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INVARIANT SETS FOR KINETIC EQUATIONS

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Some sets in the space of compositions possessing an invariance property are considered for a closed system, where a complex chemical reaction of a known mechanism proceeds. If the vector of concentrations belongs to such a set at a certain moment of time, it will remain within it at any succeeding moment. Some possible applications are discussed.

Для закрытой системы, в которой протекает сложная химическая реакция с известным механизмом, рассмаириваются множества в пространстве составов, обладающие свойством инвариантности: если вектор концентраций принадлежит такому множеству в некоторый момент времени, он будет лежать в нём и во все последующие моменты. Обсуждаются возможные приложения.

The problem of a priori evaluation of trajectories without taking into consideration the values of rate constants on the basis of the reaction mechanism itself is important when studying the dynamics of complex chemical processes. These evaluations may be obtained by studying invariant subsets of the composition spaces where the trajectories once entering at a certain moment remain inside of it at any succeeding moment.

Invariant sets (I. S.) depending only on the reaction mechanism and the location of the point of detailed equilibrium (P. D. E.) are discussed here. Special attention is paid to the I. S. which are minimal among those containing some (arbitrary) point.

Consider the system of reactions

$$\alpha_{p1} A_1 + \ldots + \alpha_{pn} A_n \rightleftharpoons \beta_{p1} A_1 + \ldots + \beta_{pn} A_n \qquad (1 \leqslant p \leqslant N) \qquad (1)$$

($A_1,\dots,A_n$ are the symbols of substances, p is the step number.) The following notations will be used: a_i is the concentration of substance A_i, a is the vector of concentrations, a^* is the P. D. E., γ_p is the stoichiometric vector of the p-th stage: $(\gamma_p)_i = \beta_{pi} - \alpha_{pi}$, $w_p^+(a)$ and $w_p^-(a)$ are, respectively, the rate of the p-th direct and reverse reactions calculated from the law of mass action, $w_p(a) = w_p^+(a) - w_p^-(a)$. Kinetic equations are of the form

$$\dot{a} = \sum_p \gamma_p w_p(a) \tag{2}$$

Hereafter, we will consider that a lies in some fixed invariant plane C, assuming that the totality of linear laws of conservation are excluded.

Definition. The closed set V is referred to as invariant with respect to mechanism (1) for a fixed P. D. E. of a^*, provided that for any set of the rate constants k_p^+ (but for fixed equilibrium constants determined by a^*) each solution (2) of a(t) with the initial conditions $a(t_0) \in V$ lies in V and $t > t_0$.

Hereafter we will refer to V as the invariant set omitting references to the mechanism and P. D. E.

Let every $a \in C$ be ascribed to the "cone of possible rates" Q_a: $\dot{a} \in Q_a$, for each $k_p^+ \geq 0$, within which the vector $\dot{a}$ lies for any values of $k_p^+ \geq 0$. Q_a is a convex envelope of rays possessing guiding vectors e_p sign $w_p(a)$, where p have the property that $w_p(a) \neq 0$ if $k_p^+ \neq 0$. No vectors e_p depend on the k_p^+ values.

The closed set $V \subset C$ is invariant then and only then, if any a belonging to the boundary V ($\partial V = V - \mathrm{int} V$) has such a neighborhood U that

$$U \cap (a + Q_a) \subset V$$

The intersection of any I. S. is also invariant, hence among the I. S. involving the given point a there exists a minimal set which will be referred to as V_a.

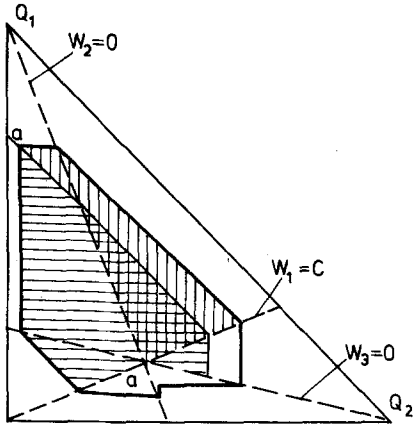

Fig. 1. Sets of V_a for isomerization mechanisms of n-butenes /2/: $A_1 \rightleftarrows A_2 \rightleftarrows A_3 \rightleftarrows A_1$ (outlined region); $A_1 \rightleftarrows A_2$; $A_1 \rightleftarrows A_3$ (horizontally shaded); $A_1 \rightleftarrows A_2 \rightleftarrows A_3$ (vertically shaded)

The sequence $s = \{s_1, \ldots, s_N\}$, each element of which is equal to 1 or -1, will be referred to as a signature. Define the set

$$P_s = \{a | s_p w_p(a) \geq 0 \ (p=1, \ldots, N)\}$$

for any signature s. The totality of s for which P_s has a non-empty interior will be referred to as S. The same set of vectors $e_p = \gamma_p s_p$ corresponds to the totality of the points belonging to $intP_s$. Hence the cone Q_a does not depend on a at $a \in intP_s$. It will be referred to as Q_s.

Describe the procedure of V_a construction. For this purpose introduce some additional definitions. Let M be a closed subset C and

$$V_o(M) = \bigcup_{s \in S} (((M \cap P_s) + Q_s) \cap P_s); \quad V_o^2(M) = V_o(V_o(M)); \ldots \quad V_M = \bigcup_{i=1}^{\infty} V_0^i(M).$$

Then V_M is the minimum I. S. involving M. Having constructed V_M for the single-point set $M = \{a\}$, one can obtain V_a. A typical example of I. S. is the set given by the inequality $G(a) \leq \varepsilon$, where G is Lyapunov's function for kinetic equations (2).

Several versions of such functions /1/, /2/ are known. The non-equilibrium free energy is the most universal Lyapunov function, which is the same for any mechanism and depends only on the P. D. E. location /3/, /4/.

We have constructed I. S. V_a for a simple case of the linear mechanism of isomerization (Fig. 1). They may greatly differ from the sets given by inequalities $G(a) \leqslant \varepsilon$. In particular, V_a are nonconfidently the neighborhoods of a^x. The most important circumstance of the above analysis is the fact that I. S. V_a is strongly dependent on the detailed reaction mechanism. This may be used for discrimination of various mechanisms under consideration.

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