Significance and Experimental Determination of Stoichiometric Number

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The concept of stoichiometric number is introduced with special reference to the applicability of the classical theorem $k'/k'' = K$ to the relation between the forward and the backward rate constants, k' and k'', and the equilibrium constant K. The significance of the stoichiometric number ν_r of the rate-determining step in determining the mechanism is illustrated.

The theoretical background of ν_r and theorems on ν_r derived from its definition are reviewed and on their basis the experimental determination of ν_r is illustrated in several cases.

INTRODUCTION

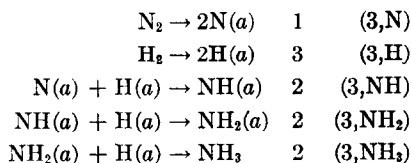The well-known theorem of kinetics

$$k'/k'' = K \tag{1}$$

was derived from the mass action law on the tacit assumption that a chemical conversion expressed by a chemical equation occurs in one act of an elementary reaction in either direction, where k' or k'' is the rate constant, respectively, of the forward or the backward act of the elementary reaction, and K is the relevant equilibrium constant.

In the following, the elementary reaction will be termed simply "step"; the set of particles involved in a step, the "reaction complex"; and the reaction complex at the state prior to or following the occurrence of the step, the "initial" or the "final complex" of the step, respectively.

We accept nowadays that a directly observed chemical conversion expressed by a chemical equation is, in general, a resultant of a relevant set of steps. The catalyzed synthesis of ammonia

$$N_2 + 3H_2 = 2NH_3 \tag{2}$$

may thus be the resultant of the set of steps:

$$
\begin{array}{llll}
N_2 \rightarrow 2N(a) & 1 & (3,N) \\
H_2 \rightarrow 2H(a) & 3 & (3,H) \\
N(a) + H(a) \rightarrow NH(a) & 2 & (3,NH) \\
NH(a) + H(a) \rightarrow NH_2(a) & 2 & (3,NH_2) \\
NH_2(a) + H(a) \rightarrow NH_3 & 2 & (3,NH_3)
\end{array}
$$

where (a) denotes the adsorbed state of an atom or an atom group on the catalyst. We see immediately that the occurrence of each step multiplied by the number of times indicated on the right results in the chemical conversion of Eq. (2) without ultimately consuming or creating any of the intermediates, $N(a)$, $H(a)$, $NH(a)$, and $NH_2(a)$. We will call the directly observed chemical conversion expressed by a chemical equation, e.g., Eq. (2), simply an "over-all reaction."

Now the question arises whether the classical theorem would hold even in the case of an over-all reaction composed of steps. This question has been discussed by Temkin and Pyzhev (1), by Manes et al. (2) and by Frost and Pearson (3) with the conclusion that the classical theorem holds only in particular cases. We might first deduce some valid relationships between the rate constants and the equilibrium constant in the particular case of Eqs. (3).

In equilibria of all steps of Eqs. (3), we have

$$k'_N a_e^{N_2} = k''_N (a_e^{N(a)})^2$$

$$k'_H a_e^{H_2} = k''_H (a_e^{H(a)})^2$$

$$k'_{NH} a_e^{N(a)} a_e^{H(a)} = k''_{NH} a_e^{NH(a)}$$

$$k'_{NH_2} a_e^{NH(a)} a_e^{H(a)} = k''_{NH_2} a_e^{NH_2(a)}$$

$$k'_{NH_3} a_e^{NH_2(a)} a_e^{H(a)} = k''_{NH_3} a_e^{NH_3}$$

where k'_N, etc., or k''_N, etc., are the forward or the backward rate constants of steps (3,N), etc., and $a_e^{N_2}$, etc., are the activities a^{N_2}, etc., of N_2, etc. at the equilibria, respectively. Raising both sides of each of the above five equations to the power of the indicated number in Eq. (3) and equating the products of the respective sides of the equations, we have

$$\left(\frac{k'_N}{k''_N}\right)^1 \left(\frac{k'_H}{k''_H}\right)^3 \left(\frac{k'_{NH}}{k''_{NH}}\right)^2 \left(\frac{k'_{NH_2}}{k''_{NH_2}}\right)^2 \left(\frac{k'_{NH_3}}{k''_{NH_3}}\right)^2$$
$$= \frac{(a_e^{NH_3})^2}{a_e^{N_2}(a_e^{H_2})^3} = K$$

where the second member equals the thermodynamic equilibrium constant of the over-all reaction, which is, of course, in equilibrium in this case. We see readily that the foregoing equation is generalized as (4)

$$\prod_{s=1}^{S} (k'_s/k''_s)^{\nu_s} = K \qquad (4)$$

where k_s' or k_s'' is the rate constant of sth constituent step $(s = 1, \ldots, S)$, ν_s is the number of times that the sth step occurs, e.g., 1,3,2,2, and 2 for the steps of Eqs. (3) to complete the over-all reaction, and K is its equilibrium constant. Equation (4) shows that the classical theorem, Eq. (1), holds in the particular case where $S = 1$ and $\nu_s = 1$. The ν_s is the stoichiometric number (5–8) of the sth constituent step.

We now examine, alternatively, the case where there exists a rate-determining step. Let, e.g. Eq. (3,H) be the rate-determining step. The forward unidirectional rate V' of the over-all reaction, Eq. (2), is proportional to the activity of H_2, i.e.,

$$V' = k'a^{H_2} \qquad (5,V')$$

where k' is the observable forward rate

constant in this case. The backward unidirectional rate V'' is proportional to the square of the activity $a^{H(a)}$ of $H(a)$, i.e.,

$$V'' \propto (a^{H(a)})^2$$

Steps other than the rate-determining one, Eq. (3,H), are approximately in equilibrium, so that

$$a^{N_2} \propto (a^{N(a)})^2 \qquad a^{N(a)}a^{H(a)} \propto a^{NH(a)}$$
$$a^{NH(a)}a^{H(a)} \propto a^{NH_2(a)} \qquad a^{NH_2(a)}a^{H(a)} \propto a^{NH_3}$$

From the above five relations we have, by eliminating $a^{N(a)}$, $a^{H(a)}$, $a^{NH(a)}$, and $a^{NH_2(a)}$

$$V'' = k''(a^{NH_3})^{2/3}/(a^{N_2})^{1/3} \qquad (5,V'')$$

where the proportionality constant k'' is the observable backward rate constant. Putting $V' = V''$ for the equilibrium of the over-all reaction, we have from Eqs. (5)

$$k'/k'' = K^{1/3} \qquad (6a)$$

on the basis of K as already defined.

Assuming Eq. (3,N) as the rate-determining step instead, we have similarly

$$k'/k'' = K \qquad (6b)$$

where k' or k'' is the forward or backward rate constant observable in this case*. Eq. (6,b) is in accordance with the classical theorem, Eq. (1), but the rate-determining step of Eqs. (3,NH) or (3.NH$_2$) or (3.NH$_3$) leads commonly to the equation

$$k'/k'' = K^{1/2} \qquad (6c)$$

We see from Eq. (6) that the exponent to K is the reciprocal of the stoichiometric number ν_r of the rate-determining step r, i.e., (8,9)

$$k'/k'' = K^{1/\nu_r} \qquad (7)$$

It is seen that the classical theorem, Eq. (1), does not necessarily hold in the general case of over-all reactions composed of steps, that the relation valid in the latter case includes stoichiometric numbers, and that the observation of ν_r provides us a sound diagnosis of mechanism; if, for instance, we find $\nu_r = 1$ or 3 with regard to

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* The rate constant k' or k'' depends, respectively, on the rate-determining step.

Eq. (2), the rate-determining step is decided to be Eq. (3,N) or Eq. (3,H), respectively, and if $\nu_r = 2$, the rate-determining step is decided to be Eq. (3,N) or Eq. (3,H), respectively, and if $\nu_r = 2$, the rate-determining step is confined to one of Eqs. (3,NH), (3,NH$_2$), and (3,NH$_3$).

We might review in what follows the theoretical background of ν_r, theorems on ν_r, and the experimental determinations of ν_r based on the theorems.

THEORETICAL BACKGROUND

The set, Eqs. (3), of steps each multiplied by the appropriate ν_s indicated on the right adds up to the chemical equation, (2), whereas the same set, Eqs. (3), of steps each multiplied by one-half of the relevant ν_s adds up similarly to the chemical equation

$$\tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 = NH_3$$

whose coefficients are commonly one-half of those of Eq. (2). The latter chemical equation is, however, identical with Eq. (2) with regard to the material balance. A set of stoichiometric numbers, which differ only by a common factor, leads thus to the same material balance; the set of stoichiometric numbers is said to define a reaction route (4). Definite values of the stoichiometric numbers should, of course, be referred to a chemical equation of definite coefficients.

In general,

$$P = S - I \qquad (8)$$

gives the number of different reaction routes for S kinds of steps and I kinds of independent intermediates involved (7,8). The number I of independent intermediates is exemplified as follows. Consider the Nernst chain, consisting of steps

$$H + Cl_2 \rightarrow HCl + Cl$$
$$Cl + H_2 \rightarrow ClH + H$$
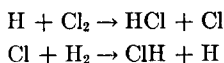
The amount of intermediate Cl formed by the steps is given by $n_1 - n_2$, whereas that of the other intermediate H formed by $n_2 - n_1$, where n_1 or n_2 is the number of occurrences of the first or the second step of the Nernst chain. If either $n_2 - n_1$ or $n_1 - n_2$ is given, the other is, of course, fixed. In such a case, the two intermediates are termed not independent, but only one of them is independent. In general, the amounts of respective intermediates formed are given as homogeneous linear functions (7,8) of the numbers of occurrence of the steps, e.g., $n_1 - n_2$ or $n_2 - n_1$ in the above example. Let I' be the number of such homogeneous linear functions each appropriate to an intermediate and I ($\leqslant I'$) among them, designated as those of I-group, have the following properties (4): (i) none of the homogeneous linear functions of the I-group is given as a linear combination* of the rest of the same group, and (ii) any of $I' - I$ homogeneous linear functions, which do not belong to the I-group, if any, is given as a linear combination of those of the I-group. We then term I the number of independent intermediates. The number I is algebraically determined for any given set of steps (7,8).

Particularly, for the set, Eqs. (3), we have $I = I' = 4$. Since $S = 5$ for Eqs. (3), we have $P = 1$ according to Eq. (8), hence the reaction route is unique in this case.

On the basis of the general theory leading to Eq. (8), it is generally shown that (4)

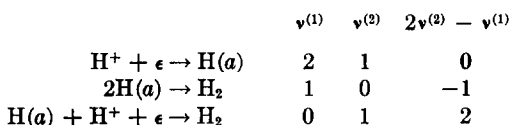$$\prod_{s=1}^{S} (k'_s/k''_s)^{\nu_s(p)} = K^{(p)} \qquad p = 1, \ldots, P.$$

where $\nu_s^{(p)}$ is the stoichiometric number of the sth step relevant to the pth reaction route and $K^{(p)}$ is the equilibrium constant of the over-all reaction, which results from the pth reaction route. The above theorem implies Eq. (4) as its special case, where $P = 1$.

However, the current concept of rate-determining step is only reasonably introduced into the case of $P = 1$.

It is a problem yet to be solved, whether the concept of the rate-determining step could be established in the other case, where $P > 1$. Simple introduction of the concept into the latter case may result in a confusion as exemplified below.

* Each of $n_1 - n_2$ and $n_2 - n_1$ is a simple example of the linear combination of the other.

Consider a set of steps

	$\mathbf{v}^{(1)}$	$\mathbf{v}^{(2)}$	$2\mathbf{v}^{(2)} - \mathbf{v}^{(1)}$
$H^+ + \epsilon \rightarrow H(a)$	2	1	0
$2H(a) \rightarrow H_2$	1	0	-1
$H(a) + H^+ + \epsilon \rightarrow H_2$	0	1	2

where ϵ is the metal electron of a hydrogen electrode and the only intermediate is $H(a)$, which is, of course, independent. $P = 2$ in this case according to Eq. (8). The two reaction routes may be $\mathbf{v}^{(1)}$ and $\mathbf{v}^{(2)}$, specified as above by the respective set of stoichiometric numbers 2, 1, 0, and 1, 0, 1 each designated under the notation of the appropriate reaction route on the right of the scheme of the relevant step. It may be noted that either reaction route, $\mathbf{v}^{(1)}$ or $\mathbf{v}^{(2)}$, results in the hydrogen electrode reaction

$$2H^+ + 2\epsilon = H_2 \qquad (9)$$
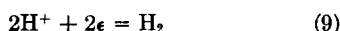
We might now examine the statement that the above over-all reaction occurs concurrently through both the reaction routes, $\mathbf{v}^{(1)}$ and $\mathbf{v}^{(2)}$, respectively, with the rate governed by the same step, $H^+ + \epsilon \rightarrow H(a)$. This statement would seem at first sight reasonable, but is associated with the following contradiction. The second and third steps, $2H(a) \rightarrow H_2$ and $H(a) + H^+ + \epsilon \rightarrow H_2$, must be far more rapid than the first one in accordance with the statement that the latter determines the rate, in either case, of the reaction routes. And the second and the third steps alone may give rise to the above over-all reaction along the reaction route $2\mathbf{v}^{(2)} - \mathbf{v}^{(1)}$ shown above, which is the vectorial linear combination of $\mathbf{v}^{(1)}$ and $\mathbf{v}^{(2)}$ with the stoichiometric numbers as the vector components. It follows that the over-all reaction should proceed far more rapidly through the reaction route $2\mathbf{v}^{(2)} - \mathbf{v}^{(1)}$, than concurrently through $\mathbf{v}^{(1)}$ and $\mathbf{v}^{(2)}$. The statement is thus self-contradictory.

THEOREMS ON ν_r

In the case $P = 1$, we have by definition of stoichiometric number

$$V = \frac{v'(s) - v''(s)}{\nu_s} \qquad s = 1, \ldots, S$$

where V is the steady rate of the over-all reaction and $v'(s) - v''(s)$ the net rate or the excess of the forward rate $v'(s)$ over the backward rate $v''(s)$ of sth step. The above equation is written for rth step and other s'th ones as

$$V = \frac{v'(r) - v''(r)}{\nu_r} = \frac{v'(s') - v''(s')}{\nu_{s'}}$$
$$s' = 1, \ldots, r - 1, r + 1, \ldots, S. \quad (10)$$

Let now both $v'(r)/\nu_r$ and $v''(r)/\nu_r$ be so small as compared with any of $v(s')/\nu_{s'}$ and $v''(s')/\nu_{s'}$ that the following conditions are practically fulfilled:

(i) The reaction is practically completed in either direction as soon as r takes place ν_r times in the appropriate direction.

(ii) The ratio of $v'(s')$ to $v''(s')$ is nearly unity.

It follows from (i) that the unidirectional rate V' or V'' of the over-all reaction is given as

$$V' = v'(r)/\nu_r \qquad V'' = v''(r)/\nu_r$$
$$(11, V'), (11, V'')$$

Hence according to Eq. (10)

$$V = V' - V'' \qquad (12)$$

The forward and backward rates, v' and v'', of a thermal step are now statistical-mechanically expressed as $(6, 10, 11)$

$$v' = \kappa(kT/h) \exp\left(-\frac{\mu^* - \mu^I}{RT}\right) \quad (13, v')$$

$$v'' = \kappa(kT/h) \exp\left(-\frac{\mu^* - \mu^F}{RT}\right), \quad (13, v'')$$

where κ is the transmission coefficient, k or h the Boltzmann or Planck constant*, μ^* the chemical potential of the critical complex, and μ^I or μ^F the chemical potential of the initial or the final complex, respectively. It is noted just for the present application that $(6, 10, 11)$ v' and v'' and the chemical potentials μ^*, μ^I, and μ^F are referred to the system, in which the step of interest is going on and that $(6, 10, 11)$ μ^*

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* The h will denote the Planck constant here only, but the amount of hydrogen everywhere else.

as well as κ is common to v' and v'' of the same step.

We have thus from Eq. (13) for sth step

$$\ln v'(s)/v''(s) = -\Delta F(s)/RT \quad (14a)$$

where

$$\Delta F(s) = \mu^{F(s)} - \mu^{I(s)} \quad (14b)$$

is by definition the increment of the free energy of the system of interest per mole occurrence of the sth step. It follows from (ii) and Eq. (14a) on the one hand approximately that

$$\Delta F(s') = 0 \quad (15,s')$$

and from Eqs. (11) and (14a) on the other hand that

$$\ln V'/V'' = -\Delta F(r)/RT \quad (15,r)$$

The increment ΔF of free energy per mole occurrence of the over-all reaction should be given as the total sum of $v_s\Delta F(s)$ over s as

$$\Delta F = \sum_{s=1}^{S} v_s\Delta F(s)$$

hence it follows from Eq. (15,s')

$$\Delta F = v_r\Delta F(r)$$

or according to Eq. (15,r)

$$\ln V'/V'' = -\Delta F/v_r RT \quad (16)$$

Further theorems are derived below from the fundamental theorem of Eq. (16).

(A) Eq. (16) is transformed as

$$V'/V'' = (Ka^L/a^R)^{1/v_r} \quad (17)$$

where K is the equilibrium constant of the over-all reaction and a^L or a^R are the activity products of the left- or the righthand side of the appropriate chemical equation; in the case of Eq. (2) for instance,

$$K = (a_e^{NH_3})^2/a_e^{N_2}(a_e^{H_2})^3, \qquad a^L = a^{N_2}(a^{H_2})^3,$$
$$\text{and} \qquad a^R = (a^{NH_3})^2$$

Equation (17) is derived from Eq. (16) as follows. ΔF is the difference of the chemical potential μ^R of the righthand side of the chemical equation minus the chemical potential μ^L of the lefthand side of the same chemical equation, i.e.,

$$\Delta F = \mu^R - \mu^L$$

The μ^R and μ^L are expressed as

$$\mu^R = \mu_1^R + RT \ln a^R$$
$$\mu^L = \mu_1^L + RT \ln a^L$$

where μ_1^R and μ_1^L are, respectively, constant at constant temperature. In equilibrium, we have $\mu^R = \mu^L$, hence

$$\mu_1^L - \mu_1^R = RT \ln a_e^R/a_e^L = RT \ln K$$

ΔF is expressed by the above four equations, as

$$\Delta F = RT \ln a^R/Ka^L \quad (18)$$

Equation (17) is obtained by substituting ΔF from Eq. (18) into Eq. (16).

Manes, Hofer, and Weller (2) have advanced the relation $V'/V'' = (Ka^L/a^R)^Z$ where Z is supposed to be a simple integer or its reciprocal, as an assumption, which sufficiently fits in with some particular examples. Eq. (17) verifies the above equation generally, elucidating the physical meaning of Z.

(B) Let the forward rate law be

$$V' = k' \prod_{m=1}^{M} (a^{B_m})^{f_m},$$

where a^{B_m} is the activity of the chemical species B_m ($m = 1, \ldots, M$) involved in the over-all reaction, f_m the appropriate exponent and k' the forward rate constant. The backward rate law is readily obtained by substituting V' from the above equation into Eq. (17) as

$$V'' = k'/K^{1/v_r} \prod_{m=1}^{M} (a^{B_m})^{f_m}/(a^L/a^R)^{1/v_r}$$

where the constant coefficient $k'/K^{1/v_r}$ is the backward unidirectional rate constant k'', i.e.

$$k'' = k'/K^{1/v_r}$$

which verifies Eq. (7) induced from the particular examples.

(C) Equation (7) leads to the relation

$$RT^2(d \ln k'/dT) - RT^2(d \ln k''/dT)$$
$$= (1/v_r)RT^2(d \ln K/dT) \quad (19)$$

between the activation energies and the heat of reaction $-RT^2 d \ln K/dT$, which should replace the well-known relation

$$RT^2(d \ln k'/dT) - RT^2(d \ln k''/dT)$$
$$= RT^2(d \ln K/dT)$$

derived from the classical theorem, Eq. (1).

Boreskov (12) introduced the concept of the molecularity of a chemical species of interest involved in an over-all reaction, which is experimentally determined, as deduced by him, as the ratio of the lefthand side of Eq. (19) to $RT^2 d \ln K/dT$ appropriate to the chemical equation of the over-all reaction with the coefficient of the chemical species of interest normalized to unity. The molecularity is thus, according to Eq. (19), the reciprocal of v_r referred to the chemical equation normalized as above to the chemical species of interest.

Boreskov (12) defined the molecularity as the number of the chemical species of interest involved in the rate-determining step. Equation (2) is now, as it is, normalized to nitrogen. The molecularity of nitrogen is hence 1, 1/3, or 1/2 by Eq. (19), according to whether (3,N) or (3,H) or one of (3,NH), (3,NH$_2$) and (3,NH$_3$), respectively, determines the rate. The first or the third value of the molecularity fits in with the definition, as N_2 is involved as a whole or by its dissociated half in the respective rate-determining step, but the second value is not, since no N_2 is involved in the relevant rate-determining step.

(D) We have from Eq. (16)

$$V = -V'_e \Delta F / v_r RT \qquad (20)$$

in the neighborhood of equilibrium, where $V = V' - V''$ is sufficiently small compared with V' or V'', hence the latter is nearly equal to the unidirectional rate $V_e' = V_e''$ in equilibrium, by expanding the lefthand side of Eq. (16) with respect to $(V' - V'')/V''$, ignoring the terms higher than the first order one and identifying the denominator V'' of the first order term with V_e'. Equation (20) shows that V is proportional to the affinity $-\Delta F$ of the reaction in the neighborhood of equilibrium.

This theorem was previously stated by Prigogine *et al.* (13) based on particular rate laws. Equation (20) states it generally, irrespective of any particular rate law.

EXPERIMENTAL METHODS OF v_r DETERMINATION

(I) If we are provided with an isotopic tracer without any isotopic difference of rates, v_r is experimentally determined by the method exemplified below by the catalyzed synthesis of ammonia.

Consider that N^{15}-shifted nitrogen, hydrogen, and ammonia is circulated over a definite portion of synthetic catalyst through a system of definite volume, and that the total number n of moles of nitrogen and the N^{15} atomic fraction Z^N in nitrogen or that Z^A in ammonia are, respectively, followed with time t. The rate of transfer of N^{15} from nitrogen to ammonia is expressed as $-d(2nZ^N)/dt$ or as $2Z^N V' - 2Z^A V''$, so that we have

$$-d(nZ^N)/dt = Z^N V' - Z^A V''$$

The rate $-dn/dt$ of decrease of nitrogen is given as

$$-dn/dt = V' - V'' \qquad (21)$$

We have from the above two equations

$$V''(Z^A - Z^N) = n dZ^N/dt \qquad (22)$$

The total amount $aZ^A + 2nZ^N$ of N^{15} in the mixture is constant and given in terms of the constant total amount $a + 2n$ of nitrogen atoms in the mixture and the atomic fraction Z_i at the equilibrium distribution of N^{15}, as

$$aZ^A + 2nZ^N = (a + 2n)Z_i \qquad (23)$$

where a is the total number of moles of ammonia in the system.* Admitted that the both sides of Eq. (23) are known from the initial values of a, n, Z^A and Z^N, the momentary values of V' and V'' are determined by Eqs. (21), (22) and (23) from observations of n and Z^N or Z^A at every

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* a, a_e etc., in this section, denote the total number of moles of ammonia in the system. a^L and a^R, and $a_e{}^L$ and $a_e{}^R$, however, are the activity products of Eq. (17).

moment along with the progress of the over-all reaction, Eq. (2).

The corresponding values of a^L and a^R on the righthand side of Eq. (17) are determined, identifying activity of the gaseous components with relevant concentration, as

$$a^L = nh^3/\varphi^4$$
$$a^R = a^2/\varphi^2$$

where h is the number of moles of hydrogen in the system and φ is the volume of the system, through which the mixture is circulated. The equilibrium constant $K \equiv a_e{}^R / a_e{}^L$ is expressed in accordance with the above equations, as

$$K = \varphi^2 a_e^2 / n_e h_e^3 \qquad (24)$$

where suffix e signifies quantities at equilibrium. The argument Ka^L/a^R of the right-hand side of Eq. (17) is now expressed by the above three equations as

$$Ka^L/a^R = (n/n_e)(h/h_e)^3/(a/a_e)^2 \qquad (25)$$

The momentary values h and a are determined from the observed momentary value of n by the stoichiometric relation in accordance with Eq. (2), i.e.,

$$n_0 - n = (h_0 - h)/3 = (a - a_0)/2, \qquad (26a)$$

where n_0, etc. are initial values of n, etc. The n_e, h_e, and a_e are evaluated by Eq. (24) and the particular case of Eq. (26a), i.e.,

$$n_0 - n_e = (h_0 - h_e)/3 = (a_e - a_0)/2 \qquad (26b)$$

Ka^L/a^R is thus evaluated by Eq. (25), hence v_r is determined at every moment at a different extent of deviation from equilibrium.

The v_r determination of Eq. (2) by this method is now being carried forward by K. Tanaka in this laboratory. The v_r of the same reaction has previously been determined according to Eq. (20) by measuring V_e' and $(V/\Delta F)_e$ with the result that $v_r = 2$ (17). Since then Bokhoven et al. (18) modified the latter method and found $v_r = 1$. The conflicting results have been discussed in further papers (19, 20).

(II) In the case of an electrode reaction, where a tracer without an isotopic differ-

ence of rate is available, the v_r is determined similarly but with ΔF in Eq. (16) expediently expressed in terms of directly observable overvoltage η as

$$\Delta F = n^\epsilon F \eta \qquad (27)$$

where F is Faraday and n^ϵ the number of electrons given out from the electrode for every act of the over-all electrode reaction.

ΔF is, e.g., $\Delta F = \mu^{H_2} - 2(\mu^{H^+} + \mu\epsilon)$ for the hydrogen electrode reaction (9), where μ^{H_2}, etc., are the chemical potentials of H_2, etc. For a reversible hydrogen electrode with hydrogen and hydrogen ion, of the same chemical potentials, we have $0 = \mu^{H_2} - 2(\mu^{H^+} + \mu_e\epsilon)$, where $\mu_e\epsilon$ is the particular value of $\mu\epsilon$ for the reversible hydrogen electrode. We have hence $\Delta F = 2(\mu_e\epsilon - \mu\epsilon)$, where $\mu\epsilon - \mu_e\epsilon$ is the work required to transfer one mole of metal electron from the reversible to the test electrode. By the definition of overvoltage,

$$\mu^\epsilon - \mu_e{}^\epsilon = -F\eta \qquad (28)$$

hence $\Delta F = 2F\eta$.

This argument is readily extended to the general case, where $\Delta F = n^\epsilon F \eta$. The n^ϵ is 2 for the zinc electrode reaction $Zn^{2+} + 2\epsilon = Zn$, as well as for the hydrogen electrode reaction (9), and it is -4 for the oxygen electrode reaction, $4OH^- = O_2 + H_2O + 4\epsilon$.

Substituting ΔF from Eq. (27) into Eq. (16), we have

$$\ln V'/V'' = -n^\epsilon F \eta / v_r RT \qquad (29)$$

The lefthand side of Eq. (29) is determined quite similarly as in Section (I) by observing isotopic contents of reactants and the over-all rate in terms of the electrode current. The v_r is determined by Eq. (29) at every moment at different values of overvoltage.

The determination of v_r of the oxygen electrode reaction on platinum is being conducted by T. Kodera in this laboratory by the method outlined above, using O^{18} as tracer.

Losev (14) has observed the transfer of radioactive zinc in a zinc amalgam electrode to $N/10$ $ZnSO_4$ (aq.) or its reversal simultaneously with the current and over-

voltage; this provides a complete requisite set of data for determining v_r. The lefthand side of Eq. (29) calculated from the observation (14) was found to vary fairly in proportion to the observed η and the relevant value of the proportionality constant was found to give $v_r = 1$ for $n\epsilon = 2$ (15). This means that the rate-determining step occurs, whatever it may be, once for every act of the over-all zinc electrode reaction, $Zn^{2+} + 2\epsilon = Zn$, amal.

(III) The v_r determination of the hydrogen electrode reaction is not conducted as in (I) or (II) by means of hydrogen isotope as a tracer because of the pronounced isotopic difference in rates. The first determination of v_r (16) was conducted with the hydrogen electrode on platinum by means of deuterium as a tracer under the assumption that the unidirectional rate of deuterium transfer is proportional to that of protium over the whole range of η observed.

An alternative v_r determination of the same kind of electrode reaction is now carried on by A. Matsuda in this laboratory without relying upon the above assumption, by observing the rate of transfer of sparse tritium from hydrogen gas to hydrogen ion, or the rate of the reverse reaction. It is admitted that (i) tritium participates in the hydrogen electrode reaction by the same mechanism as the predominant isotope, i.e., protium, and that (ii) the unidirectional rate V' of tritium transfer from the state of ion to that of gas or the V'' of the reverse reaction depends on, in addition to η, only the tritium fraction in the state from which it is transferred. Because of the sparse fraction of tritium and (i) above, the tritium transfer occurs, practically, by the over-all reaction

$$T^+ + H^+ + 2\epsilon = TH$$
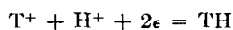
The ratio of the forward unidirectional rate V' of the latter reaction to that V'' of the reverse one is given by Eq. (16) in terms of the appropriate ΔF, i.e.,

$$\Delta F = \mu^{HT} - \mu^{H^+} - \mu^{T^+} - 2\mu^\epsilon$$

Differentiating ΔF with respect to η, we have, referring to Eq. (28)

$$\partial \Delta F / \partial \eta = 2F$$

Hence according to Eq. (16)

$$\alpha' + \alpha'' = 2/v_r$$

where

$$\alpha' = -\frac{RT}{F}\frac{\partial \ln V'}{\partial \eta}$$

$$\alpha'' = \frac{RT}{F}\frac{\partial \ln V''}{\partial \eta}$$

The α' is determined according to (ii) above from the dependence on η of the initial value of V' at a constant tritium fraction in hydrogen ion and in its absence in hydrogen gas. The α'' is similarly determined from the initial rate of tritium from hydrogen gas of constant tritium fraction to hydrogen ion free from tritium. The v_r is thus determined by the above three equations.

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