

since the overall rate of the transfer of I atoms from A to B is given by the definitions either as $m(\vec{V}_{ex} - \bar{V}_{ex})$ or as mV . It follows from (5) and (17)

$$\vec{V}_{ex} - \bar{V}_{ex} = \vec{V} - \bar{V}. \quad (18)$$

We define ν_{ex} by an equation similar to (3.b)

$$\nu_{ex} = -\Delta F / RT \ln (\vec{V}_{ex} / \bar{V}_{ex}), \quad (19)$$

which equals ν_r , if \vec{V}_{ex} and \bar{V}_{ex} equal \vec{V} and \bar{V} respectively.

It is investigated below how \vec{V} , \bar{V} and ν_r are reproduced respectively by \vec{V}_{ex} , \bar{V}_{ex} and ν_{ex} observed by means of isotope.

§ 3. Single Path Exchange

The \vec{V}_{ex} and \bar{V}_{ex} are formulated and discussed in the case of the single path, by which I atoms are handed over successively from one to another step from A to B. Let the steps of the single path be numbered as $1, \dots, n, \dots, N$, in order of them passing I from A to B. This group of steps are part or all of the set of steps, $1, \dots, s, \dots, S$, providing a single reaction route of the overall reaction. Such single path consists, e. g. of steps from (2.b) to (2.e) for nitrogen,

*) Let I or I' be for instance nitrogen or N¹⁵ respectively with regard to the overall reaction (2), in which case A \equiv N₂, B \equiv NH₃ and $m=2$.

It follows from (20), (21.a) and (22.a)

$$1/\vec{V}_{ex} = \sum_{n=1}^N \nu_n / R_{n-1} \vec{v}_n. \quad (23. a)$$

The rate $\vec{V}_{N,1}$ is given similarly as

$$1/\vec{V}_{N,1} = R_N \sum_{n=1}^N (R_{n-1} a_n \vec{v}_n)^{-1}$$

hence by (21.b) and (20)

$$1/\vec{V}_{ex} = m/\vec{V}_{N,1} = R_N \sum_{n=1}^N (\nu_n / R_{n-1} \vec{v}_n). \quad (23. b)$$

It follows immediately from (23) that

$$\vec{V}_{ex}/\vec{V}_{ex} = R_N, \quad (24)$$

or developing R_N according to (22.b) and (9), that

$$\vec{V}_{ex}/\vec{V}_{ex} = \exp\left(-\sum_{n=1}^N \Delta F_n / RT\right). \quad (25)$$

We now investigate \vec{V}_{ex} , \vec{V}_{ex} and ν_{ex} in the case, where (i) the single path of exchange comprizes the rate-determining step or (ii) not. The (ii) or (i) is the case, *e.g.* for nitrogen exchange accompanied by (2), according as (2.a) determines the rate or not.

(i) We have in this case practically

$$\sum_{n=1}^N \Delta F_n = \Delta F_r \quad (26)$$

according to (14) and (16), admitting that ν_s 's different from zero are of the order of magnitude of unity, hence according to (25)

$$\vec{V}_{ex}/\vec{V}_{ex} = \exp(-\Delta F_r / RT). \quad (27)$$

It follows from (27) and (11) that

$$\vec{V}_{ex}/\vec{V}_{ex} = \vec{V}/\vec{V},$$

hence according to (3.b) and (19)

$$\nu_{ex} = \nu_r.$$

We see now referring to (18), that \vec{V} , \vec{V} and ν_r are respectively reproduced by \vec{V}_{ex} , \vec{V}_{ex} and ν_{ex} , which are isotopically traced.

(ii) In the case, where the rate-determining step is not implied in the single path, we have according to (16)

$$-\Delta F_r \gg -\sum_{n=1}^N \Delta F_n, \quad (28)$$

since then the set of steps, $n=1, \dots, N$, is identical with or a part of the set

of steps, $s' = 1 \cdots, r-1, r+1, \cdots, S$. It follows from (28), (11) and (25)

$$\ln \bar{V}_{ex} / \bar{V}_{ex} < < \ln \bar{V} / \bar{V}, \quad (29)$$

hence according to (3.b) and (19)

$$\nu_{ex} > > \nu_r.$$

We have from (29) with reference to (18)

$$\bar{V}_{ex} > > \bar{V}, \quad \bar{V}_{ex} > > \bar{V}.$$

The latter situation, that \bar{V}_{ex} , \bar{V}_{ex} and ν_{ex} far exceed \bar{V} , \bar{V} and ν_r respectively may be actualized with nitrogen exchange through the steps of (2), if (2.a) governed the rate of the overall reaction, but not in the case of (7), where the rate-determining step is inevitably comprized in the single path of exchange as mentioned above.

§ 4. Multipath Exchange

We deal with the particular example of (8) of the multipath exchange leaving the generalization to further works.

We have in this case a double path of exchange composed of paths I and II associated with the single reaction route of (8) of the overall reaction (6); path I consists of (8.a) and (8.b), which hand over hydrogen atom successively from the state of H^+ to that of a constituent atom of H_2 and path II consists solely in (8.b), which transfers H^+ directly to the other constituent atom of H_2 .

Let \bar{V}^I or \bar{V}^{II} be the rate of I' transferred respectively through the path I or II from A to B at $x_A = 1$ and $x_B = 0$; they are expressed as

$$\bar{V}^I = \bar{v}_1 \bar{v}_2 / (\bar{v}_1 + \bar{v}_2) \quad (30. I)$$

$$\bar{V}^{II} = \bar{v}_2, \quad (30. II)$$

where \bar{v}_1 or \bar{v}_2 is the forward rate of (8.a) or (8.b) respectively and \bar{v}_1 is the backward one of (8.a). We see that (30.I) or (30.II) is the special case of $\bar{V}_{1,N}$ as given by (22.a) for $N=2$ and $a_1 = a_2 = 1$ or for $N=1$ and $a_1 = 1$ respectively. The forward rate \bar{V}_{ex} of exchange is now by definition*) the quotient of $\bar{V}^I + \bar{V}^{II}$ over $m=2$, *i. e.*

$$\bar{V}_{ex} = \frac{1}{2} \{ \bar{v}_1 \bar{v}_2 / (\bar{v}_1 + \bar{v}_2) + \bar{v}_2 \}. \quad (31. a)$$

The backward rate \bar{V}_{ex} of exchange is similarly derived as

*) Cf. § 2.

$$\bar{V}_{ex} = \frac{1}{2} \{ \bar{v}_2 \bar{v}_2 / (\bar{v}_1 + \bar{v}_2) + \bar{v}_2 \} . \quad (31. b)$$

where \bar{v}_2 is the backward rate of (8.b).

Eqs. (31.a) and (31.b) have already been derived by FRUMKIN⁽¹¹⁾ in terms of the relevant rates of electricity unidirectionally conveyed.

The ratio $\bar{V}_{ex}^{\rightarrow} / \bar{V}_{ex}$ is now according to (31)

$$\frac{\bar{V}_{ex}^{\rightarrow}}{\bar{V}_{ex}} = \frac{\bar{v}_1 \bar{v}_2 \bar{v}_1 + \frac{\bar{v}_2}{\bar{v}_2} (\bar{v}_1 + \bar{v}_2)}{2\bar{v}_1 + \bar{v}_2} ,$$

which is the weighted mean of R_n given by (22.b) for I and that for II with weights \bar{v}_1 and $\bar{v}_1 + \bar{v}_2$ respectively. Rewriting the above equation as

$$\frac{\bar{V}_{ex}^{\rightarrow}}{\bar{V}_{ex}} = \frac{\bar{v}_2}{\bar{v}_2} \cdot \frac{\bar{v}_1 + \bar{v}_1 + \bar{v}_2}{2\bar{v}_1 + \bar{v}_2} ,$$

we see that the second factor is practically unity in either case of the rate-determining step (8.a) or (8.b), where $\bar{v}_1 \ll \bar{v}_2$ and $\bar{v}_1 \ll \bar{v}_2$ or $\bar{v}_1 \neq \bar{v}_1 > \bar{v}_2$ respectively, hence by (9)

$$\bar{V}_{ex}^{\rightarrow} / \bar{V}_{ex} = \exp(-\Delta F_2 / RT) , \quad (32)$$

where $-\Delta F_2$ is the affinity of (8.b).

It follows now from (16), that

$$-\Delta F_2 \gg -\Delta F_r$$

or

$$\Delta F_2 = \Delta F_r$$

according as (8.a) or (8.b) is the rate-determining step. In the former case, we have by (11) and (32)

$$\ln \bar{V}_{ex}^{\rightarrow} / \bar{V}_{ex} \ll \ln \bar{V}^{\rightarrow} / \bar{V} , \quad (33. a)$$

hence according to (3.b) and (19)

$$\nu_{ex} \gg \nu_r \quad (33. b)$$

or with reference to (18)

$$\bar{V}_{ex} \gg \bar{V} , \quad \bar{V}_{ex} \gg \bar{V} ,$$

similarly as in the case of (ii), §3. In the latter case we have by (11) and (32)

$$\bar{V}_{ex}^{\rightarrow} / \bar{V}_{ex} = \bar{V}^{\rightarrow} / \bar{V} ,$$

hence according to (3.b) and (19)

$$\nu_{ex} = \nu_r$$

or referring to (18)

$$\vec{V}_{ex} = \vec{V}, \quad \bar{V}_{ex} = \bar{V}$$

similarly as in the case of (i), §3.

The ν_{ex} , \vec{V}_{ex} and \bar{V}_{ex} thus reproduce ν_r , \vec{V} and \bar{V} respectively, if the rate is governed by (8.b), which is shared between paths I and II, but far exceed the latter, if otherwise.

§ 5. Conclusions

So far we have investigated the method of determining \vec{V} , \bar{V} and ν_r by means of isotopic tracer in the case of overall reaction of a single reaction route with a rate-determining step. The overall reaction of such type accompanies an exchange reaction of single path or that of multipath. In the case of single path \vec{V}_{ex} , \bar{V}_{ex} and ν_{ex} respectively reproduce or exceed \vec{V} , \bar{V} and ν_r according as the single path comprises the rate-determining step of the overall reaction or not. In the case of multipath it was shown with special reference to the example of (8), that \vec{V}_{ex} , \bar{V}_{ex} and ν_{ex} respectively reproduce or exceed \vec{V} , \bar{V} and ν_r according as the rate-determining step is (8.b) or not, which is shared between the constituent paths I and II of the double path.

References

- 1) J. HORIUTI and M. IKUSIMA, Proc. Imp. Acad. Tokio, **15**, 39 (1939).
- 2) J. HORIUTI, *Chemical Kinetics*, Iwanami Series, *Physics X. C. 2*, (1940).
- 3) J. HORIUTI, This Journal, **1**, 8 (1948-51).
- 4) J. HORIUTI and T. NAKAMURA, Z. physik. Chem. N.F., **11**, 358 (1957).
- 5) J. HORIUTI, This Journal, **5**, 1 (1957).
- 6) J. HORIUTI and S. ENOMOTO, Proc. Japan Acad. Tokio, **29**, 160, 164 (1953).
- 7) S. ENOMOTO and J. HORIUTI, *ibid.* **28**, 493, 499 (1952); This journal, **2**, 87 (1951-3).
S. ENOMOTO, J. HORIUTI and H. KOBAYASHI, *ibid.*, **3**, 185 (1953-5).
- 8) J. HORIUTI and A. MATSUDA, *ibid.* **5**, 19 (1957).
- 9) J. HORIUTI, Bull. Chem. Soc. Japan, **13**, 210 (1938).
- 10) K. HIROTA and J. HORIUTI, Sci. Papers Inst. Phys. Chem. Research, Tokio, **34**, 1174 (1938).
- 11) A. N. FRUMKIN, Reports Acad. Sci. USSR, **119**, 318 (1958).