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Homogeneous reaction schemes with a great number of steady states

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Homogeneous termolecular stage reaction schemes with a great number of internal (no zero coordinates) steady states have been investigated.

The problem of determining the number of steady states in reactions, depending on the stage reached in the process, is a current topic in chemical kinetics. Reactions are characterized[1] by internal and boundary steady states, ISS and BSS, respectively. Their coordinates are defined according to a set of concentration values of substances. In BSS the concentration of some substance is equal to zero. In most cases (for example, for one-step reactions) the reaction rate in these steady states is also equal to zero. In ISS the concentrations of all substances participating in a reaction and the rate are not equal to zero. Hence, the determination of ISS number is connected with the problem of increasing the effectiveness of the precise reactions proceeding. A number of papers[2–6] are devoted to the determination of ISS number. As a rule, the estimation of ISS number or their exact value (usually not more than three) for precise mechanisms[2,3] and for some classes of reaction schemes,[4-6] are given in these papers.

In this report we have shown that in a class of homogeneous (consisting of stages with the same molecularity) schemes there exist schemes which are constructed by termolecular stages with a great number of ISS. The existence of a multiplicity of steady states (MSS) in such reactions has been under discussion.[7] The possibility of using homogeneous mechanisms for describing reactions with 5 or more ISS has not been investigated.

The analysis has shown that the following homogeneous three-step scheme with the participation of n substances admits at least $n + 1$ different ISS. In reaction (1) each of the routes is

$$\begin{array}{l} 1.3\mathrm{X}_2 \overset{k_1}{\rightarrow} \mathrm{X}_1 + 2\mathrm{X}_2,\ 1'.\mathrm{X}_1 + 2\mathrm{X}_2 \overset{k_1'}{\rightarrow} 3\mathrm{X}_2,\ 1''.2\mathrm{X}_1 + \mathrm{X}_2 \overset{k_1''}{\rightarrow} 3\mathrm{X}_1, \\ 2.3\mathrm{X}_3 \overset{k_2}{\rightarrow} \mathrm{X}_2 + 2\mathrm{X}_3,\ 2'.\mathrm{X}_2 + 2\mathrm{X}_3 \overset{k_2'}{\rightarrow} 3\mathrm{X}_3,\ 2''.2\mathrm{X}_2 + \mathrm{X}_3 \overset{k_2''}{\rightarrow} 3\mathrm{X}_2, \\ \ldots\ \ldots \overset{k_i}{\rightarrow} \ldots\ \ldots\ \ldots,\ \ldots\ \ldots\ \ldots\ \ldots \overset{k_i'}{\rightarrow} \ldots,\ \ldots\ \ldots\ \ldots\ \ldots \overset{k_i''}{\rightarrow} \ldots \\ n.3\mathrm{X}_1 \overset{k_n}{\rightarrow} \mathrm{X}_n + 2\mathrm{X}_1,\ n'.\mathrm{X}_n + 2\mathrm{X}_1 \overset{k_n'}{\rightarrow} 3\mathrm{X}_1,\ n''.2\mathrm{X}_n + \mathrm{X}_1 \overset{k_n''}{\rightarrow} 3\mathrm{X}_n. \end{array} \qquad (1)$$

given in the form of a column which contains n stages in consecutive order. k_i, k_i', k_i'' are the constants of the stage rates. At the values of stage frequencies determined *via* the parameter $p > 0$, $p \neq 1$ by relations $k_i = k = p^{n-1}$, $k_i' = k' = 1 + p^n$, $k_i'' = k'' = p$, $i = 1, ..., n$, the stationary equations for reaction (1)

$$\dot{x}_1 = k(x_2^3 - x_1^3) - k'(x_1x_2^2 - x_nx_1^2) + k''(x_1^2x_2 - x_n^2x_1) = 0,$$

$$\dot{x}_2 = k(x_3^3 - x_2^3) - k'(x_2x_3^2 - x_1x_2^2) + k''(x_2^2x_3 - x_1^2x_2) = 0,$$

$$\ldots \quad \ldots\ldots$$

$$\dot{x}_n = k(x_1^3 - x_n^3) - k'(x_nx_1^2 - x_{n-1}x_n^2) + k''(x_n^2x_1 - x_{n-1}^2x_1) = 0$$

(x_i are X_i concentrations) have n solutions of the form

$$\vec{x}_\infty = y/\ ,\quad = p(1 - p^n)/(1 - p),$$

$$\vec{y} = (p, p^2, ..., p^{n-1}, p^n), (p^2, p^3, ..., p^n, p^1), ..., (p^n, p^1, ..., p^{n-2}, p^{n-1}).$$

The coordinates of each steady state are obtained by the cyclic shift of the coordinates of the previous one. Let us check, for example, the coordinates of the first ISS:

With cyclic shifting of the vector $\vec{x}_\infty$ components the equations of the stationary state transfer from one to another.

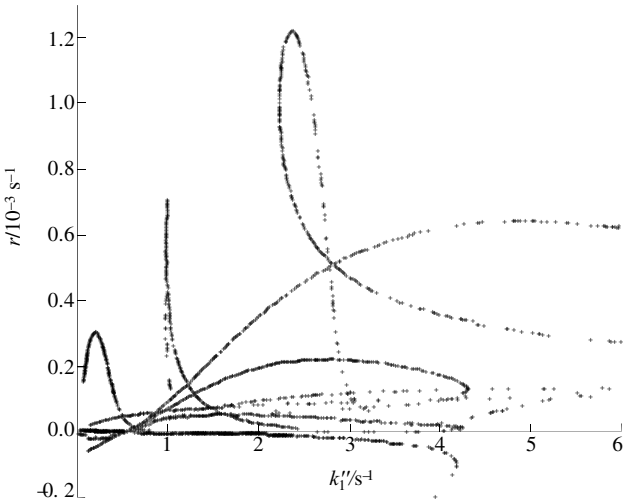

Figure 1 Dependence of 'r' rate of stage 1″ on k_1'' for the reaction proceeding *via* reaction (1) at $n = 5$, $k_1 = ... = k_n = p^{n-1}$, $k_1' = ... = k_n' = 1 + p^n$, $k_2'' = ... = k_n'' = p$, $p = 1/2$.

$$\dot{x}_1 = 0:\ p^{n-1}(p^6 - p^3) - (1 + p^n)(p^5 - p^{n+2}) + p(p^4 - p^{2n+1}) \equiv 0;$$

$$\dot{x}_i = 0:\ p^{n-1}(p^{3i+3} - p^{3i}) - (1 + p^n)(p^{3i+2} - p^{3i-1}) + p(p^{3i+1} - p^{3i-2}) \equiv 0;$$
$$1 < i < n$$

$$\dot{x}_n = 0:\ p^{n-1}(p^3 - p^{3n}) - (1 + p^n)(p^{n+2} - p^{3n-1}) + p(p^{2n+1} - p^{3n-2}) \equiv 0.$$

Therefore, the other $n - 1$ $\vec{x}_\infty$ vectors also satisfy these equations. The above-mentioned reaction also has a steady state $\vec{x}_\infty = (1/n, 1/n, ..., 1/n)$. Hence, a reaction proceeding *via* a homogeneous mechanism (1) with a limited stage molecularity (three in this case) can have any number of ISS ($n + 1$ ISS when the number of substances is equal to n).

Figure 1 shows the possibility of a number of ISS arising for a reaction proceeding according to reaction (1). The single-parameter kinetic dependence of the stage 1″ rate on parameter k_1'' given in Figure 1 is constructed based on an analysis of the system of stationary equations in reaction (1) for $n = 5$, which is achieved in the form of the MAPLE V program. Such single-parameter dependences are constructed, as a rule, for the illustration of ISS multiplicity in the form of ambiguous kinetic curves.[4-6] As seen in Figure 1 in certain regions nine or more values of reaction rate correspond to one k_1'' value.

Thus, the results obtained show that in the case of homogeneous stage schemes of limited molecularity there are schemes which can reproduce a great number of ISS. Reaction (1) can be applied in the 'construction' of specific reaction mechanisms with a prescribed number of steady states.

References

1 N. I. Koltsov, V. Kh. Fedotov and B. V. Alekseev, *Zh. Fiz. Khim.*, 1988, **62**, 1973 (*Russ. J. Phys. Chem.*, 1988, **62**, 1973).

2 N. I. Koltsov, V. Kh. Fedotov and B. V. Alekseev, *AMSE Transaction 'Scientific Siberian', Series A, Mathematical Models in Chemical Kinetics*, 1993, **8**, 131.

3 L. F. Razon and R. A. Schmitz, *Catal. Rev. Sci. Eng.*, 1986, **28**, 89.

4 B. V. Alekseev and N. I. Koltsov, *Khim. Fiz.*, 1997, **16**, 43 [*Chem. Phys. Reports* (*Engl. Transl.*), 1997, **16**, 2153].

5 N. I. Koltsov and V. Kh. Fedotov, *Heterogeneous Catalysis. Proceedings of the 8th Intern. Symp.*, Varna, 1996, part 1, p. 93.
6 N. I. Koltsov, V. Kh. Fedotov and B. V. Alekseev, *Kinet. Katal.*, 1995, **36**, 51 [*Kinet. Catal.* (*Engl. Transl.*), 1995, **36**, 42].
7 L. A. Aizenberg, V. I. Bykov, A. M. Kytmanov and G. S. Yablonskii, *Chem. Eng. Sci.*, 1983, **38**, 1561.

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