M. I. TEMKIN

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Abstract

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M. I. TEMKIN

KINETICS OF STATIONARY REACTIONS

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Complex reactions are combinations of simple reactions, which in this case are called elementary reactions, or stages. Intermediate substances enter only into the chemical equations of the stages, but not into the chemical equations describing the observed reaction. A reaction is stationary if, at constant concentrations of the initial substances and products, the concentrations of the intermediate substances are also constant. Such a reaction regime is realized in a flow system or in gradientless reactors ([1]). Reactions in a static system may in many cases be regarded as quasi-stationary (the Bodenstein method). The conditions for applicability of such a treatment were formulated by D. A. Frank-Kamenetskii ([2]) and N. N. Semenov ([3]). The following discussion concerns stationary (or quasi-stationary) reactions. In the case of heterogeneous reactions we shall assume the surface to be homogeneous. The intermediate substances for such reactions are chemisorbed atoms or molecules and free surface sites.

In order to obtain the reaction equation by adding the equations of the stages, the latter must first be multiplied by numbers called ([4]) stoichiometric numbers. In the general case these numbers may be chosen in several essentially different ways; each such way corresponds to a certain reaction route ([4]). By essentially different are meant such sets of stoichiometric numbers that cannot be obtained from one another by multiplication by a factor (which would correspond to multiplying the chemical equation of the reaction by the same factor). The stoichiometric numbers may be fractional, negative, and equal to zero; in order of magnitude they are comparable with 1.

Let x_{js} denote the coefficient of the intermediate substance X_j in the chemical equation of stage s; $x_{js} > 0$ if X_j is formed, and $x_{js} < 0$ if X_j is consumed. We denote the stoichiometric number of stage s for route p by $\nu_s^{(p)}$; these numbers are chosen so that

$$\sum_{s=1}^{S} \nu_s^{(p)} x_{js} = 0, \qquad (1)$$

where S is the total number of stages. The number of linearly independent conditions of the form (1) determines the number of independent intermediate substances I. There exist $P = S - I$ linearly independent sets of numbers $\nu_s^{(p)}$– solutions of the system of equations of the form (1), i.e., P independent reaction routes ([4]).

Sometimes different routes correspond to one and the same chemical equation. Let the numbers of such routes be 1 and 2. Then the chemical equation of route 3, formed by means of the equality $\nu_s^{(3)} = \nu_s^{(2)} - \nu_s^{(1)}$, is the equality $0 = 0$. We shall call such routes empty (Christiansen ([5]) calls them cyclic sequences). More often each independent route corresponds to its own chemical equation. From the kinetic point of view, in this case one complex reaction takes place in the system, since some stages are common to different routes.

The chemical equation of a stage is written in accordance with the course of its elementary act; by the rate of stage s in the forward direction r_s, or in the reverse direction r_{-s}, we shall understand the number of elementary ac-

of the corresponding direction of this stage, occurring per unit time in a unit volume (for a homogeneous reaction) or on a unit surface (for a heterogeneous reaction). The chemical equation of a route allows multiplication by a factor; therefore it must be specified. Assuming this has been done, we shall call a run of the reaction along a given route the disappearance of molecules of the initial substances and the appearance of molecules of products in the number indicated by the coefficients of the chemical equation. The rate of reaction $r^{(p)}$ along route p will be called the number of corresponding runs per unit time in a unit volume or on a unit surface.

The following stationarity conditions for the stages are satisfied:

$$\sum_{p=1}^{P} \nu_s^{(p)} r^{(p)} = r_s - r_{-s}. \tag{2}$$

Indeed, per unit time in a unit volume or on a unit surface there are formed

$$\sum_{s=1}^{S} x_{js}(r_s - r_{-s})$$

molecules X_j. Substituting $r_s - r_{-s}$ from (2) and taking (1) into account, we obtain that

$$\sum_{s=1}^{S} x_{js}(r_s - r_{-s}) = 0, \tag{3}$$

i.e., the amount of each intermediate substance is constant. The S equations of the form (2) determine $P + I$ unknowns, namely the P quantities $r^{(p)}$ and the I

activities of the independent intermediate substances. Of course, one may also use the stationarity conditions for the intermediate substances (3).

The transition from one set of independent routes $1, 2, \ldots$ to another $1', 2', \ldots$ is given by equations of the form

$$\begin{aligned} \nu_s^{(1')} &= C_{11}\nu_s^{(1)} + C_{12}\nu_s^{(2)} + \ldots, \\ \nu_s^{(2')} &= C_{21}\nu_s^{(1)} + C_{22}\nu_s^{(2)} + \ldots, \\ &\ldots\ldots\ldots\ldots\ldots \end{aligned} \tag{4}$$

where C_{11}, C_{12}, etc. are coefficients. The chemical equations of the routes are transformed accordingly. If $r^{(1)}, r^{(2)}$, etc. are known, then $r^{(1')}, r^{(2')}$, etc. are obtained by solving the system of equations

$$\begin{aligned} r^{(1)} &= C_{11}r^{(1')} + C_{21}r^{(2')} + \ldots, \\ r^{(2)} &= C_{12}r^{(1')} + C_{22}r^{(2')} + \ldots, \\ &\ldots\ldots\ldots\ldots\ldots \end{aligned} \tag{5}$$

composed so that the coefficients of each row of system (4) are placed in the corresponding column of system (5). Indeed, substituting the expressions (5) into equation (2) and taking the equalities (4) into account, we find that the set of quantities $r^{(1')}, r^{(2')}$, etc. satisfies the stationarity conditions for all s. We note that the left-hand side of equation (2) has the form of the scalar product of two vectors. The description of the course of a chemical transformation by means of the rates along routes may be regarded as representing a vector by the set of its components.

Let routes 1 and 2 correspond to the same chemical equation. We leave route 1 unchanged, and replace route 2 by the empty route, i.e., we take $\nu_s^{(1')} = \nu_s^{(1)}$, $\nu_s^{(2')} = \nu_s^{(2)} - \nu_s^{(1)}$; then from (5) we obtain $r^{(1')} = r^{(1)} + r^{(2)}$ and $r^{(2')} = r^{(2)}$. Consequently, the reaction rate along an empty route is in general not equal to zero (it is always equal to zero if the empty route is the only one). Although route 1 has been left unchanged, $r^{(1')} \neq r^{(1)}$; no definite value of the rate can be assigned to a given route until the set of independent routes of which it is an element has been specified.

Let us replace, in some set of independent routes, one of the

them by new ones with the aid of the equalities

$$\nu_s = \sum_{p=1}^{P} \nu_s^{(p)} r^{(p)} \Big/ \sum_{p=1}^{P} r^{(p)}, \tag{6}$$

leaving the others unchanged. Here ν_s is the stoichiometric number of the new route for stage s. Denoting the rate along this route, which we shall call the overall route, by r, we obtain from equations (5) that

$$r = \sum_{p=1}^{P} r^{(p)},$$

and the rates along the remaining routes are equal to zero. The chemical equation of the overall route describes the overall chemical transformation in the system.

In a number of cases the derivation of kinetic equations expressing $r^{(1)}, r^{(2)}$, etc., in terms of the concentrations, or activities, of the initial substances and products can be considerably facilitated in the following way. In the identity

$$(r_1 - r_{-1}) r_2 r_3 \ldots + r_{-1}(r_2 - r_{-2}) r_3 \ldots + r_{-1} r_{-2}(r_3 - r_{-3}) \ldots + \ldots = r_1 r_2 r_3 \ldots - r_{-1} r_{-2} r_{-3} \ldots \quad (7)$$

we express $(r_1 - r_{-1}), (r_2 - r_{-2})$, etc., by equation (2). Dividing both sides of the equality by $r_1 r_2 r_3 \ldots$, we obtain

$$r^{(1)} \left(\frac{\nu_1^{(1)}}{r_1} + \frac{r_{-1}\nu_2^{(1)}}{r_1 r_2} + \frac{r_{-1} r_{-2} \nu_3^{(1)}}{r_1 r_2 r_3} + \ldots \right) + \\ + r^{(2)} \left(\frac{\nu_1^{(2)}}{r_1} + \frac{r_{-1}\nu_2^{(2)}}{r_1 r_2} + \frac{r_{-1} r_{-2} \nu_3^{(2)}}{r_1 r_2 r_3} + \ldots \right) + \ldots = 1 - \frac{r_{-1} r_{-2} r_{-3} \cdots}{r_1 r_2 r_3 \cdots}. \quad (8)$$

Equation (8) may be called the equation of stationary reactions. Like equation (2), it is valid independently of the order in which the stages are numbered. This is natural, since under stationarity all stages of the reaction proceed simultaneously.

In special cases simplifications are possible. Sometimes the scheme of the reaction mechanism contains a stage for which $\nu_s^{(p)} = 0$ for all p. Such a stage is an equilibrium stage; for it $r_s = r_{-s}$, and the corresponding terms drop out of (8). If for some stage r_s is much greater than $r_s - r_{-s}$, such a stage is called fast, or quasi-equilibrium; stages for which r_s is of the same order as $r_s - r_{-s}$ are called slow. According to (2), for a fast stage $|\nu_s^{(p)} r^{(p)}| \ll r_s$, and since, moreover, $r_s \simeq r_{-s}$, the terms corresponding to the fast stage in (8) may be omitted. If some stage s is irreversible, the terms in (8) containing r_{-s} become 0.

Equation (8) makes it possible at once to eliminate some of the unknown activities (or concentrations) of intermediate substances, and sometimes all of them. For this it is necessary to arrange the equations of the stages, as far as possible, in such an order that an intermediate substance formed in some stage is consumed in the following stage. Several such arrangements make it possible to obtain the required number of equations. In this, diagrams showing the structure of the reaction mechanism may be helpful ([6,3,5]). The concentrations of intermediate substances, if necessary, are also determined with the aid of suitable sequences of stages. If there are equilibrium or quasi-equilibrium stages, the activity of the intermediate substance participating in such a stage is found with the aid of the law of mass action for equilibrium.

Applying equation (8) to the overall route, we obtain

$$r\left(\frac{\nu_1}{r_1}+\frac{r_{-1}\nu_2}{r_1r_2}+\frac{r_{-1}r_{-2}\nu_3}{r_1r_2r_3}+...\right)=1-\frac{r_{-1}r_{-2}r_{-3}\cdots}{r_1r_2r_3\dots}. \tag{9}$$

This form of the equation of stationary reactions is, evidently, directly applicable to the rate of reactions with one route.

Let us introduce, for the overall route of a complex reaction or for a reaction with one route, the concept of the rate in the forward direction r_+, defining

this quantity as the value that r assumes if the last step becomes irreversible, i.e. $r_{-s}=0$, while the remaining quantities r_s and r_{-s} retain their former values. Equation (9) gives

$$r_+\left(\frac{\nu_1}{r_1}+\frac{r_{-1}\nu_2}{r_1r_2}+\frac{r_{-1}r_{-2}\nu_3}{r_1r_2r_3}+\cdots\right)=1. \tag{10}$$

If only one step is slow (and the others are quasi-equilibrium or equilibrium), this step is called rate-limiting. For such a case we obtain from (10) the equality $r_+=r_l/\nu_l$, where l is the index of the rate-limiting step. Changing the directions of all steps and arranging them in the reverse order, and then putting $r_1=0$, we obtain an equation for the rate in the reverse direction, r_-. It is then not difficult to verify that

$$\frac{r_-}{r_+}=\frac{r_{-1}r_{-2}r_{-3}\cdots}{r_1r_2r_3\cdots}; \tag{11}$$

$$r=r_+-r_-. \tag{12}$$

According to equations (11) and (12), the quantities r_+ and r_- do not depend on the order in which the steps are arranged (since r_-/r_+ and r_+-r_- do not change when the order of the steps is changed).

When applied to sequences of steps of the special type considered by Christiansen ([5],[7]), equations (8)–(12) directly give the results of that author.

When there is only one pathway of isotope exchange, the rate of isotope exchange is described by an equation of the same form as equation (10), but including not all steps of the reaction, only the steps participating in the exchange. Such an equation was obtained by Matsuda and Horiuti ([8]).

Let us introduce, for a reaction with one route, whose chemical equation is

$$aA + a'A' + \cdots = bB + b'B' + \cdots,$$

the mean stoichiometric number $\bar{\nu}$ by means of the definition

$$\bar{\nu} = \frac{\nu_1 \Delta G_1 + \nu_2 \Delta G_2 + \cdots}{\Delta G_1 + \Delta G_2 + \cdots}. \tag{13}$$

Here ΔG_s is the change in Gibbs free energy in step s. From the theory of absolute reaction rates it follows that $\Delta G_s = -RT \ln \frac{r_s}{r_{-s}}$, and since

$$\nu_1 \Delta G_1 + \nu_2 \Delta G_2 + \cdots = \Delta G = -RT \ln K \frac{(A)^a (A')^{a'} \cdots}{(B)^b (B')^{b'} \cdots},$$

where K is the equilibrium constant, (A) is the activity of substance A, etc., equation (11) gives:

$$\frac{r_+}{r_-} = \left[K \frac{(A)^a (A')^{a'} \cdots}{(B)^b (B')^{b'} \cdots} \right]^{1/\bar{\nu}}. \tag{14}$$

In equation (13) the quantities referring to equilibrium or quasi-equilibrium steps drop out, because for them $\Delta G_s = 0$ (exactly or approximately). If the ν_s of all nonequilibrium steps are the same, $\bar{\nu}$ is equal to this common value. In particular, if there is a rate-limiting step, then $\bar{\nu} = \nu_l$, and the results of G. K. Boreskov ([9]) and J. Horiuti ([4]) are obtained.

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Note: Figure translations are in progress. See original paper for figures.