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(Note)

UNIDIRECTIONAL RATES OF REACTION OF SINGLE ROUTE

By

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The rate expressions of the forward and backward unidirectional reaction of a single route has been preliminarily presented for application in a contribution to the International Conference on The Use of Tracers Study in Heterogeneous Catalysis, August 28, 29, 1972 New York Academy of Science. Its derivation is given in the present note.

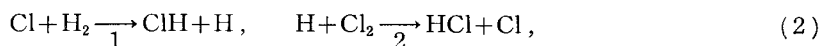
The fundamentals of the treatment are briefly reviewed below to start with. We have an *assembly*, which may be macroscopic, where elementary reactions (termed *steps*) are simultaneously going on. It is postulated that chemical species involved in the steps may be grouped in the class of distinctly longer lives and that of shorter lives; chemical species of the former or the latter class are called respectively *molecules or intermediates*. The total number, $f_{i'}$, of i' -th intermediates created by all of steps is given as

$$f_{i'} = \sum_{s=1}^S b_{i's} n_s, \quad i' = 1, \dots, I, \quad (1. a)$$

where $b_{i's}$ is the number of i' -th intermediates created (algebraically) by s -th ($1, \dots, S$) step and n_s the number of s -th step to occur. The condition of the steady state is the absence of net creation of every intermediate, *i.e.*

$$f_{i'} = 0, \quad i' = 1, \dots, I. \quad (1. b)$$

Eqs. (1. b) are not necessarily independent of one another. Let I be the number of independent equations among Eqs. (1. b), which is termed the number of *independent intermediates*. For the set, *e.g.* of steps



we have, with the annexed numbers of steps

$$f_{\text{H}} = n_1 - n_2, \quad f_{\text{Cl}} = n_2 - n_1,$$

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where n_1 and n_2 are respectively the numbers of steps 1 and 2 to occur. We see that $f_{\text{Cl}} + f_{\text{H}} = 0$ identically or that f_{Cl} and f_{H} are not independent. Physically, a definite amount of either intermediate, Cl or H, defines the amount of the other, inasmuch as one intermediate of either kind is created at the cost of just one of the other kind according to Scheme (2). Either Cl or H is thus termed independent intermediate in this case.

It may be shown generally^{1,2)} that there exist

$$P = S - I \quad (S: \text{total number of kinds of steps}) \quad (3)$$

independent solutions of Eq. (1. b), each of which is a set of numbers of steps to occur which are definite except a common factor. The eventual conversion caused by the set of steps thus specified is that among molecules which is termed *reaction*. The set of independent solutions is such that none of them is given as the linear combination of other solution or solutions. Let $(n_1, n_2, \dots, n_s, \dots, n_S)$ be one of the solutions. We have for molecules

$$\sum_{s=1}^S b_{ms} n_s = b_m, \quad m=1, \dots, M, \quad (4. a)$$

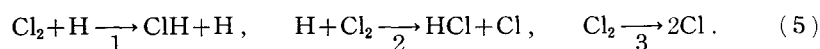
where b_{ms} or b_m is respectively the number of m -th molecules created (algebraically) by one act of s -th step or the net number of m -th molecules eventually created (algebraically) by the set of steps of the above solution.

The set of b_m 's is definite except a common factor. Let B_m be the particular value of b_m , which is the coefficient of m -th molecule on the right- or, with reverse sign, on the left-hand side of the chemical equation describing the conversion. Let ν_s be the particular value of n_s relevant to B_m in accordance with Eq. (4. a), as

$$\sum_{s=1}^S b_m \nu_s = B_m, \quad m=1, \dots, M. \quad (4. b)$$

The set of ν_s 's is termed a route of the reaction of the chemical equation and the individual value of ν_s is termed the *stoichiometric number* of s -th step referred to the latter chemical equation. The material balance of a route is given by a chemical equation, which may, however, be common to more than one route.

We now consider the particular case where $P=1$, *i.e.* there exists a unique route. We have a definite compound ratio of stoichiometric numbers different from zero. Zero stoichiometric number may arise, the relevant step being called *zero-step*. Assume that intermediate Cl in the set of Scheme (2) is created by an additional step of decomposition of Cl_2 , hence the set to deal with is



Eqs. (1) are now

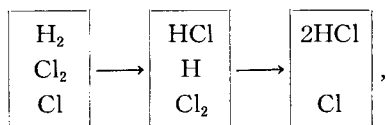
Unidirectional Rates of Reaction of Single Route

$$f_{\text{H}} = n_1 - n_2 = 0, \quad f_{\text{Cl}} = n_2 - n_1 + 2n_3 = 0,$$

hence $n_3 = 0$, or $\nu_3 = 0$, or step 3 is in perfect equilibrium, notwithstanding the steady reaction going on.

A zero-step is never connected with other step of stoichiometric number different from zero through transfer of their formations, while the latter is connected with another kindred step or steps, or/and with a molecule or molecules, insofar as the steady reaction is going on. A thread of steps of stoichiometric numbers different from zero thus starts from a reactant or reactants and ends in a product or products. A zero-step never intervenes in the latter thread of steps with stoichiometric numbers different from zero, on account of the absence of connection through transfer of their formations, but its formation may act as an intermediate without net creation like Cl in Scheme (5).

We may now set up a scheme, *e.g.* for the reaction sustained by steps of Scheme (5) as



where intermediate Cl is accompanied by reactants and products; sets of chemical species in rectangular enclosures represent posts through which the reactants mutate into products by a series of arrows each standing for $\nu_s (\neq 0)$ -times occurrence of s -th step. Posts will be so numbered that s -th post is converted into $s+1$ -th post by ν_s -times occurrence of s -th step. We have thus 1-st to $S+1$ -th posts according to Eq. (3) and the premise that $P=1$.

The unidirectional rates of the reaction in question are derived in terms of the following symbols.

V_+, V_- : forward and backward unidirectional rates of the reaction.

v_{+s}, v_{-s} : forward and backward rates of s -th step.

V_{+s}, V_{-s} : forward and backward unidirectional rates of the s -th post converted into that of $S+1$ -th post.

We see by definition that

$$V_+ = V_{+1}. \tag{6}$$

V_{+2} is connected with V_{+1} as

$$V_{+1} = (v_{+1}/\nu_1) V_{+2}/(v_{-1}/\nu_1 + V_{+2}),$$

inasmuch as ν_1 -times forward acts of the 1st step transfer the 1st post to the second post at the rate, v_{+1}/ν_1 , and every arrival at the 2nd post completes the further conversion to $S+1$ -th post with probability $V_{+2}/(v_{-1}/\nu_1 + V_{+2})$, where v_{-1}/ν_1

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is the reverse rate of v_{+1}/ν_1 . We have from the above equation

$$1/V_{+1} = \nu_1/v_{+1} + (v_{-1}/v_{+1})(1/V_{+2}).$$

Similarly we have

$$1/V_{+2} = \nu_2/v_{+2} + (v_{-2}/v_{+2})(1/V_{+3}),$$

.....

$$1/V_{+s} = \nu_s/v_{+s} + (v_{-s}/v_{+s})(1/V_{s+1}),$$

.....

$$1/V_{+(s-1)} = \nu_{s-1}/v_{+(s-1)} + (v_{-(s-1)}/v_{+(s-1)})(1/V_s),$$

and

$$V_s = v_{+s}/\nu_s$$

Eliminating V_{+2}, \dots, V_{+s} from the above S equations, we have, with reference to Eq. (6)

$$1/V_{+} = \sum_{s=1}^S (\nu_s/R_{s-1}v_{+s}), \quad (7. a)$$

where

$$R_s = \prod_{s=1}^S v_{+s}/v_{-s}, \quad R_0 = 1. \quad (7. b), (7. c)$$

The backward unidirectional rate of the reaction, V_- , is similarly derived as

$$1/V_- = V_{-S} = R_S \sum_{s=1}^S (\nu_s/R_{s-1}v_{+s}), \quad (8)$$

so that with reference to Eq. (7. a)

$$V_{+}/V_{-} = R_S.$$

No amendment is required to the derivation of the unidirectional rates through a path³⁾ implied in a route, no zero-step being capable of intervening in the thread of the path dealt with there³⁾.

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