THE STOICHIOMETRIC NUMBER OF A CHEMICAL REACTION

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Let us consider a reaction which takes place by several independent paths, each of which involves several slow nonequilibrium stages.

The following notation is used: let $A = -\sum_s f_s \mu_s$ be the De Donder affinity [1,2] of the overall reaction, where f_s are the stoichiometric coefficients of the materials in the chemical equation of the reaction; these coefficients are positive for the products and negative for the reactants; μ_s are their chemical (electro-chemical) potentials; $V = \vec{V} - \overleftarrow{V}$ is the overall reaction rate, equal to the difference in the number of its transits in the forward and reverse direction in unit time; V^0 is the exchange rate of the overall reaction, i.e. $V^0 = \vec{V} = \overleftarrow{V}$ when $A = 0$; $V_p = \vec{V}_p - \overleftarrow{V}_p$ is the overall reaction rate by path p; V_p^0 is the exchange rate of the reaction by path p; A_{pi} is the affinity of stage i in path p; ν_{pi} is the true stoichiometric number of stage pi, equal to the number of its transits occurring per transit of the overall reaction by path p; $v_{pi} = \vec{v}_{pi} - \overleftarrow{v}_{pi}$ is the rate of stage pi, equal to the difference in the number of transits of the stage in the forward and reverse directions in unit time; $V_{pi} = v_{pi}/\nu_{pi} = \vec{V}_{pi} - \overleftarrow{V}_{pi}$ is the rate of stage pi, expressed as the equivalent number of transits of the overall reaction, whence $\vec{V}_{pi} = \vec{v}_{pi}/\nu_{pi}$ and $\overleftarrow{V}_{pi} = \overleftarrow{v}_{pi}/\nu_{pi}$.

It is assumed that the same chemical equation of the overall reaction corresponds to the different paths. For heterogeneous reactions taking place on an energetically nonuniform surface with a finite number of different types of sites, at which the reaction takes place at different rates or even by a different mechanism, it is convenient to relate these parts of the surface to different independent paths.

The equation valid for the elementary stage is [3]

$$\vec{v}_{pi}/\overleftarrow{v}_{pi} = \vec{V}_{pi}/\overleftarrow{V}_{pi} = \exp(A_{pi}/RT'). \tag{1}$$

Since in stationary conditions $V_p = V_{pi}$, then

$$V_p = \overleftarrow{V}_{pi}(\vec{V}_{pi}/\overleftarrow{V}_{pi} - 1) = \overleftarrow{V}_{pi}[\exp(A_{pi}/RT) - 1].$$

Differentiating this equation with respect to A we have, at A = 0,

$$(\partial V_p/\partial A)_{A=0} = (V_{pi}^0/RT)(\partial A_{pi}/\partial A)_{A=0}. \tag{2}$$

Equation (2) can be obtained immediately by using the nonequilibrium thermodynamics equation [2]

$$V_{pi} = V_{pi}^0 A_{pi}/RT, \tag{3}$$

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which applies when $A_{pi} \ll RT$. Taking the expression for $(\partial A_{pi}/\partial A)_{A=0}$ obtained from (2) and putting it into the equation $\Sigma \nu_{pi} (\partial A_{pi}/\partial A)_{A=0} = 1$, which follows from

$$A = \sum_i \nu_{pi} A_{pi}, \tag{4}$$

we obtain $(\partial V_p/\partial A)_{A=0} = 1/RT \sum_i (\nu_{pi}/V^0_{pi})$. For independent paths $V = \sum_p V_p$ and therfore $(\partial V/\partial A)_{A=0} = \sum_p (\partial V_p/\partial A)_{A=0}$, whence

$$\left(\frac{\partial V}{\partial A}\right)_{A=0} = \frac{1}{RT} \sum_p \frac{1}{\sum_i (\nu^2_{pi}/\nu^0_{pi})} = \frac{1}{RT} \sum_p \frac{1}{\sum_i (\nu_{pi}/V^0_{pi})}. \tag{5}$$

A similar expression for the particular case of a single-path heterogeneous electrochemical reaction has been given in [4].

There is an analogy between multistage reactions and a branched electrical circuit. In the framework of this analogy the quantity $(\partial V/\partial A)_{A=0}$ can be called the conductivity of the reaction close to equilibrium. For a single-path reaction with one slow stage Horiuchi [3] has given an equation which enables the true stoichiometric number of the slow stage r to be calculated from experimental data:

$$\nu_r = (V^0/RT) / (\partial V/\partial A)_{A=0}. \tag{6}$$

The value of V^0 can be determined directly in certain cases (for example by a radiochemical method) or by extrapolating V from regions far from equilibrium. At certain slow stages the true exchange rate V^0 and the extrapolated value V^0_e must be different. In this case, at a different degree of nonequilibrium of the reaction, i.e. when A is changing, a change may be observed in the rate of the determining stage and the possibility arises of determining several values of V_e^0. If the concentrations of the intermediate reaction products in the reaction zone maintain limiting values over the whole range of A studied (i.e., when their mole fractions or degrees of surface coverage are close to 0 or 1) or are not at all dependent on A, then V_e^0 coincides with V_{pi}^0, the rate of the determining stage.

In the general case, in addition to the so-called extrapolated stoichiometric number ν', which is calculated using V_e^0, [5-8], it is useful to introduce also the value ν_{pi}^0, defined as

$$\nu^0_{pi} = (V^0_{pi}/RT)/(\partial V/\partial A)_{A=0}, \tag{7}$$

which will subsequently be called the apparent stoichiometric number of stage pi (ν_{pi}^0 will equal ν' when $V_{pi}^0 = V_e^0$). In principle it is possible to calculate as many different ν_{pi}^0 as there are slow stages pi. The possibility that several values of ν' can be calculated was mentioned in [5,6].

Putting (5) in (7) we obtain $\nu^0_{pi} = V^0_{pi} \left| \sum_p [\sum_i (\nu_{pi}/V^0_{pi})]^{-1} \right.$, from which

$$\sum_p \frac{1}{\sum_i (\nu_{pi}/\nu^0_{pi})}. \tag{8}$$

For a single-path reaction (8) has the form $\sum_i (\nu_i/\nu_i^0) = 1$, while for a reaction involving several paths, in each of which there is only one slow stage, $\sum_p (\nu^0_p/\nu_p) = 1$.

Since, by definition, ν_p and ν_{pi}^0 have the same sign, it follows from (8) that for the two cases mentioned $\nu_i^0 \geq \nu_i$ and $\nu_p^0 \leq \nu_p$. The experimental establishment of the inequalities may indicate the presence of several slow stages, which may be consecutive or parallel. It is advisable to use Eq. (8) [and also (5)] as a criterion in selecting a mechanism. When several values of ν^0 have been determined, Eq. (8) can be used to check their agreement with various probable stages in the reaction scheme. This checking should be carried out for serveral sets of concentrations of the starting materials and reaction products.

The faster any stage of the reaction, the higher its exchange rate V_{pi}^0 and therefore also ν_{pi}^0. Therefore

for a given path the terms in ν_i/ν_i^0 corresponding to the fastest stages make the smallest contribution to (8). For single-path reaction ν_i/ν_i^0 may vary from 0 to 1 and is characteristic of the relative slowness of this stage compared to others close to equilibrium. Slower stages correspond to higher values of ν_i/ν_i^0. For parallel stages the ratio ν_p^0/ν_p plays a similar role, varying over the same limits. Here the faster stage corresponds to higher ν_p^0/ν_p. It can be seen from (8) that $\nu_{pi}^0 = \nu_{pi}$ only for a reaction with a single slow limiting stage.

Let us introduce into the discussion the quantity $(\partial V_{pi}/\partial A_{pi})_{A=0} = (\partial V_p/\partial A_{pi})_{A=0}$, which we will call the conductivity of stage pi. Differentiating (3) with respect to A_{pi} and assuming $A_{pi} = 0$, we find $(\partial V_{pi}/\partial A_{pi})_{A=0} = V_{pi}^0/RT$. Comparing this expression with (7) it can be seen that ν_{pi}^0 is equal to the ratio of the conductivity of stage pi to that of the overall reaction. The use of the analogy between a complex reaction and an electrical circuit makes it possible to write down (8) immediately.

For a single-path reaction the apparent stoichiometric number also shows to what extent the affinity of the overall reaction is greater than the affinity of stage i, i.e., the quantity $1/\nu_i^0$ is the "energy fraction" of the stage in the total energy balance of the reaction close to equilibrium. Putting (2) into (7) we obtain

$$1/\nu_i^0 = (\partial A_i/\partial A)_{A=0} \tag{9}$$

(for a single slow stage ($A = \nu_i A_i$), $\nu_i^0 = \nu_i$ is equal to the number of its repetitions for one transit of the overall reaction [3,6]).

A stoichiometric number calculated using V^0 [6-8] has also been discussed in the literature (we will call this number $\bar{\nu}^0$), namely

$$\bar{\nu}^0 = (V^0/RT)/(\partial V/\partial A)_{A=0}. \tag{10}$$

Let us establish the connection between $\bar{\nu}^0$ and ν_{pi}^0. To do this we will use the relationship introduced by Temkin [9] for the overall reaction path; when the reaction paths are independent this relationship may apply to any of them:

$$\vec{V}_p\left(\frac{1}{\vec{V}_{p1}} + \frac{\overleftarrow{V}_{p1}}{\vec{V}_{p1}\vec{V}_{p2}} + \frac{\overleftarrow{V}_{p1}\overleftarrow{V}_{p2}}{\vec{V}_{p1}\vec{V}_{p2}\vec{V}_{p3}} + \cdots\right) = 1. \tag{11}$$

At equilibrium ($A = 0$, $\vec{V}_{pi} = \overleftarrow{V}_{pi}$) (11) becomes

$$1/V_p^0 = \sum_i (\nu_{pi}/v_{pi}^0) = \sum_i (1/V_{pi}^0). \tag{12}$$

Since $V^0 = \sum_p V_p^0$, then

$$V^0 = \sum_p \frac{1}{\sum_i (\nu_{pi}/v_{pi}^0)} = \sum_p \frac{1}{\sum_i (1/V_{pi}^0)}. \tag{13}$$

Comparing (7), (10), and (13) we obtain

$$\bar{\nu}^0 = \sum_p \frac{1}{\sum_i (1/\nu_{pi}^0)}. \tag{14}$$

Although for a single path reaction ν_i^0 may take as high a value as may be desired, $\bar{\nu}^0$ is limited by the highest and lowest values of ν_i. For a reaction with a single slow stage r, $\bar{\nu}^0 = \nu_r^0 = \nu_r$.

Let us consider in more detail the case of a single-path reaction. We will use the relationship

$$\vec{V}/\overleftarrow{V} = \prod_i (\vec{V}_i/V_i), \tag{15}$$

which was introduced in [9]. Combining (15) and (1) we obtain $\vec{V}/\overleftarrow{V} = \exp\left[\sum_i (A_i/RT)\right]$, from which $V = \vec{V} - \overleftarrow{V} = \overleftarrow{V} \cdot [\exp \sum_i (A_i/RT) - 1]$. Differentiating this equation with respect to A and assuming A = 0, we have $(\partial V/\partial A)_{A=0} = (V^0/RT)\left(\partial \sum_i A_i/\partial A\right)_{A=0}$. Comparing this expression with (10) it follows that

$$\overline{\nu^0} = \left(\partial A/\partial \sum_i A_i\right)_{A=0}. \tag{16}$$

The concept of an average stoichiometric number was introduced in [9]:

$$\bar{\nu} = A \Big/ \sum_i A_i. \tag{17}$$

It can easily be seen that $\overline{\nu^0}$ is the limiting value of $\bar{\nu}$ for $A \to 0$. Therefore the quantity $\overline{\nu^0}$ should be called the equilibrium average stoichiometric number of the reaction. The quantity $\bar{\nu}$ may vary as A varies, but in the particular case of the equivalence of all ν_i among themselves we will have $\bar{\nu} = \overline{\nu^0} = \nu_i$, i.e., $\bar{\nu}$ does not depend on A.

It follows from (7) and (10) that

$$V^0 / \overline{\nu^0} = V_i^0 / \nu_i^0. \tag{18}$$

Using (18) V^0 can be very easily calculated from the experimental values of V_i^0 and ν_i^0, referring here to only one determining stage rate, it being unnecessary to measure the rates for other stages under conditions of equal ν_i ($\bar{\nu} = \overline{\nu^0}$). In the general case the rate of the overall reaction close to equilibrium, in contast to [3], will be

$$V = V^0 A / \overline{\nu^0} RT, \tag{19}$$

where $V^0/\overline{\nu^0}RT = (\partial V/\partial A)_{A=0}$. Equation (5) thus establishes a connection between the phenomenological coefficient of the overall reaction [2], which is equal to its conductivity, and the same coefficients for the separate stages.

The relationships introduced in this paper are applicable to reactions with independent paths. Therefore in order to use them schemes of branched reactions (in which intermediate products formed in any one stage may be consumed in several parallel stages) must be changed into schemes with independent paths, using in particular the following stationary state conditions:

$$\sum_p V_{pi} = \sum_p V_{p,i+1} = \sum_p V_p, \tag{20}$$

where index i refers to stages right up to the point of branching, and index i + 1 to stages immediately after it. Equation (20) is analogous to Kirchhoff's law for electrical circuits.

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