Formal first-order chemical kinetics

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Dedicated to Professor Ing. J. Kováč, DrSc., in honour of his 60th birthday

Contents

Chemical kinetic systems involving the first-order reactions are investigated from the unified standpoint. Theorems are derived which are significant in the understanding of general properties of the first-order kinetic systems. A brief description is given for special type of kinetic graphs.

С помощью унифицированного подхода исследуются химические кинетические системы, включающие реакции первого порядка. Выводятся теоремы, важные для понимания общих свойств кинетических систем первого порядка. Приводится краткое описание кинетических графиков особого вида.

I. Introduction

The main purpose of this work is to give a general and unifying viewpoint on chemical kinetic systems involving only first-order reactions. Formal aspects of

chemical kinetics were initiated to be studied at the beginning of this century by the well-known communication of *Wegscheider* [1] in which he demonstrated that the condition of vanishing of time derivatives of concentrations does not necessarily coincide with the thermodynamic equilibrium condition when there are several linearly independent reactions controlled by the mass-action law. It was demonstrated that the condition of vanishing of time derivatives of concentrations coincides with the thermodynamic equilibrium conditions only if there are fulfilled special relations between the rate constants.

This situation became known as Wegscheider's paradox, was invoked by *Lewis* [2] by his very general "law of entire equilibrium", which requires that every chemical reaction should be accompanied by its retroreaction, and that their rates are balanced at equilibrium. Applying this principle of detailed balance (in physics with an analogue in a principle of microscopic reversibility) we get that the rate of overall reaction—retroreaction pair vanishes at all equilibrium points. With this constraint it is not difficult to show [3—5] that the condition of equilibrium for systems controlled by the mass-action law always coincides with the condition of thermodynamic equilibrium in ideal mixtures, so Wegscheider's paradox is removed. It can be also shown that the free energy decreases with increasing time in all non-equilibrium states (*i.e.* it plays a role of a Lyapunov function known in the theory of dynamic stability of differential equations). Hence, the condition of detailed balance ensures a consistency of formal chemical kinetics with classical thermodynamics of closed systems of ideal mixtures. It was demonstrated by *Horn* and *Jackson* [6, 7] that these properties of chemical kinetic systems restricted by the detailed-balancing condition can be considerably generalized also for systems in which the condition is not required. Recently, formal aspects of chemical kinetics are under intensive studies [8, 9] of many reasearchers from different branches of physics, biology, ecology, and economics. Moreover, some results of formal kinetics belong between fundamental reasoning examples in non-equilibrium thermodynamics and synergetics.

The present work is devoted to studies of formal aspects of closed chemical systems involving first-order reactions. We emphasize that many chemical kinetic systems involving the second and/or higher order reactions can be well approximated by the so-called pseudo-reactions when concentrations of some species (educts) are kept fixed (*e.g.* in biochemistry). This fact essentially enlarges impact and importance of obtained theoretical results for general kinetics. Furthermore, the formal chemical kinetics of first-order reactions can serve [6, 7] as a prototype for an elaboration of methods applicable for systems involving reactions of higher orders (non-linear kinetics). The present work exploits very extensively the graph theory [10, 11]. Its approaches and notions belong between progressive elements of new viewpoints on formal chemical kinetics [9], they

make possible to formulate very easy many theoretical concepts and techniques, whereas their pure algebraic (or verbal) presentation is often clumsy or almost impossible.

II. Kinetic system

Let us study the following system of three first-order reactions

$$\begin{aligned} &R_1\colon X_1 \xrightarrow{k_{12}} X_2 \\ &R_2\colon X_2 \xrightarrow{k_{23}} X_3 \\ &R_3\colon X_1 \xrightarrow{k_{13}} X_3 \end{aligned} \tag{1}$$

The symbol R_1 denotes the first-order chemical reaction transforming an educt X_1 into a product X_2, its rate is determined by a positive *rate constant* k_{12}, in a similar way there are interpreted R_2 and R_3. We postulate, if $k_{ij} = 0$, then a reaction $X_i \to X_j$ is not presented in the studied system. Since reactions $X_i \to X_i$ are irrelevant for the dynamics of system, we put $k_{ii} = 0$; *i.e.* all "diagonal" rate constants are zero. The *rate matrix* assigned to a system composed of n species $X_1, X_2, \ldots, X_n$ is a square matrix (n, n) with entries k_{ij}, $\boldsymbol{K} = (k_{ij})$. For system (*1*) its form is

$$\boldsymbol{K} = \begin{pmatrix} 0 & k_{12} & k_{13} \\ 0 & 0 & k_{23} \\ 0 & 0 & 0 \end{pmatrix} \tag{2}$$

Let $\mathscr{X} = \{X_1, X_2, \ldots, X_n\}$ be a species set, $\mathscr{R} = \{R_1, R_2, \ldots, R_m\} \subset \mathscr{X} \times \mathscr{X}$ be a non-empty subset of direct product $\mathscr{X} \times \mathscr{X}$, this set is called the reaction set. It contains only those ordered pairs of species from $\mathscr{X}$ that are different, *i.e.* if $R_a = (X_i, X_j) \in \mathscr{R}$, then $i \neq j$. We assign to each entity $R_a = (X_i, X_j)$ a positive rate constant k_{ij} from the rate matrix $\boldsymbol{K}$. The reaction set is composed of ordered pairs of species with positive rate constants

$$\mathscr{R} = \{(X_i, X_j);\ k_{ij} > 0\} \tag{3}$$

The *kinetic system* $\mathscr{K}$ is determined as an ordered triple

$$\mathscr{K} = (\mathscr{X}, \mathscr{R}, \boldsymbol{K}) \tag{4}$$

where $\mathscr{X}$ is the species set, $\mathscr{R}$ is the reaction set, and $\boldsymbol{K}$ is the rate matrix; the kinetic system assigned to (*1*) is of the form: $\mathscr{X} = \{X_1, X_2, X_3\}$, $\mathscr{R} = \{R_1 = (X_1, X_2), R_2 = (X_2, X_3), R_3 = (X_1, X_3)\}$, and the rate matrix is specified by (*2*).

1. Kinetic matrix

The *kinetic matrix* corresponding to the kinetic system (4) is defined by [6]

$$\boldsymbol{A} = \varrho(\boldsymbol{K}) = -\,\mathrm{dg}\,(\boldsymbol{K}\boldsymbol{e}) + \boldsymbol{K}^T \tag{5}$$

where $\boldsymbol{K}^T$ is the transposed rate matrix, $\boldsymbol{D} = \mathrm{dg}\,(\boldsymbol{d})$ is a diagonal matrix formed by the vector $\boldsymbol{d} = (d_1, d_2, \ldots, d_n)^T$ in such a way that $D_{ij} = d_i\delta_{ij}$, δ_{ij} is the usual Kronecker's delta. Vector $\boldsymbol{e}$ in (5) is an n-dimensional column vector composed of unit elements

$$\boldsymbol{e} = (1,\ 1,\ \ \ 1)^T \tag{6}$$

The matrix $\mathrm{dg}\,(\boldsymbol{K}\boldsymbol{e})$ contains row summations of $\boldsymbol{K}$

$$\boldsymbol{L} = \mathrm{dg}\,(\boldsymbol{K}\boldsymbol{e}) = (L_{ij}) \tag{7a}$$

$$L_{ij} = l_i\delta_{ij} \tag{7b}$$

$$l_i = \sum_{j=1}^{n} k_{ij} \tag{7c}$$

Hence, the kinetic matrix can be expressed as follows

$$\boldsymbol{A} = -\boldsymbol{L} + \boldsymbol{K}^T \tag{8}$$

Kinetic matrix of (1) is

$$\boldsymbol{A} = \begin{pmatrix} -k_{12} - k_{13} & 0 & 0 \\ k_{12} & -k_{23} & 0 \\ k_{13} & k_{23} & 0 \end{pmatrix} \tag{9}$$

It can be easily verified that ϱ is a linear transformation

$$\varrho(\lambda\boldsymbol{K}) = \lambda\varrho(\boldsymbol{K}) \tag{10a}$$

$$\varrho(\boldsymbol{K}_1 + \boldsymbol{K}_2) = \varrho(\boldsymbol{K}_1) + \varrho(\boldsymbol{K}_2) \tag{10b}$$

If $\boldsymbol{K}_1$ and $\boldsymbol{K}_2$ differ only in diagonal elements, then

$$\varrho(\boldsymbol{K}_1) = \varrho(\boldsymbol{K}_2) \tag{10c}$$

Furthermore, if $\boldsymbol{D}$ is a diagonal matrix, then

$$\boldsymbol{A}\boldsymbol{D} = \varrho(\boldsymbol{K})\boldsymbol{D} = \varrho(\boldsymbol{D}\boldsymbol{K}) \tag{10d}$$

One of the most important properties of kinetic matrix is that its column summations are vanishing

$$\sum_{i=1}^{n} A_{ij} = 0 \qquad (j = 1, 2, \ldots, n) \tag{11}$$

The rank of $\boldsymbol{A}$ is ranged by

$$1 \leq r(\boldsymbol{A}) \leq n - 1 \tag{12}$$

The defect of $\boldsymbol{A}$ is determined by $d(\boldsymbol{A}) = n - r(\boldsymbol{A})$. There exist $d = d(\boldsymbol{A})$ linearly independent vectors that are solution of the following homogeneous problem

$$\boldsymbol{f}_i^T \boldsymbol{A} = 0 \tag{13}$$

for $i = 1, 2, \ldots, d$, where $\boldsymbol{f}_i$ are elements of d-dimensional null space (kernel) of $\boldsymbol{A}^T$

2. *Kinetic graph*

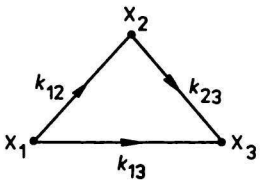
We assign to each kinetic system $\mathscr{K} = (\mathscr{X}, \mathscr{R}, \boldsymbol{K})$ an oriented graph [10, 11] (without loops and multiple edges) called *the kinetic graph* [12]

$$G(\mathscr{K}) = (\mathscr{X}, \mathscr{R}, \varphi) \tag{14}$$

where $\mathscr{X} = \{X_1, X_2, \ldots, X_n\}$ is a vertex set (species) and $\mathscr{R} = \{R_1, R_2, \ldots, R_m\}$ is an edge set (reactions). Each edge $R_\alpha \in \mathscr{R}$ is expressed by the ordered pair of vertices X_i and X_j from $\mathscr{X}$, $R_\alpha = (X_i, X_j)$, the vertex X_i (X_j) is initial (terminal) of the given edge R_α. The mapping $\varphi: \mathscr{R} \to (0, \infty)$ assigns to each edge $R_\alpha = (X_i, X_j)$ a positive number called the rate constant. Formally,

$$\varphi(R_\alpha) = \begin{cases} k_{ij} > 0 & (R_\alpha \in \mathscr{R}) \\ 0 & (R_\alpha \notin \mathscr{R}) \end{cases} \tag{15}$$

We see that the concept of kinetic graph is very closely related to the kinetic system, it visualizes the abstract notion "kinetic system", *e.g.* for (*1*) we have



(*16*)

where edges are evaluated by rate constants. One can say that kinetic graph is induced by the rate matrix $\boldsymbol{K}$, its dimension determines the number of vertices in $G(\mathscr{K})$, the edge (X_i, X_j) is presented in $G(\mathscr{K})$ when the rate constant k_{ij} from $\boldsymbol{K}$ is positive. We shall assume throughout this work that the kinetic graph is *connected* [10, 11], it contains only one component. If the kinetic graph is *disconnected* [10, 11], the corresponding kinetic system $\mathscr{K}$ may be separated in a few non-interacting subsystems which in forthcoming considerations are studied as independent kinetic systems with connected kinetic graphs.

3. *Differential equations over kinetic graph* [12—14]

A concentration of a species X_i is denoted by $x_i = x_i(t)$, where t is time-independent variable. The *concentration vector* $\boldsymbol{x}$ is determined as an n-dimensional column vector with components x_i

$$\boldsymbol{x} = (x_1, x_2, \ldots, x_n)^T \tag{17}$$

We study a kinetic system $\mathscr{K} = (\mathscr{X}, \mathscr{R}, \varphi)$ with kinetic graph $G(\mathscr{K}) = (\mathscr{X}, \mathscr{R}, \varphi)$. Let us denote by $\Gamma_+(i)$ ($\Gamma_-(i)$) a set of all vertex indices that are incident with edges outgoing (incoming) from (to) the vertex X_i. For kinetic graph (*16*) these sets are: $\Gamma_+(1) = \{2, 3\}$, $\Gamma_+(2) = \{3\}$, $\Gamma_+(3) = \emptyset$, $\Gamma_-(1) = \emptyset$, $\Gamma_-(2) = \{1\}$, $\Gamma_-(3) = \{1, 2\}$. We assign to each vertex X_i a differential equation for time derivative of x_i, $\dot{x}_i = \mathrm{d}x_i/\mathrm{d}t$,

$$\dot{x}_i = -\left\{\sum_{j \in \Gamma_+(i)} k_{ij}\right\} x_i + \sum_{j \in \Gamma_-(i)} k_{ji} x_j \tag{18}$$

where the first (second) term expresses the rate of annihilation (creation) of the species X_i. We recall the property of $\boldsymbol{K}$, its entries are vanishing if the corresponding edges are not presented at the kinetic graph, the first summation from circled brackets is equal to the entity l_i determined by (*7c*)

$$l_i = \sum_{j \in \Gamma_+(i)} k_{ij} = \sum_{j=1}^{n} k_{ij} \tag{19a}$$

Similarly, the second summation from the r.h.s. of (*18*) is essentially simplified, since $k_{ij} = 0$ for $j \notin \Gamma_-(i)$ we get

$$\sum_{j \in \Gamma_-(i)} k_{ji} x_j = \sum_{j=1}^{n} k_{ji} x_j \tag{19b}$$

Introducing (*19a—19b*) in (*18*) we arrive at

$$\dot{x}_i = -l_i x_i + \sum_{j=1}^{n} k_{ji} x_j \tag{20}$$

This system of linear differential equations determines the time evolution of kinetic system $\mathscr{K}$ for $t > 0$. The *initial conditions* of (*20*) are specified by concentrations at the time $t = 0$

$$\boldsymbol{x}(0) = \boldsymbol{x}_0 = (x_1^0, x_2^0, \ldots, x_n^0) \tag{21}$$

where $x_i^0 = x_i(0)$.

In the matrix formalism the system of differential equations (*20*) is of the form

$$\dot{\boldsymbol{x}} = \boldsymbol{A}\boldsymbol{x} \qquad [\boldsymbol{x}(0) = \boldsymbol{x}_0] \tag{22}$$

The solution of this system of differential equations is a standard task of the theory of linear differential equations, algebraically it leads to the determination of eigenvalues and corresponding strings of generalized eigenvectors of the kinetic matrix.

Let us assume that the kinetic matrix $\boldsymbol{A}$ has p different eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_p$, their multiplicities are determined by integers $n_1, n_2, \ldots, n_p$ restricted by $n_1 + n_2 + \quad + n_p = n$. A general solution of (*22*) looks like this [15]

$$x_i = c_{i1}(t)\, \mathrm{e}^{\lambda_1 t} + c_{i2}(t)\, \mathrm{e}^{\lambda_2 t} + \quad + c_{ip}(t)\, \mathrm{e}^{\lambda_p t} \tag{23}$$

where $c_{ij}(t)$ is a polynomial function of the time variable t, its order is not greater than $n_j - 1$. For simple eigenvalue λ_j ($n_j = 1$) the entity $c_{ij}(t)$ is a constant. We shall not investigate a construction of these polynomial functions from (*23*); the main purpose of the work is a qualitative study of the solution of (*22*) based on algebraical properties of the kinetic matrix $\boldsymbol{A}$. After simple integration of (*22*) and taking into account the formula (*8*) we get [4]

$$\boldsymbol{x}(t) = \mathrm{e}^{-\boldsymbol{L}t}\boldsymbol{x}_0 + \int_0^t \mathrm{e}^{-\boldsymbol{L}\vartheta}\boldsymbol{K}^T\boldsymbol{x}(t - \vartheta)\, \mathrm{d}\vartheta \tag{24a}$$

or

$$x_i(t) = \mathrm{e}^{-l_i t}\, x_i^0 + \sum_{j=1}^{n} k_{ji} \int_0^t \mathrm{e}^{-l_i \vartheta} x_j(t - \vartheta)\, \mathrm{d}\vartheta \tag{24b}$$

for $i = 1, 2, \ldots, n$. It will be demonstrated that this integral solution of (*22*) is very useful for our forthcoming qualitative theory.

III. Qualitative theory

This section is devoted to the qualitative features and properties of solutions of the fundamental differential equation (*22*). The used theoretical approach is fully based on simple algebraic properties of the kinetic matrix $\boldsymbol{A}$ without necessity of an implementation of additional physicochemical assumptions.

1. Conservation laws

The kinetic matrix $\boldsymbol{A}$ has at least one nontrivial solution of the homogeneous problem (*13*). A solution denoted by $\boldsymbol{f}_1$ can be constructed in an explicit form by making use of the property (*11*) (column summations of $\boldsymbol{A}$ are vanishing)

$$\boldsymbol{f}_1 = \boldsymbol{e} = (1, 1, \ldots, 1)^T \tag{25}$$

For $d \geq 2$ there exist further nontrivial vectors $\boldsymbol{f}_2, \boldsymbol{f}_3, \ldots, \boldsymbol{f}_d$, but their explicit form already depends on actual values of entries of the kinetic matrix.

Multiplying differential equation (*22*) from the left side by the vector $\boldsymbol{f}_i^T$ (for $i = 1, 2, \ldots, d$) we get

$$\boldsymbol{f}_i^T \dot{\boldsymbol{x}} = 0 \tag{26}$$

where the relation (*13*) was used. Its integration gives the i-th conservation law

$$\boldsymbol{f}_i^T \boldsymbol{x} = \omega_i \tag{27}$$

The integration constant ω_i is unambiguously determined by initial condition (*21*)

$$\omega_i = \boldsymbol{f}_i^T \boldsymbol{x}_0 \tag{28}$$

Without loss of generality of our considerations we can assume that the initial concentration vector $\boldsymbol{x}_0$ from (*11*) is "normalized" as follows

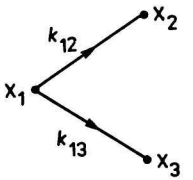
$$\boldsymbol{e}^T \boldsymbol{x}_0 = x_1^0 + x_2^0 + \quad + x_n^0 = 1 \tag{29}$$

Since the vector $\boldsymbol{f}_1$ is identical with the vector $\boldsymbol{e}$ (see eqn (*25*)), the first conservation law is

$$\boldsymbol{e}^T \boldsymbol{x} = x_1 + x_2 + \quad + x_n = 1 \tag{30}$$

for each $t \geqslant 0$. This conservation law has very important physical interpretation, the summation of concentrations assigned to individual species X_i from the kinetic system $\mathscr{K}$ is unit for each $t \geqslant 0$. It is a specific manifestation of the mass conservation law, but we have to emphasize that its validity immediately follows from the algebraic property (*11*) of the kinetic matrix $\boldsymbol{A}$. Further conservation laws (*27*) for $i = 2, 3, \ldots, d$ are not of such generality, their actual form depends on the kinetic matrix $\boldsymbol{A}$.

For illustration, let us study the kinetic graph



(*31a*)

the corresponding kinetic matrix being

$$\boldsymbol{A} = \begin{pmatrix} -k_{12} - k_{13} & 0 & 0 \\ k_{12} & 0 & 0 \\ k_{13} & 0 & 0 \end{pmatrix} \tag{31b}$$

The rank of A is $r(A) = 1$, then for defect we have $d(A) = 3 - 1 = 2$. The matrix A has two linearly independent solutions of (*13*)

$$\boldsymbol{f}_1 = (1, 1, 1)^T \tag{32a}$$

$$\boldsymbol{f}_2 = (0, k_{13}, -k_{12})^T \tag{32b}$$

Introducing these two vectors in (*27*) we get the following two conservation laws

$$x_1 + x_2 + x_3 = 1 \tag{33a}$$

$$k_{13}x_2 - k_{12}x_3 = k_{13}x_2^0 - k_{12}x_3^0 \tag{33b}$$

for each $t \geqslant 0$.

2. *Non-negativity of concentration vector*

A vector $\boldsymbol{a} = (a_1, a_2, \ldots, a_n)^T$ will be called non-negative [7] if all of its components are non-negative ($a_i \geqslant 0$ for $i = 1, 2, \ldots, n$), formally $\boldsymbol{a} \geqslant 0$. In an analogous way we define positive vector, negative vector, *etc.* Generalization of this simple terminology may be done also for matrices.

We shall start from an assumption that the initial concentration vector $\boldsymbol{x}_0$ is non-negative, $\boldsymbol{x}_0 \geqslant 0$. We have to prove that the concentration vector $\boldsymbol{x}(t)$ is also non-negative for each $t \geqslant 0$

$$\boldsymbol{x}(0) = \boldsymbol{x}_0 \geqslant 0 \Rightarrow \boldsymbol{x}(t) \geqslant 0 \tag{34}$$

Assuming $x_i^0 > 0$, from (*20*) it follows that the time derivative $\dot{x}_i(0)$ may be either positive or negative; if $x_i^0 = 0$, then $\dot{x}_i(0)$ is non-negative, $\dot{x}_i(0) \geqslant 0$. Hence, if the initial vector $\boldsymbol{x}_0 \geqslant 0$ is non-negative, then there exists such small positive number ε that for all $0 \leq t \leq \varepsilon$ the concentration vector $\boldsymbol{x}(t)$ is non-negative. Now, let us assume that $x_i(t)$ is a component of the concentration vector which first passes from positive to negative values; this means that for a time $t_0 > 0$ we have $x_i(t_0) = 0$. Following (*24b*), the concentration $x_i(t)$ can vanish for some finite t_0 only if at least another one concentration $x_j(t)$ ($j \neq i$) is negative for the time t_0. But this is in a contradiction with our initial assumption that $x_i(t)$ is the first concentration to be negative, hence all concentrations should be non-negative.

Conservation law (*30*) and the non-negativity property (*34*) can be linked at the more general property

$$\boldsymbol{x}_0 \geqslant 0 \quad \text{and} \quad \boldsymbol{e}^T\boldsymbol{x}_0 = 1 \Rightarrow \boldsymbol{x}(t) \geqslant 0 \quad \text{and} \quad \boldsymbol{e}^T\boldsymbol{x}(t) = 1 \tag{35}$$

for each $t \geqslant 0$. This immediately implies that all concentrations are ranged by

$$0 \leq x_i(t) \leq 1 \tag{36}$$

for each $i = 1, 2, \ldots, n$ and $t \geqslant 0$.

If the kinetic graph $G(\mathscr{K})$ is *strongly connected* [10] (for an arbitrary pair of vertices X_i and X_j there exist two directed paths going from X_i to X_j and from X_j to X_i) the above result (*35*) can be presented in a stronger form, a non-negativity of the initial concentration vector implies its positivity for each $t \geqslant 0$

$$\boldsymbol{x}_0 \geqslant 0 \quad \text{and} \quad \mathrm{e}^T\boldsymbol{x}_0 = 1 \Rightarrow \boldsymbol{x}(t) > 0 \quad \text{and} \quad \mathrm{e}^T\boldsymbol{x}(t) = 1 \tag{37}$$

It can be proved also by making use of the integral solution (*24b*), for strongly connected kinetic graph each vertex X_i is coincident with a vertex X_j such that the oriented edge (X_i, X_j) exists; hence for each i we have an index j such that $k_{ij} > 0$.

3. *Properties of solution at* $t = 0$ [13, 14]

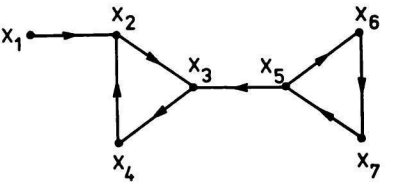
The vertex set $\mathscr{X}$ can be decomposed in two disjoint subsets $\mathscr{X}_0$ and $\mathscr{X}_+$

$$\mathscr{X} = \mathscr{X}_0 \cup \mathscr{X}_+ \tag{38a}$$

$$\mathscr{X}_0 = \{X_i \in \mathscr{X};\ x_i^0 = 0\} \tag{38b}$$

$$\mathscr{X}_+ = \{X_i \in \mathscr{X};\ x_i^0 > 0\} \tag{38c}$$

The subset $\mathscr{X}_0$ ($\mathscr{X}_+$) is composed of those vertices for which initial concentrations are vanishing (positive), *e.g.* if $X_i \in \mathscr{X}_0$ then $x_i^0 = 0$. We assign to each vertex $X_i \in \mathscr{X}_0$ a positive integer $\varkappa_i$, it expresses the length of the shortest path from $\mathscr{X}_+$ to X_i; if such a path does not exist we put $\varkappa_i = \infty$. The above definition of integers $\varkappa_i$ is naturally extended also for vertices $X_i \in \mathscr{X}_+$, we put $\varkappa_i = 0$. For illustration, let us study the following kinetic graph



(*39*)

The initial concentration vector is specified by $\boldsymbol{x}_0 = (0, 0, 0, 0, 0, x_6^0, x_7^0)$, where x_6^0 and x_7^0 are positive components. The subsets $\mathscr{X}_0$ and $\mathscr{X}_+$ from (*38*) are $\mathscr{X}_0 = \{X_1, X_2, X_3, X_4, X_5\}$ and $\mathscr{X}_+ = \{X_6, X_7\}$. We assign to each vertex $X_i \in \mathscr{X}_0$ an integer $\varkappa_i$, it specifies the length of the shortest path from $\mathscr{X}_+$ to X_i, we get $\varkappa_1 = \infty$, $\varkappa_2 = 4$, $\varkappa_3 = 2$, $\varkappa_4 = 3$, $\varkappa_5 = 1$, $\varkappa_6 = 0$, $\varkappa_7 = 0$. For instance, the shortest path from $\mathscr{X}_+$ to X_2 is a sequence of vertices and edges X_7—X_5—X_3—X_4—X_2,

its length is equal to 4. For the vertex X_1 there does not exist a path from $\mathscr{X}_+$ to X_1, hence $\varkappa_1 = \infty$. Finally, the vertices X_6 and X_7 belong to $\mathscr{X}_+$, therefore $\varkappa_6 = \varkappa_7 = 0$.

Applying this terminology we can prove in an analogous way as (*34*) that for a given initial state $\boldsymbol{x}_0$ (the decomposition $\mathscr{X} = \mathscr{X}_0 \cup \mathscr{X}_+$ is determined by $\boldsymbol{x}_0$) concentrations $x_i(t)$ for each $t \geqslant 0$ are either zero or positive depending on the value of the integer $\varkappa_i$

$$\varkappa_i = \infty \Rightarrow x_i(t) = 0 \tag{40a}$$

$$\varkappa_i < \infty \Rightarrow x_i(t) > 0 \tag{40b}$$

Physical interpretation of this result is very simple. Concentrations $x_i(t)$ assigned to those species (vertices) $X_i \in \mathscr{X}_0$ that are not reached by an oriented path from $\mathscr{X}_+$ to X_i ($\varkappa_i = \infty$) must be vanishing. There does not exist a mass flow (a path on kinetic graph oriented from $\mathscr{X}_+$) for their "deviation" from initial zero values.

The coefficients $\varkappa_i$ are proper tool for description of concentrations at the time $t = 0$. Let us investigate the kinetic system $\mathscr{K}$ with given initial concentration vector $\boldsymbol{x}_0$. At the neighborhood of time $t = 0$ each concentration $x_i(t)$ is an infinitely small entity of the order $\varkappa_i$

$$x_i(t) \to t^{\varkappa_i} v_i \qquad (\text{for } t \to 0) \tag{41}$$

where v_i is a positive constant. In order to prove (*41*) there is sufficient to show that time derivatives up to the order $\varkappa_i - 1$ are vanishing for $t = 0$

$$x_i^{(p)}(0) = 0 \qquad (p = 1, 2, \ldots, \varkappa_i - 1) \tag{42}$$

The first time derivative of $x_i(t)$ at $t = 0$ is determined by the relation (*22*), its straightforward generalization offers

$$\boldsymbol{x}^{(n)}(0) = \boldsymbol{A}^n \boldsymbol{x}(0) = \boldsymbol{A}^n \boldsymbol{x}_0 \tag{43a}$$

or in the component formalism

$$x_i^{(n)}(0) = \sum_j (\boldsymbol{A}^n)_{ij} x_j^0 \tag{43b}$$

The matrix element $(\boldsymbol{A}^n)_{ij}$ has very simple interpretation in the framework of graph theory [10], it corresponds to all possible paths (with possible repetition of edges) which are oriented from X_i to X_j. We are looking for a path with the shortest length, hence a repetition of edges is not permitted. From these simple considerations we deduce that the integer n from (*43b*) is equal to the coefficient $\varkappa_i$ assigned to the vertex X_i; we have proved the condition (*42*) from which immediately follows (*41*), the positiveness of constants v_i we get from (*40*).

4. Equilibrium concentration vector

Let us investigate the integral solution (*24b*) for $t \to \infty$. Since there exist exponential functions with negative exponents and moreover the concentrations are ranged by (*36*), for an arbitrary small $\varepsilon > 0$ we have such a time $T = T(\varepsilon) > 0$ that

$$t > T \Rightarrow |x_i(t + \tau) - x_i(t)| < \varepsilon \tag{44}$$

for each $i = 1, 2, \ldots, n$ and $\tau > 0$. This means that the concentration $x_i(t)$ for $t \gg 0$ is tending to a constant value and its time derivatives are vanishing for $t \gg 0$

$$\lim_{t \to \infty} \dot{\boldsymbol{x}}(t) = \boldsymbol{0} \tag{45}$$

Equilibrium concentration vector of the kinetic system $\mathscr{K}$ is defined as a limit value of the concentration vector for $t \to \infty$

$$\lim_{t \to \infty} \boldsymbol{x}(t) = \bar{\boldsymbol{x}} \tag{46}$$

Introducing (*45*) and (*46*) in (*22*) we get

$$\boldsymbol{A}\bar{\boldsymbol{x}} = \boldsymbol{0} \tag{47}$$

The equilibrium concentration vector $\bar{\boldsymbol{x}}$ is determined as a nontrivial solution ($\bar{\boldsymbol{x}} \neq 0$) of the homogeneous problem (*47*), it must simultaneously satisfy the condition (*35*)

$$\bar{\boldsymbol{x}} \geqslant 0 \quad \text{and} \quad \boldsymbol{e}^T\bar{\boldsymbol{x}} = 1 \tag{48}$$

For $r(\boldsymbol{A}) = n - 1$ the equilibrium concentration vector is determined by (*47*) unambiguously (the null space if $\boldsymbol{A}$ is 1-dimensional). If $r(\boldsymbol{A}) \leqslant n - 2$ (*i.e.* $d(\boldsymbol{A}) \geqslant 2$) the dimension of null space of $\boldsymbol{A}$ is greater than or equal to 2, this means that in order to construct the equilibrium concentration vector $\bar{\boldsymbol{x}}$ we have to use further conservation laws determined by vectors $\boldsymbol{f}_2, \boldsymbol{f}_3, \ldots, \boldsymbol{f}_d$.

For illustration let us construct the equilibrium concentration vector for the kinetic system specified by the graph (*31a*), solving (*47*) we get

$$\bar{\boldsymbol{x}} = (0, \alpha, \beta)^T \tag{49}$$

where α, β are arbitrary non-negative constants. The vectors $\boldsymbol{f}_1$ and $\boldsymbol{f}_2$ are determined by (*32a—32b*), the equilibrium concentration vector is

$$\bar{\boldsymbol{x}} = \left(0, \frac{k_{13}x_2^0 - k_{12}(x_3^0 - 1)}{k_{12} + k_{13}}, \frac{k_{12}x_3^0 - k_{13}(x_2^0 - 1)}{k_{12} + k_{13}}\right)^T \tag{50}$$

What is the physical interpretation of obtained theoretical results? An arbitrary kinetic system is tending for $t \to \infty$ to an equilibrium concentration vector with vanishing time derivatives of all its components. Sustained concentration oscillations are not, a priori, permitted. Only damped oscillations can occur and they are damped by an exponential factor $e^{-\alpha t}$, where $\alpha > 0$. Therefore, the kinetic systems (closed and involving only first-order reactions) can be verbally characterized as "quasi-thermodynamic", they are spontaneously tending to equilibrium state. For $r(\boldsymbol{A}) = n - 1$ these equilibrium states are determined unambiguously, whereas for $r(\boldsymbol{A}) \leqslant n - 2$ they depend on initial concentration vectors (Fig. 1).

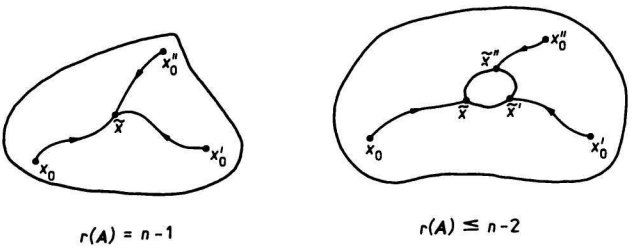


Fig. 1. Schematic trajectories of differential equations (*22*). For $r(\boldsymbol{A}) = n - 1$ the equilibrium state (terminus of trajectory) is determined unambiguously. All trajectories end at the same equilibrium point independently of their initial states. For $r(\boldsymbol{A}) \leqslant n - 2$ equilibrium states are not determined unambiguously, the trajectory terminus depends on its initial state.

5. *Pseudo-Lyapunov function*

Very general approach for the construction of Lyapunov function was suggested by *Horn* [6], his technique has strong limitation — it is applicable only for kinetic systems with strongly connected graphs. Recently, *Yablonskii et al.* [16] introduced the so-called *pseudo-Lyapunov function* (which is only continuous, standard Lyapunov function should be also smooth, *i.e.* its time derivative is continuous), they did not present a proof of a negativeness of the first time derivative on intervals of its smoothness.

Let us define the so-called l_1-norm of a vector $\boldsymbol{a} = (a_1, a_2, \ldots, a_n)^T$

$$|\boldsymbol{a}| = \sum_{i=1}^{n} |a_i| \tag{51}$$

The following three properties are satisfied

$$|\boldsymbol{a}| \geqslant 0 \qquad (= 0 \text{ only for } \boldsymbol{a} = \boldsymbol{0}) \tag{52a}$$

$$|\alpha \boldsymbol{a}| = |\alpha|\,|\boldsymbol{a}| \tag{52b}$$

$$|\boldsymbol{a} + \boldsymbol{b}| \leqslant |\boldsymbol{a}| + |\boldsymbol{b}| \tag{52c}$$

where α is a complex number. Pseudo-Lyapunov function is determined as follows [16]

$$\mathrm{L}(t) = |\boldsymbol{x}(t) - \bar{\boldsymbol{x}}| = \sum_{i=1}^{n} |x_i(t) - \bar{x}_i| \tag{53}$$

Applying (*52a*) and (*52c*) we get

$$0 \leqslant \mathrm{L}(t) \leqslant 2 \qquad (\text{for each } t \geqslant 0) \tag{54a}$$

$$\lim_{t \to \infty} \mathrm{L}(t) = 0 \tag{54b}$$

Pseudo-Lyapunov function is a positive and continuous function, for $t \to \infty$ it asymptotically tends to zero. The basic property of this function is its monotonous decreasing for increased time t (Fig. 2)

$$\mathrm{L}(t + \tau) < \mathrm{L}(t) \qquad (\text{for } \tau > 0) \tag{55}$$

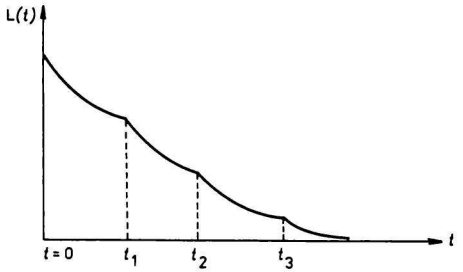


Fig. 2. Illustrative plotting of the pseudo-Lyapunov function L(t) defined by (*53*), at the time points $t = t_1, t_2, t_3$ its first time derivatives do not exist (though the function is continuous for each $t \geqslant 0$).

The function L(t) is interpreted as a "distance" (in l_1 metrics) between the point $\boldsymbol{x}(t)$ lying on trajectory of differential equation (*22*) and the equilibrium point $\bar{\boldsymbol{x}}$ (terminus of the trajectory). Following (*55*) this distance is monotonously decreasing and vanishing for $t \to \infty$ (for $\boldsymbol{x} = \bar{\boldsymbol{x}}$).

Let us have a set of points $\{t_0 = 0, t_1, t_2, \ldots, t_\alpha, \ldots\}$ on time axis, they are determined in such a way that for $t_{\alpha-1} < t < t_\alpha$ ($\alpha = 1, 2, \ldots$) the differences $x_i(t) - \bar{x}_i$ from (*53*) have the same sign, this sign may be changed only at the points $t = t_\alpha$ for $\alpha = 1, 2,$ Let the time t be ranged by $t_{\alpha-1} < t < t_\alpha$, then the relation (*53*) is

$$\mathrm{L}(t) = \sum_{i=1}^{n} \omega_i [x_i(t) - \bar{x}_i] \tag{56a}$$

where the coefficients ω_i are

$$\omega_i = \begin{cases} 1 & (\text{for } x_i(t) > \bar{x}_i) \\ -1 & (\text{for } x_i(t) < \bar{x}_i) \end{cases} \tag{56b}$$

The time derivative of $L(t)$ for a time $t_{\alpha-1} < t < t_\alpha$ is

$$\dot{L}(t) = \sum_{i=1}^{n} \omega_i \dot{x}_i(t) \tag{57}$$

Applying (*20*) and after simple algebraic manipulations we arrive at

$$\dot{L}(t) = \sum_{i,j=1}^{n} k_{ij}(\omega_i\omega_j - 1)\,\omega_i[x_i(t) - \bar{x}_i] \tag{58}$$

Since for an arbitrary kinetic system there exists at least a pair of indices i and j such that $k_{ij}\omega_i[x_i(t) - \bar{x}_i]$ is positive and $(\omega_i\omega_j - 1)$ is negative, the right-hand side of (*58*) must be negative

$$\dot{L}(t) \leqslant 0 \tag{59}$$

The time derivative of $L(t)$ is vanishing only if $x_i = \bar{x}_i$ for all i's (taking place for $t \to \infty$). Hence, we have proved that the pseudo-Lyapunov function for $t_{\alpha-1} < t < t_\alpha$ is monotonously decreasing, at the point $t = t_\alpha$ (for $\alpha = 1, 2, \ldots$) the time derivative does not exist. Since it is continuous, the pseudo-Lyapunov function should be monotonously decreasing on the whole positive time axis (Fig. 2).

The pseudo-Lyapunov function $L(t)$ may be simply generalized also for two trajectories $\boldsymbol{x}_A(t)$ and $\boldsymbol{x}_B(t)$ of the same kinetic system $\mathscr{K}$ where their initial points are different

$$L_{AB}(t) = |\boldsymbol{x}_A(t) - \boldsymbol{x}_B(t)| = \sum_{i=1}^{n} |x_i^A(t) - x_i^B(t)| \tag{60}$$

In a completely analogous way as above one can prove that this function is monotonously decreasing

$$L_{AB}(t + \tau) < L_{AB}(t) \qquad (\tau > 0) \tag{61}$$

and

$$\lim_{t \to \infty} L_{AB}(t) = |\bar{\boldsymbol{x}}_A - \bar{\boldsymbol{x}}_B| \tag{62}$$

where $\bar{\boldsymbol{x}}_A$ ($\bar{\boldsymbol{x}}_B$) is an equilibrium state of the trajectory $\boldsymbol{x}_A(t)$ [$\boldsymbol{x}_B(t)$]. For $r(\boldsymbol{A}) = n - 1$ these equilibrium points are identical, $\bar{\boldsymbol{x}}_A = \bar{\boldsymbol{x}}_B$, the pseudo-Lyapunov function is asymptotically vanishing for $t \to \infty$. For $r(\boldsymbol{A}) \leqslant n - 2$ equilibrium concentrations depend on the initial condition, then it asymptotically tends to $|\bar{\boldsymbol{x}}_A - \bar{\boldsymbol{x}}_B| > 0$ for $t \to \infty$. Summarizing the obtained results, the distance (in l_1 metrics) between two points from the trajectories $\boldsymbol{x}_A(t)$ and $\boldsymbol{x}_B(t)$ monotonously decreases to $|\bar{\boldsymbol{x}}_A - \bar{\boldsymbol{x}}_B|$ for $t \to \infty$.

Finally, let us define this special form of the pseudo-Lyapunov function

$$L_p(t) = |\boldsymbol{x}^{(p)}(t)| = \sum_{i=1}^{n} |x_i^{(p)}(t)| \tag{63}$$

for $p = 1, 2, \ldots$, where $x_i^{(p)}(t)$ is the p-th time derivative of the concentration vector. Generalizing (*20*) by induction we get $\boldsymbol{x}^{(p+1)} = \boldsymbol{A}\boldsymbol{x}^{(p)}$, where $\boldsymbol{x}^{(0)}(t) = \boldsymbol{x}(t)$ is original concentration vector. This pseudo-Lyapunov function is continuous and monotonically decreasing to zero

$$L_p(t + \tau) < L_p(t) \tag{64a}$$

$$\lim_{t \to \infty} L_p(t) = 0 \tag{64b}$$

Hence, single parameters of curvature monotonically decrease and asymptotically tend to zero.

IV Special forms of kinetic graph

For some special forms of kinetic graph qualitative properties of studied systems can be proved in much more stronger form than for general kinetic systems with unrestricted graphs (considered in the previous third section).

1. Acyclic kinetic graph

The *acyclic kinetic graph* does not contain oriented cycles. For kinetic systems determined by such graphs we are able to solve differential equations (*22*) in a compact analytical form [12]. One of the fundamental properties of acyclic graphs is that the vertices can be labelled in such a way that for each directed edge $(X_i, X_j) \in \mathscr{R}$ we have $i < j$ [10]. The vertex classified as the source (sink) should be indexed by 1 (n). Illustrative examples of acyclic graphs are (*16*) and (*31a*), where the vertices were already labelled in accordance with the above-mentioned property. As a consequence of this labelling of vertices is that the corresponding kinetic matrix is triangular, its entries above the main diagonal are zero. Eigenvalues of the kinetic matrix $\boldsymbol{A}$ are determined by $\det(\boldsymbol{A} - \lambda) = (-1)^n(\lambda + l_1)(\lambda + l_2)\ldots(\lambda + l_n)$, where $-l_i$ are diagonal entries of $\boldsymbol{A}$ determined by (*19a*)

$$\lambda_i = -l_i \qquad (i = 1, 2, \ldots, n) \tag{65}$$

Hence, for an acyclic kinetic graph the eigenvalues of $\boldsymbol{A}$ are determined by its

diagonal elements, their multiplicity is, in general, unit. A solution of (*22*) will be looked for in the form (*cf.* eqn (*23*))

$$x_i(t) = \sum_{p=1}^{i} N_{ip}\, \mathrm{e}^{-l_p t} \qquad (i = 1, 2, \ldots, n) \tag{66}$$

where N_{ip} are constant coefficients and the summing index p is ranged by $1 \leq p \leq i$ (since the kinetic graphs are acyclic one can simply verify that $N_{ip} = 0$ for $p = i + 1, i + 2, \ldots, n$). In order to simplify our forthcoming considerations we shall assume that the studied kinetic graph contains only one source (a vertex indexed by 1 and which is incident only with outgoing edges). Furthermore, we assume that the initial concentration vector is $\boldsymbol{x}_0 = (1, 0, \ldots, 0)^T$, *i.e.* at the time $t = 0$ the concentration of x_1 is unit while remaining vertices are zero. The differential equation (*22*) for x_1 gives $\dot{x}_1 = -l_1 x_1$, and $x_1(0) = 1$, then we get $x_1 = \mathrm{e}^{-l_1 t}$

$$N_{11} = 1 \tag{67}$$

Introducing (*66*) in (*20*) we arrive at

$$N_{ip} = \frac{1}{l_i - l_p} \sum_{j=1}^{i-1} k_{ji} N_{jp} \tag{68}$$

for $i = 1, 2, \ldots, n$ and $p = 1, 2, \ldots, i - 1$. This relation is determined only for $i \neq p$, diagonal coefficients N_{ii} (for $i = 2, 3, \ldots, n$) are constructed by making use of the initial condition $x_i(0) = 0$ (for $i = 2, 3, \ldots, n$)

$$N_{ii} = -\sum_{p=1}^{i-1} N_{ip} \tag{69}$$

Relations (*67*) to (*69*) are useful for recurrent determination of coefficients N_{ip}. At the first step we calculate coefficients N_{ip} for vertices that are adjacent by an edge to the source X_1. At the next (second) step we calculate these coefficients for forthcoming new vertices that are adjacent to previous ones, and so on.

The outlined purely algebraic approach for the construction of coefficients N_{ip} is essentially simplified by making use of the graph-theory notions. This is based on the observation [12] that the coefficient N_{ip} is simply equal to the sum of coefficients $N_{ip}^{(t)}$, where $N_{ip}^{(t)}$ is assigned to an oriented path directed from the source X_1 to the vertex X_i; coefficients $N_{ip}^{(t)}$ are expressed by simple algebraic formula. Hence, the solution of differential equations (*22*) for acyclic kinetic graph is transformed to a procedure involving only simple graph-theory considerations over corresponding kinetic graph.

The pseudo-Lyapunov function (*53*) for kinetic systems with acyclic kinetic graph can be transformed in a smooth form (the first time derivative is con-

tinuous). For simplicity, let us assume that the kinetic graph contains only one sink X_n (a vertex incident only with incoming edges). Then the equilibrium concentration vector is $\bar{x} = (0, 0, \ldots, 0, 1)^T$ The pseudo-Lyapunov function (*53*) is essentially simplified as follows

$$L(t) = x_1(t) + x_2(t) + \quad + x_{n-1}(t) - (x_n(t) - 1) \tag{70}$$

Applying the first conservation law (*30*) we get

$$L(t) = 2 - 2x_n(t) \tag{71}$$

The time derivative of $x_n(t)$ assigned to the source X_n should be positive (this immediately follows from (*20*) due to $l_n = 0$)

$$\dot{L}(t) = -2\dot{x}_n(t) \leqslant 0 \qquad (= 0 \text{ for } t \to \infty) \tag{72}$$

We have demonstrated that the pseudo-Lyapunov function (*53*) for kinetic systems with acyclic graph is smooth and asymptotically vanishing for $t \to \infty$, *i.e.* it has all attributes of standard Lyapunov functions.

2. *Strongly connected kinetic graph*

In section III.*2* we have proved that for kinetic systems with strongly connected graphs the concentration vector should be positive (*cf.* eqn (*37*)), since this property is satisfied for each $t > 0$, the equilibrium concentration vector should be also positive, $\bar{x} > 0$. The positiveness of equilibrium concentration vectors offers very important approach how to construct the Lyapunov function for kinetic systems with strongly connected graphs.

Let us define the diagonal matrix

$$\boldsymbol{D} = \mathrm{dg}\,(\bar{\boldsymbol{x}}) \tag{73}$$

which is nonsingular and its inverse matrix $\boldsymbol{D}^{-1}$ does exist. The matrix differential equation (*22*) can be transformed in the form

$$\dot{\boldsymbol{y}} = \boldsymbol{A}'\boldsymbol{y} \tag{74}$$

where $\boldsymbol{y} = \boldsymbol{D}^{-1}\boldsymbol{x}$, $\boldsymbol{A}' = \boldsymbol{D}^{-1}\boldsymbol{A}\boldsymbol{D}$, and the initial condition is specified by $\boldsymbol{y}_0 = \boldsymbol{y}(0) = \boldsymbol{D}^{-1}\boldsymbol{x}_0$. The equilibrium vector of (*74*) is determined by

$$\bar{\boldsymbol{y}} = \boldsymbol{D}^{-1}\bar{\boldsymbol{x}} = \boldsymbol{e} = (1, 1, \ldots, 1)^T \tag{75}$$

where

$$\lim_{t \to \infty} \boldsymbol{y}(t) = \bar{\boldsymbol{y}} = \boldsymbol{e} \tag{76}$$

Let us define a Lyapunov function as follows [6]

$$\mathrm{L}(t) = \bar{\boldsymbol{x}}^T \boldsymbol{\varphi}(\boldsymbol{y}) = \sum_{i=1}^{n} \bar{x}_i \varphi(y_i) \tag{77}$$

where $\boldsymbol{\varphi}(\boldsymbol{y})$ is a column vector with components $\varphi(y_i)$, $\boldsymbol{\varphi}(\boldsymbol{y}) = (\varphi(y_1), \ldots, \varphi(y_n))^T$, and $\varphi(\ )$ is an arbitrary positive, smooth and convex function. The first time derivative of (*77*) is

$$\dot{\mathrm{L}}(t) = \bar{\boldsymbol{x}}^T \,\mathrm{dg}\,(\dot{\boldsymbol{\varphi}}(\boldsymbol{y}))\dot{\boldsymbol{y}} = \boldsymbol{e}^T \,\mathrm{dg}\,(\dot{\boldsymbol{\varphi}}(\boldsymbol{y}))\, \varrho(\boldsymbol{DK})\boldsymbol{y} \tag{78}$$

where the property (*10d*) was used. We shall demonstrate that the derivation $\dot{\mathrm{L}}(t)$ is non-positive (vanishing only for $\boldsymbol{y} = \bar{\boldsymbol{y}} = \boldsymbol{e}$)

$$\dot{\mathrm{L}}(t) \leqslant 0 \qquad (= 0 \text{ for } t \to \infty) \tag{79}$$

This means that the function $\mathrm{L}(t)$ is applicable as a criterion of the "quasi-thermodynamic" behaviour of kinetic systems with strongly connected graphs.

Let us study the so-called renormalized rate matrix $\boldsymbol{K}' = \boldsymbol{DK}$ from (*78*), its entries are

$$k'_{ij} = \bar{x}_i k_{ij} \tag{80}$$

We assign to this matrix a kinetic graph denoted by $G'(\mathscr{K})$, which has the same "topology" as the original graph $G(\mathscr{K})$, they are different only in the evaluation of edges. Each edge $(\mathrm{X}_i, \mathrm{X}_j)$ from $G'(\mathscr{K})$ is evaluated by the renormalized rate constant k'_{ij}. The graph $G'(\mathscr{K})$ satisfies very important property which will be essential in our considerations, for each vertex X_i $(i = 1, 2, \ldots, n)$ the sum of evaluations of incoming edges is equal to the sum of evaluations of outgoing edges

$$\sum_{j=1}^{n} k'_{ij} = \sum_{j=1}^{n} k'_{ji} \tag{81}$$

This relation is a consequence of (*47*) applied for kinetic systems with strongly connected graphs.

We have to emphasize that not all renormalized rate constants are independent, they are restricted by (*81*). Minimal number of independent renormalized rate constants will be determined by a procedure specified below. Since the graph $G'(\mathscr{K})$ is strongly connected, each its edge belongs to a cycle [10]. We construct for $G'(\mathscr{K})$ a minimal set of cycles $C_1(\mathscr{K})$, $C_2(\mathscr{K})$, ..., $C_p(\mathscr{K})$ in such a way that each cycle contains an edge which is not contained in other cycles. If we have such a cycle for which each edge is contained in other cycles, then this cycle should be omitted as redundant. In Fig. 3 are shown cycles of the graph $G'(\mathscr{K})$, minimal sets of cycles are $\{C_1(\mathscr{K}), C_2(\mathscr{K})\}$ and $\{C_3(\mathscr{K}), C_4(\mathscr{K})\}$, respectively. We assign to each cycle $C_i(\mathscr{K})$ a positive coefficient ξ_i, its value is

unambiguously determined by the evaluation of the edge occurring merely in this cycle $C_i(\mathscr{K})$. In the case that there exist more of such edges than one, we choose arbitrary of them. Let (X_r, X_s) be the selected edge, then $\xi_i = \bar{x}_r k_{rs}$. Each edge in $G'(\mathscr{K})$ is evaluated by the sum of coefficients ξ_i assigned to cycles in

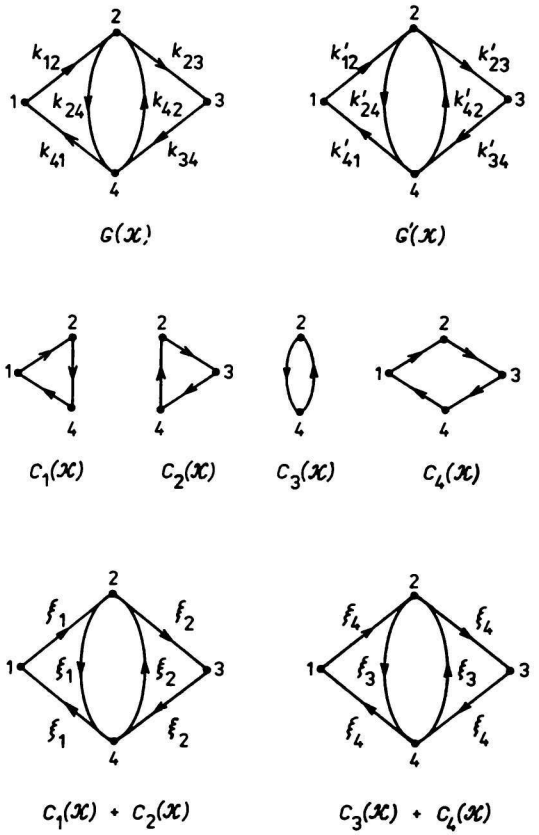


Fig. 3. A kinetic graph $G'(\mathscr{K})$ can be constructed from the original graph $G(\mathscr{K})$ if evaluations of edges are changed by renormalized rate constants k'_{ij}; for all vertices of $G'(\mathscr{K})$ the condition (*81*) should be fulfilled. For graph $G'(\mathscr{K})$ four different cycles $C_{1\to4}(\mathscr{K})$ can be constructed. Coefficients ξ_i are determined by two independent ways, the first (second) one corresponds to cycles $C_1(\mathscr{K})$ and $C_2(\mathscr{K})$ ($C_3(\mathscr{K})$ and $C_4(\mathscr{K})$).

which the corresponding edge is appearing. In fact, we have constructed a minimal set of independent renormalized rate constants evaluating edges in $G'(\mathscr{K})$; the condition (*81*) is automatically fulfilled as a result of the construction of coefficients ξ_i. The matrix of renormalized rate constants may be expressed as follows

$$\boldsymbol{K}' = \sum_{i=1}^{p} \xi_i \boldsymbol{K}_i' \tag{82}$$

where $\boldsymbol{K}_i'$ is the adjacency matrix [10] of cycle $C_i(\mathscr{K})$, its element $(\boldsymbol{K}_i')_{pq}$ is equal to 1 (0) if the edge (X_p, X_q) is contained (not contained) in the cycle $C_i(\mathscr{K})$. The result (*82*) is of great importance for our proof of the property (*79*), we note that the proved formula is a consequence of strong connectivity of the kinetic graph $G(\mathscr{K})$.

Let us assume that the kinetic graph is composed of one cycle denoted by $C_1(\mathscr{K})$, then

$$\boldsymbol{K}' = \xi_1 \boldsymbol{K}_1' \tag{83}$$

In this simplest case all renormalized rate constants are the same and equal to the coefficient ξ_1. Assume that the indexing of vertices was carried out in such a way that edges (X_n, X_1) and (X_i, X_{i+1}) (for $i = 1, 2, \ldots, n-1$) form the graph $G(\mathscr{K})$, introducing (*83*) in (*78*) we get

$$\begin{aligned} \dot{\mathrm{L}}(t) &= \xi_1 \boldsymbol{e}^T \,\mathrm{dg}\,(\dot{\boldsymbol{\varphi}}(\boldsymbol{y}))\, \varrho(\boldsymbol{K}_1')\boldsymbol{y} \\ &= \xi_1 \boldsymbol{\Phi}(y_1, y_2, \ldots, y_n) \end{aligned} \tag{84a}$$

where

$$\begin{aligned} \boldsymbol{\Phi}(y_1, y_2, \ldots, y_n) &= \dot{\varphi}(y_1)(y_n - y_1) + \dot{\varphi}(y_2)(y_1 - y_2) \\ &+ \quad + \dot{\varphi}(y_n)(y_{n-1} - y_n) \end{aligned} \tag{84b}$$

Defining the Lyapunov function (*77*) we have postulated a convexity of $\varphi(\cdot)$, *i.e.* its first derivative $\dot{\varphi}(\cdot)$ should be monotonously increasing function, then one can prove [7] by a mathematical induction an inequality

$$\boldsymbol{\Phi}(y_1, y_2, \ldots, y_n) \leqslant 0 \qquad (= 0 \text{ for } y_1 = y_2 = \quad = y_n) \tag{85}$$

where the equality of all "concentrations" y_i is fulfilled for cyclic system only for equilibrium state $y_1 = y_2 = \quad = y_n = 1$. Inserting (*85*) in (*84a*) we get the following condition for kinetic systems represented by simple cyclic graph

$$\dot{\mathrm{L}}(t) \leqslant 0 \qquad (= 0 \text{ for } \boldsymbol{y} = \bar{\boldsymbol{y}} = \boldsymbol{e}) \tag{86}$$

which is in accordance with the relation (*79*). Applying this specific result there is easy to prove the relation (*79*) fulfilled for general strongly connected kinetic graphs. Introducing (*82*) in (*78*) we get the time derivative $\dot{\mathrm{L}}(t)$ expressed by a sum of time derivatives of Lyapunov functions constructed for single cycles $C_i(\mathscr{K})$ from $G(\mathscr{K})$

$$\dot{\mathrm{L}}(t) = \sum_{i=1}^{p} \dot{\mathrm{L}}_i(t) \tag{87}$$

where every term satisfies separately the inequality (*86*), hence we have proved (*78*), which was to be demonstrated. Summarizing, for kinetic systems with strongly connected graphs there exists broad class of positive Lyapunov functions which are in the course of time evolution of system monotonously convexly decreasing and vanishing in the equilibrium state.

3. *Symmetrizable kinetic matrix* [3—5]

Kinetic systems with *symmetrizable kinetic matrix* are special case of those systems that are represented by strongly connected graphs. This is the reason for what we shall not study Lyapunov functions, their functional form is formally contained at (*77*) introduced for systems with strongly connected kinetic graphs.

A kinetic system with symmetrizable kinetic matrix is specified by the following two conditions:

1. The rate matrix is sign symmetrical, for an arbitrary pair of indices either first or second condition should be fulfilled

$$k_{ij} > 0 \Rightarrow k_{ji} > 0 \tag{88a}$$

$$k_{ij} = 0 \Rightarrow k_{ji} = 0 \tag{88b}$$

2. There exists such a diagonal positive matrix $\boldsymbol{R} = \mathrm{dg}\,(r_1, r_2, \ldots, r_n)$ that

$$\boldsymbol{RK} = \boldsymbol{K}^T\boldsymbol{R} \tag{89a}$$

or in the component formalism

$$r_i k_{ij} = r_j k_{ji} \tag{89b}$$

for each pair of indices.

Since the matrix $\boldsymbol{R}$ from (*89a*) is positive, it should be nonsingular and matrices $\boldsymbol{R}^{\pm 1/2}$ do exist. We transform (*22*) in the form

$$\dot{\boldsymbol{z}} = \boldsymbol{A}'\boldsymbol{z} \tag{90a}$$

where

$$\boldsymbol{A}' = \boldsymbol{R}^{-1/2}\boldsymbol{A}\boldsymbol{R}^{1/2} \tag{90b}$$

$$\boldsymbol{z} = \boldsymbol{R}^{-1/2}\boldsymbol{x} \tag{90c}$$

Symmetrized kinetic matrix $\boldsymbol{A}'$ is similar with original (symmetrizable) matrix $\boldsymbol{A}$, their eigenvalues should be identical. Matrix elements of $\boldsymbol{A}'$ are

$$A'_{ii} = A_{ii} = -l_i \tag{91a}$$

$$A'_{ij} = (r_i/r_j)^{1/2} k_{ij} = (k_{ij}k_{ji})^{1/2} \tag{91b}$$

where, for the construction of last relation, eqn (*89b*) was used. Matrix A' is negatively semidefinite, its eigenvalues are real and non-positive. Let $t = (t_1, t_2, \ldots, t_n)^T$ be an arbitrary column vector, then

$$\boldsymbol{t}^T\boldsymbol{A}'\boldsymbol{t} = \sum_{ij} t_i A'_{ij} t_j = -\sum_i t_i^2 l_i + \sum_{ij} (k_{ij}k_{ji})^{1/2} t_i t_j =$$

$$= -\sum_{i<j} (t_i k_{ij}^{1/2} - t_j k_{ji}^{1/2})^2 \leqslant 0 \qquad (92)$$

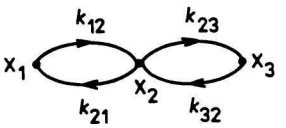
We have proved that the matrix A' is negatively semidefinite. Since the matrices A and A' are similar, the matrix A should be also negatively semidefinite and its eigenvalues are real and non-positive. This means that for kinetic systems with symmetrizable kinetic matrix any type of concentration oscillations is strictly forbidden.

For kinetic systems with symmetrizable kinetic matrix the rate constants are restricted by the so-called *Wegscheider's conditions* [1]. Assume that a kinetic graph $G(\mathscr{K})$ contains two cycles $C(\mathscr{K})$ and $C'(\mathscr{K})$ which are formed from p edges ($p \geqslant 3$), and these edges are incident with the same vertex set composed of p vertices. Their existence is ensured by the condition (*88a*) and they are of the opposite orientation. Let cycles $C(\mathscr{K})$ and $C'(\mathscr{K})$ be formed of sequence of p vertices and p edges: $X_{i1} - X_{i2} - \quad - X_{ip} - X_{i1}$ and $X_{i1} - X_{ip} - \quad - X_{i2} - X_{i1}$. Applying the condition (*89b*) to these cycles we get *Wegscheider's conditions* [1]

$$k_{i1i2}k_{i2i3} \ldots k_{ipi1} = k_{i2i1}k_{i3i2} \ldots k_{i1ip} \qquad (93)$$

Similar conditions can be constructed for all pairs of cycles with opposite orientations and induced by the same set of vertices. Summarizing, in order a kinetic system be determined by the symmetrizable kinetic matrix all rate constants should fulfil conditions (*93*) constructed for each pair of cycles with opposite orientation.

In the forthcoming part of this subsection we demonstrate two kinetic systems which satisfy conditions (*88*) and (*89*). Let us consider a kinetic system which satisfies the condition (*88*) and its kinetic graph contains merely cycles of the length two. For these systems an existence of the matrix $\boldsymbol{R}$ is ensured by solving the condition (*89b*). For example, let us study a kinetic graph



From (*89b*) we get

$$r_1 k_{12} = r_2 k_{21}, \quad r_2 k_{23} = r_3 k_{32}$$

then

$$r_2 = \frac{k_{12}}{k_{21}} r_1, \quad r_3 = \frac{k_{23}}{k_{32}} r_2 = \frac{k_{12} k_{23}}{k_{21} k_{32}} r_1$$

From this simple illustrative example we see that for kinetic systems with symmetrizable kinetic matrix and with graphs involving merely cycles with the length two, an existence of $\boldsymbol{R}$ is ensured in such a way that the homogeneous system of equations (*89b*) is solvable and resulting elements r_i are positive.

As a second example of systems with symmetrizable kinetic matrix we shall study systems satisfying the so-called condition of *detailed balance*. These systems are determined by the condition (*88*) (*i.e.* their kinetic matrices are sign symmetrical) and single components of equilibrium concentration vector $\bar{\boldsymbol{x}} = (\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_n)^T$ and rate constants k_{ij} satisfy the condition of detailed balance

$$\bar{x}_i k_{ij} = \bar{x}_j k_{ji} \tag{94}$$

For these systems the matrix $\boldsymbol{R}$ is identical with a diagonal matrix $\boldsymbol{D}$

$$\boldsymbol{R} = \boldsymbol{D} = \mathrm{dg}\,(\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_n) \tag{95}$$

The requirement of detailed balance ensures simple construction of the symmetrized kinetic matrix $\boldsymbol{A}'$, and moreover, Wegscheider's conditions are now an immediate consequence of the detailed balance.

V. Conclusion

We have demonstrated that an arbitrary closed kinetic system of first-order reactions asymptotically tends to an equilibrium state in which all time derivatives of concentrations are vanishing. An equilibrium state for $r(\boldsymbol{A}) = n - 1$ is determined unambiguously, it does not depend on initial concentrations. If the rank of kinetic matrix satisfies $r(\boldsymbol{A}) \leqslant n - 2$, then an equilibrium state is not determined unambiguously, it depends on initial concentrations. These kinetic systems have infinitely many equilibrium states, their actual form is dependent on initial concentrations. Sustained concentration oscillations are for closed kinetic systems involving first-order reactions strictly forbidden.

We have defined the so-called pseudo-Lyapunov function, which is continuous, positive, and monotonously vanishing for $t \to \infty$. It can be interpreted as a measure of distance (in l_1-metrics) between a concentration vector and the

equilibrium state. If a kinetic system has a strongly connected graph, then we can define a standard Lyapunov function which is not only continuous but also smooth for each positive time (in contrast to the pseudo-Lyapunov function which is not in general a smooth function). In a telling way, kinetic systems are "quasi-thermodynamic", they are spontaneously tending to an equilibrium state. As a special case of kinetic systems with strongly connected graphs we have studied systems with symmetrizable kinetic matrix. These systems are closely related to thermodynamic closed systems of ideal mixtures in which first-order reactions are running. We have proved that for systems with symmetrizable kinetic matrix even damped concentration oscillations cannot occur (eigenvalues of the kinetic matrix are non-positive).

In the course of our theoretical study we have used extensively the graph-theory formalism. It offers very simple and straightforward formalism how to present many concepts and notions, whereas their pure algebraic theory is very clumsy.

Though we have been mainly focused on chemical systems, the elaborated theory might be of general validity [9] for different arrays of physics, biology, ecology, and economics, the time evolution of these systems is described by similar differential equations with those used in chemical kinetics. Moreover, many concepts are immediately applicable [6, 7] for a theoretical study of nonlinear systems involving chemical reactions of higher than first order.

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