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THERMODYNAMIC FUNCTION ANALOGUE FOR REACTIONS PROCEEDING WITHOUT INTERACTION OF VARIOUS SUBSTANCES

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Abstract—A function similar to Lyapunov's function has been constructed for reactions with $\alpha A_i \rightarrow \sum \beta_j A_j$ stages. This provides for the quasi-thermodynamics of the appropriate kinetic model, which implies steady-state uniqueness and global stability in the reaction polyhedron. The kinetic law generalizing the Marcelin–de Donder kinetics has been written for a separate stage. Explicit Lyapunov thermodynamic functions have been written for various conditions of the reaction proceeding in closed systems. The matrix of linear approximation close to equilibrium is expressed by means of the introduced scalar product. Particularly, the absence of damped oscillations as equilibrium is approached as shown.

INTRODUCTION

The equilibrium point in detailed balanced systems is known to be unique and stable (by the given values of linear conservation laws) (Zel'dovich, 1938; Shapiro and Shapley, 1965; Wei, 1962; Wei and Prater, 1962; Vasil'ev *et al.*, 1973; Vol'pert and Khudyaev, 1985; Gorban', 1980, 1984; Gorban' *et al.*, 1980; Yablonskii *et al.*, 1983). Another example of the above systems are complex-balanced systems (Horn, 1972; Horn and Jackson, 1972; Feinberg, 1972b; Feinberg and Horn, 1974; Orlov, 1980; Orlov and Rozonoer, 1980), such as complex reactions proceeding via a linear mechanism, i.e. monomolecular reaction systems (Wei and Prater, 1962).

There is another type of reaction mechanism with "quasi-thermodynamics", i.e. with a unique and asymptotically stable steady state at given values of the conservation laws. These are reactions in which various substances do not interact with each other. The uniqueness and stability of the steady state in these reactions were proved by Bykov *et al.* (1975), Slin'ko *et al.* (1976) and Vol'pert *et al.* (1975). Isolated mechanisms are defined as the totality of elementary reactions of the type

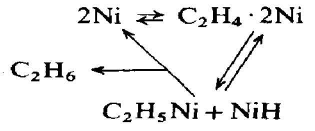
$$\alpha A_i \rightarrow \sum_{j=1}^{n} \beta_j A_j \tag{1}$$

where $A_1, A_2, \ldots, A_n$ are symbols of the substances, α and β_i are stoichiometric coefficients (integers, $\alpha > 0$, $\beta_j \geqslant 0, j = 1, 2, \ldots, n$), and n is the number of reagents. There is one initial substance in each elementary reaction (1), though $\alpha > 1$ is also possible. Linear reaction mechanisms are typical examples of this type of reaction. However, nonlinear reaction mechanisms without interaction of the various substances are also of common occurrence; for example, transformation of intermediates via the Eley–Rideal mechanism (impact) of CO oxidation on Pt:

$$2\mathrm{Pt} \xrightarrow{+O_2} 2\mathrm{PtO}; \quad \mathrm{PtO} \xrightarrow{+CO} \mathrm{Pt}\,(+\mathrm{CO_2}\uparrow). \tag{2}$$

Kinetic models corresponding to type (2) mechanism are non-linear ones. However, in this case the steady state is still unique and stable.

Systems without interaction of the various substances are not obligatorily complex-balanced. In turn, complex-balanced systems may consist of the steps of intermediate interactions. An example is the Twigg mechanism (Twigg, 1950) of ethylene hydrogenation on nickel:



(3)

According to the criteria suggested by Horn (1972), Horn and Jackson (1972) and Feinberg (1972b), system (3) is always complex-balanced.

For detailed and complex-balanced systems global Lyapunov functions exist. These functions are determined in the whole reaction polyhedron. The latter is given for the non-negative concentration condition and linear laws of conservation [for a detailed analysis of the structure, see Gorban' (1984)].

The aim of this work was to find Lyapunov's functions for systems without interactions between the various substances, and to investigate the dynamics of such systems both in steady and unsteady-state external conditions. Besides, based on the kinetic law of

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individual steps and generalization of Marcelin–de Donder kinetics, thermodynamic Lyapunov's functions have been written in their explicit form for closed systems in various conditions. The absence of damped oscillations in the linear equilibrium area is demonstrated by the introduced scalar product.

LYAPUNOV'S FUNCTION. UNGROWTH

Let the reaction mechanism be

$$\alpha_{s1}A_1 + \dots + \alpha_{sn}A_n \rightarrow \beta_{s1}A_1 + \dots + \beta_{sn}A_n, \qquad s = 1, \dots, S \qquad (4)$$

where s is an elementary reaction number and α_{si} and β_{si} are non-negative integers (stoichiometric numbers). The direct and reverse reactions in eq. (4) are written separately. Let us denote the concentration of A_i (in mol/m^3 for homogeneous reactions and in mol/m^2 for heterogeneous reactions) by c_i, and the concentration vector by c.

Suppose that the reaction proceeds in isothermal conditions. Reactions proceeding in unsteady-state conditions (including non-isothermic external ones) will be considered below. It should be noted that in nonisothermal conditions critical phenomena may be observed even for linear reactions (Vaganov *et al.*, 1978). Let us correlate each reaction (4) with its rate $W_s(c) \geqslant 0$, which is a non-negative function of the concentrations.

The main assumption is that for a type (1) reaction, $W(c) = W(c_i)$ is a smooth, monotonically growing function of c_i, $W(0) = 0$. This is valid, for example, when the rate of reaction (1) is calculated by the law of mass (surface) action: $W(c) = kc_i^{\alpha}$, where k is the rate constant.

Let $A_1, \dots, A_n$ be surface substances for heterogeneous catalytic reactions; (4) is the transformation mechanism. Assuming the composition of the gas phase to be constant, we may write down

$$\dot{c}_i = \sum_s \gamma_{s_i} W_s(c) \qquad (5)$$

or in vector form

$$\dot{c} = \sum_s \gamma_s W_s(c) \qquad (6)$$

where $\gamma_{si} = \beta_{si} - \alpha_{si}$, γ_s is a vector with components and γ_{si} is a stoichiometric vector of the s-th reaction. The same kinetic equations [(5) and (6)] may also be written for heterogeneous reactions proceeding at a constant volume. The results below are valid for this case as well.

At least one positive linear law of conservation should exist for eqs (5) and (6). It is possible to find a set of numbers $m_i > 0$ $(i = 1, \dots, n)$ such that for any s

$$\sum_i m_i \gamma_{si} = 0 \quad \text{and} \quad \sum_i m_i c_i = \text{constant}.$$

The numbers m_i may be proportional to the molecular weights of the reagents A_i. In our case, it seems more convenient to use new variables $a_i = m_i c_i$; then eq. (5) may be rewritten as

$$\dot{a}_i = m_i \sum_s \gamma_{si} W_s. \qquad (7)$$

Using $g_{si} = m_i \gamma_{si}$ (g_s is a vector with components g_{si}), we may represent eq. (7) as

$$\dot{a}_i = \sum_s g_{si} W_s \qquad (7a)$$

or in vector form as

$$\dot{a} = \sum_s g_s W_s. \qquad (7b)$$

It should be borne in mind that in eqs (7a) and (7b) $\sum_s g_{si} = 0$ and $\sum_i a_i = \text{constant}$.

Suppose that all reactions (4) have the form (1), i.e. the s-th elementary reaction is

$$\alpha_s A_{i_s} \rightarrow \sum_i \beta_{si} A_i. \qquad (8)$$

Now, let us consider the Jacobian matrix corresponding to eq. (7):

$$J(a) = \left(\frac{\partial \dot{a}_i}{\partial a_j}\right). \qquad (9)$$

It can be shown that for any positive a (all $a_i \geqslant 0$) diagonal elements of the J matrix are negative ($\partial \dot{a}_i / \partial a_i \leqslant 0$), non-diagonal elements J are positive ($\partial \dot{a}_i / \partial a_j \geqslant 0$, if $i \neq j$) and the sum of the elements is zero in any column $\left(\sum_{i=1}^{n} \partial \dot{a}_i / \partial a_j = 0\right)$. Actually,

$$J(a) = \frac{\partial \dot{a}_i}{\partial a_j} = \sum_s g_{si} \frac{\partial W_s}{\partial a_{i_s}} \delta_{i_s j} \overset{\text{def}}{=} \sum_s J_s(a) \qquad (10)$$

where

$$\delta_{i_s j} = \begin{cases} 1, & \text{if } i_s = j \\ 0, & \text{if } i_s \neq j. \end{cases}$$

Matrix $J_s(a)$ in eq. (10) is the product of a positive scalar $\partial W_s / \partial a_{i_s}$ and the constant matrix J_s°

$$(J_s^{\circ})_{ij} = g_{si}\, \delta_{i_s j}. \qquad (11)$$

In matrix J_s°, whose elements are determined in eq. (11), only the column i_s differs from zero. It is the same as vector column g_s. The components of the latter, $g_{si} \geqslant 0$, if $i \neq i_s$, $\sum_i g_{si} = 0$; the diagonal component $g_{si_s} < 0$. These facts follow from the above-mentioned properties of matrix $J(a)$.

Thus, for each positive matrix $J(a)$ represents an infinitesimal matrix of a certain Markovian process (Dynkin, 1959; Kemeney and Snell, 1960). This analogy will be widely used below.

Let $a(t)$ be an arbitrary positive solution of eq. (7). Upon linearizing eq. (7) in the neighbourhood of $a(t)$, we consider solutions $a(t) + \Delta(t)$ close to $a(t)$, with the same value of the conservation law $\left(\sum_{i=1}^{n} \Delta_i = 0\right)$.

In the linear approximation

$$\frac{d}{dt}\Delta(t) = J(a(t))\,\Delta(t). \tag{12}$$

It is well known from the theory of Markov processes that for equations of type (12) there exists a function, ungrowing along solutions

$$\mathscr{L}(\Delta) = \sum_{i=1}^{n} |\Delta_i|. \tag{13}$$

In eq. (13), $\mathscr{L}(\Delta)$ is the sum of absolute values of Δ_i.

Function $\mathscr{L}(\Delta)$ does not grow along solutions (12) if matrix $J(a(t))$ depends smoothly on t and has the above formulated properties: diagonal members are negative, non-diagonal members are positive, and the sum of the elements in each column equals zero.

Function $\mathscr{L}(\Delta)$ is a norm in R^n: $\mathscr{L}(\alpha\Delta) = |\alpha|\mathscr{L}(\Delta)$, $\mathscr{L}(\Delta_1+\Delta_2) \leqslant \mathscr{L}(\Delta_1)+\mathscr{L}(\Delta_2)$, $\mathscr{L}(\Delta) = 0$ only for $\Delta = 0$. From this we conclude that for any two positive solutions $a^{(1)}(t)$ and $a^{(2)}(t)$, of system (7) for the condition $\sum_{i=1}^{n} a_i^{(2)} = \sum_{i=1}^{n} a_i^{(1)}$, function $\mathscr{L}(a^{(1)}(t) - a^{(2)}(t))$ does not increase with time because $\mathscr{L}(\Delta)$ does not grow along solutions (12).

The role of function

$$\begin{aligned}\mathscr{L}(a^{(1)}-a^{(2)}) &= \sum_{i=1}^{n} |a_i^{(1)}-a_i^{(2)}| \\ &= \sum_{i=1}^{n} m_i|c_i^{(1)}-c_i^{(2)}|\end{aligned} \tag{14}$$

determined in eq. (13) for the dynamics of systems without interaction of the various substances is the same as that of Lyapunov's thermodynamic functions in the dynamics of closed systems. $\mathscr{L}(a^{(1)}-a^{(2)})$ is the function determined by two points $a^{(1)}$ and $a^{(2)}$. One may, however, choose a stable point of eq. (7) as $a^{(2)}$ and consider $\mathscr{L}(a^{(1)}-a^{(2)})$ as function $a^{(1)}$. It should be noted that as $\mathscr{L}$ is not differentiated everywhere, the obtained function $\mathscr{L}(a^{(1)}-a^{(2)})$ ($a^{(2)}$ is a stable point) cannot be strictly regarded as Lyapunov's function for system (7) (see, for example, Tikhonov *et al.*, 1980). In practice, this difference is of no significance, only the monotony of the variation of $\mathscr{L}$ with time and the convexity of $\mathscr{L}$ being important. Below we separate the cases when $\mathscr{L}(a^{(1)}(t)-a^{(2)}(t)) \to 0$ at $t \to \infty$ for any $a^{(1)}$ and $a^{(2)}$ with the same condition $\left(\sum_{i=1}^{n} a_i^{(1)}(t) = \sum_{i=1}^{n} a_i^{(2)}(t) = \text{constant}\right)$, and consider Lyapunov's thermodynamic functions for closed systems in terms of the generalized Marcelin–de Donder kinetics (Van Rysselberghe, 1958; Feinberg, 1972a).

LYAPUNOV'S THERMODYNAMIC FUNCTIONS

Let us consider again the general scheme

$$\alpha_{si}A_1 + \ldots + \alpha_{sn}A_n \rightleftharpoons \beta_{si}A_i + \ldots + \beta_{sn}A_n,$$
$$s = 1, \ldots, S$$

where, as in eq. (4), α_{si} and β_{si} are stoichiometric numbers, s is the stage number and $A_1, \ldots, A_n$ are symbols of the substances.

$N_1, \ldots, N_n$ (the amounts of substances $A_1, \ldots, A_n$) are the main variables that characterize the state of a mixture in the given fixed conditions. The rest variables may be expressed by vector N (the elements of which are N_i) and by values which are constant in these conditions.

The rate W_s corresponds to each (s-th) step. The rate of step W_s is a value which is defined as a function of concentration and temperature $W_s(c, T)$. The following way of determining $W_s(c, T)$ permits one to generalize the approach suggested by Van Rysselberghe (1958) and Feinberg (1972a) and to describe both ideal and nonideal systems in different conditions (isothermal or adiabatic, isochoric or isobaric, etc.). Catalytic systems of nonideal kinetics are considered by Zyskin *et al.* (1981a, b).

Let n functions, $\mu_1(c, T), \ldots, \mu_n(c, T)$, be prescribed. They are determined and smooth at $T > 0$ and all positive c (if all $c_i > 0$). Feinberg (1972a) calls them pseudo-chemical potentials. In all familiar cases, $\mu_i(c, T)$ is the chemical potential of substance A_i divided by RT.

We assume that

$$W_s(c, T) = W_s^0(c, T)\left(\exp\sum_i \alpha_{si}\,\mu_i - \exp\sum_i \beta_{si}\,\mu_i\right) \tag{15}$$

where $W_s^0(c, T)$ is a certain positive function (arbitrary in other respects).

Let us write the kinetic equation

$$\dot{N} = V\sum_s \gamma_s W_s(c, T) \tag{16}$$

where V is the system volume and γ_s is the stoichiometric vector of the s-th stage: $\gamma_{si} = \beta_{si} - \alpha_{si}$.

In general, the equations describing the concentration dynamics are more cumbersome than eqs (16). At the given reaction conditions the concentration vector c and temperature T may be expressed through the composition N and constants characteristic of these conditions. Equations (16) become closed. Let the conditions be fixed and functions $c(N, \ldots)$, $T(N, \ldots)$, $\mu_i(N, \ldots)$ be determined. Here, the dots stand for constants which are different for different conditions. Thus, for example, for an isochoric, adiabatic process the inner energy U (which also includes chemical energy) and volume V should be inserted instead of the dots. Functions $\mu_i(N, \ldots)$ should satisfy the following requirements (if $N_i > 0$, $T(N, \ldots) > 0$):

(1) Symmetry:

$$\frac{\partial \mu_i}{\partial N_j} = \frac{\partial \mu_j}{\partial N_i}. \tag{17}$$

(2) Positive determinancy:

(a) The quadric form

$$\sum_{i,j=1}^{n} x_i \frac{\partial \mu_i}{\partial N_j} x_j \tag{18}$$

is non-negatively determined in R^n.

(b) Quadric form (18) is positively (strictly positively) determined in any hyperplane of positive, normal v (all $v_i > 0$).

When conditions (1) and (2) are fulfilled, a convex Lyapunov's function $G(N, \ldots)$ is used for eqs (16). Function $G(N, \ldots)$ is determined from the expression with an accuracy of constant

$$\frac{\partial G(N, \ldots)}{\partial N_i} = \mu_i. \tag{19}$$

According to condition (2b), G is strictly convex in the limitation to any hyperplane of positive normal.

Taking eqs (16) into account

$$\dot{G} = -\sum_s W_s \ln \frac{W_s^+}{W_s^-} \leqslant 0 \tag{20}$$

where W_s^+ and W_s^- are the rates of the direct and the reverse reaction of the s-th step:

$$W_s^+ = W_s^\circ(c, T) \exp \sum_{i=1}^{n} \alpha_{si}\, \mu_i(c, T)$$

$$W_s^- = W_s^\circ(c, T) \exp \sum_{i=1}^{n} \beta_{si}\, \mu_i(c, T).$$

As follows from eq. (20), $\dot{G} = 0$ provided that $W_s = 0$ for all $s = 1, 2, \ldots, s$. This is the principle of the detailed equilibrium.

The validity of (1) and (2) in various conditions will limit the possible form of function μ_i. For example, let us consider the reaction in an ideal classical gas. The equation of state is

$$PV = RT \sum_{i=1}^{n} N_i \tag{21}$$

where P is the gas pressure.

Suppose that at constant volume and temperature the kinetics obey the law of mass action. Based on the validity of limitation (1), we obtain

$$\mu_i(c, T) = \ln c_i + \frac{u_i}{RT} - \frac{C_{vi}}{R} \ln T + \delta_i \tag{22}$$

where u_i (in J/mol) is the energy of the normal state of A_i, C_{vi} (in J/mol degree) is the specific partial heat capacity and δ_i is an arbitrary constant.

Thus, functions $\mu_i(c, T)$ are determined with an accuracy of the constants. The numbers δ_i depend on the system and are associated with the equilibrium compositions, for which $\sum_i \gamma_{si}\, \mu_i = 0$.

Let us write down functions G for various conditions.

(1°) $V, T =$ constant, $G = \sum_{i=1}^{N} N_i(\mu_i - 1)$.

(2°) $P, T =$ constant, $G = \sum_{i=1}^{n} N_i\, \mu_i$.

In (1°) and (2°), functions G are found to be proportional to the classical thermodynamic potentials of Helmholtz (free energy) and Gibbs (free enthalpy).

(3°) $V, U =$ constant (the system is heat-insulated):

$$G = \sum_{i=1}^{n} N_i(\ln(N_i/V) + \delta_i - 1) - \frac{C_v}{R}(\ln T + 1) \tag{23}$$

where

$$C_v = \sum_{i=1}^{n} C_{vi}\, N_i, \quad T = \left(U - \sum_{i=1}^{n} u_i N_i\right) \Big/ C_v.$$

(4) $P, H =$ constant (H is the enthalpy, the system is heat-insulated):

$$G = \sum_{i=1}^{n} N_i\left(\ln N_i - \ln \sum_{i=1}^{n} N_i + \delta_i - \ln \frac{R}{P}\right)$$
$$- \frac{C_p}{R}(\ln T + 1) \tag{24}$$

where

$$C_p = \sum_{i=1}^{n} (C_{vi} + R) N_i, \quad T = \left(H - \sum_{i=1}^{n} u_i N_i\right) \Big/ C_p.$$

The above formulae, (22)–(24), can easily be generalized for variable specific partial heat capacities, for more complete equations of state, and for non-ideal kinetics of $V, T \neq$ constant.

Formula (15) is a general form of the kinetic law which is in agreement with thermodynamics [another general form is given by Orlov (1980) and Orlov and Rozonoer (1980)].

It should be noted that the linear approximation to eqs (16), close to equilibrium (Gorban', 1979; Bykov *et al.*, 1979a, b), may easily be written using the quadric form (18).

Let us introduce a scalar product into

$$\langle x | y \rangle = \sum_{i=1}^{n} x_i \frac{\partial \mu_i}{\partial N_j} x_j \tag{25}$$

Denote a certain equilibrium composition by N^*, the corresponding concentrations by c_i^*, the temperature by T^* and the volume by V^*. From eq. (20), $N = 0$ only in those positive points where $W_s = 0$ for all s (the detailed equilibrium principle).

The linear approximation of W_s close to equilibrium is

$$W_s = -W_s^\circ(c^*, T^*) \left[\exp \sum_i \alpha_{si}\, \mu_i(c^*, T^*)\right]$$
$$\times \sum_{i,j} \gamma_{si} \frac{\partial \mu_i}{\partial N_j}(N_j - N_j^*). \tag{26}$$

Denote

$$W_s^* \overset{\text{def}}{=} W_s^\circ(c^*, T^*) \exp \sum_i \alpha_{si}\, \mu_i(c^*, T^*)$$
$$= W_s^\circ(c^*, T^*) \exp \sum_i \beta_{si}\, \mu_i(c^*, T^*). \tag{27}$$

W_s^* is the equilibrium exchange rate in the s-th stage. One may observe these values (their linear combinations) in experiments on isotope exchange (Gorban' and Yablonskii, 1981). Using the scalar product (25), formula (26) is reduced to

$$W_s = -W_s^* \langle \gamma_s | N - N^* \rangle. \tag{28}$$

Equation (16) in the linear approximation is

$$\dot{N} = -V^* \sum_s W_s^* \gamma_s \langle \gamma_s | N - N^* \rangle \overset{\text{def}}{=} K(N - N^*). \tag{29}$$

It is convenient to write the matrix of linear approximation K using bracket designations:

$$K = -V^* \sum_s W_s^* | \gamma_s \rangle \langle \gamma_s |. \tag{30}$$

As can be seen from eq. (30), K is self-conjugated about the scalar product (25). Matrix K is nonpositively determined in the limitation on invariant subspace, which is a linear shell of vectors $\gamma_s (s = 1, \ldots, S)$. Hence, damped vibrations are impossible in the neighbourhood of the equilibrium, and point N^* is a stable "knot" in the invariant linear manifold (reaction polyhedron).

The general properties of the dynamics of system (16) with the kinetic law (15) are found to be the same as those proved by Feinberg (1972a), Bykov *et al.* (1979a) and Akramov *et al.* (1975) for Marcelin–de Donder kinetics.

LYAPUNOV'S FUNCTIONS. DECREASE

Let us consider again the systems without interaction of various substances. As shown above, function $\mathscr{L}(a^{(1)}(t) - a^{(2)}(t))$ does not increase with time for any two solutions, $a^{(1)}(t)$ and $a^{(2)}(t)$, of system (7) with the same values of the conservation law $\sum_{i=1}^{n} a_i^{(1)} = \sum_{i=1}^{n} a_i^{(2)}$. Let us assume that

$$\mathrm{d}W_s/\mathrm{d}c_{i_s} > 0, \quad \text{if } c_{i_s} > 0. \tag{31}$$

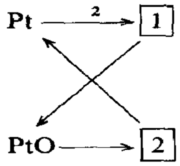
A sufficient condition is $\mathscr{L}(a^{(1)}(t) - a^{(2)}(t)) \to 0$ at $t \to \infty$. It implies that in the initial period ($t = 0$) some substance from $A_1, \ldots, A_n$ is in the mixture, whereas at $t > 0$ all the substances are present ($c_i(t) > 0$ at $t > 0$). In other words, any substance A_i produces any other A_j during the reaction. Such a transformation of A_i to A_j seems to result from the successive occurrence of several elementary reactions.

Let us give a strict formulation. The reaction mechanism under consideration will be compared with a two-fraction graph (Vol'pert, 1972; Clark, 1980) having two types of tops. The first type corresponds to substances, the second one to elementary reactions. Only the tops of the different types are connected by edges. The top substance A_i is connected to the top reaction by an edge.

$$\alpha_{si} A_1 + \ldots + \alpha_{sn} A_n \to \beta_{si} A_1 + \ldots + \beta_{sn} A_n$$

if $\alpha_{si} \neq 0$ or $\beta_{si} \neq 0$. The edge is oriented from the top substance to the top reaction if $\alpha_{si} \neq 0$, and vice versa if $\beta_{si} \neq 0$. If both $\alpha_{si} \neq 0$ and $\beta_{si} \neq 0$, the top substance and top reaction are connected with the opposite oriented arrows. A number, corresponding to the stoichiometric coefficient α_{si} or β_{si} is indicated by the figures above the arrow.

For the impact mechanism of CO oxidation the two-fraction graph of intermediates transformations on Pt (2) is as follows:



(32)

The graph is oriented and bound if one may pass from one top to another by arrows. Graph (32) is proved to be oriented and bound.

Let us formulate the condition for the decrease of function $\mathscr{L}(a^{(1)}(t) - a^{(2)}(t))$.

Let there be no stages of interaction of the various substances in the reaction mechanism, and let the graph of the latter be oriented and bound. Let $a^{(1)}(t)$, $a^{(2)}(t)$ be the solution of kinetic eqs (7) and $\sum_{i=1}^{n} a_i^{(1)} = \sum_{i=1}^{n} a_i^{(2)}$. Then

$$\mathscr{L}(a^{(1)}(t) - a^{(2)}(t)) \overset{\text{def}}{=} \sum_{i=1}^{n} |a_i^{(1)}(t) - a_i^{(2)}(t)| \to 0 \quad \text{at } t \to \infty. \tag{33}$$

Hence, function $\mathscr{L}(a^{(1)} - a^{(2)})$ decreases for the reaction whose mechanism graph is orientally bound.

This may be proved as follows. For any $t \geqslant 0$, $\tau > 0$ and $a^\circ = \sum_{i=1}^{n} a_i$, shift operator $F(t + \tau, t) : \Delta(t) \to \Delta(t + \tau)$ for eq. (12) is positive (all elements f_{ij} of matrix F are above zero) and stochastic (the sum of the elements in any column is 1) due to the oriented bond. Furthermore, such $\varepsilon = \varepsilon(\tau, a^\circ) > 0$ exists that for any t, $f_{ij}(t + \tau, t) \geqslant \varepsilon > 0$. Hence, $\|\Delta(t + \tau)\| < (1 - \varepsilon)\|\Delta(t)\|$, where $\|\Delta\| = \sum_{i=1}^{n} |\Delta_i|$. From this equation the required statement may easily be obtained. All of the above is also valid for systems without interaction of the various substances in unsteady states. Let the external conditions (temperature, pressure, etc.) be variable. Then for a type (8) reaction, $W_s = W_s(c_{i_s}, t)$. Let condition (31) be uniformly fulfilled with respect to t:

$$\frac{\partial W_s}{\partial c_{i_s}} > \delta(c_{i_s}) > 0, \quad \text{if } c_{i_s} > 0 \tag{34}$$

where $\delta(c_{i_s})$ is independent of t.

Let us assume the reaction mechanism graph to be orientally bound. Let $a^{(1)}(t)$, $a^{(2)}(t)$ be solutions of kinetic eqs (7) into which $W_s = W_s(c, t)$ is substituted. If $\sum_{i=1}^{n} a^{(1)}(0) = \sum_{i=1}^{n} a^{(2)}(0)$, then eq. (33) is valid. Thus, even in external conditions, initial conditions are "forgotten" for systems without interaction of the various substances, except for the conservation law value: $\sum_{n=1}^{n} a_i(0) = \sum_{i=1}^{n} a_i(t)$. Note that for systems without interaction of the various substances there exists a single (with an accuracy of proportionality) linear law of conservation, provided that the reaction mechanism graph is oriented and bound.

CONCLUSION

Systems without the interaction of various substances represent generalized linear systems (systems of monomolecular reactions). In these systems, the distance $\mathscr{L}(a^{(1)}(t) - a^{(2)}(t))$ between trajectories $a^{(1)}(t)$ and $a^{(2)}(t)$ in a norm $\|x\| = \mathscr{L}(x) = \sum_{i=1}^{n} |x_i|$ does not increase with time. If the reaction mechanism graph is orientally bound, this distance tends to 0 and $t \to \infty$, the trajectories draw closer to each other. This is valid for systems without interaction between the various substances both in fixed and in labile external conditions. In constant external conditions (kinetic equations are autonomous) there exists a single, asymptotically stable steady state in each invariant simplex $\mathscr{S} = \left\{ a \,\middle|\, \sum_{i=1}^{n} a_i = \varepsilon, a_i \geqslant 0 \right\}$.

A distinct feature of these systems is the existence of a norm in which the trajectories draw closer to each other. There is no such norm in closed systems of a general form. Only the existence of Lyapunov's function is a valid statement for them. At present, criteria of uniqueness and stability of the steady state are known which are based on the study of the structure of the reaction mechanism graph (Clark, 1980; Ivanova, 1979; Ivanova and Tarnopol'skii, 1979). However, it remains unclear whether there are such norms in other types of reaction mechanisms. This is particularly important when studying reactions in labile external conditions.

Chemical systems with nontrival dynamics have recently received great attention. In particular, reactions with a multiplicity of steady states (see, for example, Bykov and Yablonskii, 1981b; Bykov *et al.*, 1981; Yablonskii *et al.*, 1984) and self-oscillations (for the corresponding mathematical models, see Bykov *et al.*, 1978, 1979b; Bykov and Yablonskii, 1981a; Ivanova *et al.*, 1978; Yablonskii *et al.*, 1984) have been found in catalysis. Anomalously slow relaxations are also possible (see Elokhin *et al.*, 1980; Yablonskii *et al.*, 1984; for the mathematical theory, see Gorban' and Cheresiz, 1981; Chap. 3 in Yablonskii *et al.*, 1984). Nontrival dynamics of the lumped system produce interesting effects in the distributed systems "kinetics + diffusion" (Aris, 1975; Pismen, 1980; Gorban' *et al.*, 1980). The results obtained in this work prove that the steps of the interaction between various substances are necessary for the appearance of such interesting phenomena.

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NOTATION

A_i	symbols of substances
a_i	$= m_i c_i, i = 1, 2, \ldots, n$
$\dot{a}_i$	$= \mathrm{d}a_i/\mathrm{d}t$
a	vector with components a_i
c_i	concentrations of A_i
$\dot{c}_i$	$= \mathrm{d}c_i/\mathrm{d}t$
c	vector of concentrations
c^*	equilibrium concentration
C_{vi}	specific partial heat capacity
$G(N)$	thermodynamic Lyapunov's function
$\dot{G}$	$\mathrm{d}G/\mathrm{d}t$
g_s	vector with components $g_{si} = m_i \gamma_{si}, s = 1, 2, \ldots, S$
H	enthalpy
$J(a)$	Jacobian matrix
K	matrix of linear approximation
$\mathscr{L}$	function defined by eq. (13)
m_i	molecular weights of A_i
N_i	amounts of substances A_i
N	vector with coordinates N_i
N_i^*	equilibrium N_i
$\dot{N}$	$= \mathrm{d}N/\mathrm{d}t$
P	pressure
R	universal gas constant
$\mathscr{S}$	invariant simplex
t	time
T	temperature
T^*	equilibrium temperature
U	inner energy
u_i	energy of the normal state of A_i
V	volume of the system
V^*	equilibrium volume
W_s	rate of s-th reaction
$W_s^\circ(c, t)$	certain positive function in eq. (15)
W_s^+	rate of direct s-th reaction
W_s^-	rate of reverse s-th reaction
W_s^*	function denoted by eq. (27)
$\langle x \mid y \rangle$	scalar product defined by (25)
$\|\|x\|\|$	norm of the vector x
$\|x\|$	module of the vector x

Greek letters

α, β	stoichiometric coefficients
γ_s	stoichiometric vector of the s-th reaction
γ_{si}	$= \beta_{si} - \alpha_{si}$
δ_{ij}	Kroneker's symbol
δ_i	arbitrary constant in eqs (22), (23) and (24)
$\delta(c)$	arbitrary positive function in eq. (34)
$\Delta_i(t)$	little function
$\Delta(t)$	vector function $(\Delta_i(t))$
μ_i	chemical potential of substance A_i divided by RT
μ	vector (μ_i)
τ	time increment
ε	little value

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