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APPLICATION OF THE STOICHIOMETRIC NUMBER METHOD TO INVESTIGATION OF MULTISTEP REACTIONS

By

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On the basis of the non-equilibrium thermodynamics the regularities of a complex reaction close to equilibrium is examined. It is shown that the rate of any separate step can always be written as proportional to the electrochemical affinity of the same step only. The formula for the phenomenological coefficient of the overall reaction is derived. This formula is a generalization of the Horiuti's formula for the case of multiroute multi-step reactions. The expression interrelating the experimental values of the extrapolated stoichiometric numbers of the reaction is obtained. This expression can be used as a criterion of validity of the suggested reaction mechanism. The physical meaning of the experimental stoichiometric number in the case of consecutive and parallel steps is discussed.

As a matter of fact Horiuti proposed his concept of stoichiometric number in the very first issue of this Journal¹⁾ though it can be considered as further development of the ideas already outlined in the literature²⁾. In his paper¹⁾ Horiuti introduced the notion of the stoichiometric number of the step (henceforth called the true stoichiometric number of the step), which is equal to the number of its occurrences for the overall reaction to occur once, and derived the formula for calculation of the true stoichiometric number of the rate determining step of the reaction

$$\nu = \frac{V^0}{RT} \left(\frac{\partial V}{\partial A} \right)_{A=0} \quad \text{or} \quad \nu = \frac{nFI^0}{RT} \left(\frac{\partial I}{\partial \eta} \right)_{\eta=0}, \quad (1)$$

where $V(I)$ is the process rate (the electric current); $V^0(I^0)$ is the exchange rate (current); A is the electrochemical affinity according to De Donder; η is the overpotential; n is the total number of electrons transferred for one overall reaction as written. The exchange current can be determined, for instance, by extrapolation from the Tafel plot to the equilibrium potential.

It is evident, however, that equation (1) is applicable only to single-route reactions involving a single slow step. But in the general case the

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quantity $(\partial V/\partial A)_{A=0}$ (as well as $(\partial I/\partial \eta)_{\eta=0}$) is determined by all irreversible reaction steps. Moreover, there arises an uncertainty as to what quantity should be used as I^0 in (1) — the exchange current of the overall reaction, or the exchange current obtained by extrapolation from the Tafel plot. In the case of the reaction involving several slow steps neither of the quantities thus determined coincides with the number of occurrences of the rate determining step. In the present communication based on the papers^{3~6} the course of a complex reaction close to equilibrium is examined and a relation is given for the phenomenological coefficient of the overall reaction $(\partial V/\partial A)_{A=0}$ expressed in terms of those of the separate steps. This relation is a generalization of equation (1) to reactions with an arbitrary number of routes and slow steps. This suggests a possibility of using equation (1) for investigation of such reactions. The reasoning is similar in some aspects to that reported.^{7,8} Our approach is based on some relations of non-equilibrium thermodynamics and on this account it has an advantage that it does not depend on any physical models (such as, for instance, the transition state theory), *i.e.* it does not involve any particular dependences of the reaction parameters (activation energy, surface coverage by intermediates, reaction rate) on the electrode potential.

Consider a certain multistep reaction running along several routes, all corresponding to the same stoichiometric equation. We now introduce the following designations. Let the overall reaction rate, as generally accepted, be defined as $V \equiv d\xi/d\tau$, where τ is the time, and ξ is the extent of the overall reaction. In exactly the same way we can define the rate of a step i as $v_i \equiv d\xi_i/d\tau$, ξ_i is its extent. Here ξ and ξ_i are calculated with regard to stoichiometric coefficients in the chemical equations of the overall reaction and the step i , respectively. Then we can write for the overall reaction current $I = nFV$. The overall reaction rate is the sum of its rates along all the routes

$$V = \sum_p V_p, \quad (2)$$

where p denotes the serial number of a route, and V_p is the overall reaction rate along the route p . The total number of the routes in (2) is equal to the number of independent routes P , which can be determined by formula⁷

$$P = I - S \quad (3)$$

where I is the total number of different steps, and S is the number of the kinds of intermediates. Similarly the rate of any step i can be regarded as the sum of its rates along each route

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$$v_i = \sum_p v_{pi} \quad (4)$$

Let v_{pi} and ν_{pi} denote the rate and the true stoichiometric number of a step i in a route p . Then for the given route p the effective rates of all the steps (*i.e.* expressed in terms of the overall reaction rate) $V_{pi} \equiv v_{pi}/\nu_{pi}$ are identical and equal to the overall reaction rate along the route p

$$V_{pi} = V_p \quad (5)$$

Formula (5) can be regarded as the steady-state condition for the route p . Formulae (4) and (5) give the steady-state condition of the overall reaction in the form;

$$v_i = \sum_p \nu_{pi} V_p, \quad (6)$$

which was derived by other methods in the literature.⁷⁻¹¹

It was shown¹² that for a single-route reaction, involving a single slow step, the expression

$$V = \left(\frac{\partial V}{\partial A} \right)_{A=0} A \quad (7)$$

is valid, if the reaction affinity A is rather small; the quantity $(\partial V/\partial A)_{A=0}$, called the phenomenological coefficient of the reaction, does not depend on A . The applicability of equation (7) to complex multiroute reactions has not been investigated, though substantial difficulties may arise here. Moreover, it is not clear if the equation of the type of (7) is applicable even to a separate step of a complex process. Indeed, in the general case the rate of a separate step i can in principle depend on the affinities of all reaction steps, that is

$$v_i = \sum_j^I g_{ij} A_j, \quad (8)$$

where g_{ij} are constants if A_j are small. In ref.¹², a single-route reaction, consisting of steps with the true stoichiometric numbers equal to 1, is considered. Postulating $g_{ij}=0$ with $i \neq j$, the authors¹² showed for an ideal system, that $(\partial v_i / \partial A_i)_{A=0} = v_i^0 / RT = g_{ii}$, whence in accordance with (7) $(\partial V / \partial A)_{A=0} = (\sum_i g_{ii}^{-1})^{-1}$. We now show that the expression of the type of (7) is applicable to a separate step of a complex reaction in the general case.

With the help of (4), (6) and (8) the effective rates of the steps for a route p can be written as

$$\begin{aligned} V_{p1} &= a_{11}^{(p)} A_1 + \cdots + a_{1I}^{(p)} A_I \\ &\dots, \\ V_{pI} &= a_{I1}^{(p)} A_1 + \cdots + a_{II}^{(p)} A_I \end{aligned}$$

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where $a_{ij}^{(p)}$ are constants; i is the serial number of a step; or in the form of the matrix equation $\|a_{ij}^{(p)}\| \cdot \|A_j\| = \|V_{pi}\|$, $p=\text{const}$. Hence $\|A_j\| = \|b_{ji}^{(p)}\| \cdot \|V_{pi}\|$, where $\|b_{ji}^{(p)}\| = \|a_{ij}^{(p)}\|^{-1}$. Taking into consideration the steady-state condition (5), we obtain the following simultaneous equations

$$\begin{aligned} A_1 &= V_A \sum_j^I b_{1j}^{(p)} \\ &\dots, \\ A_I &= V_p \sum_j^I b_{Ij}^{(p)} \end{aligned}$$

whence, assuming $A_j=0$ for all j with $A=0$, we have $(\partial V_p / \partial A_i)_{A=0} = (\partial V_{pi} / \partial A_i)_{A=0} = \left(\sum_j^I b_{ij}^{(p)}\right)^{-1}$. Thus the phenomenological coefficient of a separate step is a constant independent of the change of affinity of other steps. Close to equilibrium $V_p = \left(\sum_j^I b_{ij}^{(p)}\right)^{-1} A_i$ is valid, and allowing for (6)

$$v_i = -\frac{v_i^o}{RT} A_i \quad (9)$$

where

$$v_i^o = \sum_p v_{pi}^o; \quad v_{pi}^o \equiv v_{pi} RT (\partial V_{pi} / \partial A_i)_{A=0} \quad (10)$$

The derived relations are valid also for non-ideal systems to the extent that the involved quantities v_i^o and v_{pi}^o are independent of A_i close to equilibrium. It should be noted, that in the general case (e.g., for branched reactions) v_{pi}^o as well as v_i^o can not be identified with the diagonal elements a_{ii} and g_{ii} of the matrices $\|a_{ij}\|$ and $\|g_{ij}\|$, as it sometimes done, *i.e.* the non-diagonal elements of the matrix $\|g_{ij}\|$, characterising the interrelationship between the generalized fluxes or rates of different steps, can also make a contribution to the exchange rate (current) of a separate step.

The dependence of the phenomenological coefficient of the overall reaction $(\partial V / \partial A)_{A=0}$ on the phenomenological coefficients of the separate steps is of interest. These are understood to mean the quantities $(\partial V_{pi} / \partial A_i)_{A=0} = (\partial V_p / \partial A_i)_{A=0}$. It is convenient to introduce the exchange rates of steps defined as $V_{pi}^o = v_{pi}^o / v_{pi}$ (henceforth called effective). Then close to equilibrium it follows from (9) that

$$V_{pi} = \frac{V_{pi}^o}{RT} A_i. \quad (11)$$

Differentiating (11) with respect to A , we have

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$$(\partial V_{pi}/\partial A)_{A=0} = (V_{pi}^o/RT)(\partial A_i/\partial A)_{A=0} \quad (12)$$

We use the expression for the overall reaction affinity^{7,8)}

$$A = \sum_i \nu_{pi} A_i, \quad (13)$$

which is also differentiated with respect to A

$$\sum_i \nu_{pi} (\partial A_i / \partial A)_{A=0} = 1 \quad (14)$$

Besides it follows from (5), (12) and (14) that

$$(\partial V_p / \partial A)_{A=0} = [RT \sum_i \nu_{pi} / V_{pi}^o]^{-1}, \quad (15)$$

and from (2) that

$$(\partial V / \partial A)_{A=0} = (\partial V_p / \partial A)_{A=0}. \quad (16)$$

Substituting (15) into (16) we have the following expression

$$\left(\frac{\partial V}{\partial A} \right)_{A=0} = \frac{1}{RT} \sum_p \left[\sum_i (\nu_{pi} / V_{pi}^o) \right]^{-1} = \frac{1}{RT} \sum_p \left[\sum_i (\nu_{pi}^2 / V_{pi}^o) \right]^{-1}, \quad (17)$$

the particular form of which for the single-route reaction was derived in the literature.^{9,13~15)} We rewrite (17) in electrical terms. For this purpose we write the corresponding expressions for A , V and V_{pi}^o : $A = nF\eta$; $I = nFV$; $I_{pi}^o = nFV_{pi}^o$; besides $i_{pi}^o = n_i Fv_{pi}^o$ (whence $I_{pi}^o = i_{pi}^o n / \nu_{pi} n_i$). Hence n_i is the number of electrons participating in one act of a step i ; i_{pi}^o is the exchange current of the step i in a route p ; I_{pi}^o is the effective exchange current of the step pi . Then

$$\left(\frac{\partial I}{\partial \eta} \right)_{\eta=0} = n^2 F^2 \left(\frac{\partial V}{\partial A} \right)_{A=0} = \frac{nF}{RT} \sum_p \left[\sum_i (\nu_{pi} / I_{pi}^o) \right]^{-1}, \quad (18 \text{ a})$$

and

$$\left(\frac{\partial I}{\partial \eta} \right)_{\eta=0} = \frac{n^2 F}{RT} \sum_p \left[\sum_i (\nu_{pi}^2 n_i / i_{pi}^o) \right]^{-1} \quad (18 \text{ b})$$

Formulae (17) and (18) are the generalization of Horii's formulae (1) and reduce to these in the case of a single-route reaction involving a single irreversible step. In the case of reactions involving slow chemical steps it is advisable to use formula (18), in which the exchange currents of the steps are expressed in electrical terms.

In the case of a single-route reaction formulae (18) reduce to

$$\left(\frac{\partial I}{\partial \eta} \right)_{\eta=0} = \frac{nF}{RT} / \sum_i (\nu_i / I_i^o) = \frac{n^2 F}{RT} / \sum_i (\nu_i^2 n_i / i_{pi}^o), \quad (19 \text{ a})$$

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and in the case of a reaction consisting of parallel routes, where each route involves a single slow step, we have

$$\left(\frac{\partial I}{\partial \eta} \right)_{\eta=0} = \frac{nF}{RT} \sum_p \frac{I_p^o}{v_p} = \frac{n^2 F}{RT} \sum_p \frac{i_p}{v_p^2 n_p}, \quad (19 \text{ b})$$

where n_p is the number of electrons participating in one act of the slow step in a route p .

The use of (17) and (18) presumes knowledge of the exchange rates or currents in the separate routes, which can be determined with the help of relations (2)-(7), (9)-(11), (13) and (17). This approach is rather cumbersome, though it corresponds to the graphical representation of the overall reaction as an analogue of an electric circuit with parallel branches-routes, in which the consecutive sections correspond to separate steps. The quantities V_{pi}^o/RT represent the conductivities of these sections. The knowledge of the extent of participation of each step in different routes as well as of the distribution of the overall reaction affinity among the steps may be useful. Furthermore, in most important particular cases formulae (17) and (18) can be easily simplified (*e.g.*, see (19)). It is expedient however to derive a formula for $(\partial V/\partial A)_{A=0}$ directly expressed in terms of the exchange rates of the steps $-v_i^o$. This can be done in the following way.

It follows from (6) and (9) that $\sum_p v_{pi} V_p = v_i^o A_i/RT$ whence $A_i = RT \sum_p v_{pi} V_p / v_i^o$. Substituting this expression into (13), we have

$$\sum_i \frac{v_{pi}}{v_i^o} \sum_p v_{pi} V_p = A/RT \quad (20)$$

This equation conforms to the following simultaneous equations

$$RT \cdot \begin{vmatrix} c_{11} & \cdots & \cdots & c_{1P} \\ \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots \\ c_{P1} & \cdots & \cdots & c_{PP} \end{vmatrix} \begin{vmatrix} V_1 \\ \vdots \\ \vdots \\ V_P \end{vmatrix} = \begin{vmatrix} A \\ \vdots \\ \vdots \\ A \end{vmatrix}, \quad (21)$$

where a certain chosen equation with the serial number k can be written in the form

$$\sum_i \sum_p \frac{v_{ki} v_{pi}}{v_i^o} V_p = A/RT. \quad (22)$$

Formula (22) was derived in a different way in ref. (9). It should be noted that in agreement with Onsager's reciprocal relations the matrix $||c||$ in (22) is symmetrical $c_{kj} = c_{jk} = \sum_i \frac{v_{ki} v_{ji}}{v_i^o}$. Solving (21) with respect to V_1, \dots, V_P ,

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differentiating the obtained values with respect to A and substituting the derivatives into (16) we can determine $(\partial V/\partial A)_{A=0}$.

Relations (17), (18) and (20), (21) reflect different approaches to the analysis of the reaction, which have their advantages and shortcomings. Apparently relations (20), (21) are more convenient for calculation of $(\partial V/\partial A)_{A=0}$ in the case of branched reactions, where an intermediate can participate in several routes, whereas (17), (18) are preferable in the case of single-route reactions and multi-route reactions, in which each route involves only one slow step. Moreover, as mentioned before, formulae (17) and (18) have a clear physical meaning showing that the procedure of calculating the phenomenological coefficient of the overall reaction from the phenomenological coefficients of the steps is similar to calculating the conductivity of a complex electric circuit from the conductivities of its separate sections (see eqs. (18) and (19)).

Formulae (17) and (18) can be used to analyse a multistep reaction scheme. The combination of these relations with formula (1) opens a convenient way for this analysis. However, as mentioned earlier, its use involves the necessity of introducing at least two kinds of ν corresponding to two different definitions of the exchange current I^0 appearing in (1). These are the mean stoichiometric number $\bar{\nu}$ obtained by substituting the exchange rate (current) of the overall reaction into (1), which will not be considered in detail here*) (see, refs. (3, 4)) and the effective stoichiometric numbers ν_{pi}^o obtained by substituting the values of I_{pi}^o (or V_{pi}^o) into (1), *i.e.*

$$\nu_{pi}^o \equiv \frac{V_{pi}^o}{RT} / \left(\frac{\partial V}{\partial A} \right)_{A=0} = \frac{nFI_{pi}^o}{RT} / \left(\frac{\partial I}{\partial \eta} \right)_{\eta=0}. \quad (23)$$

The quantities ν_{pi}^o are of interest first of all for the reason that in many practically important cases they coincide with the stoichiometric numbers calculated by using the extrapolated exchange current in (1). Indeed, for instance, in the case of an electrochemical reaction involving several slow steps the polarisation curve usually consists of several Tafel sections, each of which corresponds to its own rate determining step. Transition from

*) The methods of determination of $\bar{\nu}$ in the case of single-route reactions are based on the relation $\bar{V}/\hat{V} = \exp(A/\bar{\nu}RT)$, \bar{V} and \hat{V} close to equilibrium being determined either by the tracer method or from the deviation of the polarisation curve from the Tafel plot (see e.g. refs. 16, 17) under the assumption of the constancy of the apparent transfer coefficient in the potential region under investigation (for some difficulties involved here see ref. 5). If an intermediate participates in several routes, then the value of the overall reaction exchange current and consequently $\bar{\nu}$ (but not its phenomenological coefficient) become indefinite, though they still have to comply with certain restrictions.

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one section to another is thus caused by the change of the rate determining steps either in the set of consecutive steps of one route or in the case of a change of the route itself. Since each Tafel section corresponds to its own extrapolated exchange current, it is possible to calculate for each section by formula (1) its stoichiometric number (called sometimes the extrapolated stoichiometric number^{18,19}). In the case of the Langmuir adsorption isotherm of an electroactive intermediate the exchange currents, estimated by extrapolation from different Tafel sections, usually coincides with the effective exchange currents of the corresponding rate determining steps. Therefore the extrapolated stoichiometric numbers calculated by formula (1) using the extrapolated exchange currents coincide with the effective stoichiometric numbers defined by (23).

Comparing (23) and (17) or (18) it is easy to obtain the expression correlating the ν_{pi}^o values of all reaction steps

$$\sum_p \left[\sum_i (\nu_{pi}/\nu_{pi}^o) \right]^{-1} = 1. \quad (24)$$

In the case of a single-route reaction it reduces to

$$\sum_i \frac{\nu_i}{\nu_i^o} = 1. \quad (24 \text{ a})$$

In particular, if a reaction involves two consecutive slow steps with true stoichiometric numbers equal to 1 ($\nu_1 = \nu_2 = 1$) the following equivalent formulae obtained from (24 a) can be used

$$\frac{1}{\nu_1^o} + \frac{1}{\nu_2^o} = 1; (\nu_1^o - 1)(\nu_2^o - 1) = 1; \nu_1^o + \nu_2^o = \nu_1^o \cdot \nu_2^o.$$

In the case of a multi-route reaction, where each route involves a single slow step, the following formula holds true

$$\sum_p \frac{\nu_p^o}{\nu_p} = 1. \quad (24 \text{ b})$$

The presence of several Tafel sections on the polarisation curve in cathodic and/or anodic potential regions makes it possible, as mentioned earlier, to calculate several values of the extrapolated stoichiometric numbers. If changes of the polarisation curve slope are caused by the change of the rate determining steps (also in some other causes⁹), then neither of the extrapolated stoichiometric numbers is equal to the true stoichiometric number, and consequently not equal to the number of the occurrences of the rate determining step. Formulae (24) make it possible to use the experimental values of the extrapolated stoichiometric numbers. Assuming various

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possible mechanisms, *i.e.* substituting various sets of true stoichiometric numbers ν_{pi} into (24) we can determine which one satisfies these formulae. Therefore, formulae (24) actually represent a quantitative criterion of the multistep reaction mechanism. In this connection the impossibility of an adequate choice of the true reaction scheme, *i.e.* the set of the true stoichiometric numbers, satisfying (24), shall mean, that the slope change on the polarisation curve is caused not by the change of the rate determining step, but, *e.g.*, by the change of the surface nature, by the change of the true transfer coefficient of the rate determining step, if it is the same for several sections of the polarisation curve, by non-Langmurian character of the adsorption isotherm of an intermediate etc.

Naturally, for a more or less definite conclusion about the reaction mechanism it is necessary to have at one's disposal some data on the reaction orders, the values of the apparent transfer coefficient *etc.*, *i.e.* to use in analysis as large a variety of experimental data as possible.

Relations (24) were used in investigating the kinetics of the chlorine reaction on graphite and DSA.^{20,21}

Now we analyse the physical meaning of (24). As it is seen from (23) and (24 a) the terms ν_i/ν_i^o , corresponding to the slowest steps (with the least values of V_i^o or I_i^o and consequently the most values of A_i close to equilibrium) make the largest contribution to (24 a). From (12) and (13) it is easy to obtain

$$1/\nu_i^o = (\partial A_i / \partial A)_{A=0}. \quad (25)$$

Thus, ν_i/ν_i^o represents the contribution of the given step *i* to the total deviation of the overall reaction from equilibrium. The larger is the ratio ν_i/ν_i^o , the slower is the step *i* in comparison with other consecutive reaction steps. The sum of all the relative contributions is equal to 1.

Similarly, for a reaction with parallel routes it follows from (5), (12), (15) and (23) that

$$\nu_p^o/\nu_p = (\partial V_p / \partial A)_{A=0}, \quad (26)$$

i.e. the quantity ν_p^o/ν_p represents the contribution of a given route *p* to the total rate of the overall reaction close to equilibrium.

It should be noted, that the effective stoichiometric number ν_{pi}^o and the mean stoichiometric number $\bar{\nu}$ are fundamentally different. For example, in the case of a single-route reaction the following formula is valid for $\bar{\nu}$ ^{3,4,10,11}

$$\bar{\nu} = \sum_i \nu_i A_i / \sum_i A_i = A / \sum_i A_i \quad (27)$$

(*cf.* (25)). It is necessary to bear in mind this difference in analysing the

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reaction mechanism using simultaneously the stoichiometric number values estimated by different methods. The values of ν and ν_i^o coincide in the case of a single-route reaction involving a single slow step (see also ref. (6) concerning restrictions in the θ value).

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