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Analyzing a Sequence of Reactions by the De Donder Equation

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In the kinetic analysis of the mechanism postulated simplified assumptions are often made. These assumptions are generally verified by comparing the simplified kinetic description with experimental data. In this study consideration is given to the idea of constructing a "quantitative" measure for the "qualitative" assessment of the assumption (approximation), which makes it possible to examine its adequacy at an arbitrary moment of the reaction. The adopted measures are defined as criteria for steady-state and equilibrium (quasi-equilibrium) approximations.

Key words: kinetics, steady-state approximation, quasi-equilibrium, criteria of applicability

When analyzing the schemes of chemical reactions, use is made of various assumptions – that of the steady-state concentration for one or more intermediates, that of the equilibrium (quasi-equilibrium) of some reaction steps, or that of the reaction step which controls (limits) the reaction rate. Verification is carried out *a posteriori,* on the basis of experiments.

So far, many attempts have been made to formulate the criteria of applicability. Answers have been sought to the following major questions: Which of the two methods applies to the postulated reaction scheme – steady-state approximation or equilibrium-state approximation? Are these methods applicable in each instance or only under strictly defined conditions? Particular consideration has been given to the following issues: If the reaction yields more than one intermediate, which of them will reach its steady-state concentration and which will not? If the reaction involves more than one step, which of them can be assumed to run at an equilibrium state? How accurate is the approximation adopted? Relevant investigations have been carried out for many decades. In the nineteen-fifties and nineteen-sixties, the steady-state approximation method has raised particular interest [1-6]. In spite of this, no general procedure has been developed to solve the about problems adequately. Numerical methods, which make it possible to solve the so-called stiff differential equations, have distracted the attention from the problems itemized above. Since the questions of interest are still open, we approach them in this paper. This approach is based on the chemical affinity of reaction $\mathcal{A}$, equal (with a minus sign) to the free enthalpy of reaction. $\mathcal{A}$ is related to the reaction rate by the De Donder formula [7], which has been considered in analyzing the mechanism of the reactions that occur *via* a closed sequence of steps [8,9,10]. And this relation was adopted in our analysis.

RESULTS AND DISCUSSION

Chemical affinity is defined as

$$\mathcal{A} = -\left(\frac{\partial G}{\partial \xi}\right)_{p,T} \tag{1}$$

where G is free enthalpy and ξ is the extent of reaction. $\mathcal{A}$ is related to the rates of the forward and backward reaction of an elementary step r_+ and r_- by De Donder equation [7]:

$$\mathcal{A} = RT\ln\left(\frac{r_+}{r_-}\right) \tag{2}$$

where $r_+ - r_- = r$ denotes the net rate of the elementary step.

For a sequence of elementary reactions, being part of the mechanism governing a composite reaction, if the assumption under analysis is that of the equilibrium (quasi-equilibrium) for a given elementary step, chemical affinity $\mathcal{A}$ of this step is considered directly. If the assumption under analysis is that of steady-state concentration for an intermediate product X, then – if the intermediate X forms in one elementary step only – we relate the quantity $\mathcal{A}$ to this step; but if the intermediate X forms in more than one elementary step, we take into account the sum of chemical affinities $\mathcal{A}_i$ of all the elementary steps at which the intermediate is formed. $\mathcal{A}$ defined *via* the above route (*i.e.* related either to a single elementary reaction or to the sum of affinities of the steps at which the intermediate forms) is assigned the subscript **d**. Besides the quantity $\mathcal{A}_d$, an approximate quantity $\mathcal{A}_p$ is established by substituting the condition for the equilibrium of the given step (or the steady-state concentration X) into the expression for $\mathcal{A}$.

If the approximation is adequate, the rates of change of the two chemical affinities $\mathcal{A}$ will take the form:

$$\frac{d\mathcal{A}_d}{dt} \approx \frac{d\mathcal{A}_p}{dt} \tag{3}$$

The change of the chemical affinity given by the approximate relationship should not substantially differ from the one described by the exact relationship. (3) is used as a basis for the idea of how to assess the adequacy of equilibrium (pe) or steady-state (ss) approximation. The assessment is quantitative, as (3) can always be written as a relevant criterion. The method of establishing the criteria proposed in this paper is shown on a generalized example of a consecutive reaction.

A composite reaction occurs in a closed system, which is an ideal solution. The transition from substrates to products proceeds in two steps *via* the intermediate X:

$$\text{(substrates)} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{X} \quad \text{step 1;} \qquad \text{X} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \text{(products)} \quad \text{step 2} \tag{I}$$

The rates of the steps, r_1 and r_2, include the rate of the forward reaction (subscript +) and the rate of the backward reaction (subscript –). Hence, we have

$$r_1 = r_{+1} - r_{-1} \quad \text{and} \quad r_2 = r_{+2} - r_{-2} \tag{4}$$

Let us now consider three different assumptions – that of the equilibrium between the intermediate and the substrates, that of the steady-state concentration of the intermediate and that of quasiequilibrium, *i.e.* of the equilibrium within steady-state approximation.

The assumption of equilibrium in step 1 of scheme (I) is equivalent to the condition

$$r_1 \approx 0 \tag{5}$$

The expression for the chemical affinity of step 1 becomes

$$\mathcal{A}_d = RT\ln\left(\frac{r_{+1}}{r_{-1}}\right) \tag{2a}$$

The relation yields the accurate value of $\mathcal{A}$, *i.e.* the quantity $\mathcal{A}_d$. The approximate quantity $\mathcal{A}_p$ is such a quantity $\mathcal{A}$ for which the condition of (5) is fulfilled. Hence,

$$\mathcal{A}_p \approx RT \cdot \ln(1) = 0 \tag{2b}$$

Thus, the rate of change of chemical affinity takes the form

$$\frac{d\mathcal{A}_d}{dt} = RT\left(\frac{\frac{dr_{+1}}{dt}}{r_{+1}} - \frac{\frac{dr_{-1}}{dt}}{r_{-1}}\right) \quad \text{and} \quad \frac{d\mathcal{A}_p}{dt} \approx 0 \tag{6}$$

because $r_{+1} \approx r_{-1}$. Comparing the two expressions, by the general condition (3), we obtain

$$\frac{dr_{+1}}{dt} \approx \frac{dr_{-1}}{dt} \tag{7}$$

(7) can be written as the ratio of r_1 to r_2. The expression obtained *via* this route depends on the character of the elementary reactions involved in step 1 of scheme (I). Thus, if step 1 consists of first-order reactions:

$$S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} p \tag{IA}$$

the ratio of r_1 to r_2 will take the form

$$\frac{r_1}{r_2} \approx \frac{k_{-1}}{k_1 + k_{-1}} \tag{8}$$

If step 1 involves a second-order reaction, directed to the right-hand side and a first-order reaction running in the opposite direction, *i.e.* if scheme (I) consists of the following reaction:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} X \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C + D \tag{IB}$$

the ratio of r_1 to r_2 can be written as

$$\frac{r_1}{r_2} \approx \frac{k_{-1}}{k_1(c_A + c_B) + k_{-1}} \tag{9}$$

If step 1 is described by another elementary reaction, differing from those mentioned above, the r_1/r_2 ratio will also take another form. The left-hand side is the rate ratio for equilibrium step 1 and for step 2 and can be adopted as a criterion for the adequacy of assumption (5). Thus, the lower is the value of the criterion, the closer to equilibrium is step 1. The numerical value of the criterion is given by the right-hand sides of the relations (8) and (9).

Using a similar procedure, we derive a criterion, which verifies the assumption of equilibrium for step 2 in scheme (I). Hence, we can write:

$$\frac{r_2}{r_1} = \frac{k_2}{k_2 + k_{-2}} \quad \text{in reaction (IA);} \qquad \frac{r_2}{r_1} = \frac{k_2}{k_2 + k_{-2}(c_C + c_D)} \quad \text{in reaction (IB).}$$

The assumption that the comparatively low concentration of the intermediate reaches a steady-state within a short time after initiation of the reaction indicates, that the rate of intermediate product formation and the rate of intermediate product disappearance become equal:

$$r_1 \approx r_2 \tag{10}$$

This means that the expression for chemical affinity $\mathcal{A}_d$ incorporates two steps of intermediate product (X) formation:

$$\mathcal{A}_d = RT\ln\left(\frac{r_{+1}r_{-2}}{r_{-1}r_{+2}}\right) \tag{11}$$

Considering (10), we obtain the approximate affinity $\mathcal{A}_p$:

$$\mathcal{A}_p \approx RT\ln\left(\frac{r_{+1}}{r_{-1}}\,\frac{r_{+2}-(r_{+1}-r_{-1})}{r_{+2}}\right) \tag{12}$$

Condition (3), after suitable transformation, reduces to the equation of rate derivatives for step 1 and step 2:

$$\frac{dr_1}{dt} \approx \frac{dr_2}{dt} \tag{13}$$

From (13) we can derive a criterion, which defines the relative difference between the rate of intermediate product disappearance and the rate of intermediate product formation. In the schemes of reaction (IA) and reaction (IB) this criterion becomes:

$$\frac{r_2 - r_1}{r_1} \approx \frac{k_1 - k_{-2}}{k_{-1} + k_2 + k_{-2}} \qquad \text{and} \qquad \frac{r_2 - r_1}{r_1} \approx \frac{k_1(c_A + c_B) - k_{-2}(c_C + c_D)}{k_{-1} + k_2 + k_{-2}(c_C + c_D)} \tag{14}$$

Thus, the smaller is the value of the criterion, the more justified is the assumption that $r_1 \approx r_2$, which formulates the steady-state approximation.

The proposed criteria enable a quantitative assessment of the equilibrium (pe) state or steady-state (ss) assumption. The equilibrium approximation is related to a defined elementary step. The steady-state approximation holds for a defined intermediate and, by virtue of the expression for chemical affinity, is related to one, or to more than one, step. In some instances, *e.g.* in the analyzed scheme (I), the expression for $\mathcal{A}_d$ incorporates the rates of all steps of a composite reaction. Hence, the meaning of the steady-state approximation criterion seems to be more comprehensive than that of the pre-equilibrium approximation criterion, particularly because steady-state approximation may coexist with equilibrium approximation (in the sense defined below).

Let us consider a case where – besides the approximate equality (10) – there exists assumption (5) describing the equilibrium course of step 1 in scheme (I), or there is an assumption (equivalent to (5)) describing the equilibrium course of step 2 in scheme (I). Assumption (10) means that the rate of intermediate formation and the rate of intermediate disappearance are equal. In (5) the rate of formation of product X is negligible. There is no inconsistency between these two assumptions. This exists when the components of the rate of step 1, r_{+1} and r_{-1}, are substantially greater than the components of rate r_{+2} and r_{-2}. Although the differences between these components are identical (steady-state), step 1 is much closer to such a step for which the difference ($r_{+1} - r_{-1}$) can be regarded as negligibly small (compared, for example, to rate r_{+1}). Such an equilibrium is referred to as the quasi-equilibrium of step 1 [11] or as the pre-equilibrium [12].

The criteria of equilibrium for step 1, defined by the (8) and (9), can be rewritten in the form of

$$\frac{r_1}{r_{+1}} = \frac{k_{-1}}{k_1 + k_{-1}} \frac{r_2}{k_1 c_S} \qquad \text{in reaction (IA)}$$

$$\text{and} \quad \frac{r_1}{r_{+1}} = \frac{k_{-1}}{k_1 (c_A + c_B) + k_{-1}} \frac{r_2}{k_1 c_A c_B} \qquad \text{in reaction (IB)} \tag{15}$$

The lower is the value of the criterion, the more justified is the assumption of the quasi-equilibrium of step 1. The quasi-equilibrium for step 2 can be considered in a similar way. Then, we obtain the following criteria

$$\frac{r_2}{r_{+2}} = \frac{k_{-1} + k_2}{k_2 + k_{-2}} \frac{r_1}{k_1 c_S + k_{-2} c_P} \qquad \text{in reaction (IA)}$$

$$\text{and} \quad \frac{r_2}{r_{+2}} = \frac{k_{-1} + k_2}{k_2 + k_{-2}(c_C + c_D)} \frac{r_1}{k_1 c_A c_B + k_{-2} c_C c_D} \qquad \text{in reaction (IB)} \tag{16}$$

When the chemical reaction involves more than one step, attempts are often made to identify the step that exerts the strongest influence on the total rate. Such step is called a rate-controlling, a rate-determining, or a rate-limiting step. In this paper, this step is referred to as proposed by Laidler [13]. The rate-controlling step is such that its rate constants appear directly in the equation describing the rate of product formation. The rate constants of other steps do not occur at all or take the form of ratios of appropriate rate constants, *i.e.* the form of equilibrium constants.

In particular, if we can assume the existence of a given approximation, we can also formulate an approximate expression for the rate of product formation, at least in some simple cases. Thus, we can indirectly indicate the controlling step. In the reaction occurring by a two-step mechanism

$$S \rightleftarrows X \longrightarrow P$$

for the approximation of $pe_{(1)}$, step 2 is the controlling (limiting) one; ss, step 1 is the controlling (determining) one; (ss + $pe_{(1)}$), step 2 is the controlling (limiting) one.

The proposed criteria (8) and (9), (14), as well as (15) and (16), enable a quantitative assessment of the error caused by the given approximation (pe), (ss) or (ss + pe), for an arbitrary combination of concentrations of the reacting mixture. The application of the proposed procedure is exemplified by analyzing the reaction of thermal decomposition of ozone:

$$M + O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M + O_2 + O, \qquad O + O_3 \xrightarrow{k_2} 2O_2 \tag{II}$$

where M may be O_2, O_3, N_2, etc. The rate equations are given by

$$\frac{dc_{O_3}}{dt} = -r_1 - r_2, \qquad \frac{dc_{O_2}}{dt} = r_1 + 2r_2, \qquad \frac{dc_O}{dt} = r_1 - r_2 \tag{17}$$

where $r_1 = k_1 c_M c_{O_3} - k_{-1} c_M c_{O_2} c_O$ and $r_2 = k_2 c_{O_3} c_O$.

Rate constants were taken from Kondratev tables [14]. Considered were only ozone-oxygen mixtures.

The values found for the rate constants are as follows:

for M equal to O_2: $k_1^{ox} = 7.76 \cdot 10^8 \exp(-11670/T)$, $k_{-1}^{ox} = 5.37 \cdot 10^1 \exp(210/T)$;

for M equal to O_3: $k_1^{oz} = 8.51 \cdot 10^9 \exp(-12200/T)$, $k_{-1}^{oz} = 6.02 \cdot 10^1 \exp(300/T)$;

and $k_2 = 3.71 \cdot 10^6 \exp(-1865/T)$.

Concentration and time one expressed in mol/m^3 and seconds, respectively.

In (II) we can develop some criteria which verify the equilibrium, the steady-state and quasiequilibrium approximations. These criteria take the form

for equilibrium

$$\frac{r_1}{r_2} = \frac{k_1^{ox}(2x - y) - 2k_1^{oz}x + k_{-1}^{ox}y(y - 4z) + k_{-1}^{oz}(y(x + z) - 2xz)}{k_1^{ox}(y - x) + 2k_1^{oz}x + k_{-1}^{ox}y(y + 2z) + k_{-1}^{oz}(y(x - z) + xz)} \tag{18}$$

for steady-state

$$\frac{r_2 - r_1}{r_1} = \frac{(k_1^{ox} - k_{-1}^{oz}z)(2y - 3x) + 4k_1^{oz}x + z(6k_{-1}^{ox}y - 2k_2)}{(k_1^{ox} - k_{-1}^{oz})(2x - y) + k_{-1}^{oz}xy - 2k_1^{oz}x + k_{-1}^{ox}y(y - 4z) + k_2(x + z)} \tag{19}$$

for quasiequilibrium

$$\frac{r_1}{r_{+1}} = \frac{k_1^{ox}(2x - y) - 2k_1^{oz}x + k_{-1}^{ox}y(y - 4z) + k_{-1}^{oz}(y(x + z) - 2xz)}{k_1^{ox}(y - x) + 2k_1^{oz}x + k_{-1}^{ox}y(y + 2z) + k_{-1}^{oz}(y(x - z) + xz)} \; \frac{k_2 z}{k_1^{ox}y + k_1^{oz}x} \qquad (20)$$

where $x = c_{O_3}$, $y = c_{O_2}$ and $z = c_O$.

To obtain numerical estimates it has been assumed that ozone decomposes in an ozone-oxygen mixture of an initial ozone and oxygen concentration of 4 mol/m^3 and 12 mol/m^3, respectively and at of 373 K. Figure 1 shows the error of estimation for the steady-state concentration of the intermediate, *i.e.* the oxygen atoms. The difference between exact and approximate (steady-state) concentration is related to the exact concentration value. The figure also includes the plots of the steady-state criterion. Figure 2 provides the equilibrium criterion and quasi-equilibrium criterion. The relative error of estimation of the intermediate concentration decreases monotonically to reach small values after a short time. In the example presented here, the error was lower than 3% after 30 μs already (the conversion of ozone being as poor as $2.3 \cdot 10^{-6}$%).

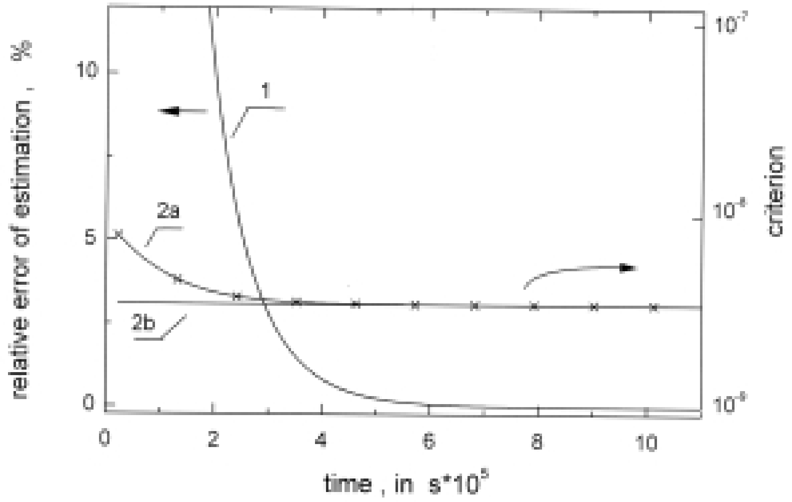

Figure 1. The relative error of estimation for the steady-state concentration of intermediate (1) and values of the steady-state criterion; from exact solution (2a), from steady-state approximation (2b).

The steady-state criterion is defined by the right side of (19). Curve 1 is obtained from the exact solutions of (17). This exact expression is compared with the approximate expression obtained from the use of the steady-state approximation (curve 2). The approximate rate equation in the steady-state takes the form

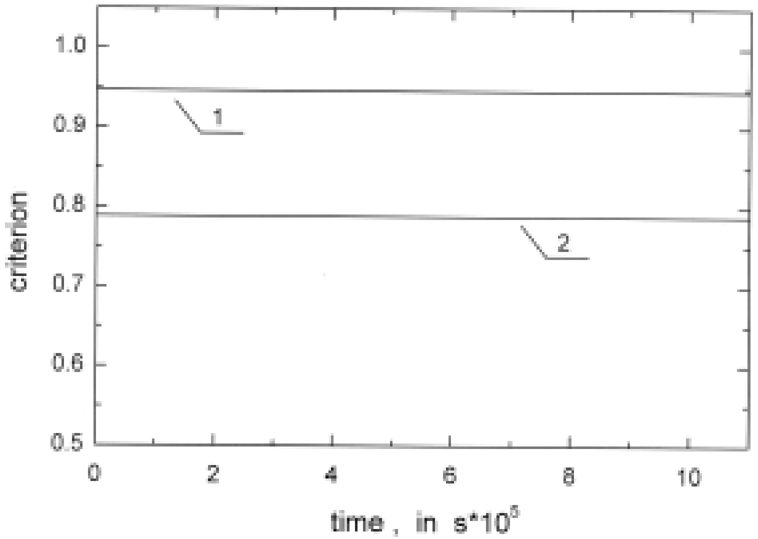

Figure 2. The values of the equilibrium criterion (1) and quasi-equilibrium criterion (2) for thermal ozone decomposition reaction.

$$-\frac{1}{2}\frac{dc_{O_3}}{dt} \approx \frac{1}{3}\frac{dc_{O_2}}{dt} = k_2 c_{O_3} c_O \qquad (21)$$

where the steady-state concentration of oxygen atoms is given by

$$c_O = \frac{k_1^{ox} c_{O_2} + k_1^{oz} c_{O_3}}{(k_{-1}^{ox} c_{O_2} + k_{-1}^{oz} c_{O_3}) c_{O_2} + k_2 c_{O_3}} c_{O_3} \qquad (22)$$

This equation describes very well the experimental results obtained with various mixtures of inert gases. And for this equation Benson and Axworthy established a set of rate constants k_1, k_{-1} and k_2. They also determine the relative efficiencies of O_2, N_2, CO_2 and He in activating O_3 (compared to O_3 itself); they are 0.44; 041; 1.06 and 0.34, respectively. The values found for the rate constants are (for M equal to O_3) [15]: $k_1 = 4.61\cdot10^9\cdot\exp(-24000/(RT))$ m^3/(mole·s), $k_{-1} = 6.00\cdot10^1\cdot\exp(+600/(RT))$ m^6/(mole^2·s), $k_2 = 2.96\cdot10^7\cdot\exp(-6000/(RT))$ m^3/(mole·s).

Let us formulate the ranges of applications:

(a) In the analysis of steady-state approximation we can consider the steps of intermediate product formation in the way shown in here. But we can also analyze the steps of intermediate product disappearance. Both approaches give the same results.

(b)The procedure described here applies to an arbitrary reaction scheme. It may be not only an open sequence of reactions (such as the one included in scheme (I)), but also a closed sequence (such as that of chain or catalytic reactions).

(c) The criterion for steady-state approximation is valid for a defined intermediate, but it may be constructed for any intermediate product separately.

(d) The equilibrium/quasiequilibrium criterion holds for a defined step; it may be constructed for any step separately.

Thus, a procedure for assessing the "quality" of steady-state approximation and equilibrium-state approximation in the postulated scheme of elementary reactions was described. The procedure was exemplified by a generalized consecutive reaction, occurring in two steps with one intermediate product. The criteria derived in this study make it possible to verify the assumption of a defined approximation for particular cases, when there is one intermediate, and the reaction during which the intermediate forms is either a first-order or a second-order reaction. This procedure can be transposed onto a composite reaction of an arbitrary mechanism [16].

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