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GRADIENT SYSTEMS ARE CROSS-CATALYTIC

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If the kinetic differential equation of a chemical mechanism is a gradient system, the mechanism is essentially cross-catalytic. Consequently, "rather few" conservative (in the Horn-Jackson sense) mechanisms have a kinetic differential equation of the gradient type. Relations with thermodynamics are only briefly mentioned.

Если кинетическое дифференциальное уравнение химического механизма является градиентной системой, то механизм, по сушеству, является перекрестным каталитическим. Поэтому "достаточно мало" консервативных (в смысле по Хорну-Джэксону) механимов имеют кинетическое дифференциальное уравнение градиентного типа. Слегка останавлтваются на связях с термодинамикой.

INTRODUCTION AND DEFINITIONS

In the qualitative theory of differential equations, especially in the so called "catastrophe theory", it has turned out that differential equations of the gradient type are relatively easy to deal with (cf. Ref. /9/, p. 55/). Furthermore – and this may prove more relevant – it has been proposed sometimes (see e.g. Refs. /4/ and /2/) that only gradient systems are worth studying in thermodynamics. Is this kind of differential equations relevant to reaction kinetics? How is it related to genuine kinetic properties? These are the questions to be answered in this paper.

First, some introductory definitions are needed. Most of the notions and notations introduced by Feinberg, Horn and Jackson will be used without repeating their definition /3, 10, 11/.

DEFINITION 1. The differential equation $\dot{x} = f \circ x$ (where $f = :(f_1, \ldots, f_M) \in C^1(R^M, R^M)$) is of the gradient type if there exists a function $V \in C^2(R^M, R)$ (called potential) such that $f = \text{grad } V$. A complex chemical reaction (or mechanism) is a gradient system, if its kinetic differential equation is of the gradient type.

DEFINITION 2. A mechanism is cross-catalytic if for each elementary reaction $C(j) \rightarrow C(i) (i, j \in \{1, \ldots, N\},\ i \neq j,\ k(i, j) > 0)$ either

(i) the coordinates of the elementary reaction vector $x(i, j) := y(i) - y(j)$ are nonnegative and there is at least one positive among them, or

(ii) the reactant complex vector is a multiple of one of the base vectors of R^M.

In other words, in a cross-catalytic mechanism there does not exist any chemical component causing the decrease of another. Nothing has been claimed about the effect of components on themselves.

DEFINITION 3. A mechanism is essentially cross-catalytic, if the canonic mechanism related to its kinetic differential equation (see /5/) is cross-catalytic.

If the reader does not feel it necessary to make a distinction between cross-catalytic and essentially cross-catalytic mechanisms, he may disregard this difference.

DEFINITION 4. A mechanism is weakly realistic if its reactant complexes $C(i) (i \in \{1, 2, \ldots, N\})$ belong to one of the following two types:

(i) there is an $m \in \{1, 2, \ldots, M\}$ such that $C(i) = y^m(i)A(m)$;

(ii) $C(i) = \sum_{m=1}^{M} y^m(i)A(m)$; $y^m(i) = 0$ or 1 for all $m \in \{1, 2, \ldots, M\}$.

It is easy to see that realistic mechanisms, i.e. those with reactant complexes not longer than two (/10/, p. 288) belong to the class of weakly realistic ones, and generalized compartment systems (/11/) are also weakly realistic.

RESULTS

THEOREM. A weakly realistic mechanism of the gradient type is essentially cross-catalytic.

Proof. Let us suppose, on the contrary, that there is a term $-kx_m x_{m'} P$ on the right side of the m-th equation of the kinetic differential equation system: here $k \in R_+$, $m, m' \in \{1, 2, \ldots, M\}$, $m \neq m'$ and P is a – possibly void – product of certain x_i-s ($i \neq m, m'$). A well-known necessary and sufficient condition for the existence of a potential for the equation $\dot{x} = f \circ x$, where $f = : (f_1, \ldots, f_M)$, is: $\partial_{i j} f = \partial_{j i} f$ $(i, j \in \{1, 2, \ldots, M\})$(7 , 10.35 Remarks). In our case

$$\partial_{m,m} f = -kx_m P + \ldots = \partial_{m m} f,$$

should hold, i.e. f_m, should contain the term $-kx_m^2 P/2$. This is impossible, because this term has a negative coefficient and it does not contain x_m, (see /5/).

A generalization of obeying to the atomic balance is conservativity, a notion introduced by Horn and Jackson (see /6/, p. 89, or /10/, p. 251).

DEFINITION 5. A mechanism is conservative if there exists a vector $r \in R^M$ with positive coordinates, orthogonal to all of the elementary reaction vectors (or to the stoichiometric space).

Obviously, if a cross-catalytic mechanism contains elementary reactions of type (i) (Def. 2), too, then it is not conservative. A consequence of this fact is worth underlinig.

COROLLARY. Conservative gradient systems may be found in only two classes of mechanisms:

(i) in the class of non-weakly realistic and non-cross-catalytic ones, and

(ii) in the class of those cross-catalytic ones that contain elementary reactions of type (ii) (Def. 2) only.

An example of type (ii) of the Corollary is a closed compartment system with a symmetric reaction rate matrix. This is in contrast to the conclusion of Ref. /1/ (p. 165) due to the differences between our definitions. However, although the second example in Ref. /1/ (p. 166) is a conservative, non-weakly realistic, and non-cross-

catalytic mechanism, it is not a gradient system in the sense of our Definition 1, and this statement is in accordance with Ref. /1/.

Relations between earlier works and our results remain to be studied. At present, as we see (cf. /8/, pp. 38-41) the usual procedure is as follows: a transformation $y := g \cdot x$ is performed on the equation $\dot{x} = f \circ x$, so as to obtain $f \circ x = V' \circ y$, where $V \in C^2(R^M, R)$. Naturally, $\dot{x} = V' \circ y$ is not a gradient system. It would help to clarify the situation if we could determine in which case will a gradient system be obtained by a transformation of the above type?

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